

**HANDBOOK OF SOLID
STATE DIFFUSION:
VOLUME 2**

HANDBOOK OF SOLID STATE DIFFUSION: VOLUME 2

Diffusion Analysis in Material Applications

Edited by

ALOKE PAUL

SERGIY DIVINSKI



elsevier.com

Elsevier

Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

Copyright © 2017 Elsevier Inc. All rights reserved

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-12-804548-0

For information on all Elsevier publications
visit our website at <https://www.elsevier.com>



Working together
to grow libraries in
developing countries

www.elsevier.com • www.bookaid.org

Publisher: Matthew Deans

Acquisition Editor: Christina Gifford

Editorial Project Manager: Jennifer Pierce

Production Project Manager: Jason Mitchell

Designer: Mark Rogers

Typeset by VTeX

BIOGRAPHIES

Editors and contributors:

Professor Alope Paul heads a research group working on various aspects of diffusion in solids in the Department of Materials Engineering, Indian Institute of Science, Bangalore, India. Major research areas include developing new phenomenological models, materials in electronic packaging, bond coat in jet engine applications, the growth of A15 intermetallic superconductors, etc. He teaches a postgraduate level course on Diffusion in Solids. He has guided several PhD and ME students and coauthored around 100 articles in various international journals. During his PhD studies under the guidance of Prof. Frans J.J. van Loo and Dr. Alexander Kodentsov (Eindhoven University of Technology), he was part of one of the most important discoveries of recent times on previously unknown phenomena related to the Kirkendall effect. After joining the Indian Institute of Science, his group developed new methods for estimation of the diffusion coefficients, for example, a physicochemical approach that relates microstructural evolution with the rate of diffusing components and a pseudo-binary method in multicomponent diffusion. These methods are included in the course curriculum of many universities and also in the books written on this topic. Professor Paul has also coauthored a textbook titled *Thermodynamics, Diffusion and the Kirkendall effect in Solids*. Currently, he is an editorial board member of *Journal of Electronic Materials*, published by Springer-TMS, and of *Scientific Reports*, published by Nature Publishing Group.



Dr. Sergiy Divinski is a Privat-Dozent at the Institute of Materials Physics, University of Münster, Germany, where he leads the radiotracer laboratory, which represents one of the most reputed and internationally recognized diffusion schools. His research is focused on diffusion and especially grain boundary diffusion in metals and alloys. He teaches graduate and postgraduate courses on Diffusion in Solids, Numerical methods in Material Science and different aspects of Materials Science. He has coauthored more than 150 articles in various international journals, several book chapters in the field of Diffusion in Solids, and a textbook titled *Thermodynamics, Diffusion and the Kirkendall effect in Solids*.



Contributors:

Dr. Alain Portavoce received his PhD in Materials Science in 2002. He was offered a permanent position by the French National Center of Scientific Research (CNRS) in 2005, for joining the Institute of Materials Microelectronics and Nanoscience of Provence (Marseille), where he leads the “Reactivity and Diffusion at Interfaces” research team. His expertise includes elaboration (molecular beam epitaxy, sputtering, etc.) and characterization (secondary ion mass spectrometry, Auger electron spectroscopy, Atom Probe Tomography, etc.) of thin films and nanostructures. His work mainly concerns nanometer scale solid state diffusion, segregation and reaction in materials involved in the fabrication of microelectronic devices (semiconductors, silicides, germanides, etc.). He has coauthored 89 scientific publications and is regularly invited to give lectures on atomic redistribution.



Mr. Jacques Perrin Toinin received his Master's degree in Materials Science at the Aix-Marseille University in 2013. He is currently completing PhD studies at the Institute of Materials Microelectronics and Nanoscience of Provence (IM2NP, Marseille). His research is focused on atomic diffusion and segregation in semiconductors after ionic implantation, as well as on atomic redistribution during electrical contact production via reactive diffusion. He has coauthored several papers in international journals dealing with implantation-mediated defects in Ge, and gave several lectures in international conferences on atomic redistribution during diffusion and reactive diffusion.



Dr. Khalid Hoummada received his PhD in Materials Science in 2007. He was hired by the Aix-Marseille University in 2009 as an associated professor and joined the “Reactivity and Diffusion at Interfaces” team of the Institute of Materials Microelectronics and Nanoscience of Provence (IM2NP, Marseille). His current work focuses on segregation and interfacial reaction in materials involved in microelectronic device fabrication (semiconductors, silicides, etc.). His expertise includes the fabrication (evaporation, sputtering, etc.) and the characterization of thin films, especially combining in situ X-ray diffraction and atom probe tomography



measurements. He has coauthored more than 60 papers in international journals and conference proceedings.

Professor Andriy Gusak works at the Department of Physics at Cherkasy National University, Ukraine. He graduated from Moscow State University in 1976 with honors, specialized in theoretical physics. During 1978–1982 he was a PhD student at the Institute of Metallurgy of Academy of Sciences of USSR (Moscow). Prof. Gusak holds a PhD degree since 1983 and Dr. Hab. degree since 1992. He is a full professor since 1994. Since 1996 prof. Gusak is an Honored worker of science and technology of Ukraine. He works mainly in the field of theory and modeling of interdiffusion, solid-state reactions and phase transformations in nanosystems. Prof. Gusak and his team are involved in wide international cooperation. He worked, as an invited professor, at universities and research institutes of Los Angeles, Grenoble, Muenster, Marseille, Cracow, Singapore, Goettingen, Dijon, Debrecen, Eindhoven, Dubna. His publications can be found at https://scholar.google.com.ua/citations?user=dsM_M8gAAAAJ&hl=en, <http://www.scopus.com/authid/detail.url?authorId=7005107923>, <http://orcid.org/0000-0002-2594-5559>, https://www.researchgate.net/profile/A_Gusak. Among them are books published by Wiley (jointly with King Ning Tu), Wiley-VCH, chapters in the books published by Wiley-VCH, Pan Stanford, Trans Tech.



Dr. Nadiia V. Storozhuk is an Assistant Professor at the Department of Physics at Cherkasy National University, Ukraine. She has got her Master's degree in 2009 (with honors) from Cherkasy National University, and her PhD degree in 2014 from the Institute of Metal Physics (National Academy of Sciences, Kiev, Ukraine). She works mainly in the field of interdiffusion modeling, Kirkendall and Frenkel effects, phase transformations in binary alloys.



Dr. Tomi Laurila received his DSc degree (with honors) in 2001 and an adjunct professorship in 2006, both from Helsinki University of Technology (HUT). Currently he acts as Associate Professor in the field of microsystem technology in Aalto University. His research is focused on the study of interfacial reactions between dissimilar materials used in microsystems, biocompatibility issues related to different types of (bio)materials, properties and synthesis of hybrid carbon nanomaterials and electrochemical measurements of different biomolecules under in vitro and in vivo conditions. He has contributed to two text books dealing with interfacial compatibility issues and thermodynamics of solid state diffusion as well as published over 80 scientific papers and several book chapters.



Dr. Vesa Vuorinen received his DSc degree in Electronics Production Technology from the Helsinki University of Technology in 2006. The thesis was focused on the common interfacial reactions encountered in lead-free electronics. Since then he has been working as a research scientist and senior university lecturer in the group of Electronics Integration and Reliability at Aalto University. His research includes manufacturing and reliability of high-density electronics assemblies with emphasis on interconnection metallurgy. He has also been responsible for teaching physics of failure and reliability assessment in electronics and direct research co-operation with the industrial partners for the last 20 years. He has been involved in the creation of international electronics assembly technology standards (IEC) and contributed to two textbooks dealing with interfacial compatibility issues and thermodynamics of solid state diffusion, as well as published over 35 scientific papers and several book chapters.



Dr. Hongqun Dong is a postdoctoral researcher in the Department of Electronics, Aalto University School of Electrical Engineering, Espoo, Finland. She received her doctoral degree in Electronics Integration and Reliability from the Aalto University. Since 2006, she has been focusing on designing interconnect materials for electronic packaging with the method of thermodynamic calculations. She has strong background in Materials Science and Engineering, and thermodynamics, as well as considerable knowledge in Electronic packaging, Mechanics and Numerical Computation. Her



current research interests include: developing a reliable metallization bonding system for 3D-stacking; finding out the factor that would affect the mechanical properties of the bonding joints; using the combined Thermodynamics–Kinetics approach to predict the evaluation of the bonding joints thus to provide a clue for the packaging reliability, and the recovering the metals elements from WEEE.

Praveen Kumar received his BTech degree from the Indian Institute of Technology, Kanpur, India, in 2003, and his PhD degree in Mechanical Engineering from the University of Southern California, Los Angeles, USA in 2007. He is currently an assistant professor at the Department of Materials Engineering at Indian Institute of Science, Bangalore, India. His current interests include materials and mechanics related reliability issues in microelectronics and MEMS devices and mechanical behavior, including effect of electric field or electro-mechanical coupling on the mechanical behavior of materials at different length scales. He teaches graduate level courses on mechanical behavior, finite element analysis and materials design and development, and an undergraduate level lab course on mechanical behavior. He has published more than 50 journal papers in different areas and 3 book chapters on mechanics and materials related issues microelectronic packaging.



Dr. Alexandre Kodentsov (formerly with Eindhoven University of Technology) is at present affiliated with the Development & Testing department of Mat-Tech BV (The Netherlands). His primary research interests are in thermodynamics and kinetics of solid-state reactions, phase transformations in solids, joining of dissimilar materials, corrosion, electron microscopy, electron-probe microanalysis, X-ray and electron diffraction. The scientific activity resulted in more than 140 publications, including a number of patent applications.



Dr. Arijit Laik is a scientist at the Materials Science Division of Bhabha Atomic Research Centre, Mumbai, India since 2000. His major field of research is solid state diffusion in metals and alloys, reactions at the interfaces between dissimilar materials and advanced joining techniques. He is also an adjunct faculty member of the Homi Bhabha National Institute, Mumbai where he teaches courses on solid state diffusion, phase transformation and welding science and technology. He has coauthored over 30 articles in various international journals. He is the recipient of Homi Bhabha Prize (2000), Young Engineer Award (2007) by the Department of Atomic Energy of India and Young Metallurgist of the Year (2011) by the Ministry of Steel, Government of India.



Dr. Gautam Kumar Dey is a Distinguished Scientist and the Director of the Materials Group of Bhabha Atomic Research Centre (BARC), Mumbai, India. He is also the Dean-Academic (Engineering Sciences) for BARC and a Senior Professor at Homi Bhabha National Institute, Mumbai. He obtained his BTech and PhD degrees from Banaras Hindu University. The areas of his research interest are phase transformation in zirconium and nickel based alloys, amorphous alloys, rapidly solidified crystalline and quasicrystalline alloys, and defect characterization using high resolution electron microscopy. He has more than 300 scientific publications to his credit. He has been a Visiting Scientist at University of Osaka, Japan and Institut für Festkörperforschung, Jülich, Germany. He is the recipient of several awards such as the Young Scientist award of Indian National Science Academy (1989), MRSI Medal by Materials Research Society of India (2001), Metallurgist of the Year award by Ministry of Steel (2003). He is a fellow of the Indian National Science Academy, Indian National Academy of Engineering, Indian Academy of Science, Electron Microscopy Society of India, and Asia Pacific Academy of Materials.



Dr. Dominique Mangelinck is a CNRS research director in the Institute Materials Microelectronics Nanosciences of Provence, National Center for Scientific Research and Aix-Marseille University. He was leading the reaction and diffusion at interfaces project until 2013, and now he is in charge of the atom probe platform. He is teaching master courses on materials and process for microelectronics. His research is focused on reactions and diffusion in thin film, particularly for microelectronics and on phase transformations in steels, alloys, and nanomaterials. He has coauthored more than 140 articles in various international journals, holds several patents, and has written a book chapter in the field of Diffusion in Solids.



PREFACE

Diffusion in solids is one of the most important topics in Materials Science and Solid State Physics. Understandably, numerous books were written in last 100 years by different authors. After going through the books available, one can easily understand that the topics covered in a particular book are naturally biased towards the research fields and the knowledge of the authors. There are no books available which cover many important aspects with equal importance from basic fundamentals and materials applications, experimental methods, and simulations to diffusion in ordered compounds, thin films, and nanomaterials. There are few books available which introduce the methods, estimation steps, and a particular analysis in various material systems in such a way that students and researchers can learn these by reading from a single book. Various types of diffusion coefficients and their physical significance may not be easy to follow from the existing literature.

Therefore, this book was planned such that the important aspects mentioned above were covered in one place with equal importance. As the title suggests, the topics are introduced in a very concise manner with a straightforward guidance for estimation of the data and their analysis. Chapters in Volume 1 mainly include the fundamental methods, whereas studies in various materials systems are covered in Volume 2. It is true that most of the chapters are mainly written on metallic systems, since, as a first step, we had to make this effort possible. In the next edition, many new topics and material systems will be included.

ACKNOWLEDGMENT

We are grateful to all the authors of this book for making it successful. Along with scientific contributions, their continuous and unconditional support to clear all the hurdles we have faced is greatly acknowledged. We do not find proper (or enough) words to thank all of them.

We thank our mentors, Prof. Frans J.J. van Loo and Dr. Alexander Kodentsov, Eindhoven University of technology (of Alope Paul), Prof. Leonid N. Larikov, National Academy of Science. Kiev, Ukraine and Prof. Christian Herzig, University of Münster, Germany (of Sergiy V. Divinski) for teaching us this fascinating subject. We were very lucky to work with such pleasant and knowledgeable personalities. We still cherish those golden periods! Even today our thinking and analysis of the scientific problems are greatly influenced by them.

We thank our students, collaborators, and colleagues for their help on many aspects throughout our professional careers.

Professional career and achievements are meaningless without an excellent personal life. In that sense, we are fortunate for all the support and joyful moments that were given to us by our families:

Bhavna, wife, Pihu, daughter of Alope Paul;

Sveta, wife, Veronika and Alisa, daughters of Sergiy Divinski.

CHAPTER 1

Diffusion Measurements in Nanostructures

Alain Portavoce, Jacques Perrin-Toinin, Khalid Hoummada

IM2NP, CNRS & Universités d'Aix-Marseille et de Toulon, France

Tens-of-nanometers-thick films, heterogeneous nanostructures, and embedded nanoobjects (nanowires, nanodots, etc.) are increasingly used in different industries (microelectronic, photovoltaic, advanced metallurgy, etc.) [1–12], to produce materials and devices exhibiting unique properties or functionalities. As usual for technology development, it is important (i) to be able to simulate the processes allowing for the fabrication of the desired material for economic reasons, and (ii) to be able to predict the material ageing for reliability reasons, as a material's properties (mechanical, electrical, thermoelectrical, opto-electrical, etc.) depend on atomic structure and distribution. In both cases, during fabrication processes and ageing, the knowledge of atomic diffusion coefficients is essential in order to predict atomic redistribution by means of technology computer-aided design (TCAD) tools [13–20]. However, the knowledge of bulk diffusion coefficients is not enough to model atomic redistribution in the case of nanostructures, since size reductions involve the possibility for atoms to use new diffusion paths, such as interfaces (particularly nanointerfaces), and interface intersections. In addition, atomic transport in nanovolumes (such as nanocrystals) may be different from usual bulk diffusion (different point defect concentrations, for example). For instance, in current microelectronic devices, the interconnections are made of Cu lines exhibiting a very thin width (nanometric scale). Cu was already used to reduce atomic electromigration in Al interconnections in previous technologies [21–24], and thus, Cu electromigration was expected to be negligible in the more recent technologies. Unfortunately, due to size reduction, electromigration is now principally taking place at interfaces between the interconnection lines and the dielectrics. Consequently, electromigration is still a problem, even in technologies using pure Cu lines [23,25–28]. Experimental measurement of atomic diffusion in nanomaterials is quite challenging. Classical measurement methods (comparison between atomic distribution before and after annealing) may not be relevant in nanostructures, since the diffusion length ($\sim$ nanocrystal size) can be similar to the depth resolution of conventional chemical analysis techniques such as secondary ion mass spectrometry (SIMS), for example. In addition, the few techniques that allow chemical measurement in nanovolumes to be performed (such as atom probe tomography) are destructive, and due to the small analysis scale, correspond to a reduced statistic,

increasing the measurement error on the diffusion coefficient. In particular, each profile before and after annealing is measured in different nanocrystals without (or with very small) average data. Thus, nanocrystal inhomogeneities (size, composition, etc.) can lead to a significant error of the diffusion coefficient measured from atomic distributions obtained in two different nanocrystals, before and after annealing. Due to experimental issues, today's atomic diffusion studies in nanostructures have been mainly performed in nanocrystalline materials (bulk and nanofilms) [29–36], giving access to diffusion coefficients in nanograins (i.e., nanocrystals) [33], in nanograin boundaries (GBs) (i.e., interfaces between crystals of same nature) [37], as well as in triple junctions (TJs) (i.e., interface intersections) [37]. Atomic diffusion coefficients were measured in different types of nanocrystalline materials (metals [32], semiconductors [35,37], etc.), and under different conditions: (i) at thermodynamic equilibrium [37], (ii) out of equilibrium [38], (iii) during GB migration [39,40], and (iv) during interfacial reaction [41]. This chapter focuses on the experimental methods that have been used to date to quantitatively measure atomic transport kinetic in nanocrystalline materials.

1.1 ANALYTICAL SOLUTIONS

Classically, diffusion coefficients are measured using the comparison between the initial atomic distribution measured in the sample before annealing and the final atomic distribution measured in the same sample after annealing. Usually, these distributions are measured in one dimension (1D) using a profiling technique, such as secondary ion mass spectrometry (SIMS), allowing the impurity 1D profile versus depth to be determined in the sample. In the case of regular polycrystalline materials, the lattice diffusion coefficient in grains is considered to be the same as the lattice diffusion coefficient measured in monocrystals. The GB diffusion coefficient is thus measured using analytical solutions corresponding to the two-dimensional (2D) Fisher model in the kinetic regime *B* (from Harrison classification [42]), taking into consideration either a constant diffusion source (complementary error function) or an instantaneous source (Gaussian function) [43]. It may be noted that only the diffusion profile (after annealing) needs to be measured in this case, as analytical solutions generally assume an initial diffusion source located on the surface of the sample [44–46]. As GB diffusion is several orders of magnitude faster than lattice diffusion, diffusion experiments are in general performed at significantly higher temperatures (*T*) for monocrystals compared to polycrystalline materials [47, 48]. Consequently, a first drawback of the method is the use of high-temperature lattice coefficients as diffusion coefficients in grains, extending the Arrhenius law measured at high temperatures to the low temperatures at which GB coefficients are measured. In doing so, the lattice diffusion mechanism in grains is assumed to be the same at high and low temperatures, which is not evident since point defect concentrations (and thus proportions) can vary significantly between low and high temperatures (with a larger

concentration of monovacancies at low T and a larger concentration of divacancies at high T , for example). A second drawback of the technique is that the Fisher model does not consider the influence of TJs. Consequently, the use of the classical analytical solutions in the kinetic regime B does not allow the measurement of diffusion coefficients in nanograins and triple junction in nanocrystalline materials. However, in the case of diffusion studies in bulk nanocrystalline materials, in specific kinetic regimes ($C-A$, $C-B$, etc. [49]) in which diffusion in grains is negligible, the usual solutions of the diffusion equations can be used to investigate nano-GB diffusion and TJ diffusion. Usual experimental techniques exhibit a good statistic on atomic distribution in grains and grain boundaries. Indeed, SIMS measurements or radiotracer experiments performed on nanocrystalline materials give average atomic distributions related to a large number of nano-GBs and TJs, allowing for the measurement of average diffusion coefficients in both types of diffusion paths. Diffusion experiments performed in kinetic regime C (between the grains and the GBs) allow solutions corresponding to homogeneous matrices to be used (1D model, no need for 2D Fisher model), such as the instantaneous (Gaussian function) and the constant (Error function) source solutions [28]. In this regime, an effective diffusion coefficient can be measured. Thus, assuming a kinetic regime A between GBs and TJs, the diffusion coefficient can be expressed as a function of the GB diffusion coefficient D_{gb} and of the TJ diffusion coefficient D_{tj} using the classical Hart equation

$$D_{eff} = (1 - f)D_{gb} + fD_{tj} \quad (1.1)$$

or using a Maxwell–Garnet-type relation

$$D_{eff} = D_{gb} \frac{2(1 - f)D_{gb} + (1 + 2f)D_{tj}}{(2 + f)D_{gb} + (1 - f)D_{tj}} \quad (1.2)$$

with f being the volume fraction of triple lines in the sample. These two equations do not take into account the segregation of impurities in the GBs or in the TJs. In the case of $f \ll 1$ and assuming $D_{gb}/D_{tj} \ll 1$, Eq. (1.2) can be reduced as follows:

$$D_{eff} \cong D_{gb} + \frac{2}{3}fD_{tj}, \quad (1.3)$$

$$D_{tj} = \frac{3}{2} \frac{1}{f} (D_{eff} - D_{gb}). \quad (1.4)$$

For example, Ni GB diffusion in bulk nanocrystalline Cu was measured in the $C-A$ kinetic regime using radiotracer experiments [50]. Nanocrystalline Cu was prepared by spark plasma sintering, and was made of ~ 40 nm-wide grains. Fig. 1.1A presents the Ni diffusion profiles (symbols) measured in nanocrystalline Cu at different annealing temperatures, and Fig. 1.1B shows the effective GB diffusion coefficients (symbols) measured in nanocrystalline Cu compared with Ni GB diffusion in regular polycrystalline

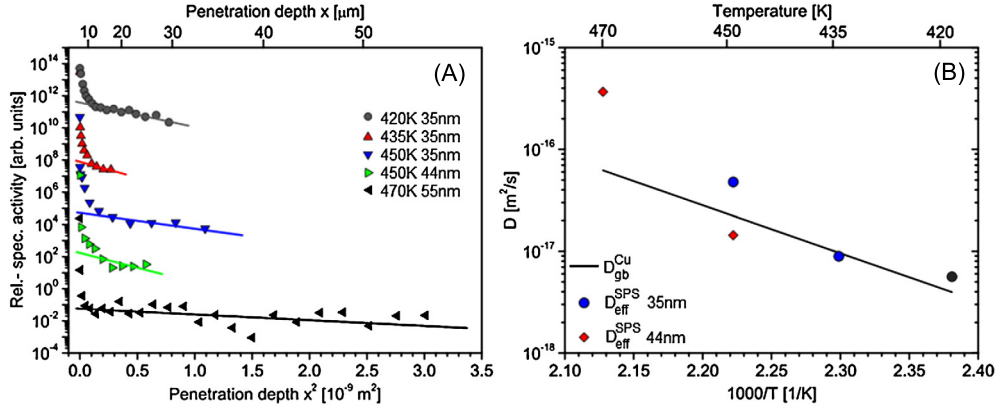


Figure 1.1 Ni GB diffusion in nanocrystalline Cu: (A) Ni diffusion profiles (solid symbols) at different temperatures, and (B) Ni diffusion coefficients compared to Ni GB diffusion in regular polycrystalline Cu (solid line). From Wegner et al. [50].

Cu (solid line). Nano-GB diffusion was found to be similar to micro-GB diffusion. GB size reduction has no influence on atomic transport in GBs. TJ diffusion coefficients were also determined from the coefficients presented in Fig. 1.1B using Eqs. (1.1) and (1.4). On average, D_{TJ} was found to be about 500 times larger than D_{gb} at the same temperature. Ni GB diffusion was also studied in nanocrystalline Cu prepared by severe plastic deformation (SPD) [51] which is expected to produce out-of-equilibrium materials [52–54]. In this study, the grains exhibited an average lateral size between 100 and 500 nm, depending on the investigated samples. The diffusion profiles exhibited two linear portions with different slopes when plotted versus the square of depth, corresponding more to a C – B kinetic regime. Two different diffusion coefficients were obtained from the two slopes corresponding to a fast GB diffusion and a slow GB diffusion. Fig. 1.2 presents the Ni GB diffusion coefficients measured in SPD nanocrystalline Cu (solid symbols for slow diffusion and open symbols for fast diffusion) compared to Ni GB diffusion in regular polycrystalline Cu (solid line). The slower diffusion coefficient is in good agreement with classical GB diffusion, confirming that atomic transport in nano-GBs is similar to classical GB diffusion. The faster diffusion coefficient is about one to two orders of magnitude larger than GB diffusion. This diffusivity was not attributed to TJ diffusion due to the size of the grains, considered to be too large to cause a significant effect of TJs ($100 \leq d \leq 500$ nm). The origin of this fast diffusion in SPD nanomaterials is still under discussion, but this faster diffusivity was proposed to be related to atomic transport in nonequilibrium GBs. Further experiments [55] concluded that in the case of metallic nanocrystalline materials, the production methods can cause the formation of “new” types of diffusion paths, exhibiting faster atomic transport kinetics than GBs. Nanocrystalline materials can thus be considered as made of

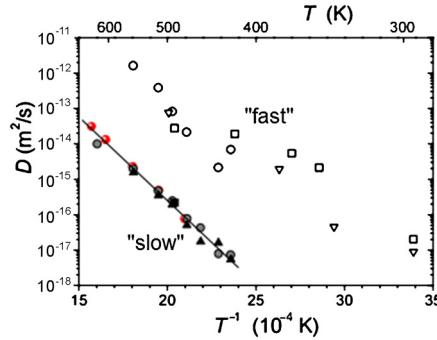


Figure 1.2 Ni GB diffusion coefficients measured in nanocrystalline Cu produced via SPD (2D symbols) compared with Ni GB diffusion in high-purity coarse-grained polycrystalline Cu (spheres and solid line). From Divinski et al. [51].

several interconnected networks of short-circuit diffusion paths, as presented in Fig. 1.3. For example, Ni GB self-diffusion coefficients (radiotracer method) and Au GB diffusion coefficients (Rutherford backscattering profiles) were measured in nanocrystalline Ni made of 50 to 70 nm-wide grains [56]. The nanocrystalline Ni was obtained by the evaporation–condensation method. The diffusion coefficients were measured using conventional analytical diffusion solutions in the kinetic regime *C*, and in the kinetic regime *C–B* (Suzuoka’s and Whipple’s solutions [57]). Two different diffusivities were also observed. The slowest corresponded to GB diffusion, while the fastest exhibited activation energies similar to surface diffusion activation energies. The sample structure was thus proposed to contain interagglomerate boundaries as well as pores, as shown in Fig. 1.3, in which atomic transport mechanisms could be of same type as on a surface. Similar diffusion paths as interagglomerate boundaries or cluster boundary and pores observed in nanocrystalline metals can also be encountered in nanostructures made of dense arrays of nanodots or nanowires produced via different fabrication processes [1–3, 5,6,9,10,58,59].

1.2 SIMULATIONS

Due to the smaller size-difference between GB width ($\delta \sim 0.5$ nm) and grain width (d) in nanocrystalline layers, the use of diffusion simulations, instead of the use of analytical solutions of the diffusion equation, to fit experimental profiles and extract diffusion coefficients is technically easier. Indeed, the use of analytical solutions allows exact results to be obtained in a very short time. However, in order to obtain an analytical solution of the diffusion equation, the geometry (nanocrystal in our case) and the diffusion conditions (boundary limits) are generally simplified. Consequently, the use of solutions is

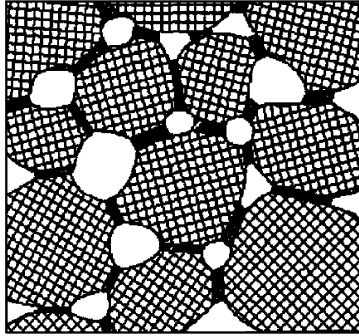


Figure 1.3 Schematic showing in addition to regular GBs (thin black lines), new diffusion paths resulting from sample fabrication, such as interagglomerate boundaries (thick black lines) and voids (white surfaces). From Bokstein et al. [56].

restricted to a very narrow set of experiments, for which the kinetic diffusion regime is well known (A , B , or C , etc. [42]). In contrast, simulations allow the investigation of all geometry types (with TJs, for example) and all boundary condition types (with GB migration, for example), and do not require the knowledge of the exact diffusion kinetic regime. However, in order to fit diffusion experimental profiles, simulations must be performed at the laboratory scale (time, sample size, etc.). The simulations are time consuming and can reduce the effectiveness of the experimental profile fitting procedure. In addition, numerical simulations, such as finite element simulations (FES), only provide an “approached” result containing numerical errors that depend on the quality of the simulation settings (shape, size, number, and distribution of finite elements, for example). The main limitation of simulations is the calculation time (computer performances). Thus, the reduction of the grain size in nanocrystalline materials, as well as the reduction of the thickness of the matrix (nanolayers) encourage the use of simulations as opposed to regular polycrystalline materials, in which diffusion needs to be simulated simultaneously in a very narrow region such as the GB and in a significantly larger region such as the grain, in a sample of several tens of microns, increasing the number of finite elements needed to get a valid results via FES. The use of simulations allows different scenarios to be investigated, meaning that the geometry and the diffusion model can be changed (static GBs, all the GBs moving, only a fraction of GBs moving, cluster formation or not, clusters dissolution or not, GB segregation or not, etc.) and the respective simulation results can be compared to the experiments, in order to determine the diffusion mechanisms (lattice diffusion, GB diffusion or mixed lattice and GB diffusion, for example) involved in the case of interest, before extracting the diffusion coefficient. Additional parameters such as impurity solubility and cluster dissolution kinetics can also be extracted independently from the diffusion coefficient. For example, B diffusion was studied in a 100 nm-thick Si nanocrystalline layer made of 40 nm-wide grains [36].

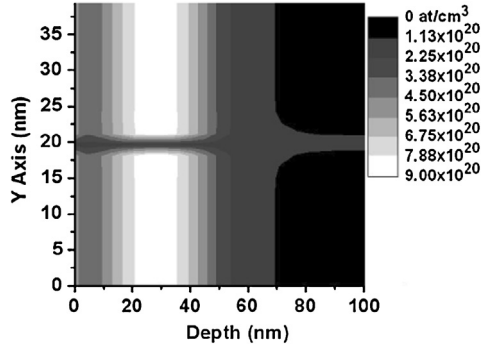


Figure 1.4 2D model used to simulate B diffusion in a 100 nm-thick nanocrystalline Si layer [36]. The model corresponds to the Fisher geometry with a GB located between two half of a grain. The gray scale corresponds to the B concentration variations in the simulation cell after annealing at 650°C for 2570 minutes.

In this study, several experimental conditions prevented the use of classical analytical solutions to measure the B diffusion coefficient: (i) the B atom source was implanted in the sample instead of being located on the sample surface, (ii) the diffusion kinetic was unknown (considering that lattice diffusion could be different in nanograins), and (iii) the sample was a thin film and not a semi-infinite substrate. 2D simulations using the Fisher geometry were performed using a grain size and a GB size set to $d = 40$ nm and $\delta = 0.5$ nm, respectively (Fig. 1.4). Different scenarios were simulated leading to the conclusion that the best way to fit the experimental profiles required that B clusters were formed at the very beginning of annealing for concentrations larger than 2×10^{20} at cm^{-3} , and that these clusters did not dissolve during the rest of the annealing time. The simulations also concluded that the diffusion occurred in the kinetic regime B. One of the most important contributions of this work was to demonstrate that the two diffusion coefficients in the grains (D_g) and in the GBs (D_{gb}) could be independently adjusted in the simulation in order to fit each single experimental profile (Fig. 1.5). Only a single set of D_g and D_{gb} coefficients could reproduce the shape of each given profile, due to the fact that D_g and D_{gb} influence differently the shape of the simulated profile. Thus, the lattice diffusion coefficient in 40 nm-wide nanocrystals and the GB diffusion coefficient in nano-GBs could be measured. The values of D_g and D_{gb} were found to be $9 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$ and $5 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 650°C, respectively. These results are similar to the diffusivities measured in regular polycrystalline Si [60–63]: at the same temperature, D_g is expected to be comprised between $9.8 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$ and $5.6 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$, and D_{gb} is expected to be comprised between $9 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ and $2.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. No obvious differences in atomic transport kinetic were observed in this work between an infinite crystal and a nanocrystal, nor between regular GBs and nano-GBs. However, one has to note that diffusion coefficients were measured

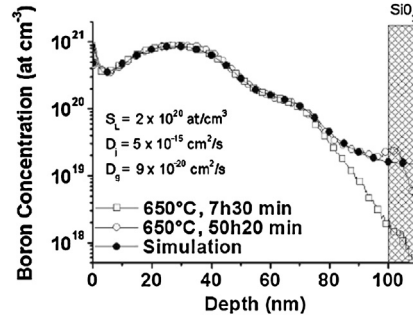


Figure 1.5 B diffusion experimental profiles measured by SIMS in a 100 nm-thick nanocrystalline Si layer (open symbols) compared to the simulated profile (solid symbols) obtained using the model presented in Fig. 1.4, considering a B solubility limit $S_L = 2 \times 10^{20}$ at cm^{-3} , $D_g = 9 \times 10^{-20}$ $\text{cm}^2 \text{s}^{-1}$ and $D_{gb} = 5 \times 10^{-15}$ $\text{cm}^2 \text{s}^{-1}$ [36].

at a single temperature (no Arrhenius plot) over a very short distance (diffusion length ~ 30 nm), and TJs were not considered. According to this work, the diffusion coefficients in grains and GBs in nanocrystalline layers can be simultaneously measured by performing FES based on the Fisher geometry. In a first step, the 2D geometry containing, for example, half a grain and half a GB is defined using the experimental sizes of the layer, of the grains (average size), and of the GBs (commonly accepted to be 0.5 nm [64]). The geometry needs to conserve the correct (experimental) proportion between atoms in grains and GBs in order that an average 1D profile can be calculated at the end of the 2D simulation to be compared with the 1D experimental profile measured after annealing. In addition, the system symmetry should be used to reduce as much as possible the size of the simulation cell, so as to reduce the calculation time. Thus, the finite elements are chosen to take into account the geometry properties (size difference between grains and GBs, for example) as best as possible, as well as the concentration variation amplitudes in the simulated sample (concentration variations at the grain/GB interface, for example), see, e.g., Fig. 1.6. With regular profiling methods, experiments only provide a 1D profile resulting from the concentration average between concentrations in grains and in GBs. Thus, the initial distribution is assumed to be identical in grains and GBs before annealing. The experimental profile measured before annealing is then used as the initial distribution in the entire simulation cell as shown in Fig. 1.7. At that point, the diffusion can be simulated considering the Fick's equation (constant diffusion coefficients in grains and GBs) resolved in the two space directions of the simulation cell (x and y in Figs. 1.6 and 1.7), considering Neumann boundary conditions allowing for atomic diffusion through the grain/GB interface and flux reflection at the exterior boundary (along the symmetry boundaries). The simulation time is fixed to be the same as the experimental annealing time, leaving only two unknown parameters to be determined, D_g and D_{gb} . A segregation effect at the grain/GB interface can be

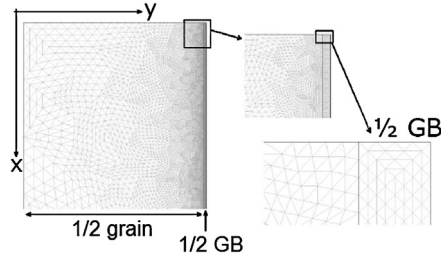


Figure 1.6 Example of the 2D geometry used for 2D FES aiming to simultaneously measure D_g and D_{gb} in a nanocrystalline layer. The geometry contains half a grain and half a GB in order to conserve the correct proportion between atoms in grains and GBs when calculating the 1D average profile to be compared with an experimental profile. The finite elements filling the simulation cell are shown.

added if needed [65], considering either the Henry law or the McLean law [66–68]. Fig. 1.8 presents the impurity concentration in the 2D geometry after annealing simulation. The concentration variations between the grain and the GB are easily observed due to the significant difference between the diffusion coefficients in the grain and in the GB. The diffusion profile in the GB is almost flat, while a Gaussian distribution is still visible in the grain. The isoconcentration lines shown in Fig. 1.8B are similar to the ones obtained with the analytical solution of the Fisher model corresponding to an instantaneous source in kinetic regime B [64]. After the simulation, the 2D distribution can be averaged in the depth direction in order to obtain a 1D concentration profile that can be compared to the experimental profile measured after annealing. Fig. 1.9

shows the 1D average profile corresponding to the 2D distribution presented in Fig. 1.8 as well as the concentration profiles in the grain and in the GB. Thus, the fitting procedure consists of (i) adjusting the values of D_g and D_{gb} independently, (ii) performing 2D simulation, (iii) calculating the 1D simulated profile, and (iv) comparing the simulated and experimental profiles, until a satisfactory agreement is reached. This method was shown to give diffusion coefficients with a typical error comprised between 5 and 20%. Using this technique, the lattice diffusion coefficient in grains can be determined at the same temperature as the GB diffusion coefficient. Despite the use of a profiling technique that could not provide the resolution to study atomic transport over a short diffusion length in the tens-of-nanometer scale, the lattice diffusion coefficients can be measured for such short distances because the overall concentration profile is significantly dependent on the diffusion from the GB to the grain. For this reason, in this type of experiments, lattice diffusion coefficients can be measured at lower temperatures than during regular experiments studying diffusion in monocrystals. For example, As diffusion was studied in a 250 nm-thick Ni_2Si layer made of columnar grains with an average width of 210 nm using the same technique [34]. The As source was implanted in the sample. As the Ni_2Si layer was located between two SiO_2

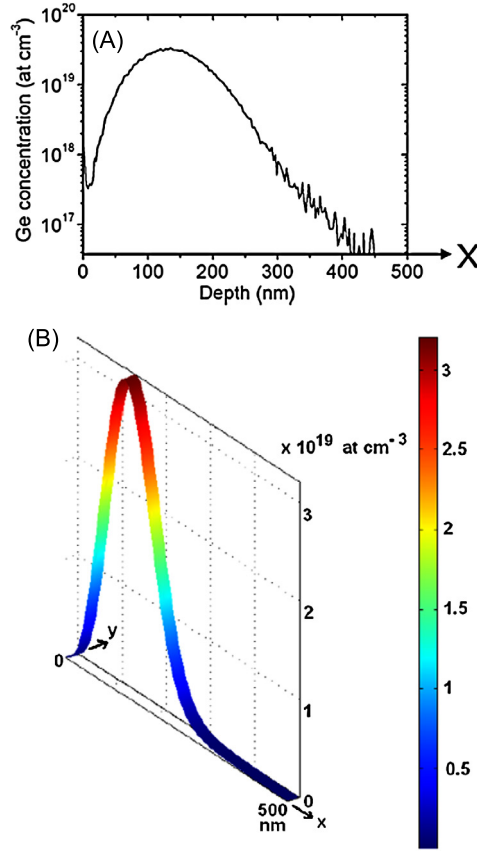


Figure 1.7 (A) 1D Ge experimental profile measured by SIMS in a Si nanocrystalline layer before annealing. (B) The same profile used as initial distribution in grains and GBs in the 2D geometry used for diffusion simulation. From [65,107].

layers acting as diffusion barriers, the simulations were performed using a 2D geometry taking into account a fast atomic diffusion along the $\text{Ni}_2\text{Si}/\text{SiO}_2$ interfaces. The As diffusion coefficients were found to be $D_g = 1.5 \times 10^{-1} \exp(-2.72 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ and $D_{gb} = 1.8 \times 10^5 \exp(-3.07 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. Fig. 1.10 presents the As diffusion coefficients simultaneously measured in the nanofilm (solid circles) with Ni self-diffusion coefficients measured in bulk materials (solid squares) [69] for comparison. Despite the fact that the Ni lattice self-diffusion is two orders of magnitude faster than the As lattice diffusion in Ni_2Si , one can note that the lowest temperature at which the Ni lattice diffusion coefficient was measured in a bulk sample was $\sim 650^\circ\text{C}$, whereas using the 2D simulations, the As lattice diffusion coefficient could be measured at a temperature $\sim 100^\circ\text{C}$ lower. The diffusion length of As atoms in grains during the different annealing

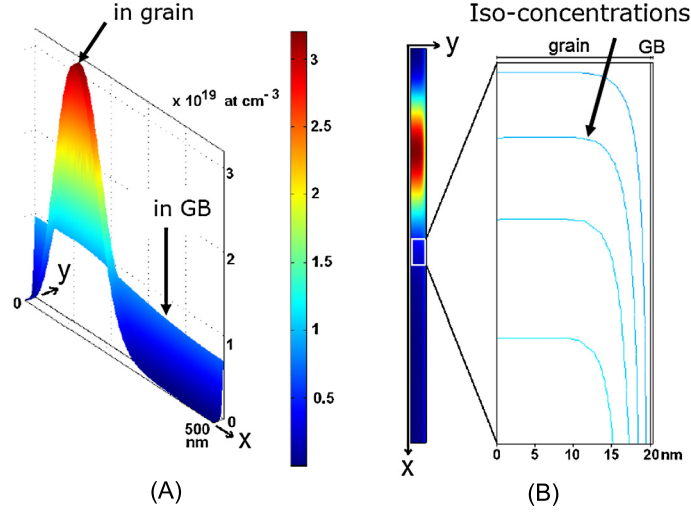


Figure 1.8 Concentration of the impurity in the 2D geometry after annealing simulation: (A) 3D view [65,107] and (B) 2D view showing also isoconcentration lines in an enlarged region located in the grain.

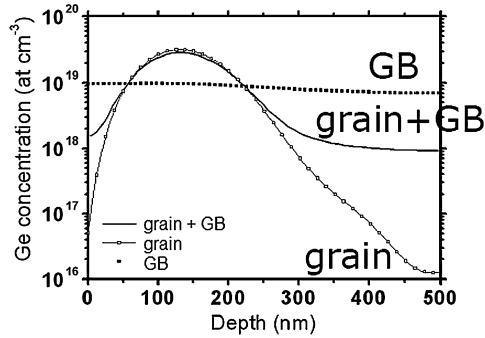


Figure 1.9 1D concentration profiles measured in the 2D geometry after annealing: the solid squares, the open squares, and the solid line correspond respectively to the concentration profiles in the GB, in the grain, and to the average profile [33,107].

allowing the As lattice diffusion coefficient to be measured was between 18 and 36 nm. The same remark can be made concerning the B lattice diffusion coefficient measured using the profiles presented in Fig. 1.5. In this case, D_g was measured at 650°C, corresponding to a B diffusion length in the grains of ~ 1.2 nm, while B diffusion in Si monocrystal is usually studied at temperatures higher than 750°C. Until recently, due to the low density of TJs in polycrystals, the influence of TJs on the effective diffusion coefficient in polycrystalline materials was thought to be negligible if the grains exhibited sizes larger than 10 nm [70]. However, the influence of TJs does not depend only

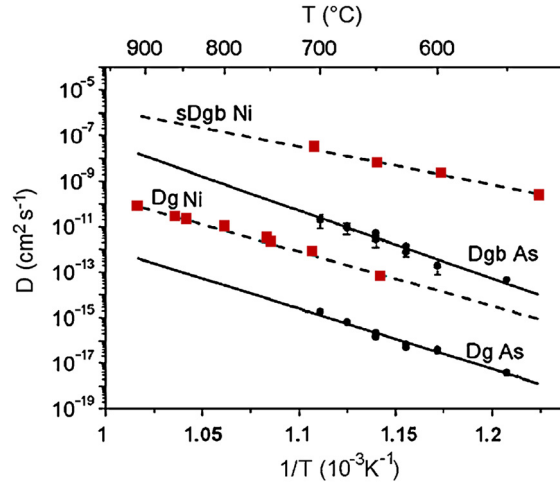


Figure 1.10 Diffusion coefficient measured in Ni_2Si . The squares correspond to Ni self-diffusion measured in bulk samples. The circles correspond to As diffusion measured in a 250 nm-thick film [34,65, 69,107].

on the TJs density in the material but also on the kinetic of atomic transport in TJs. Recent calculations suggested that TJs can influence atomic diffusion in nanocrystalline materials made of 100 nm-wide grains [71–73]. Furthermore, experiments shown that TJ diffusion can be three orders of magnitude faster than GB diffusion [74]. The same procedure described for 2D simulations can be used to perform 3D simulations that allow TJ diffusion to be taken into account in addition to grain and GB diffusion. For example, the diffusion of Ge atoms in a 500 nm-thick Si nanocrystalline layer made of 40 nm-wide grains was studied using both a 2D geometry and a 3D geometry, and compared to the diffusion coefficients measured in microcrystalline Si [33,37]. Ge diffusion in Si is fundamentally interesting since Si(Ge) layers can be produced with the same very high purity for mono-, micro-, and nanocrystalline layers, allowing for a relevant comparison between these different materials. In addition, Ge and Si are totally miscible, preventing any clustering effect during diffusion, and Ge segregation has not been observed in Si GBs. Finally, the Ge lattice diffusion mechanism in Si is known to be mainly vacancy-mediated up to 1000°C [75,76]. Fig. 1.11 presents the 3D geometry used to simulate diffusion in the Si nanocrystalline layer. It corresponds to the Fisher geometry defined in 3D with rectangular grains. Using the system symmetry, the simulation cell was reduced to a triangular volume containing 1/8th grain, 1/4th GB, and 1/8th TJ. After simulation, a 1D average profile was determined and compared to the experimental profile, as for 2D simulations. The study showed that without considering the TJs, the Ge lattice diffusion in the nanocrystals was one order of magnitude faster than in the Si monocrystal, and the Ge GB diffusion coefficient was found to be one order of

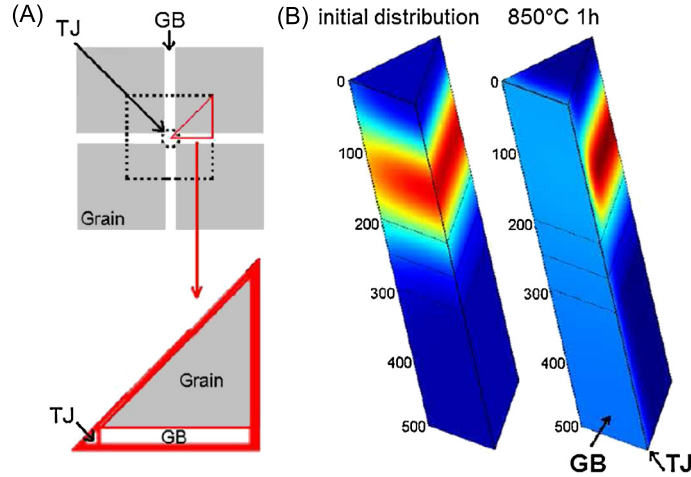


Figure 1.11 3D geometry used to measure Ge TJ diffusion in nanocrystalline Si [107]: (A) top view showing the reduction of the cell using symmetries; (B) 3D view before and after annealing [65].

magnitude larger than the GB diffusion coefficient measured in regular Si polycrystals. 3D Simulations shown that Ge GB diffusion was the same in nano- and micro-GBs, in agreement with former experiments [34,77–79]. Thus, using the D_{gb} measured in Si polycrystalline samples via analytical solutions, D_g and the TJ diffusion coefficient (D_{tj}) could be simultaneously measured from each experimental profile. Fig. 1.12A presents the diffusion coefficients measured in the sample versus temperature. In this case, D_g was found to be the same as the lattice coefficient measured using the 2D geometry, exhibiting a value about 10 times larger than in macroscopic Si crystals. D_{tj} was found to be three orders of magnitude larger than D_{gb} (with an average $D_{tj}/D_{gb} \sim 4.7 \times 10^2$), confirming that TJs are different defects from GBs [80–83]. These results show that, in nanocrystalline materials made of 40 nm-wide grains, the contribution of TJ diffusion to atomic transport is not negligible, and the study of atomic transport kinetic in this type of materials without taking into account TJs can lead to an erroneous overestimation of the GB diffusion coefficients. The diffusion enhancement observed in the 40 nm-wide nanocrystals needs to be further investigated. However, these results also lead to the conclusion that size reduction does not significantly modify the nature of interfaces, but can have an impact on the properties of point defects in crystals (change the concentration, for example). In the case of a semiconductor such as Si, the diffusion enhancement noted in nanocrystalline materials (at equilibrium) does not result from an increase of diffusion kinetic in GBs, but from a faster diffusion in TJs and a diffusion increase in nanocrystals. Fig. 1.12B shows the Arrhenius plots corresponding to $D_g = 1.97 \times 10^{-4} \exp(-2.92 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$, $D_{gb} = 31.65 \times 10^1 \exp(-3.34 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$, and $D_{tj} = 5.72 \times 10^4 \exp(-3.24 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. Ge diffusion coefficients measured in

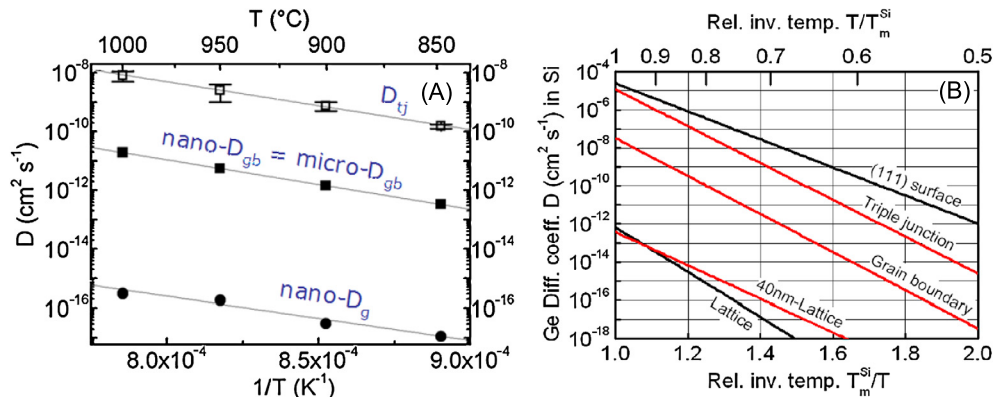


Figure 1.12 Ge diffusion measured in nanocrystalline Si: (A) diffusion coefficients in 40 nm-wide nanocrystals (solid circles), nano-GBs (solid squares), and nano-TJs (open squares) [37,65,107]; (B) comparison between diffusion kinetics measured in the Si nanocrystalline layer and in the Si monocrystal and on the Si (111) surface (T_m is the Si melting temperature) [107].

the Si nanocrystalline layer present convincing characteristics. Indeed, due to the Ge diffusion mechanism in Si, an increase of Ge diffusion in the nanograins could be explained by an increase of the vacancy concentration in the nanograins compared to a microscopic crystal. It was shown that reducing nanocrystal size can lead to a decrease of both the formation and the migration energy of Si vacancies [64,84–91]. It is thus expected that at high temperatures, close to the melting temperature, due to the significant increase of vacancy concentration in the Si crystal, the vacancy concentration difference between the microscopic and nanoscopic crystals should be negligible. This is indeed what is observed in Fig. 1.12B: $\text{nano-}D_g \sim D_g$ at high temperature. In addition, the Ge diffusivity found in TJs is larger than GB diffusion, but it is smaller than the Ge diffusion at the Si surface. One can note that Ge TJ diffusion is very close to the Ge surface diffusion at the melting temperature. This is in agreement with the premelting phenomenon that is expected to start first at the surface, and was shown to occur in TJs before extending to GBs [81]. After annealing, the dislocation density is expected to be smaller in nanograins due to the significant GB density allowing for dislocation annihilation. However, the increase of Ge lattice diffusion in 40 nm nanocrystals could still be also explained by the presence of extended defects in the nanograins. In order to investigate this possibility, atom probe tomography (APT) measurements were performed on the sample in which D_g , D_{gb} , and D_{tj} were measured using 2D and 3D simulations. Fig. 1.13 presents APT results measured in a sample annealed at 850°C for one hour. As shown in Fig. 1.13A, the distribution of Ge atoms was found to be entirely random and no Ge accumulation in any extended defects such as dislocation and GBs could be observed. In addition, Fig. 1.13B shows that the Ge profile measured by APT is in good agreement with the SIMS profile used to measure the diffusion

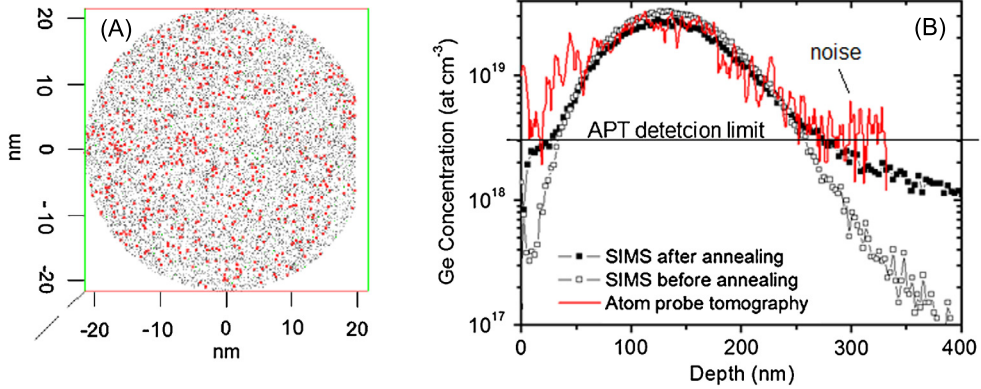


Figure 1.13 APT measurements performed in the Si noncrystalline samples in which the Ge lattice, GB and TJ diffusion coefficients were measured: (A) top view of the Ge (large red dots) and Si (small gray dots) atom distributions in a sample volume of $\sim 40 \times 40 \times 350 \text{ nm}^3$, and (B) comparison between the 1D profile measured in the same APT volume and the SIMS profile used to extract the diffusion coefficient using FES. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

coefficients. Consequently, the first part of the profile, which is principally dependent on lattice diffusion (and used to adjust D_g in the simulations), corresponds to Ge atoms randomly distributed in the grains, meaning that Ge atom diffusion in grains was not mediated by extended defects that would favor atomic distributions dependent on the symmetries of the extended defect (lines for dislocations, planes for GBs, etc. [92–95]). Consequently, the lattice diffusion increase in Si nanocrystals could be interpreted as an increase of vacancy concentration. Despite the prediction of decreased vacancy formation and migration energy in Si nanocrystals, this type of effect was expected to occur in nanocrystals exhibiting sizes of few nanometers [84,85,90]. Equilibrium point defect concentration in a crystal is reached thanks to point defect reactions in bulk and in extended defects such as surfaces, GBs, and interfaces [76,96–99]. The formation energy of point defects in extended defects is known to be smaller than in bulk, and the equilibrium concentration of point defects in extended defects and in their vicinity is known to be larger than in bulk. However, equilibrium point defect concentration measurements in bulk materials lead to different values with significant variations depending on the measurement methods [76], and equilibrium point defect concentration in extended defects are generally not quantitatively measured. In the case of Si, Si(111) surface melting was shown to occur at $T_{sm} = 0.84T_m$ (with T_m the Si bulk melting temperature), corresponding to $\Delta T_m = T_m - T_{sm} \sim 200^\circ\text{C}$ [100]. Considering that the vacancy concentration in a given material is proportional to its melting temperature, in a first approximation, the vacancy equilibrium concentration at a given temperature T at the Si surface could be considered to be equal to the bulk equilibrium concentration

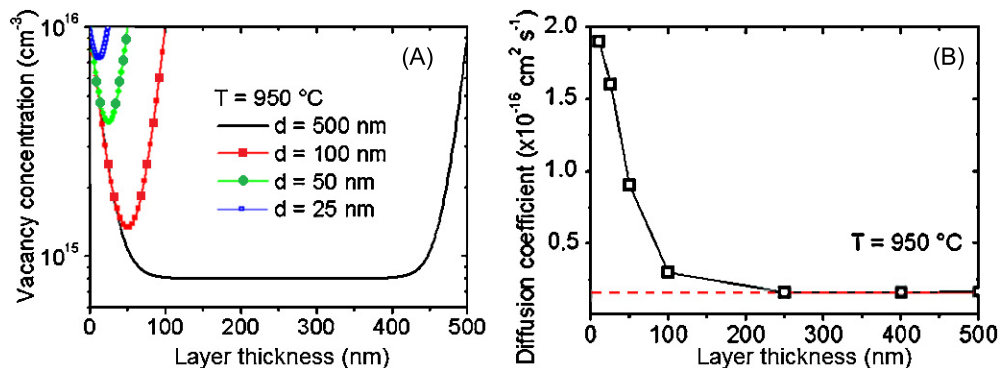


Figure 1.14 Simulations using the vacancy bulk equilibrium concentration and the vacancy diffusion coefficient from the literature, and a bulk vacancy annihilation/formation rate of $5 \times 10^2\text{ s}^{-1}$ [102]. The Ge diffusion was assumed to occur via the direct vacancy mechanism. (A) Vacancy concentration profile in a Si monocrystal versus its thickness, and (B) Ge lattice diffusion variations in the same Si crystal versus its thickness. The dash red line corresponds to the Ge lattice diffusion coefficient measured in the macroscopic Si monocrystal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

at $(T + \Delta T_m)$. For example, at 950°C , the vacancy bulk equilibrium concentration in Si should be $\sim 8 \times 10^{14}\text{ cm}^{-3}$ [101], and thus the surface equilibrium concentration would be $\sim 1 \times 10^{16}\text{ cm}^{-3}$. This difference is about one order of magnitude, which is typically the diffusivity difference found between the nanocrystal and the microscopic crystal. Following this approach, it was shown that depending on the vacancy diffusion coefficient and on the vacancy formation/annihilation rate in the material, the Si vacancy concentration could increase in a nanocrystal of tens-of-nanometers, with a value approaching the surface equilibrium value [102]. For example, Fig. 1.14 shows the variations of the vacancy concentration and the variations of the effective Ge diffusion coefficient versus the thickness of an Si monocrystal, considering the vacancy diffusion coefficient given in the literature and a bulk vacancy annihilation/formation rate of $5 \times 10^2\text{ s}^{-1}$. For these simulations, the Ge lattice diffusion was assumed to occur via the direct vacancy mechanism [64]. For a thickness of 500 nm, the bulk vacancy concentration is the same as the bulk equilibrium concentration, but close to the surface the vacancy concentration increases up to the surface equilibrium concentration. If the distance between the two surfaces of the crystal decreases, the vacancy concentration in the center of the crystal increases towards the surface equilibrium concentration value. Consequently, the Ge lattice diffusion coefficient increases when the crystal thickness decreases to values smaller than 100 nm. The simulations show that this phenomenon does not result only from a difference of vacancy equilibrium concentration between the bulk and the surface, but depends significantly on the vacancy diffusivity and the bulk vacancy annihilation/formation rate.

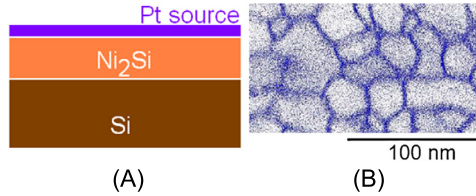


Figure 1.15 (A) Schematic of a sample made of a 65 nm-thick Ni₂Si nanocrystalline layer containing Pt atoms, and (B) top view of an APT volume measured in this sample: only Pt atoms (dots) are shown [107].

1.3 ATOM PROBE TOMOGRAPHY

Analytical solution of the diffusion equation and the use of FES can allow the diffusion coefficients to be measured in nanostructures, and in particular in nanocrystalline materials, using 1D diffusion profiles measured in the samples with classical tools such as SIMS for example. However, a second approach consists of using the same method based on the fit of 1D profiles to measure diffusion coefficients, but by means of original experimental tools that possess the resolution to measure diffusion profiles in nanostructures, and in particular in interfaces. APT is one of the rare techniques able to determine the chemical composition of a sample at the atomic scale, in the three space directions (x , y , and z). During an APT experiment, the atoms composing the sample are ionized and evaporate one by one, allowing the reconstruction of the sample (shaped as a tip with a diameter varying typically between 40 and 250 nm) at the atomic scale [103–106]. Classically, 50% of all the atoms composing the sample are collected, identified thanks to time-of-flight mass spectrometry, and positioned in the sample volume thanks to a 2D detector (x and y coordinates) and a reconstruction procedure (z coordinates) [103–105]. This technique allows composition profile measurements in nanovolumes, in GBs (interfaces) and in triple joints. For example, Fig. 1.15 presents the schematic of a sample made of a 65 nm-thick Ni₂Si nanocrystalline layer containing Pt atoms, as well as an APT volume measured in this sample [94,107]. After the formation of the Ni₂Si layer via the reaction of an Ni layer with a Si substrate, Pt atoms located on the Ni₂Si surface could diffuse in the Ni₂Si layer during annealing at 250°C. In Fig. 1.15B only Pt atoms (dots) are shown. Pt atoms are principally located in Ni₂Si GBs, revealing the columnar nanograins forming the Ni₂Si layer (top view). TJs can be easily detected. APT allows direct concentration measurements in the three spatial directions without the need for calibration, and without matrix effect and mixing effect, generally involved with classical profiling methods [10–105]. Usually, APT microscopy allows a magnification of 10^6 times, a lateral resolution between 0.05 and 0.3 nm at an analyzing temperature lower than 100 K, a depth resolution smaller than 0.07 nm in best cases, and a field of view between 50 and 250 nm. With a detection yield of 50%, the detection limit varies between $\sim 10^{18}$ and 5×10^{19} at cm^{-3} depending on the size of the analyzed volume.

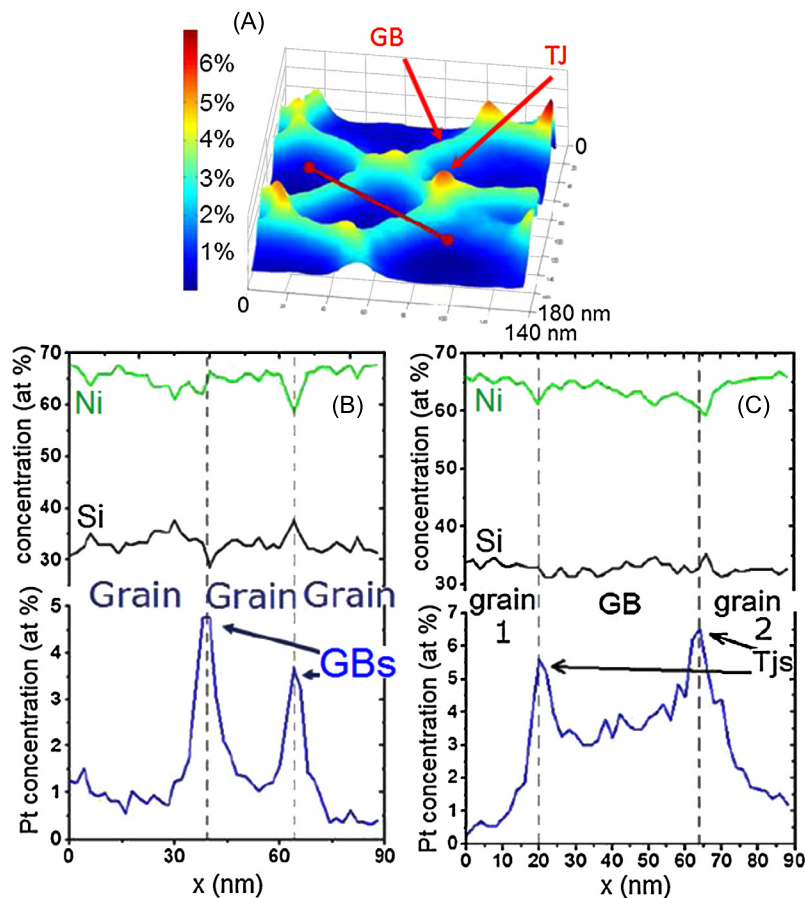


Figure 1.16 APT analyses performed on the sample presented in Fig. 1.15: (A) 2D composition map (at.%) of Pt atoms in the vicinity of a Ni_2Si nanograin; (B) 1D composition profiles (at.%) across three nanograins and two GBs along the red line shown in (A); and (c) 1D composition profiles (at.%) across two TJs and one GB [107]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

From the 3D atomic distribution measured by APT as shown in Fig. 1.15B (each dot is a single atom), 2D and 1D composition analyses can be performed. For example, Fig. 1.16A presents a 2D composition map of Pt atoms in the vicinity of a nanograin in the Ni_2Si layer shown in Fig. 1.15. The Pt composition in grains is lower than 1 at.%, while the composition in GBs can reach 2 at.%, and the TJs composition is larger than 4 at.%. One can note that Pt composition in grains is quite homogeneous, while significant composition variations are observed between GBs and TJs, showing that despite bulk properties seeming quite homogeneous in the sample (independent of grain orientation), the properties of GBs (i.e., interfaces) and of TJs (i.e., interface intersections)

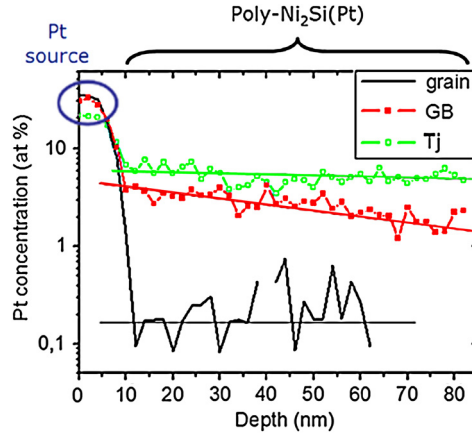


Figure 1.17 1D Pt concentration profiles measured by APT in the sample presented in Fig. 1.15: the solid line corresponds to a profile measured in a single nanograin, the solid symbols correspond to a profile measured in a single GB, and the open symbols correspond to the profile measured in a single TJ [107].

may vary with the crystalline orientation of such extended defects. Fig. 1.16B presents the 1D composition profile measured along the red line shown in Fig. 1.16A, crossing two GBs. The Ni (66 at.%) and Si (33 at.%) composition in the grains corresponds to the Ni_2Si stoichiometry. In the GBs the Ni or Si composition decreases (depending on the GB) and the Pt composition increases. Similar composition profiles can be also measured between TJs. For example, Fig. 1.16C shows the Pt concentration variations between two TJs across a single GB. The Pt concentration in the TJs is found to be larger than in the GBs. Assuming that the Pt concentration in the nanocrystalline Ni_2Si layer results only from diffusion, the fact that the concentration is larger in TJs than in GBs and that the concentration is larger in GBs than in grains could be interpreted by a faster diffusion kinetic in TJs than in GBs, in agreement with a faster diffusion in GBs than in nanograins. APT diffusion profiles can be measured in a single nanocrystal, along an interface and along the intersection of several interfaces. For instance, Pt diffusion profiles can be measured in the considered Ni_2Si nanocrystalline layer in a single nanograin, in a single GB and in a single TJ, as shown in Fig. 1.17. In the present case, the Pt profile in the nanograin is abrupt, showing that the Pt lattice diffusion coefficient is small in Ni_2Si at $T = 250^\circ\text{C}$. However, the Pt penetration profile measured in a neighboring GB shows that Pt diffused in the GB from the Pt source up to the Si substrate. The Pt profile is linear and presents a small slope from the source to the bottom of the layer, corresponding to a concentration gradient of ~ 2 at.%. The linear shape of the diffusion profile can result from the finite size of the layer, since at that temperature Pt atoms did not diffuse into the Si monocrystalline substrate. The Pt profile in the TJ is flat, meaning that Pt atoms could fully diffuse in the TJ until reaching the equilibrium

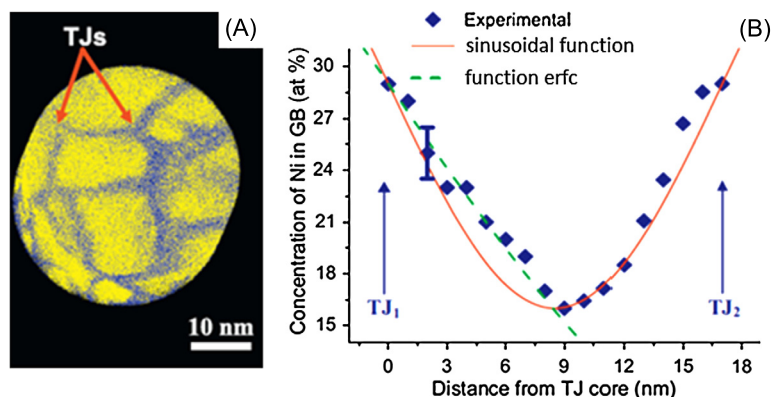


Figure 1.18 APT measurements performed in nanocrystalline Cu: (A) 3D-view showing Cu GBs enriched with Ni atoms that diffused into the Cu layer; (B) Ni concentration profile measured in a GB between the two TJs shown in (A) (solid diamonds) compared to diffusion profiles modeled via two different analytical solutions (solid and dashed lines, respectively). From Chellali et al. [109].

state without concentration gradient. These observations also lead to the conclusion that atomic diffusion is faster in TJs than in GBs. This type of measurement could be used to measure quantitatively atomic diffusion kinetic in nanostructures. However, APT is not a technique currently used for diffusion measurements. One of the disadvantages of using APT is that, due to its high resolution, it offers very small statistics. For example, because the sample is destroyed by the analysis, the initial profile before diffusion and the final profile after diffusion cannot be measured in the same nanograin in a nanocrystalline layer. Thus, in order to get an average diffusion coefficient in nanograins, it is necessary to perform the same measurement in several nanograins. A solution to this problem is to perform diffusion experiments using a diffusion source located on the sample surface. This way, there is no need to measure an initial profile (no impurity in the sample bulk before annealing), and only the final profile needs to be measured in several nanograins. The diffusion profiles measured by APT can be fitted using either diffusion analytical solutions or numerical simulations. However, experiments that used APT profiles to measure diffusion coefficients are very rare [108–110]. The few experiments reported in the literature mainly focused on diffusion coefficient measurements in GBs and TJs. For example, the GB and TJ diffusion of Ni was studied in nanocrystalline Cu using APT measurements [109]. 15 nm-thick Ni/Cu bi-layers were deposited by ion beam sputtering on tungsten tips. These layers were nanocrystalline, containing 10 to 20 nm-wide grains. The samples were annealed at temperatures comprised between 290 and 380°C, at which Ni lattice diffusion in Cu cannot occur. Fig. 1.18A presents a 3D view of a typical sample after annealing. Ni atoms (dark dots) are located in the GBs and in the TJs of the Cu (bright dots) nanocrystalline layer. Fig. 1.18B presents a typical 1D Ni concentration profile measured between the two TJs through a single GB (solid

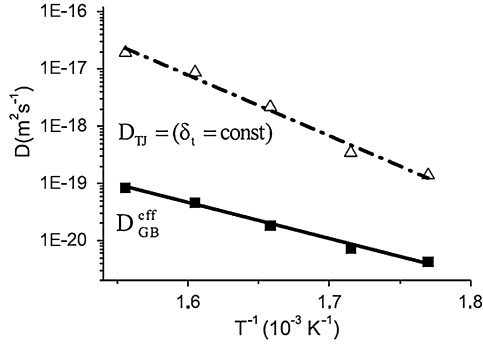


Figure 1.19 Ni diffusion coefficients measured in Cu nano-GBs (solid squares) and TJs (open triangles) using APT. From Chellali et al. [109].

symbols). In order to extract the diffusion coefficients in TJs and GBs from this type of composition profile, two different analytical solutions were used, corresponding to either (i) the so-called *C–B* kinetic regime (*C* between grains and GBs, and *B* between GBs and TJs) characterized by fast transport along the TJ and slow leakage from the TJ into the neighboring GBs, and no diffusion into the bulk, or (ii) a kinetic regime leaning toward the so-called *C–A* kinetic regime (*C* between grains and GBs, and *A* between GBs and TJs). In the first case, the diffusion profile can be fitted with a complementary error function, while in the second case the diffusion profile can be fitted with a sinusoidal function. These two types of solutions were used to fit the Ni profile presented in Fig. 1.18B, the complementary error function corresponding to the dashed line and the sinusoidal function corresponding to the solid line. Using this method, the Ni diffusion coefficients in Cu nano-GBs and TJs were measured, and are presented in Fig. 1.19. TJ diffusion coefficients were found to be 100–300 times larger than GB diffusion coefficients, with an activation energy of 2.10 ± 0.26 eV and 1.24 ± 0.16 eV in TJs and GBs, respectively. However, it is important to note that the GB diffusivity measured by APT is about 10^6 times slower than the Ni GB diffusivity measured by conventional methods [111]. This result indicates a possible problem for measuring diffusion profiles in interfaces and TJs by APT. Indeed, GBs and TJs are generally detected in APT volumes if the concentration of the impurity of interest is higher in the extended defects than in the bulk (need impurity accumulation). Thus, usually, the GBs and TJs studied by APT are very rich and may not correspond to the case of diluted impurity diffusion. For example, the Pt concentration in GBs and TJs in the Ni_2Si layer presented in Figs. 1.16 and 1.17 is between 1 and 5 at.%, and the Ni concentration in GBs and TJs in the Cu layer presented in Fig. 1.18 is between 15 and 30 at.%. These concentrations do not correspond to diluted atoms. Diffusion coefficients may be concentration dependent at these concentration levels. Thus, the profiles measured by APT between GBs and TJs,

or between nanograins and GBs, may correspond to interdiffusion profiles instead of diffusion profiles.

1.4 ATOMIC TRANSPORT KINETIC MEASUREMENTS

As previously mentioned, diffusion coefficients are usually experimentally determined by measuring the diffusion length of atoms. Typically, the measurements are based on the knowledge of the atomic distribution in the studied sample before and after a controlled (temperature, time, atmosphere) thermal annealing. However, the possibility of measuring these distributions becomes quite challenging in nanostructures and nanoobjects due to the resolution of the available experimental tools. In addition, the measurement of very short diffusion lengths involves a larger error of the diffusion coefficients. In order to be able to measure the diffusion coefficient in a nanofilm or in a nanoobject, another methodology can consist of directly measuring the atomic transport kinetic instead of measuring the diffusion length. For example, this can be performed by measuring in situ and in real time the composition variations of the element of interest on the nanostructure surface during the dissolution of the element in the nanostructure bulk, or during the surface segregation of the element from the nanostructure bulk. This type of measurement was already performed on regular polycrystalline materials using in situ Auger electron spectroscopy (AES) under ultrahigh vacuum (UHV), since it is one of the few methods allowing the GBs diffusion coefficient to be directly measured in the kinetic regime C [77,112–114]. This technique provides the exact value of the diffusion coefficient if it is concentration independent, or the average coefficient if it is concentration dependent. It has no thickness limitation if the correct model is used to extract the diffusion coefficient from the time-dependent composition variations recorded during annealing. It also allows self-diffusion coefficients to be measured in alloys. The main limitation of this technique is the need to use “purified” samples, or at least those exhibiting reduced contaminations, since contaminants can segregate on the sample surface, modifying the dissolution or the segregation kinetics of the element of interest. Diffusion coefficient measurements via in situ UHV AES are based on two experimental observations. First, segregation kinetic was shown to not be strongly connected to the equilibrium segregation isotherm ($C_{surf} = f(C_{vol})$ with $T = \text{constant}$), even for Fowler–Guggenheim surface segregation [111,115]. Second, at the beginning of surface segregation, the kinetic of the surface enrichment was shown to be linear with the time root mean square. This is due to the fact that, in this regime, the variations of the surface concentration (C_{surf}) and of the bulk concentration (C_{vol}) of a material versus time are principally driven by bulk diffusion, even if the ratio C_{surf}/C_{vol} is constant during diffusion (local equilibrium). Indeed, the surface concentration variations during surface segregation (or dissolution from the surface) result from atomic diffusion deeper than the distance between the two regions respecting the segregation equilib-

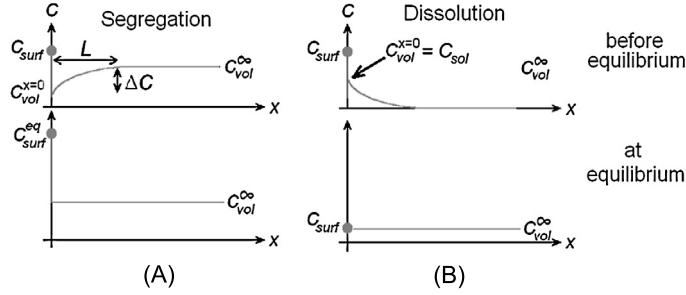


Figure 1.20 Schematics picturing the concentration variations of an impurity versus depth in a homogeneous material before and after equilibrium: (A) during segregation, and (B) during dissolution.

rium $C_{surf} = sC_{vol}$, with $s = f(T)$ the segregation coefficient. Thus, bulk diffusion is the limiting (slower) phenomenon during the segregation or dissolution kinetics. Analytical solutions of atomic diffusion during surface segregation or dissolution were developed in order to extract bulk diffusion coefficients from in situ AES measurements. For example, in the case of surface segregation on a homogeneous solid solution, the solution of the Fick equation is the complementary error function $C(x, t) = \text{erfc}(x, t)$. Thus, the surface enrichment versus time can be expressed as

$$C_{surf}(t) = C_{surf}(t=0) + 2[C_{vol}^{\infty} - C_{vol}^{x=0}] \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}. \quad (1.5)$$

$C_{vol}^{x=0}$ is the bulk concentration directly in equilibrium with the surface concentration (subsurface atomic plane), and C_{vol}^{∞} is the impurity concentration deep into the volume of the solid solution. This equation was obtained considering C_{vol}^{∞} and $C_{vol}^{x=0}$ to be constant. Fig. 1.20A schematically presents the concentration variations of the impurity versus depth in the solid solution before and after reaching equilibrium between the surface and the bulk. As observed experimentally, Eq. (1.5) predicts a linear concentration increase at the surface of the sample versus time root mean square. A similar equation can be obtained for the dissolution process (Fig. 1.20B). In the case of surface segregation, experimental conditions can be chosen in order to neglect $C_{vol}^{x=0}$ (which is experimentally unknown) compared to C_{vol}^{∞} , which is particularly the case at the beginning of the segregation kinetic (Fig. 1.20A). In the case of dissolution, $C_{vol}^{x=0}$ is usually taken as the solubility limit of the considered element in the considered substrate at the experimental temperature, which is the highest concentration that can limit the dissolution kinetic. Thus, when the kinetic of the surface concentration variations during segregation or dissolution are controlled by bulk atomic diffusion $C_{surf} = f(t^{1/2})$ is linear and the slope of the plot allows D to be measured knowing either C_{vol}^{∞} for segregation

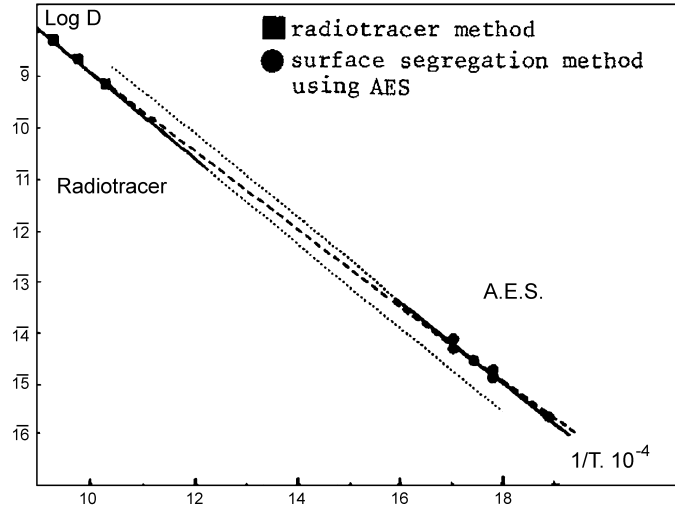


Figure 1.21 Pb diffusion coefficients measured in 50% Ag–Pb using radiotracer (solid squares) or thanks to surface segregation studies by AES (solid circles). From Rolland and Bernardini [112].

or $C_{vol}^{x=0}$ for dissolution, using the equations:

$$C_{surf}(t) = C_{surf}(t=0) + 2C_{vol}^{\infty} \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}, \quad (1.6)$$

$$C_{surf}(t) = C_{surf}(t=0) - 2C_{vol}^{x=0} \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}. \quad (1.7)$$

The measurements by in situ UHV AES of same diffusion coefficients, performed either during surface segregation or during surface dissolution, compared to radiotracer experiments, have shown that diffusion coefficient measurements performed during surface segregation exhibit in general a higher accuracy than during dissolution. For example, Fig. 1.21 presents a comparison between Pb self-diffusion coefficients measured by radiotracers and by in situ AES in a 50% Ag–Pb solid solution [112]. Despite the different temperature ranges between the two types of measurements, the Arrhenius law $D_{AES} = 1.5 \exp(-0.399 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ obtained by AES is quite close to the one $D_{TRC} = 0.38 \exp(-0.401 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ obtained by radiotracer experiments. In particular, the data from the radiotracer and the AES experiments can be fitted by a single Arrhenius law, giving $D = 0.08 \exp(-0.370 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. Few experimental studies were reported in the literature concerning the use of in situ UHV AES to study nanofilm dissolution [116–120] or atomic diffusion in nanocrystalline films [77, 113]. For example, in situ UHV AES was used to study Si and Pd self-diffusion in a 42 nm-thick nanocrystalline Pd₂Si film made of 44 nm-wide grains on average [41].

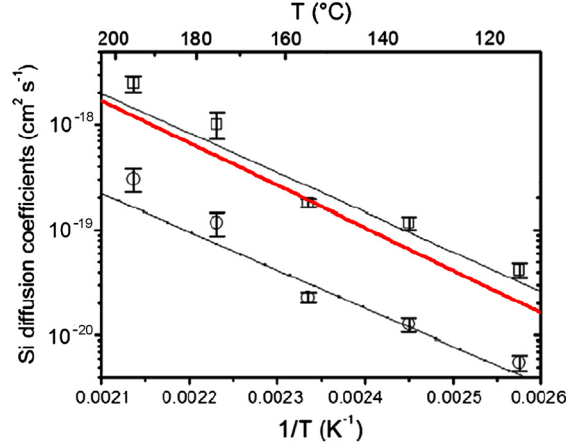


Figure 1.22 Si GB self-diffusion coefficients measured in nanocrystalline Pd_2Si using in situ UHV AES, assuming either a full Si GB solubility (open circles) or an Si GB solubility of 34.5% (open squares). The solid line corresponds to literature measurements using radiotracers [41].

The layer was grown on an Si substrate that acted as an infinite reservoir of Si atoms at the $\text{Pd}_2\text{Si}/\text{Si}$ interface. The Pd self-diffusion coefficient was measured during the dissolution of a few Pd monolayers in the Pd_2Si film using Eq. (1.7), while the Si self-diffusion coefficient was measured in the same sample and in the same experimental conditions, after the Pd dissolution, during Si surface segregation, using Eq. (1.6). The experiments were performed at $115 \leq T \leq 195^\circ\text{C}$, corresponding to the kinetic regime C. Thus, the Pd_2Si self-diffusion coefficients could be measured using Eqs. (1.6) and (1.7) only if the Si and Pd solubility was known in the GBs. The parameters C_{vol}^∞ and $C_{vol}^{x=0}$ do not significantly influence the activation energy of the diffusion coefficient, but modify the diffusion coefficient's prefactor. This study showed that the rule proposed by Bokstein et al. [121] was applicable in the present case. For example, Fig. 1.22 presents the Si GB self-diffusion obtained by AES assuming either an Si GB solubility of 100% ($C_{vol}^\infty = 1$, open circles), or of 34.5% ($C_{vol}^\infty = 0.345$, open squares) corresponding to the Pd_2Si stoichiometry. The data is compared to the Si self-diffusivity measured in a previous work using radiotracers (solid line) [122]. The AES measurements are in better agreement with the radiotracer measurements in the case of an Si solubility equal to the Pd_2Si stoichiometry as proposed by Bokstein et al. The maximum error between the two measurements is $\sim 50\%$, with $D_{AES} = 1.56 \times 10^{-10} \exp(-0.746 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$ and $D_{TRC} = 5 \times 10^{-10} \exp(-0.8 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. Thus, the Si and Pd diffusion coefficients in Pd_2Si nano-GBs were measured with $C_{vol}^\infty = 0.345$ and $C_{vol}^{x=0} = 0.667$ in Eqs. (1.6) and (1.7), respectively. Pd GB self-diffusion was fitted by the Arrhenius law $D_{Pd} = 2.64 \times 10^{-8} \exp(-0.90 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$. As shown in Fig. 1.23, Si and Pd self-diffusions were found to be similar as observed using markers during Pd_2Si growth via

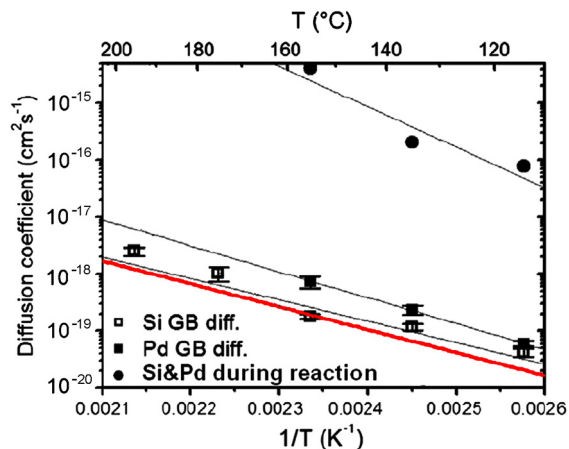


Figure 1.23 Pd₂Si GB self-diffusion coefficients measured by in situ UHV AES at equilibrium (open squares for Si and solid squares for Pd) and during Pd₂Si growth via Pd/Si reactive diffusion (solid circles) [41].

Pd/Si reactive diffusion [123]. In the case of lattice diffusion measurements, an error of 10% on diffusion coefficients is generally considered to be the result of the typical temperature measurement error. In the case of GB diffusion, a larger measurement error is generally accepted due to the use of the lattice diffusion coefficient (which can vary from experiments reported in the literature) in order to determine D_{gb} from the Fisher model analytical solutions. However, the difference between the Si GB diffusion coefficients measured using radiotracers and using AES can also be interpreted as being due to the TJ contribution. In this case, assuming that the diffusion occurred in the kinetic regime C–A during in situ AES experiments, the Si diffusion coefficient measured by AES can be considered as an effective coefficient that can be written as $D_{eff} = \beta D_{ij} + (1 - \beta)D_{gb}$ with $\beta = \delta/2d$ in case of square nanograins. Thus, the TJ diffusion coefficient D_{ij} can be determined knowing D_{gb} from radiotracer measurements. The Arrhenius laws of the three diffusion coefficients D_{gb} , D_{eff} , and D_{ij} are presented in Fig. 1.24. It is interesting to note that a difference of about 50% between the two GB diffusion coefficients is enough to justify the effect of TJs with a diffusion coefficient $D_{ij} = 1.38 \times 10^{-6} \exp(-0.91 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$, about two orders of magnitude larger than for GB diffusion. A main interest of this study on Pd and Si self-diffusion in Pd₂Si [41] was to show that self-diffusion can be measured in the same sample and in the same experimental conditions during the growth of a compound by interfacial reactive diffusion (out of equilibrium) and after the growth (at equilibrium) using in situ UHV AES measurements. Indeed, in the case of nanostructures, the sample may be so far from equilibrium that interfaces can migrate during thermal annealing, modifying the atomic distribution in the nanostructure, as well as the physical properties of

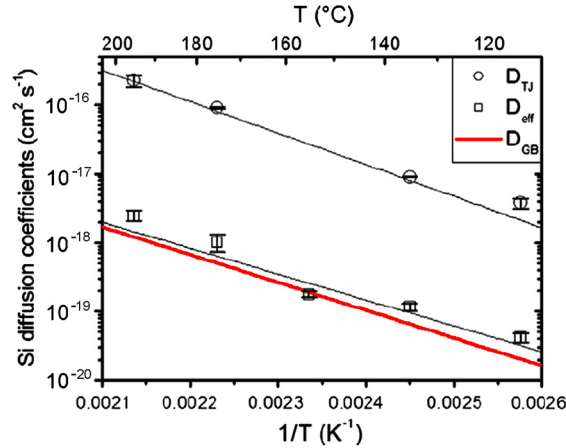


Figure 1.24 Si diffusion coefficients measured in Pd_2Si versus $1/T$. The solid line corresponds to GB diffusion, the open squares correspond to the effective diffusion coefficient measured in kinetic regime C–A, and the open circles correspond to TJ diffusion [41].

the nanostructure. Thus, the influence of mobile interfaces on atomic transport is an important subject to understand the fabrication and the stability of nanostructures and of embedded nanoobjects. The influence of GB migration on atomic redistribution is already well documented in the literature [124–131]. In particular, the GB diffusion coefficients measured in stationary GBs and mobile GBs were shown to be similar in some systems [132,133], and mobile GBs were shown to mainly modify atomic redistribution in grains [123,124]. In addition, the modification of diffusion profiles by mobile GBs is well known in the case of regular polycrystalline materials, and needs to be taken into account when using a 1D diffusion profile to extract a diffusion coefficient (in kinetic regime B, for example) [65]. However, an original phenomenon was observed in the case of GB diffusion in ultrafine-grain polycrystalline materials and nanocrystalline layers that was attributed to GB migration [39,134]. Indeed, the diffusion profile in these materials was shown to present, in some cases, a kink that could be interpreted either by concentration-dependent GB diffusion coefficients (or by the presence of several types of GBs with different diffusivities) or as a significant decrease of GB diffusivity (of several orders of magnitude). Analytical models as well as numerical simulations have actually shown that this type of diffusion profile can be reproduced with constant GB diffusion coefficients similar to coefficients measured in stationary GB, but taking into account the GB displacements (and their effects on atomic redistribution in nanograins) in the direction normal to the direction in which the diffusion profile is measured (usually along the depth of the sample). The same results are obtained for gliding GBs or for grain growth. For example, Fig. 1.25 presents experimental profiles measured in nanocrystalline Ni and in nanocrystalline Si. The first case corresponds to

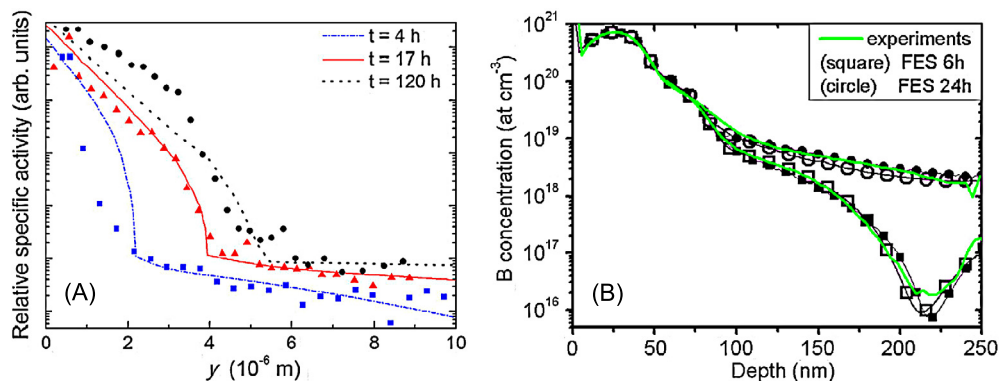


Figure 1.25 Diffusion profiles measured in nanocrystalline materials and compared to simulations: (A) Ni self-diffusion measured by radiotracers (symbols) in kinetic regime C, the fit was obtained with an analytical model (solid lines) considering 200 nm-wide grains (from Prokoshkina et al. [39]); (B) B diffusion in a 250 nm-thick nanocrystalline Si layer made of 50 nm-wide grains measured by SIMS (solid lines) in kinetic regime B, the fit was obtained using FES (symbols) [40].

GB self-diffusion, while the second case corresponds to GB diffusion of an impurity that segregates in the GBs. In the second case, it is interesting to note that the GB migration velocity was found to be inversely proportional to the impurity concentration. This observation was interpreted as an effect of B segregation in the Si GBs, the GB velocity decreasing when the B concentration in the GB increases. The effect of this type of interface migration was not found to modify atomic transport kinetics, but to modify atomic redistribution in the nanograins. In the case of the study of Pd and Si self-diffusion in Pd_2Si (Fig. 1.23), during Pd/Si reactive diffusion, the two interfaces, Pd/ Pd_2Si and Pd_2Si /Si, are moving and at the same time the reaction $\text{Si} + 2\text{Pd} \rightarrow \text{Pd}_2\text{Si}$ occurs at the two interfaces [135]. Interfacial reactions were shown to modify atomic transport due to point defect accumulation (or depletion) at the reacting interfaces. However, it was mainly observed in monocrystalline semiconductors [136–139]. For example, Pd/Si reactive diffusion was shown to inject Si self-interstitials in the Si substrate from the Pd_2Si /Si interface [136,140], but no studies concerning the injection of point defects in the Pd_2Si layer and its effect on GB self-diffusion in the Pd_2Si layer have been reported. Thanks to the use of in situ UHV AES, the Pd and Si effective GB self-diffusion coefficient piloting the growth of Pd_2Si could be measured and compared to Pd and Si equilibrium GB diffusion, in the same samples and experimental conditions. Fig. 1.23 presents a comparison between Pd and Si GB diffusivities during Pd_2Si growth (circles) and after Pd_2Si growth (squares). GB self-diffusion was found to be several orders of magnitude faster during reaction. Due to the measurement conditions, this effect cannot be attributed to a contamination effect due to different impurity concentrations in the different samples [141,142]. However, due to the very low tem-

perature of the reaction ($115 \leq T \leq 195^\circ\text{C}$, diffusion in kinetic regime C), point defect annihilation is expected to be slow even in extended defects such as GBs. Thus, the significant increase of GB diffusion during interfacial reaction can be interpreted as an injection of point defects from the reacting interfaces, due to a point-defect concentration gradient between these mobile interfaces and the center of the growing layer. One could expect a stationary regime to be reached during growth, between point defect formation at interfaces and point defect annihilation in the bulk of the layer, leading to a constant average effective GB self-diffusion coefficient. It is interesting to note that atomistic simulations have shown that the point defect concentration ratio between vacancies and self-interstitials is different in bulk and GBs, and that the contribution of interstitial diffusion in GBs is not negligible even in metals [143,144]. Consequently, the GB diffusion mechanism could be modified due to interfacial reaction. For example, Pd_2Si self-diffusion is expected to principally use the vacancy mechanism in grains and in GBs. However, the Si self-interstitial concentration was shown to be significantly increased at the reacting $\text{Pd}_2\text{Si}/\text{Si}$ interface, and Si self-interstitials were shown to diffuse in the Si monocrystal. Thus, if point defect injection from interfaces results from point-defect diffusion due to the concentration gradient between the interface and the bulk, Si atoms could use also an interstitial-mediated mechanism in Pd_2Si GBs during Pd_2Si growth.

CONCLUSION

The knowledge of atomic transport kinetic in nanostructures is essential in order to understand and predict the formation (growth, reaction, etc.) and the ageing of nanostructures. It is thus necessary to measure diffusion coefficients in nanocrystals, in interfaces and in interface intersections. To date, experiments providing diffusion coefficients in such types of paths were mainly performed on nanocrystalline materials. Indeed, in these types of materials, the nanograins (3D matrix) correspond to nanocrystals, the GBs (2D matrix) correspond to interfaces, and TJs (1D matrix) correspond to interface intersections. Different methods were employed in order to quantitatively determine atomic transport kinetic in such diffusion paths. Analytical solutions of the diffusion equation can be used principally in the case of diffusion profiles measured using classical profiling methods in bulk nanocrystalline materials. These solutions were used to measure nano-GB and nano-TJ diffusion coefficients. Numerical simulations, such as FES, allow the study of atomic transport in samples with a structure, or during experimental conditions, more complex than those offered by analytical solutions. Numerical simulations were principally used to study atomic diffusion in nanocrystalline thin films, allowing diffusion coefficients in nanograins, in nano-GBs and in nano-TJs to be measured. 2D FES using the Fisher geometry were shown to allow lattice diffusion coefficients in nanograins to be simultaneously measured with nano-GB diffusion

coefficients from same experimental profiles. Furthermore, 3D FES allows TJ diffusion to be taken into account in addition to grain and GB diffusion. In particular, 3D simulations were shown to provide the simultaneous measurement of the lattice diffusion coefficient in nanograins and of the TJ diffusion coefficient, knowing the GB diffusion coefficient (measured in coarse-grain material). An important benefit of using FES is the possibility of measuring lattice diffusion coefficients at the same temperature as GB diffusion coefficients, and thus, at lower temperatures as during usual experiments performed in monocrystalline samples. Atom probe tomography allows composition profiles to be measured in nanograin, nano-GB and nano-TJ. This technique is thus expected to be well adapted to diffusion coefficient measurements in nanostructures. It has been used to measure diffusion coefficients in nanocrystalline samples. In particular, nano-GB and nano-TJ diffusion coefficients were measured using analytical diffusion solutions. However, the GB diffusion coefficients measured by APT were shown to not correspond to the coefficients measured by regular methods such as radiotracers. This effect may be due to the composition of the GBs and the TJs observed by APT that is too high to correspond to the diluted impurity case, the coefficients available by APT corresponding to interdiffusion coefficients instead of diffusion coefficients. In situ ultrahigh vacuum Auger electron spectroscopy allows the direct measurements of atomic transport kinetic without the need to measure impurity diffusion profiles. For this reason, this technique is well adapted for diffusion coefficient measurements in diffusion paths such as nanocrystals, interfaces and interface intersections. It has been used to measure nano-GB diffusion coefficients in ultra-thin nanocrystalline films. In particular, this technique can be used to measure atomic transport kinetics during the reactive diffusion growth of a given thin film (out-of-equilibrium) and after the thin film growth (equilibrium), in the same sample and in the same experimental conditions, in order to investigate point-defect concentration variations due to interfacial reactions. To date, the different experiments reported in the literature show that nano-GB diffusion is identical to classical GB diffusion. This means that size reductions do not significantly modify the nature of interfaces. TJs diffusion was found to be about two orders of magnitude faster than GBs diffusion. Lateral growth of nanograins (i.e., GB migration) during annealing was shown to modify atomic distribution in nanograins, and thus to modify the diffusion profiles in nanocrystalline materials. However, simulations show that atomic diffusivity in mobile nano-GBs is probably the same as in stationary GBs, in agreement with previous experiments concluding that impurity diffusion in stationary and mobile GBs exhibit the same coefficients. Diffusion measurements in nanocrystals are very rare. The one-order-of-magnitude faster diffusion kinetics observed in Si 40 nm-wide nanocrystals is still under discussion. The reason for the increase of Ge atomic transport kinetic in Si nanocrystals compared to monocrystalline Si was suggested to be due to an increase of the vacancy concentration, resulting from the average bulk equilibrium vacancy concentration approaching the nanocrystal interface (or surface)

equilibrium vacancy concentration when the nanocrystal lateral size decreases. The increase of self-diffusion in thin films during low-temperature reactive diffusion is still also under debate. This increase of atomic transport kinetic was suggested to be related to point-defect injections from the mobile reactive interfaces into the growing film.

REFERENCES

- [1] M. Mehran, S. Mohajerzadeh, *Microelectr. J.* 46 (2015) 166.
- [2] X. Li, P.-C. Li, L. Ji, C. Stender, S. Rao Tatavarti, K. Sablon, E.T. Yu, *Sol. Energ. Mat. Sol. C* 143 (2015) 567.
- [3] H.J. Pandya, S. Chandra, A.L. Vyas, *Sensor. Actuat. B-Chem.* 161 (2012) 923.
- [4] J. Jie, W. Zhang, I. Bello, C.-S. Lee, S.-T. Lee, *Nano Today* 5 (2010) 313.
- [5] Q. Zhang, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu, S. Yang, *Prog. Mater. Sci.* 60 (2014) 208.
- [6] R. Inguanta, S. Piazza, C. Sunseri, *Electrochem. Commun.* 10 (2008) 506.
- [7] A. Fissel, A. Laha, E. Bugiel, D. Kühne, M. Czernohorsky, R. Dargis, H.J. Osten, *Microelectr. J.* 39 (2008) 512.
- [8] P. Kervalishvili, A. Lagutin, *Microelectr. J.* 39 (2008) 1060.
- [9] N. Iqbal, A. Afzal, N. Cioffi, L. Sabbatini, L. Torsi, *Sensor. Actuat. B-Chem.* 181 (2013) 9.
- [10] R.G. Parkhomenko, A.I. Plekhanov, A.S. Kuchyanov, S.V. Trubin, B.M. Kuchumov, I.K. Igumenov, *Surf. Coat. Tech.* 230 (2013) 279.
- [11] M. Meyyappan, *J. Vac. Sci. Technol. A* 31 (2013) 050803.
- [12] G. Pennelli, M. Macucci, *J. Appl. Phys.* 114 (2013) 214507.
- [13] C. Zechner, N. Zographos, *Mat. Sci. Semicon. Proc.* 42 (2016) 230.
- [14] H. Oh, J. Kim, J. Lee, T. Rim, C.-K. Baek, J.-S. Lee, *Microelectron. Eng.* 149 (2016) 113.
- [15] G.-F. DallaBetta, L. Pancheri, M. Boscardin, G. Paternoster, C. Piemonte, N. Cartiglia, F. Cenna, M. Bruzzi, *Nucl. Instrum. Meth. A* 796 (2015) 154.
- [16] I. Martin-Bragado, S. Tian, M. Johnson, P. Castrillo, R. Pinacho, J. Rubio, M. Jaraiz, *Nucl. Instrum. Meth. B* 253 (2006) 63.
- [17] I. Bork, V. Moroz, L. Bomholt, D. Pramanik, *Mater. Sci. Eng. B* 124–125 (2005) 81.
- [18] P. Pfäffli, P. Tikhomirov, X. Xu, I. Avci, Y.-S. Oh, P. Balasingam, S. Krishnamoorthy, T. Ma, *Microelectron. Reliab.* 52 (2012) 1761.
- [19] F. Boucard, F. Roger, I. Chakarov, V. Zhuk, M. Temkin, X. Montagner, E. Guichard, D. Mathiot, *Mater. Sci. Eng. B* 124–125 (2005) 409.
- [20] S. Selberherr, *Southern African Journal of Physics* 16 (1993) 1.
- [21] S.M. Sze, in: A.E. Elken (Ed.), *VLSI Technology*, McGraw-Hill Book Company, New York, 1988, p. 409, Chap. 9.6.4.
- [22] C.M. Tan, A. Roy, *Mater. Sci. Eng. R* 58 (2007) 1.
- [23] C.S. Hau-Riege, *Microelectron. Reliab.* 44 (2004) 195.
- [24] D. Gupta, *Can. Metall. Quart.* 34 (1995) 175.
- [25] M. Stangl, M. Liptak, J. Acker, V. Hoffmann, S. Baunack, K. Wetzig, *Thin Solid Films* 517 (2009) 2687.
- [26] S.P. Murarka, I.V. Verner, R.J. Gutmann, *Copper-Fundamental Mechanisms for Microelectronic Applications*, John Wiley & Sons, New York, 2000.
- [27] C. Steinbrüchel, B.L. Chin, in: A.R. Weeks Jr. (Ed.), *Copper Interconnect Technology*, SPIE Press, Washington, 2001.
- [28] C.-K. Hu, D. Canaperi, S.T. Chen, L.M. Gignac, S. Kaldor, M. Krishnan, S.G. Malhotra, E. Liniger, J.R. Lloyd, D.L. Rath, D. Restaino, R. Rosenberg, J. Rubino, S.-C. Seo, A. Simon, S. Smith, W.-T. Tseng, *Thin Solid Films* 504 (2006) 274.

- [29] J. Bernardini, C. Girardeaux, Z. Erdelyi, C. Lexcellent, J. Metastable Nanocryst. Mater. 19 (2004) 35.
- [30] W.P. Tong, N.R. Tao, Z.B. Wang, J. Lu, K. Lu, Science 299 (2003) 686.
- [31] T. Suzuoka, Jpn. I. Met. 2 (1961) 25.
- [32] Yu.R. Kolobov, G.P. Grabovetskaya, I.V. Ratochka, K.V. Ivanov, Nanostruct. Mater. 12 (1999) 1127.
- [33] A. Portavoce, G. Chai, L. Chow, J. Bernardini, J. Appl. Phys. 104 (2008) 104910.
- [34] I. Blum, A. Portavoce, D. Mangelinck, R. Daineche, K. Hoummada, J.L. Lábár, V. Carron, C. Perrin, J. Appl. Phys. 104 (2008) 114312.
- [35] A. Portavoce, D. Mangelinck, R. Simola, R. Daineche, J. Bernardini, Defect. Diffus. Forum 289–292 (2009) 329.
- [36] A. Portavoce, R. Simola, D. Mangelinck, J. Bernardini, P. Fornara, Defect. Diffus. Forum 264 (2007) 33.
- [37] A. Portavoce, L. Chow, J. Bernardini, Appl. Phys. Lett. 96 (2010) 214102.
- [38] S.V. Divinski, F. Hisker, Y.-S. Kang, J.-S. Lee, C. Herzig, Interface Sci. 11 (2003) 67.
- [39] D. Prokoshkina, L. Klinger, A. Moros, G. Wilde, E. Rabkin, S.V. Divinski, Acta Mater. 69 (2014) 314.
- [40] A. Portavoce, Scripta Mater. 99 (2015) 37.
- [41] A. Portavoce, K. Hoummada, F. Dahlem, Surf. Sci. 624 (2014) 135.
- [42] L.G. Harrison, Trans. Faraday Soc. 57 (1961) 1191.
- [43] I. Kaur, Y. Mishin, W. Gust, Fundamentals of Grain and Interphase Boundary Diffusion, Wiley, Chichester, West Sussex, 1995.
- [44] Z.B. Wang, K. Lua, G. Wilde, S.V. Divinski, Acta Mater. 58 (2010) 2376.
- [45] S.V. Divinski, G. Reglitz, H. Rösner, Y. Estrin, G. Wilde, Acta Mater. 59 (2011) 1974.
- [46] S.V. Divinski, G. Reglitz, G. Wilde, Acta Mater. 58 (2010) 386.
- [47] H. Gleiter, Phys. Status Solidi 172 (1992) 41.
- [48] W. Dickenscheid, R. Birringer, H. Gleiter, O. Kanert, B. Michel, B. Gunther, Solid State Commun. 79 (1991) 683.
- [49] S.V. Divinski, J.S. Lee, Chr. Herzig, J. Metastable Nanostr. Mater. 19 (2004) 55.
- [50] M. Wegner, J. Leuthold, M. Peterlechner, X. Song, S.V. Divinski, G. Wilde, J. Appl. Phys. 116 (2014) 093514.
- [51] S.V. Divinski, G. Wilde, Mater. Sci. Forum 584 (2008) 1012.
- [52] G. Salishchev, R. Zaripova, R. Galeev, O. Valiakhmetov, Nanostruct. Mater. 6 (1995) 913.
- [53] R.Z. Valiev, Y. Estrin, Z. Horita, T.G. Langdon, M.J. Zehetbauer, Y.T. Zhu, JOM-J. Min. Met. Mat. S 58 (2006) 33.
- [54] S. Divinski, G. Wilde, E. Rabkin, Y. Estrin, Adv. Eng. Mater. 12 (2010) 779.
- [55] S.V. Divinski, Defect. Diffus. Forum 289 (2009) 623.
- [56] B.S. Bokstein, H.D. Bröse, L.I. Trusov, T.P. Khvostantseva, Nanostruct. Mater. 6 (1995) 873.
- [57] T. Suzuoka, J. Phys. Soc. JPN 19 (1964) 839.
- [58] J. Perrin Toinin, A. Portavoce, K. Hoummada, M. Texier, M. Bertoglio, S. Bernardini, M. Abbarchi, L. Chow, Beilstein J. Nanotechnol. 6 (2015) 336.
- [59] K. Shin, K.A. Leach, J.T. Goldbach, D. Ha Kim, J.Y. Jho, M. Tuominen, C.J. Hawker, T.P. Russell, Nano Lett. 2 (2002) 933.
- [60] R.B. Fair, Concentration profiles of diffused dopants in silicon, in: F. Wang (Ed.), Impurity Doping Processes in Silicon, North Holland, 1981, p. 135.
- [61] J.S. Christensen, H.H. Radamson, A.Yu. Kuznetsov, B.G. Svensson, Appl. Phys. Lett. 82 (2003) 2254.
- [62] T.I. Kamins, J. Manoliu, R.N. Tucker, J. Appl. Phys. 43 (1972) 83.
- [63] K. Sakamoto, K. Nishi, T. Yamaji, T. Miyoshi, S. Ushio, J. Electrochem. Soc. 132 (1985) 2457.
- [64] H. Mehrer, Diffusion in Solids, Springer-Verlag, Berlin, Heidelberg, 2007.

- [65] A. Portavoce, I. Blum, L. Chow, J. Bernardini, D. Mangelinck, *Defect. Diffus. Forum* 309–310 (2011) 63.
- [66] D. McLean, *Grain Boundaries in Metals*, Oxford Univ. Press, Oxford, 1957.
- [67] B. Legrand, G. Tréglia, F. Ducastalle, *Phys. Rev. B* 41 (1990) 4422.
- [68] R.H. Fowler, E. Guggenheim, *Statistical Thermodynamics*, Cambridge Univ. Press, Cambridge, UK, 1960.
- [69] I. Blum, A. Portavoce, D. Mangelinck, R. Daineche, K. Hoummada, J.L. Lábár, V. Carron, J. Bernardini, *Micro. Eng.* 87 (2010) 263.
- [70] Y. Wang, Z. Su, D. Ping, *J. Mater. Sci. Technol.* 26 (2010) 1047.
- [71] Y. Chen, C.A. Schuh, *J. Appl. Phys.* 101 (2007) 063524.
- [72] H. Wang, W. Yang, A.H.W. Ngan, *Scripta Mater.* 52 (2005) 69.
- [73] Y. Chen, C.A. Schuh, *Scripta Mater.* 57 (2007) 253.
- [74] B. Bokstein, V. Ivanov, O. Oreshina, A. Peteline, S. Peteline, *Mater. Sci. Eng. A* 302 (2001) 151.
- [75] G. Hettich, H. Mehrer, K. Maier, *Inst. Phys. Conf. Ser.* 46 (1979) 500.
- [76] P. Pichler, *Intrinsic Point Defects, Impurities, and Their Diffusion in Silicon*, Springer-Verlag, Wien, Austria, 2004.
- [77] Z. Balogh, Z. Erdélyi, D.L. Beke, A. Portavoce, C. Girardeaux, J. Bernardini, A. Rolland, *Appl. Surf. Sci.* 255 (2009) 4844.
- [78] Z. Balogh, Z. Erdélyi, D.L. Beke, A. Portavoce, C. Girardeaux, J. Bernardini, A. Rolland, *Defect. Diffus. Forum* 289–292 (2009) 763.
- [79] B.S. Bokstein, H.D. Bröse, L.I. Trusov, T.P. Khvostantseva, *Nanostruct. Mater.* 6 (1995) 873.
- [80] A.H. King, *Interface Sci.* 7 (1999) 251.
- [81] T. Frolov, Y. Mishin, *Phys. Rev. B* 79 (2009) 174110.
- [82] S. Costantini, P. Alippi, L. Colombo, F. Cleri, *Phys. Rev. B* 63 (2000) 045302.
- [83] H.-E. Schaefer, R. Würschum, R. Birringer, H. Gleiter, *Phys. Rev. B* 38 (1988) 9545.
- [84] W.H. Qi, M.P. Wang, *Physica B* 334 (2003) 432.
- [85] S.P. Beckman, J.R. Chelikowsky, *Physica B* 401–402 (2007) 537.
- [86] J.-H. Eom, T.-L. Chan, J.R. Chelikowsky, *Solid State Commun.* 150 (2010) 130.
- [87] W. Luo, W. Hu, S. Xiao, *J. Chem. Phys.* 128 (2008) 074710.
- [88] M. Mirjalili, J. Vahdati-Khaki, *J. Phys. Chem. Solids* 69 (2008) 2116.
- [89] M. Wautelet, *Phys. Lett. A* 246 (1998) 341.
- [90] X. Yu, Z. Zhan, J. Rong, Z. Liu, L. Li, J. Liu, *Chem. Phys. Lett.* 600 (2014) 43.
- [91] H. Delavari, H.R. Madaah Hosseini, A. Simchi, *Physica B* 406 (2011) 3777.
- [92] O. Cojocaru-Mirédin, F. Cristiano, P.-F. Fazzini, D. Mangelinck, D. Blavette, *Thin Solid Films* 534 (2013) 62.
- [93] S. Duguay, A. Colin, D. Mathiot, P. Morin, D. Blavette, *J. Appl. Phys.* 108 (2010) 034911.
- [94] D. Mangelinck, K. Hoummada, A. Portavoce, C. Perrin, R. Daineche, M. Descoins, D.J. Larson, P.H. Clifton, *Scripta Mater.* 62 (2010) 568.
- [95] K. Hoummada, G. Tellouche, I. Blum, A. Portavoce, M. Descoins, D. Mangelinck, *Microelectron. Eng.* 107 (2013) 184.
- [96] I.J. Beyerlein, M.J. Demkowicz, A. Misra, B.P. Uberuaga, *Prog. Mater. Sci.* 74 (2015) 125.
- [97] M.J. Aziz, *Appl. Phys. Lett.* 70 (1997) 2810.
- [98] Y. Lamrani, F. Cristiano, B. Colombeau, E. Scheid, P. Calvo, H. Schäfer, A. Claverie, *Nucl. Instrum. Meth. B* 216 (2004) 281.
- [99] S.M. Hu, *Mater. Sci. Eng. R* 13 (1994) 105.
- [100] A. Natori, H. Harada, *Surf. Sci.* 438 (1999) 162.
- [101] H. Bracht, N.A. Stolwijk, H. Mehrer, *Phys. Rev. B* 52 (1995) 16542.
- [102] A. Portavoce, J. Perrin-Toinin, K. Hoummada, *Vacancy-mediated atomic transport in nano-crystals, Reviews on Advanced Materials Science* (2017), to be published.

- [103] M.K. Miller, *Atom-Probe Tomography*, Kluwer Academic/Plenum Publisher, New York, 2000.
- [104] M.K. Miller, R.G. Forbes, *Atom-Probe Tomography: The Local Electrode Atom Probe*, Springer, New York, 2014.
- [105] D.J. Larson, T.J. Prosa, R.M. Ulfing, B.P. Geiser, T.F. Kelly, *Local Electrode Atom Probe Tomography*, Springer, New York, 2013.
- [106] B. Gault, M.P. Moody, J.M. Cairney, S.P. Ringer, *Atom-Probe Tomography*, Springer-Verlag, New York, 2012.
- [107] A. Portavoce, I. Blum, K. Hoummada, D. Mangelinck, L. Chow, J. Bernardini, *Defect. Diffus. Forum* 322 (2012) 129.
- [108] P. Stender, Z. Balogh, G. Schmitz, *Ultramicroscopy* 111 (2011) 524.
- [109] M.R. Chellali, Z. Balogh, L. Zheng, G. Schmitz, *Scripta Mater.* 65 (2011) 343.
- [110] M.R. Chellali, Z. Balogh, G. Schmitz, *Ultramicroscopy* 132 (2013) 164.
- [111] T.J. Renouf, *Philos. Mag.* 22 (1970) 359.
- [112] A. Rolland, J. Bernardini, *Scripta Metall. Mater.* 19 (1985) 839.
- [113] J. Bernardini, C. Lea, E.D. Hondros, *Scripta Metall. Mater.* 15 (1981) 649.
- [114] Z. Erdélyi, C. Girardeaux, G.A. Langer, D.L. Beke, A. Rolland, J. Bernardini, *J. Appl. Phys.* 89 (2001) 3971.
- [115] A. Rolland, J. Bernardini, G. Moya, C. Girardeaux, *Surf. Sci.* 566–568 (2004) 1163.
- [116] H. Oughaddou, C. Léandria, B. Aufray, C. Girardeaux, J. Bernardini, G. Le Lay, J.P. Bibérian, N. Barrett, *Appl. Surf. Sci.* 212–213 (2003) 291.
- [117] Z. Erdélyi, C. Girardeaux, Z. Tôkei, D.L. Beke, C. Cserháti, A. Rolland, *Surf. Sci.* 496 (2002) 129.
- [118] A. Portavoce, B. Lalmi, G. Trégliat, C. Girardeaux, D. Mangelinck, B. Aufray, J. Bernardini, *Appl. Phys. Lett.* 95 (2009) 023111.
- [119] B. Lalmi, C. Girardeaux, A. Portavoce, C. Ottaviani, B. Aufray, J. Bernardini, *Phys. Rev. B* 85 (2012) 245306.
- [120] H. Oughaddou, B. Aufray, J.P. Bibérian, J.Y. Hoarau, *Surf. Sci.* 429 (1999) 320.
- [121] B.S. Bokstein, A.O. Rodin, A.N. Smirnov, *Zeit. Fur. Metallk.* 10 (2005) 1094.
- [122] J.M. Egan, C.M. Comrie, *Phys. Rev. B* 40 (1989) 11670.
- [123] W.K. Chu, S.S. Lau, J.W. Mayer, H. Müller, K.N. Tu, *Thin Solid Films* 25 (1975) 393.
- [124] M. Hillert, G.R. Purdy, *Acta Metall. Mater.* 26 (1978) 333.
- [125] J.W. Cahn, J.D. Pan, R.W. Balluffi, *Scripta Metall. Mater.* 13 (1979) 503.
- [126] R.W. Balluffi, J.W. Cahn, *Acta Metall. Mater.* 29 (1981) 493.
- [127] R. Le Gall, G. Liao, G. Saindrenan, *Scripta Mater.* 41 (1999) 427.
- [128] Y.-W. Rhee, H.Y. Lee, S.-J.L. Kang, *Journal of the European Ceramic Society* 23 (2003) 1667.
- [129] F. Liu, G. Yang, H. Wang, Z. Chen, Y. Zhou, *Thermochim. Acta* 443 (2006) 212.
- [130] B. Sivaiah, S.P. Gupta, *Mater. Charact.* 59 (2008) 1141.
- [131] S.S. Shenouda, G.A. Langer, G.L. Katona, L. Daróczy, A. Csik, D.L. Beke, *Appl. Surf. Sci.* 320 (2014) 627.
- [132] P. Zieba, *Local Characterization of the Chemistry and Kinetics in Discontinuous Solid State Reactions*, Polish Academy of Sciences, Cracow, 2001.
- [133] P. Zieba, *Interface Sci.* 11 (2003) 51.
- [134] D. Prokoshkina, L. Klinger, A. Moros, G. Wilde, E. Rabkin, S.V. Divinski, *Scripta Mater.* 101 (2015) 91.
- [135] K.-N. Tu, J.W. Mayer, L.C. Feldman, *Electronic Thin Film Science*, Macmillan Publishing Company, New York, 1992, Chaps. 11 and 12.
- [136] P. Fahey, R.W. Dutton, M. Moslehi, *Appl. Phys. Lett.* 43 (1983) 683.
- [137] M. Seibt, K. Graff, *J. Appl. Phys.* 63 (1988) 4444.
- [138] J.E. Masse, P. Knauth, P. Gas, A. Charai, *J. Appl. Phys.* 77 (1995) 934.

- [139] S.B. Herner, V. Krishnamoorthy, K.S. Jones, T.K. Mogi, M.O. Thompson, H.-J. Gossmann, *J. Appl. Phys.* 81 (1997) 7175.
- [140] M. Ronay, R.G. Schad, *Phys. Rev. Lett.* 64 (1990) 2042.
- [141] D. Prokoshkina, V.A. Esin, G. Wilde, S.V. Divinski, *Acta Mater.* 61 (2013) 5188.
- [142] S.V. Divinski, G. Reglitz, G. Wilde, *Acta Mater.* 58 (2010) 386.
- [143] I.M. Razumovskii, Yu. Mishin, C. Herzig, *Mater. Sci. Eng. A* 212 (1996) 45.
- [144] M.R. Sørensen, Y. Mishin, A.F. Voter, *Phys. Rev. B* 62 (2000) 3658.

CHAPTER 2

Diffusion-Controlled Phase Transformations in Open Systems

Andriy Gusak, Nadiia Storozhuk

Cherkasy National University, Cherkasy, Ukraine

2.1 GENERAL REVIEW OF FLUX-DRIVEN TRANSFORMATIONS

Initial title of this chapter was “Flux-driven phase transformations in diffusion zone”. Yet, in the process of writing the text we took a risk to suggest a somewhat more general title. The main reason is that the term “diffusion zone” is commonly regarded as a region of mutual (or sometimes one-sided) penetration of contacting materials in the standard diffusion couple. Yet, the progress of the last decade in the study of phase and structure transformations in materials proceeding due to and via atomic migration demonstrates a lot of various possibilities in the interaction between materials. For example, point contact reactions between nanowires of Si and nanowires or nanodots of metals like Ni or Pt demonstrate penetration of metallic atoms into Si via practically point contact, but reaction (formation of silicide) starts rather far from the contact place. Another example is amorphous solution of P in Ni which can be regarded as an end-member (marginal side) of diffusion couple in reaction with Sn. The main diffusion zone is a zone of reaction between Sn and Ni with the formation of compound Ni_3Sn_4 . Yet, the most interesting story in this interaction happens with a marginal side of this diffusion couple. Namely, it finds itself depleted with Ni or, in other words, supersaturated with P and, hence transforms into crystalline Ni_3P . In these two examples the main words are not the “diffusion zone” but the “open system”. Open system is a well-known term in general physics, nonequilibrium thermodynamics, and synergetics, meaning that a system which is under investigation has nonzero fluxes of matter or/and energy at its boundaries. Diffusion zone is a very good example of an open system, but there exist various open systems which cannot be treated as just diffusion zones. Regularities which we want to discuss in this chapter are valid not only for the standard diffusion zone but for majority of open systems,

Phase Transformation (Transition) is a very general concept. For example, the origin of our Universe (Big Bang) was actually a result of phase transition of the unstable physical vacuum. In social events, revolutions can often be treated as the phase transformations when a metastable society with old economic and social order transforms into more stable society with more favorable economic and social order (for example, feudalism into capitalism). In our chapter, we don't go so far and treat more usual physical and

chemical systems like diffusion couples, reactive foils, multilayers, powders, multiphase alloys, etc. Theory of phase transformations in condensed matter is very well developed by such classics as Gibbs, Landau, Volmer, Zeldovich, Cahn, and many others [1].

According to common understanding, all phase transformations are governed by two “powers” – thermodynamics and kinetics. Thermodynamics is something like parliament – it decides in what state any system should find itself under fixed external conditions, “at the end of the day”. Kinetics is something like government – it determines the rate of each transformation, different for each transformation. Rather often the rate of some transformations is so slow that the “end of the day” is never reached, and some transient state appears to be practically the final one. Most of the phase transformations are of the first order, which means that the old and new phase states can coexist and are separated by some barrier which should be overcome. Overcoming needs some time (depending on the height of nucleation barrier and rate of atomic migration) and includes 3 main stages: (i) nucleation of the new phase within the matrix of old phase, (ii) growth of more or less isolated precipitate of the new phase within the old phase, and (iii) coarsening (ripening) of the regions of new phase driven by the tendency to minimize the interface energy.

In the 1980s, a new concept of Driven Phase Transformations became popular. It was introduced, first of all, by the team of George Martin who then worked at the Nuclear Centre in Saclay (France). His team studied the behavior of the walls of nuclear reactors under irradiation from the reactor. They noticed that under irradiation the alloys have different criteria of metastability and instability, in comparison with alloys without irradiation. Roughly speaking, under some irradiation (expressed as an average number of displacements per atom per unit time) a system behaves as if it is exposed to higher temperature. To explain and describe this fact, Martin et al. introduced the concept of so-called “ballistic” jumps as an alternative to common thermally activated jumps [2]. This step enabled them to write the modified master equations for probabilities and to generalize the concept of phase transformations into Driven Phase Transformation in Open Systems. Later it was applied to the systems under ball milling (for example, amorphizing under ball milling) [3]. In other words, for open systems, the thermodynamics and kinetics are not so-well distinguished as in the classical approach. Instead, external fluxes may lead to “**kinetically dependent thermodynamics.**” At least one additional example of kinetically dependent thermodynamics will be described in Section 2.4, where the flux-dependent effective nucleation barrier is introduced.

During the last 15 years we, jointly with prof. King-Ning Tu at UCLA, have been developing the next step in the generalization of phase transformations – Flux-Driven Phase Transformations in **Sharply Inhomogeneous** Open systems. So, the main difference from Martin’s approach is the presence of sharp gradients of concentrations and chemical potentials across open systems and, respectively, the fluxes across the system.

Common diffusion-controlled first-order phase transformations in alloys consist of three well-known stages: nucleation, growth, and Ostwald ripening (coarsening). **Nucleation** means overcoming of the nucleation barrier due to fluctuations in the size space (changes of size due to random attachments and detachments of structure units – monomers). Nucleation in the globally homogeneous systems is determined by a thermodynamic factor (height of nucleation barrier) and kinetic factor (frequency of monomers attachment) [4]. **The growth** of new phase in binary and multicomponent alloys includes a change of local concentrations by diffusive redistribution, and, most often, is diffusion-controlled (if attachment at moving interface proceeds fast enough). It may be of two types: (i) growth of initially isolated precipitates with diffusive redistribution in the bulk of the parent phase or via the grain boundaries of the parent phase [5], (ii) cellular precipitation – growth of lamellar colonies with reaction and redistribution between lamellae along the moving interface [6]. **Ripening** is, in principle, well described by LSW (Lifshitz–Slezov–Wagner) theory [7,8] with a subsequent account of effects caused by finite volume fractions, non-equilibrium vacancies anisotropy and stresses (diffusive screening, short-range-order, etc.). Classical (conservative) ripening in a closed system is driven by the tendency of surface energy minimization at almost the constant volume of the new phase.

In this chapter, we will consider formation, growth and coarsening of the new phases in the contact zone of two materials or under intensive energy fluxes (**reactive diffusion**). From a **chemical** point of view, reactive diffusion is a **solid-state reaction** controlled by the supply of reagents through the layers of reaction products. From a **physical** point of view, reactive diffusion is a chain of competitive phase transformations in the concentration gradient within diffusion zone. The emerging phases are formed within diffusion zone (which initially has a width of a few nanometers). These new (intermediate) phases are actually the open systems, from the very beginning they find themselves in the sharp gradients of concentration and chemical potentials, as well as in the field of significant fluxes of matter and/or energy passing through the transformation zone. In this case, all stages of transformations change their behavior drastically [9]. The list and a brief review of Flux-Driven Phase Transformations in Open systems are presented.

2.1.1 Flux-Driven Ripening of Cu_6Sn_5 Scallops During Reaction Cu/Liquid Solder

State-of-the-art. Theory of Flux-Driven Ripening (FDR) is actually a kinetic theory of soldering. It was first suggested by one of the authors of this chapter (AG) jointly with prof. King-Ning Tu [10,11]. It introduced the concept of non-conservative ripening proceeding simultaneously with reactive growth due to diffusion via a system of liquid channels of molten solder between grains of growing phase. Term “non-conservative” here means that during this type of ripening the new phase volume is far from being

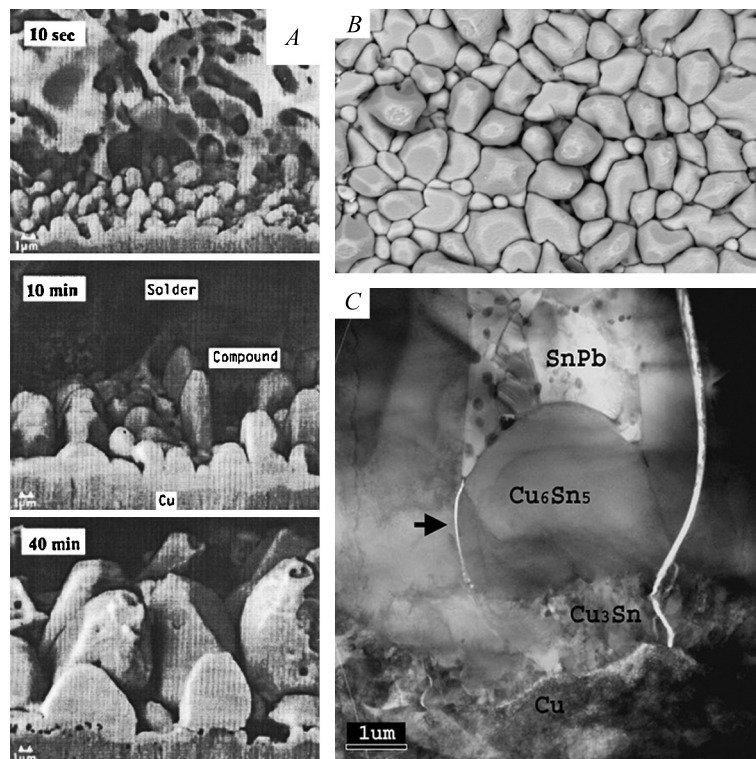


Figure 2.1 Simultaneous growth and ripening of Cu₆Sn₅: (A) SEM images of Cu₆Sn₅ scallops after 10 seconds, 10 minutes, and 40 minutes of reflow; (B) SEM image of a top view of scallops after etching of solder; (C) TEM-image of a cross section of scallops and channel. (Figure is taken from [10].)

constant, but instead is growing with time as $t^{1/3}$, and the interface is not tending to a minimum, but instead tends to constant.

Ripening rate (as well as growth rate) appeared to be independent on interface surface tension and proportional to the driving force of reaction and to the channel width. There was an intensive discussion about the nature of channels between scallops (liquid channels or ordinary grain boundaries or “prewetted” grain boundaries). Recent experimental work [12,13] – comparison of copper reaction at the same temperature 222°C with solid Sn and with metastable supercooled liquid Sn – seems to finalize this problem: liquid channels with width of a few nanometers and their joints are the main mechanism of transport for Cu+liquid Sn reaction through the reaction zone.

Unsolved problems. So far our model [10] works fine only for a few minutes of reflow when scallops reach sizes of a few microns. After this stage scallops become more and more elongated, the growth law of $t^{1/3}$ is not valid anymore. There is no generally accepted theory for this general case.

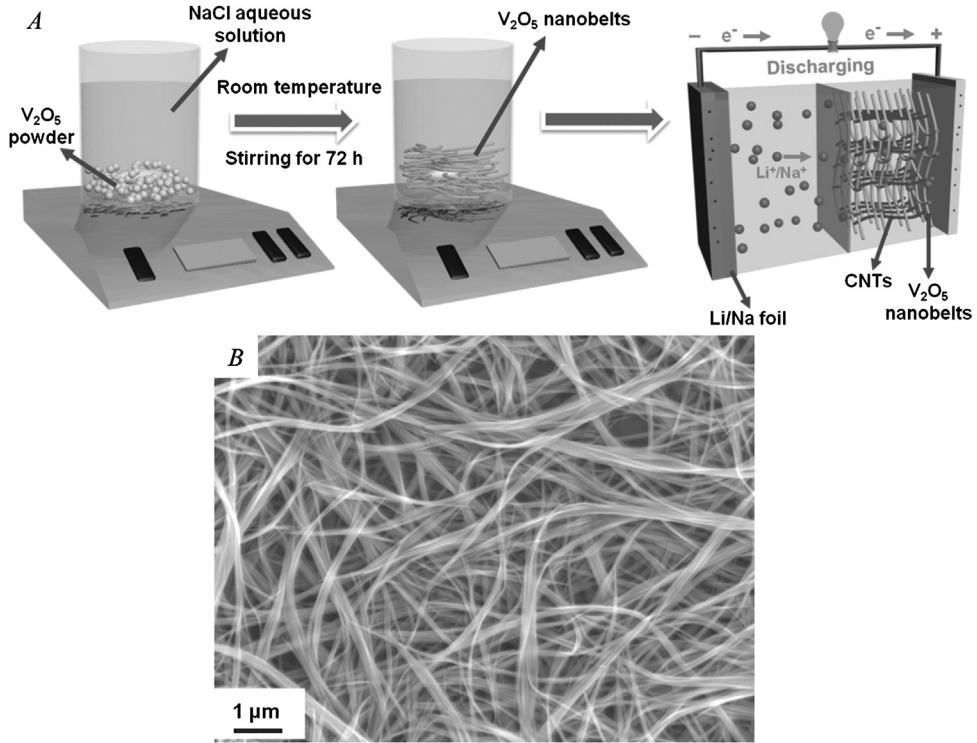


Figure 2.2 (A) Schematic diagram of the room-temperature synthesis and assembly of V_2O_5 nanobelts as cathode materials for flexible, lightweight Li(Na)-ion batteries; (B) FESEM. (Figure is taken from [14].)

2.1.2 “Anti-Ripening”: Stirring-Driven Dissolution-Recrystallization With Formation of Nanobelts

State-of-the-art. The effect of “anti-ripening” was discovered very recently by the groups from Singapore and Oslo [14]. Intensive stirring of an aqueous solution of, say, NaCl, finally leads to the dissolution of initial more or less equiaxial (several microns sized) grains of V_2O_5 , and recrystallization into long nano-belts with the total surface area up to 14 times larger than the initial one. It means that instead of minimizing the interface surface (typical for usual ripening), in this case, it grows. So, this process can be called “anti-ripening” (see Fig. 2.2).

Unsolved problems. So far no reasonable theories were suggested, excluding calculations of surface tensions for different faces of V_2O_5 crystals. One may try to use the concept of ballistic diffusion [2,3] as an addition to common thermally induced diffusion. First of all, it is necessary to investigate, how the ballistic factor can change the well-known equilibrium Wulff construction [15] and, then, the ripening kinetics.

2.1.3 Flux-Driven Anti-Phase Domains Coarsening During Reaction

State-of-the-art. It is common empirical understanding that in reactive diffusion the mean lateral size of grains of the growing compound layer is about the same as the thickness of this layer. Strange enough, but this property has not been theoretically described. In [16] we tried to present some elementary model and Monte Carlo simulation for the case when grains are actually the anti-phase domains of the growing ordered FCC phase A3B. We found that the lateral coarsening during reactions proceeds faster than the coarsening in a closed system. This result is in part similar to the Flux-Driven Grain Growth during deposition [17].

Unsolved problems. So far we can see that the flux through the growing phase layer helps the larger grains to consume the neighboring smaller grains, but we do not have a clear understanding of the reasons for this phenomenon, as well as its regularities.

2.1.4 Flux-Driven Cellular Precipitation of Porous Lamellar Structures in Cu–Sn Reactions

State-of-the-art. In 2014 J. Panchenko et al. found a new type of porous structure (sponge-like, lamellar one) formation at the late stage of reaction in the sandwich Cu/liquid Sn/Cu [18]. In [19] we (jointly with K.N. Tu from UCLA and Chih Chen, Hsinchu, Taiwan) demonstrated that formation of the mentioned structure can be treated as the flux-induced cellular precipitation during reaction $\text{Cu}_6\text{Sn}_5 - 3\text{Sn} \rightarrow 2\text{Cu}_3\text{Sn} + 3\text{V}$ with formation of lamellae of Cu_3Sn and lamellar voids due to outflux of tin from Cu_6Sn_5 .

Indeed, if some driving force sucks out tin atoms from the Cu_6Sn_5 compound, it leads simultaneously to two effects: (a) supersaturation with vacancies at the tin sublattice, (b) supersaturation with copper with respect to tin so that atomic fraction becomes closer to Cu_3Sn phase. Both of these factors should lead to decomposition with the formation of Cu_3Sn and of voids. Namely, we suggested a new mechanism of the Cu_6Sn_5 compound transformation into a lamellar structure consisting of the mutually penetrating layers of compound Cu_3Sn and of elongated voids (“void phase”). The suggested mechanism can be called a flux-driven cellular decomposition. Here the flux which drives the decomposition is an outgoing flux of Sn realized by the surface diffusion along the percolating array of the “void phase” surface. One of the main differences from the common cellular decomposition of supersaturated solid solution into two crystalline phases is that the transformation is complete, no residual phase Cu_6Sn_5 is left. Another evident difference is that the average composition of the system changes, due to loss of tin.

Unsolved problems. So far we have doubts about the nature of the driving force of Sn out-flux – it can be some chemistry related to composition of surrounding flux (gumboil) used to avoid oxidation [18], or it can be reaction of tin with side walls of

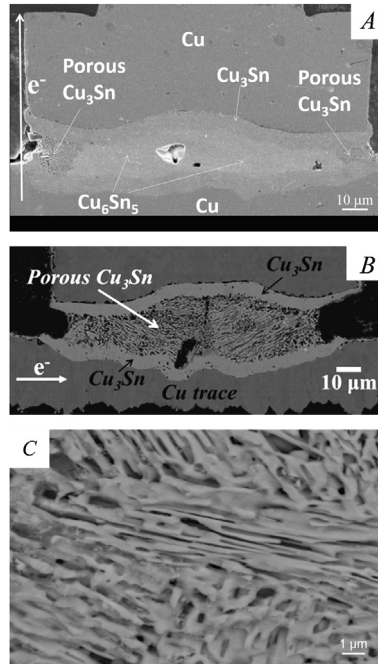


Figure 2.3 Formation of second-type Cu_3Sn porous structure in Cu–Sn–Cu reaction: (A) starting stage – cross-sectional view, (B) final stage – cross-sectional view, (C) plan view of the sponge-like lamellar porous structure. (Figure is taken from [19].)

copper due to surface diffusion of tin [19]. The answer can be found by repeating the same experiment with Cu–Sn–Cu sandwich in a vacuum instead of flux (gumboil).

2.1.5 Flux-Driven Crystallization of Amorphous NiP During Reaction With Tin-Based Solders

State-of-the-art. In solder contacts, usually, copper is too intensively reacting with tin, forming too big grains of IMC, which decrease the reliability of solder contact. Therefore, copper is often covered by nanolayer of Ni, whose interaction with tin with the formation of Ni_3Sn_4 is more moderate. Yet, due to nanostructure of Ni film, copper diffuses via the numerous grain boundaries of Ni to react with tin, so that big grains of Cu_6Sn_5 , nevertheless, use to cap the smaller grains of Ni_3Sn_4 . To prevent penetration of copper through grain boundaries of Ni, one can use electroless nickel (amorphous solution of phosphorus in nickel). Amorphous phase does not contain paths of fast diffusion (like grain boundaries) and therefore is used as a diffusion barrier. Yet, this barrier also appeared to be unstable with time. Namely, the reaction of amorphous Ni–P alloy with tin-based solder proceeds, by using part of Ni for reaction with tin and formation

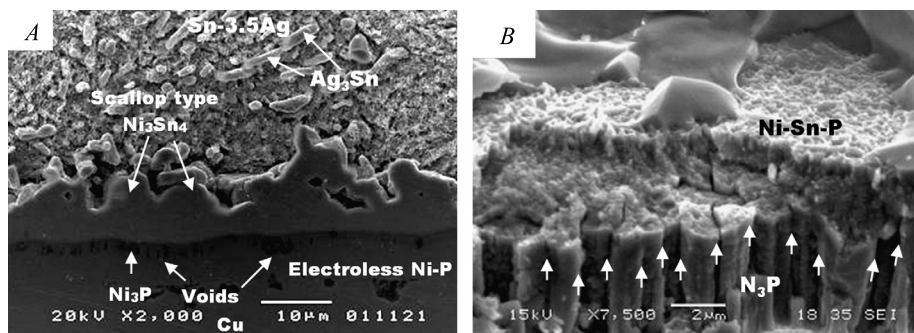


Figure 2.4 (A) SEM images showing the uneven IMCs growth at the electroless Ni-P/Sn-3.5Ag interface after reflow at 245°C for 1 min; (B) Fracture surface of electroless Ni-P/Sn-3.5Ag solder joint aged at 200°C for 100 h showing micron-size columnar Ni₃P grains. The arrows indicate the diffusion paths in the grain boundaries of Ni₃P grains. (Figure is kindly provided by prof. Chen Zhong, NTU, Singapore.)

of Ni₃Sn₄ [20]. Out-flux of Ni from amorphous Ni-P induces its flux-induced **decomposition** into crystalline compound Ni₃P. The newly-formed layer of crystalline Ni₃P contains an ensemble of lamellar voids, partially similar to that in Section 2.1.4 (see Fig. 2.4).

Unsolved problems. So far there is no theory of the mentioned process.

2.1.6 Nucleation in Sharp Concentration Gradients

State-of-the-art. Phase formation in thin films A/substrate B or bi-layers A/B over the inert substrate, or in multilayers, as a rule, proceeds “one-by-one” (sequentially). It means that reaction starts from the formation of a single phase. Then each of the next intermetallic compounds starts growing when the previous growing compound consumes at least one of materials necessary for compound construction. At each moment the film consists of one growing phase and two terminal phases being consumed by the growing phase. “At the end of the day,” the film consists of a single compound (if its average concentration is stoichiometric) or of two phases in equilibrium (if average concentration corresponds to the two-phase region).

Such sequential (one-by-one) growth has at least three possible explanations:

(a) “Low growth rate”. According to this explanation, theoretically, all phases grow simultaneously. Yet, the growth rate of each phase depends, first of all, on the diffusivities of both components in it. Diffusivities of the same component in two phases, typically, differ by one or even several orders. Therefore, the growth rate of neighboring phases may also differ by orders. In this case, the first phase to be formed is just the phase with fast atomic migration (according to F. d’Heurle, “fast is the first”). According to this concept, other phases also grow (simultaneously) but too slowly. Corresponding layers are so thin that it is almost impossible to detect them experimentally.

(b) “Competitive phase growth controlled by interfacial barriers” [21]. Accumulation of migrating atoms near interfaces, due to interfacial barriers, may cause the initial linear phase growth. It happens when the “waiting time” for atoms of at least one component, before crossing the interface, is longer than the migration time across the phase layer. In the case of two intermediate phases, the barriers between them and with terminal materials may slow down the growth rate of some phase layers and, formally, make it negative. Practically, of course, it means that such phases will not even start growing, and will be absent for some time.

(c) “Diffusion competition and suppression of critical nuclei”. In this explanation, one takes into account that any new phase in solid state reaction, as a first-order transformation, should start from the formation of the critical nucleus [22,23]. According to this concept, nature provides the unlimited source of heterophase nucleation events. The fate of each nucleus after its formation depends on the diffusive interaction with neighbors. In closed systems, all nuclei which passed the nucleation barrier (including kT-region in the vicinity of the saddle-point), are growing further without problems. In an open inhomogeneous system with gradients of concentrations and chemical potentials, the growth of “thermodynamically critical” nuclei is not guaranteed. These nuclei, appearing at the interface, have different neighboring phases “left” and “right”. The diffusion fluxes pass through the newly formed nuclei as well as through their neighbors. Diffusion fluxes change abruptly when passing across each newly formed boundary of the newly born nucleus, and thus drive the boundary movement. Such interface movement due to flux steps is typical for diffusion couples (Stephan problem) and means diffusive interactions between neighboring phases. In a common Stephan problem of the multiphase diffusion, formally, all phase layers grow parabolically (proportionally to the square root of time) from zero thickness. In our approach, it is important that the initial width of each phase is taken to be the critical nucleus size (instead of zero). In this case (if phases start from critical sizes instead of zero thickness), due to the diffusive interaction between the critical nucleus and neighboring phases, the width of some phase nucleus (distance between left and right boundaries) can decrease as well as increase. If it decreases, the nucleus becomes subcritical and should disappear. Usually, it happens if the neighboring phases have larger diffusivity and comparative thickness. We called such “aggressive” neighbors the “vampires” (Francois d’Heurle suggested to call them “sharks”). Such phases-“vampires” destroy and consume all of the newly forming nuclei, making the new phase be present only virtually in the form of constantly forming (due to heterophase fluctuations) and vanishing (due to diffusive suppression by the neighbors) embryo. A simple mathematical scheme was built, predicting the sequence of phase formation and even the values of suppression (incubation) periods. The above-mentioned scheme leads to suppression/growth criterion which predicts the first phase to grow and, then, the phase formation sequence, from the ratio of integral (Wagner)

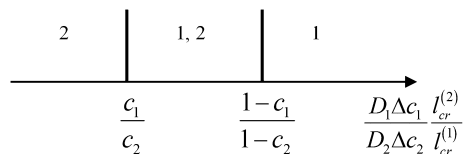


Figure 2.5 Suppression and growth criteria for two intermediate compounds (IMCs): right region corresponds to growth of IMC 1 and suppression of IMC 2; left region corresponds to growth of IMC 2 and suppression of IMC 1; and central region corresponds to simultaneous nucleation and growth of both compounds.

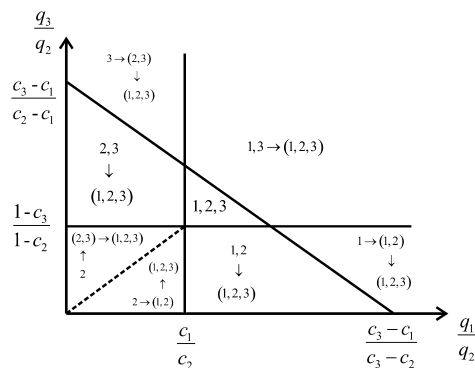


Figure 2.6 Suppression and growth criteria – case of three intermediate phases between almost pure components.

diffusivities and the critical sizes. An example of such criterion for competition of two intermediate phases is shown in Fig. 2.5.

The numbers denote phases that grow from the very beginning. Similarly, we can find the criteria for the suppression and growth in case of three intermediate phases between mutually insoluble A and B. The corresponding graphical representation of the criterion is given in Fig. 2.6. The arrows indicate the sequence of phase composition change in the diffusion zone.

Actually, both models ((b) and (c)) (published simultaneously) predict suppression/growth criteria and a certain critical thickness of the first growing phase under which growth of other phases is kinetically suppressed. Yet, in model (b) the growth/suppression criterion is determined not by diffusivities and critical nuclei sizes, but instead by the ratio of interface kinetic parameters (flux across the interface is taken as proportional to the deviation of concentration at the interface from its equilibrium value, with interface kinetic parameter as a coefficient).

In our first, primitive model of phase competition [22,23], we had taken the inhomogeneity of the nucleation region into account only to some extent: we considered the diffusive interactions of the newborn nuclei, but we had not considered the change

of the nucleation barrier caused by the very fact of the existence of a sharp concentration gradient. We had also not taken into account the change of the nucleus shape (aspect ratio) due to nucleation in sharply inhomogeneous conditions. Later we reconsidered the thermodynamics of nucleation in a concentration gradient. The first version of “nucleation in concentration gradient” theory was published in [24]. The idea of this theory was very simple: if prior to intermediate phase formation a narrow layer of the metastable solid solution or amorphous alloy is formed at the base of the initial interface, the sharp concentration gradient inside this layer will provide the decrease of the total bulk driving force of nucleation. Of course, the change of driving force leads to the change of the nucleation barrier. The spherical nuclei were considered as appearing in the inhomogeneous concentration profile of the parent phase. It means that the local driving force of transformation could change significantly from the left to the right along the diameter of the nucleus. This effect is not negligible because the intermediate phases have a sharp concentration dependence of the Gibbs free energy. It leads to a new size dependence of the Gibbs free energy. This new dependence contained, in addition to the terms of second order (surface energy, positive) and third order (bulk driving force, negative), a new term proportional to the 5th power of size and the squared concentration gradient,

$$\Delta G = \gamma \cdot 4\pi R^2 - \Delta g \frac{4\pi R^3}{\Omega} + \kappa (\nabla c)^2 R^5.$$

If the concentration gradient is large enough, the size dependence of Gibbs energy becomes monotonically increasing. It means the infinitely high nucleation barrier or, in other words, the thermodynamic suppression of nucleation by the concentration gradients. Thus, at an initial stage of reactive diffusion, nucleation can be suppressed not only by diffusive competition but also due to a too narrow space region, which is favorable for transformation. Pierre Desre et al. [25] published similar results. This approach had been applied to the description of solid state amorphizing reactions. The concept of nucleation suppression by the sharp concentration gradients may explain why stable intermetallics appear in the diffusion zone only after the amorphous layer exceeds some critical thickness. Gibbs energy size dependence in [24] and [25] were very similar, but the corresponding models of nucleation in concentration gradient treated different nucleation mechanisms (nucleation modes). In [24] we treated a polymorphous mode, by keeping in mind the following picture: The preliminary diffusion leads to the formation of a metastable parent solution with a sharp concentration profile. When this profile becomes smooth enough to provide sufficient space for compositions favorable for a new intermediate phase, this very phase nucleates just by reconstruction of atomic order, without changing immediately the concentration profile (at “frozen” diffusion) polymorphic transformation. P. Desre suggested the so-called transversal nucleation mode:

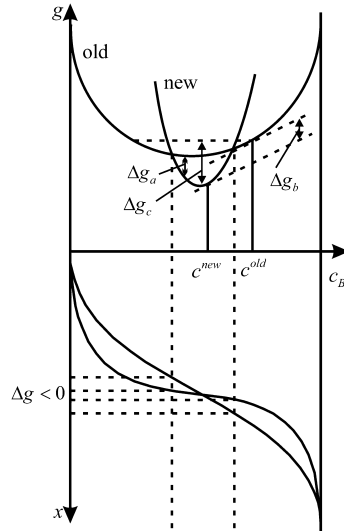


Figure 2.7 Schematic dependence of the driving force per atom of the nucleus for polymorphic (a), transversal (b), and longitudinal (c) modes.

each thin slice of the newly formed nucleus, perpendicular to the direction of the concentration gradient, is considered as a result of decomposition in a corresponding thin infinite slice of the parent solution, leading to a redistribution of atoms among new and old phases. In this transversal mode, the redistribution proceeds within each slice, independently of others (see Fig. 2.7).

Models of both nucleation modes were developed with an account of shape optimization, stresses, ternary systems, heterogeneous nucleation at grain boundaries, at interphase boundaries. Description of the mentioned development can be found in the monograph [9]. The polymorphic mode with restricted shape optimization or without shape optimization fits the experimental data for Co_2Al_9 formation [27]. Recently optimistic results were obtained by the groups of Guido Schmitz and Zoltan Erdelyi for nucleation in Cu–Si reactions [28].

Unsolved problems. So far we have no clear understanding of the choice procedure between three possible nucleation modes.

2.1.7 Flux-Driven Nucleation at Interfaces (FDN)

State-of-the-art. Nucleation of intermediate phases (compounds) and of voids at interfaces during reactive diffusion proceeds under the influence of the flux divergence in the nucleation regions. It can be described as an additional term for drift in Fokker–Planck equation for size distribution in the size space [29]. It is possible to construct the effective Gibbs nucleation barrier which may increase to infinity meaning the full

suppression of nucleation. Alternatively, the effective barrier may decrease assisting the nucleation. The introduced effective nucleation barriers depend on kinetic factors – on the ratio of diffusivities in nucleating and in neighboring phases.

Unsolved problems. So far we did not make a detailed comparison of theory with experiment.

2.1.8 Flux-Driven Self-Regulated Repeating Nucleation in Silicon Nanowires During Point-Contact Reaction With Metallic Nanowires or Nanoparticles

State-of-the-art. We distinguish reaction as a point contact if the contact of two materials, ideally, corresponds to a single point: a sphere with a sphere (initial stage of two powder particles joining), a sphere with the plane, a sphere with the cylinder, a cylinder with the cylinder. The most interesting seem to be the point contact reactions between silicon nanowires (covered by natural oxide) and metallic nanowires or nanoparticles [30]. Formation of epitaxial silicide in nanowire of Si was observed by high-resolution transmission electron microscopy. One may notice the following peculiarities of such reactions: (i) the first phase to form is different from that in thin film or bulk reactions (for example, in Ni–Si point contact reactions, the forming silicide phase is NiSi or NiSi₂, depending on the orientation of Si, instead of the Ni₂Si phase in thin film reactions); (ii) the new phase is formed outside the point contact zone – near the nanowire tip or between two point contacts; and (iii) the epitaxial growth of silicide inside the silicon nanowire is a “stop-and-go” process, consisting of a long waiting time (equal to incubation time of forming the critical disk of each new atomic layer of silicide), followed by a rapid, almost instant lateral growth of this new layer (see Fig. 2.8).

Practically, point contact reactions are very promising since they may provide the possibility of nano-heterostructure and nanogap production. For fundamental research, point contact reactions represent a new class of chemical reactions between solids, as an alternative to the standard bulk diffusion couples and layered thin films.

In [31] we used the classical nucleation theory and applied it to the repeating nucleation events in point contact reactions between metal and silicon nanowires. There we suggested that the nucleation under a constant source of metallic atoms in the silicon leads to auto-oscillations of metal atoms concentrations in the silicon. This approach was continued in [32]. The modified theory predicts the rate of repeating nucleation at the nanoscale level.

Unsolved problems. So far there is no clear understanding why nucleation of silicides does not proceed in the vicinity of point contact.

2.1.9 Flux-Driven Ordering

State-of-the-art. In 1998 we found a possibility of oscillating ordering in the contact zone at the initial stage of interdiffusion [33]. In 2008 Beke, Erdelyi and Taranovskyy,

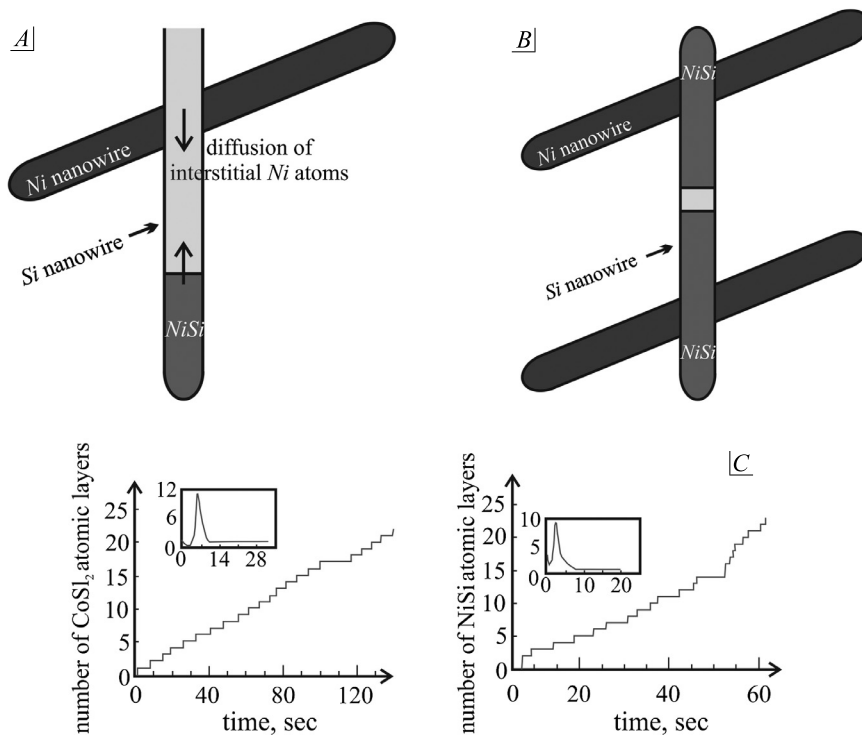


Figure 2.8 (A) Scheme of point contact reaction between Ni or Co nanowire and Si nanowire with nucleation of silicide far from the contact point, at the end of silicon nanowire; (B) Possibility of nanoheterojunction Si-silicide-Si formation using two point contacts; (C) Stepwise growth of silicide by self-regulated repeating nucleation and growth of each new atomic layer.

when simulating the formation of B2 intermediate phase in highly asymmetrical diffusion couple (by kinetic mean-field method), found that the ordering in such a system may start rather far from ideal stoichiometry [34]. It means that ordering under external fluxes behaves differently, in comparison with homogeneous ordering in the closed system.

Unsolved problems. So far the mentioned schemes were realized for artificial quasi-one-dimensional or two-dimensional lattices. It is necessary to model a Flux-Driven Ordering by simulation by just invented Stochastic Kinetic Mean-Field Model [35].

2.1.10 Self-Organization of Two-Phase Structures Under Electromigration and Thermomigration

State-of-the-art. Electromigration in metals (first of all, Al and Cu) is known as the main reason for failures of integrated circuits due to formation and growth of voids

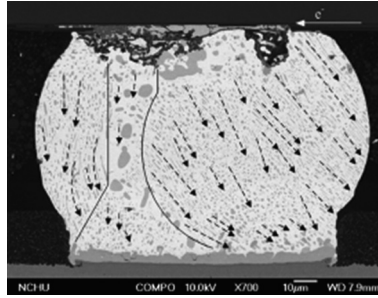


Figure 2.9 Solder bump morphology under electromigration.

and hillocks. Electromigration in solid solutions may lead to a small redistribution of components. Electromigration in two-phase structures is much more interesting. For example, electromigration studies in eutectic tin–lead solder bumps as well as in composite bumps (high-Pb solder and eutectic SnPb solder) demonstrate the formation of fibrous structures under direct current or alternative current of density about 10000 amperes per square centimeters and higher (see Fig. 2.9). The fibrous structures are formed as colonies (more or less parallel to the local current direction) and seem to be more or less monosized (small dispersion of radial sizes) inside each colony. Preliminary theoretical considerations have led us to the following preliminary conclusions (hypotheses) [36]:

1. Electromigration in a two-phase structure may cause a redistribution of phases closer to the parallel connection (so that energy dissipation goes to a minimum).
2. Thermomigration in a eutectic two-phase structure also may lead to the microstructure instability, due to the lack of chemical potential gradient in the two-phase mixture to counteract the temperature gradient.

Unsolved problems. Theory of the fibrous and lamellar structure formation under electromigration and/or thermomigration is still under discussion.

2.1.11 Hollow Nanostructures Formation and Collapse Driven by Kirkendall Effect [37–39]

State-of-the-art. In most solid state reactions the vacancy fluxes appear as a result of different mobilities of diffusing species. The divergence of vacancy fluxes leads to competing Frenkel (Kirkendall) voiding and Kirkendall shift, depending on the relative efficiency of voids and dislocation kinks as vacancy sinks/sources. Competition of Frenkel and Kirkendall effects recently (in 2004) found interesting applications in the new method of hollow nanoshell production by solid state reactions (by the group of Paul Alivisatos). In this method, metallic nanoparticles react with oxygen or sulfur, forming a compound in which metal atoms diffuse outside faster than oxygen or sulfur

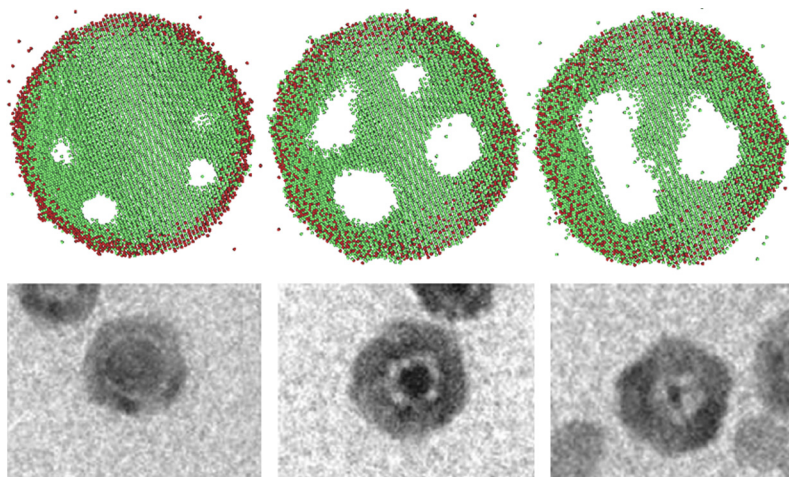


Figure 2.10 Nanoshell formation versus experiment (Yadong Yin, Robert M. Rioux, Can K. Erdonmez, Steven Hughes, Gabor A. Somorjai, A. Paul Alivisatos, *Science*, Vol. 30430, 711–714 (2004)).

inside. Thus, the vacancy flux inside eventually leads to a hollow nanostructure with a central symmetric void (see Fig. 2.10).

Of course, hollow structures should be unstable due to the Gibbs–Thomson effect (which was simultaneously noticed by Goesele and Tu). Namely, the vacancy formation at the inner shell boundary leads to shrinking of the inner void and, therefore, to a decrease of surface energy: the vacancy formation at external boundary leads to increase of surface energy. Therefore, the vacancy concentration at the inner shell boundary should be higher than that at the external one. Therefore a vacancy gradient should exist, leading to vacancy outflux and corresponding void shrinkage. Together with Tu and Zaporozhets, we analyzed the process of formation and collapse of nanoshells taking into account not only Frenkel, Kirkendall, and Gibbs–Thomson effects, but the inverse Kirkendall effect as well (segregation in the vacancy flux and corresponding damping of shrinking rate). Actually, the Gibbs–Thomson effect is important not only at the stage of shrinking but also at the stage of formation and may suppress the formation itself.

Experimental results of Nakamura et al. (2008) proved that the shrinkage process is real. The topic is very close to the problem of drug delivery – medical procedure using nanocapsules for transportation the drugs against cancer to certain places in the organism.

Unsolved problems. In cylindrical case (hollow nanowires formation and collapse) there is an additional problem of Rayleigh instability of hollow cylinder and transformation of this hollow cylinder into the chain of isolated voids.

Now we will mention some other types of flux-driven structure evolution, which have also been treated by the authors of this chapter and which, strictly speaking, are

not phase transformations, but rather have many features common with real flux-driven phase transformations.

2.1.12 Diffusion Induced Bifurcations and Instabilities of Kirkendall Planes [40,41]

State-of-the-art. There is one more interesting problem of the flux-induced morphology evolution in solid state reactions – it is a problem of bifurcation and instability of Kirkendall planes. The honor of the discovery of multiple Kirkendall planes (K-planes) – the latest great discovery in classical diffusion – belongs to the Eindhoven diffusion group (F. van Loo, A. Kodentsov, M. van Dal, C. Cserhati). One of the authors of the present chapter was lucky to take a very small and modest part in this discovery – to come to the right place (Eindhoven) at the right time (beginning of 2000) and to understand that in the case of several K-planes some of them can be stable and others can be unstable. Moreover, a situation is possible when only a single unstable K-plane exists, leading to a broadening crowd of markers instead of a plane. Later such a situation was experimentally verified. Actually, the problem is fundamental and exciting: The initial concentration step in the standard diffusion couple contains all the future of this couple like the initial fireball of Big Bang contained the future of our Universe. Moreover, like the small scales in the modern nonhomogeneous structure of the Universe, small fluctuations of inert Kirkendall marker distribution in the vicinity of the initial interface can lead to bifurcations and instabilities of Kirkendall planes. From a naive, purely intuitive point of view, it seems strange that markers, at first “overlapping” the whole concentration range of the diffusion couple, afterwards gather into a single plane corresponding to only one fixed (constant in time) composition, this plane is usually called a Kirkendall plane. It is commonly adopted that the Kirkendall plane represents the initial contact plane moving according to the parabolic law, its velocity being proportional to the difference of partial diffusivities and to the concentration gradient in the vicinity of the fixed composition. The existence of such a K-plane implies that this plane is a kind of attractor for markers. It is natural to ask why a system should have only one attractor. Is it possible for a binary diffusion couple to have two or more attractors? Is there any possibility for a system to interdiffuse without any attractors at all (without a stable K-plane), with a broadening in a time of the distribution of markers? In the latter case, a system should “forget” the initial contact interface, which should lead to the especially tight bonding of the starting materials. Thus, the problem of bifurcations and instabilities of K-planes arose. It was solved and now has a strong experimental background.

Stable and unstable K-planes. The position of a K-plane at an arbitrary time moment can be easily predicted in the case of the parabolic regime of interdiffusion from the equation $(D_B - D_A) \frac{\partial c_B}{\partial X} \Big|_{X_{K\text{-plane}}} = \frac{X_{K\text{-plane}}}{2t}$. It can be easily seen that for the case

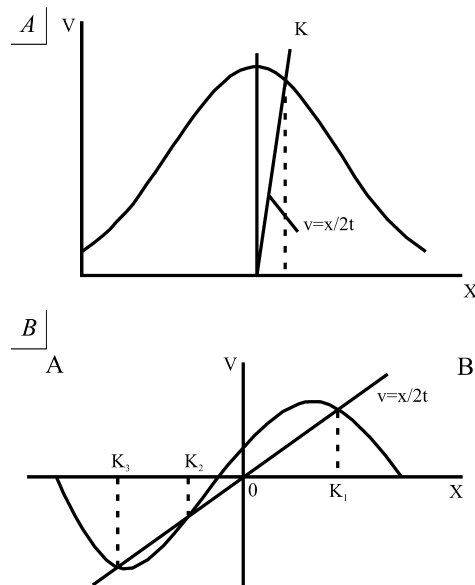


Figure 2.11 Prediction of K-planes and their stability from the marker velocity curve: (A) velocity curve for a single stable K-plane; (B) velocity curve for the case of three K-planes: two of them are stable (1, 3) and one is unstable (2).

shown in Fig. 2.11A, the K-plane is a stable one. Indeed, if due to some incidental noise one of the markers is found to be slightly ahead of the K-plane (Fig. 2.11A), its velocity will be less than that of the K-plane, so the marker will come back to the plane. If the marker is located behind the K-plane, its velocity will increase and it will also reach the K-plane. Therefore, if a K-plane is fixed with an intersection in the region with a negative slope of velocity curve it will be a moving attractor for markers.

There are several systems for which the difference $D_A - D_B$ can change its sign depending on the compound: for example, for the β -phase of Au–Zn, Ni–Al, Co–Ga, etc. In such a case, the straight line $U = \frac{1}{2t}x$ and marker velocity plot may have three intersections rather than only one (Fig. 2.11B), and three possible K-planes. We can say that K_1 and K_3 must be stable while K_2 -plane must be “virtual”, i.e., unstable. Indeed, it corresponds to the positive slope of the velocity curve. So, a marker placed in front of the K-plane will move faster than it and won’t return to it. A marker located behind the K-plane will have a smaller velocity and will also leave it. Thus, all markers that could belong to K_2 would be captured by K_1 and K_3 .

Unsolved problems. So far all derivations and experimental data on K-planes instabilities and bifurcations deal with the strictly parabolic regime of inter- and/or reactive diffusion. On the other hand, in most cases, the parabolic law is not valid at the initial stage.

2.1.13 Flux-Driven Grain Growth During Deposition [17]

State-of-the-art. Typically, at thin film deposition the mean lateral grain size is of the same order as the film thickness. Thus, the thicker the film, the larger the grains. It means that the very process of deposition somehow helps the grains grow laterally during deposition. Actually, lateral grain growth during deposition means that some grains overlap other grains. If the deposition rate is constant and mean lateral size is proportional to thickness then it means that the lateral growth rate is linear in time. It is different from common models of grain growth providing the parabolic time dependence for average grain size. One can easily check that if the mean lateral grain radius is proportional to the film thickness, then the total grain boundary area remains constant during grain growth. Hence we have a unique case of grain growth in which the total surface area is constant but the volume increases. We call it the flux-driven grain growth (FDGG). The rate of FDGG depends on the deposition flux. This is quite different from the normal grain growth in which the total volume of the grains is constant, but the grain boundary area decreases and the grain growth rate is parabolic. In Section 2.1.1, we discussed a kinetic theory of ripening during reaction, flux-driven ripening (FDR), in which the ripening occurs under a constant surface area but growing volume. It is different from the classic Lifshits–Slezov–Wagner (LSW) ripening wherein the emerging phase keeps the total volume almost constant and, instead, reduces its total surface area. The driving force of flux-driven ripening is the gain of bulk Gibbs free energy of intermetallic compound formation instead of the decrease of surface energy. FDR and FDG look very similar; both processes proceed under the conditions of the constant surface but growing volume.

We suggested the so-called “mushroom” effect as a possible mechanism of FDGG: When atoms are being deposited onto the film surface, they become adatoms. These adatoms remain migrating over the surface for some time, looking for a suitable place to join the lattice of one of the grains. We assume that the migration length of adatoms is short enough so that they tend to attach to the “home” grain surface at the place of their “landing.” We also assume that the only place where a landing atom has the choice of its future “host” grain, is a narrow band in the vicinity of a junction where a grain boundary meets the surface. Let the width of this band be $2d$, and take d_{sink} as a distance to the nearest sink (surface step) for an adatom to join the lattice. We assume that each atom, landing within the mentioned narrow band, chooses the larger grain as its “host” grain and joins the lattice of this grain.

Hence, the larger grain is overlapping its neighbor by a distance d during the building up of a new atomic layer. This leads to a linear grain growth rate proportional to the thickening rate. We assume that the reason for an adatom to choose the larger grain is simply a smaller curvature, and hence, a lower potential energy of corresponding sites. Thus, the deposition flux helps the larger grain grow due to the “mushroom effect.”

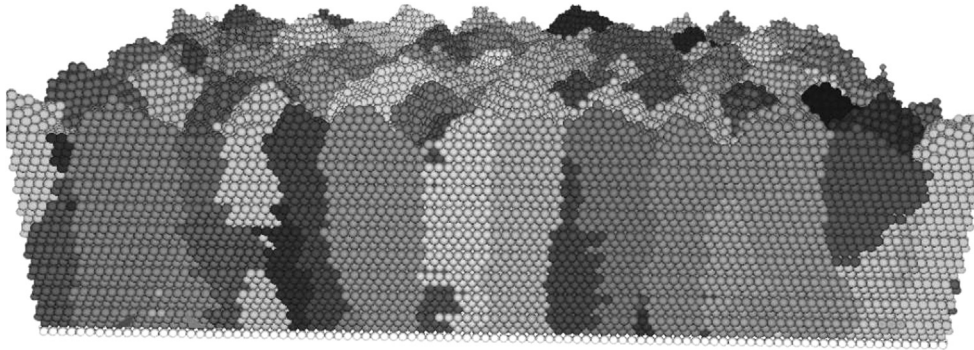


Figure 2.12 Kinetic Monte Carlo simulation of lateral grain growth during deposition of the thin film. Results illustrate the “mushroom effect” theoretically predicted in [17]. (Simulation made by coauthor of [17] – I. Sobchenko.)

This effect was demonstrated by KMC simulations of thin film deposition (Fig. 2.12, courtesy of Ihor Sobchenko).

Unsolved problems. So far the models of lateral grain growth used by our team were rather artificial.

2.1.14 Severe Deformation Induced Formation of Low-Viscosity “Phase” in KOBO Process [42]

State-of-the-art. The last two decades were the time of fast progress for various methods of Severe Plastic Deformation (SPD). Most popular SPD methods are equal-channel angular pressing (ECAP) and high-pressure torsion (HPT). Industrial use of materials produced by SPD is limited by the low production rate, a small amount of the material and inhomogeneity of structure. Some time ago Korbel and Bochniak suggested one more way of SPD, called KoBo. KoBo method resembles HPT (pressure is applied simultaneously with torsion), with a very important difference: torsion is oscillating with a frequency of several hertz and amplitude about 5–7 degrees. Such a complex method of plastic straining causes the highly heterogeneous flow of metals in the strongly shortened zone of deformation and as a result of radial flow in the direct vicinity of the die. An associated drastic decrease in the extrusion force, which depends on frequency and amplitude of the die rotations, deforms metals with very large strains at low temperature, which makes the method unique. During the KoBo extrusion process, the metal billet undergoes reversible plastic twisting just before entering the cross-section, reducing the die (Fig. 2.13A).

We developed a model [42] which confirms that the Severe Plastic Deformation in KoBo process may be interpreted as a non-equilibrium phase transition. In this transition, the system demonstrates an abrupt drop of viscosity within some zone, which

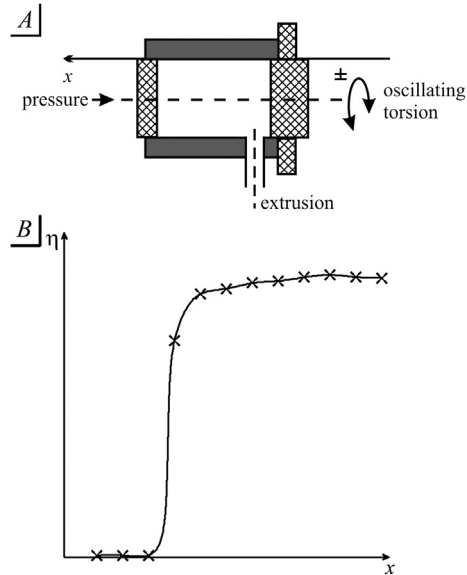


Figure 2.13 KOBO method of severe plastic deformation: (A) scheme of KOBO process; (B) sharp transition to low viscosity in a narrow region. (Figure is taken from [42].)

is determined by the intensity of deformation (Fig. 2.13B). In this zone, an intensive lateral rotational movement generates a large number of point defects, which in a self-organized manner make rotation possible, decreasing viscosity.

2.1.15 Electromigration Induced Grain Rotation Under Electron Wind in Anisotropic Conducting Beta-Tin [43]

State-of-the-art. According to [44], the resistivity of tin line under electromigration (atoms transfer due to electron wind) during one day (at constant current) decreased. It means that some structural changes proceeded in tin during electromigration. To study the evolution of the grain structure in thin film tin lines under electromigration, the local microdiffraction of synchrotron radiation was used in [43]. Evolution of surface morphology demonstrated the possibility of grain rotation. The classical driving force of rotation exists because grain boundary energy depends on the misorientation angle between the neighboring grains. We proposed an additional reason of rotation and corresponding mechanism of the grain rotation under electromigration – EDGR (Electromigration-Driven Grain Rotation). The resistivity of the line consists of bulk resistivity of grains plus resistivity of grain boundaries. Tin lattice is anisotropic; its bulk conductance depends on orientation. Grain rotation leads to the drop in bulk conductance. Grain rotation may also lead to the merging of neighboring grains; it leads to a drop of grain boundaries resistivity. Grain rotation requires a torque equal to the product

of a force and a moment arm. Electromigration-induced vacancy fluxes are proportional to current density, but the mobilities of atoms are different in neighboring grains, due to the anisotropy of diffusivity in tin. Therefore, the vacancy fluxes in neighboring grains have different values. This difference (singular flux divergence) leads to supersaturation with vacancies of the boundary at one side of the grain, and undersaturation at the other. Since the top surface of the tin line is stress-free and can be considered as a good sink/source of vacancies, it must have the equilibrium vacancy concentration. That's why the vacancy gradients and fluxes should generate in vertical directions. Vertical vacancy gradients are proportional to the vertical stress gradients along the grain boundaries. Vertical stress gradients indicate transversal forces (up and down) acting on each atom at the grain boundaries. This pair of forces is the origin of the torque. Then the diffusion along the grain boundaries will result in grain rotation.

In Sections 2.2–2.4 we will discuss in more details only three examples of Flux Driven Transformations in Diffusion zone – flux-driven ripening, flux-driven growth, and finally flux-driven nucleation.

2.2 STANDARD MODEL OF THE SIMULTANEOUS, DIFFUSION-CONTROLLED PHASE LAYERS GROWTH IN THE DIFFUSION COUPLE

2.2.1 The Standard Model for an Arbitrary Number of Intermediate Phases

First of all, we consider the standard model of diffusion-controlled reactive diffusion in common diffusion couple at high temperature (so that bulk diffusion is the main mechanism) and during sufficiently long annealing time. “Sufficiently long” time means that (i) all intermediate phases, which are thermodynamically favorable at a given temperature, have nucleated and grown simultaneously forming the parallel phase layers, (ii) the thicknesses of all layers are large enough so that the time for migration of atoms from the “left” interface to the “right” interface of any phase layer (“diffusion time”) is substantially longer than the time needed to pass the interfaces (“reaction time”). In this case the chemical potentials of each component, μ_A , μ_B (Gibbs free energy change due to addition of one atom of A or B), as well as the reduced chemical potential $\tilde{\mu} = \mu_B - \mu_A$ (Gibbs free energy change due to extracting one atom A and adding instead the atom B) should be almost the same at both sides of each interface between two neighboring phases layers:

$$\tilde{\mu}^{(i-1)}(X_{i-1,i} - 0) \approx \tilde{\mu}^{(i)}(X_{i-1,i} + 0), \quad i = 1, \dots, N, N + 1. \quad (2.1)$$

Here $i = 0$ corresponds to the solution of B in A, $i = N + 1$ corresponds to the solution of A in B, $i = 1, 2, \dots, N$ correspond to stable intermediate phases present at the equilibrium phase diagram at fixed temperature.

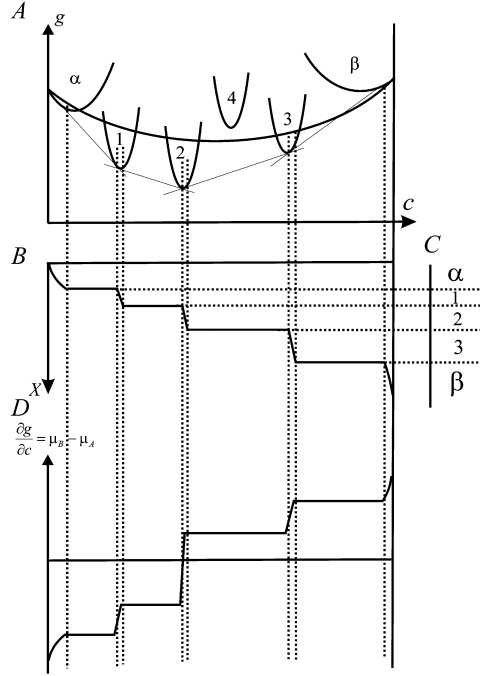


Figure 2.14 Phase spectrum of a binary system in the standard model of reactive diffusion: (A) schematic dependence of Gibbs free energy (per one atom) $g(c)$ on the composition of intermediate phase (c axis in Fig. 2.14(A) is horizontal); (B) concentration profile $c(x)$ in the diffusion zone; (X axis in Fig. 2.14(B) is vertical, c axis is horizontal); (C) reduced chemical potential $\tilde{\mu} = \mu_B - \mu_A$ versus concentration; (D) sequence of layers of growing stable phases (X axis in Figs. 2.14(B, D) is vertical).

Condition (2.1) is usually called the local quasiequilibrium condition at the interfaces. It means the validity of the common tangent rule for each pair of neighboring phases (Fig. 2.14). Note that in the standard model each neighbor in the real space is a neighbor at the equilibrium phase diagram—there is no missing (suppressed) phases or extra (metastable) phases. In Fig. 2.14 and below in this chapter, concentration C is an atomic fraction of B. Tangent points of each common tangent define two compositions in neighboring phases at which these two phases are in equilibrium between each other:

$$c_R^{(i-1)} = c(X_{i-1,i} - 0) \approx c_{eq}^{(i-1)/i}, \quad c_L^{(i)} = c(X_{i-1,i} + 0) \approx c_{eq}^{i/(i-1)}. \quad (2.2)$$

Of course, some small jumps of chemical potentials $\delta\tilde{\mu}^{(i-1)/i} \equiv \tilde{\mu}^{(i)}(X_{i-1,i} + 0) - \tilde{\mu}^{(i-1)}(X_{i-1,i} - 0)$ at any interface remain (as well as corresponding small deviations of compositions from the values determined by the common tangents) — otherwise, any flux across the interfaces would be impossible. Yet, in diffusion-controlled reactions these jumps of chemical potentials are much smaller than the change of chemical po-

tential across the phase layer:

$$\begin{aligned} |\delta\tilde{\mu}^{(i-1)/i}| &< |\tilde{\mu}^{(i)}(X_{i,i+1} - 0) - \tilde{\mu}^{(i)}(X_{i-1,i} + 0)|, \\ |\delta\tilde{\mu}^{(i-1)/i}| &< |\tilde{\mu}^{(i-1)}(X_{i-1,i} - 0) - \tilde{\mu}^{(i-1)}(X_{i-2,i-1} + 0)|. \end{aligned}$$

Further, we will denote by $\Delta\tilde{\mu}^{(i)}$, $\Delta c^{(i)}$ the differences of reduced chemical potential and of atomic fraction of B-component between the right and the left interfaces of i th phase layer:

$$\Delta\tilde{\mu}^{(i)} \equiv \tilde{\mu}^{(i)}(X_{i,i+1} - 0) - \tilde{\mu}^{(i)}(X_{i-1,i} + 0), \quad \Delta c^{(i)} \equiv c(X_{i,i+1} - 0) - c(X_{i-1,i} + 0). \quad (2.3)$$

The concentration ranges of the intermediate phases are, as a rule, very narrow ($\Delta C^{(i)} \ll 1$), instead, the range of reduced chemical potential $\Delta\tilde{\mu}^{(i)}$ for each of these phases (for example, in comparison with mixing enthalpy) is not small at all. One can see it in Fig. 2.14 – slopes of common tangents change very substantially.

In the laboratory reference (Matano) frame, the volume flux density across the phase layer is:

$$\begin{aligned} \Omega J_B &= -\tilde{L} \frac{\partial \tilde{\mu}}{\partial x} = -\tilde{L} \frac{\partial \tilde{\mu}}{\partial c} \frac{\partial c}{\partial x} = -\tilde{D} \frac{\partial c}{\partial x}, \\ \tilde{D} &= \tilde{L} \frac{\partial \tilde{\mu}}{\partial c} = \tilde{L} \frac{\partial^2 g}{\partial c^2}. \end{aligned} \quad (2.4)$$

Usually, Darken approximation for the Onsager coefficient for laboratory reference frame and for the interdiffusivity is sufficient:

$$\begin{aligned} \tilde{L} &= (c_A D_B^* + c_B D_A^*) \frac{c_A c_B}{kT}, \quad c_A + c_B = 1, \\ \tilde{D} &= (c_A D_B^* + c_B D_A^*) \frac{c_A c_B}{kT} \frac{\partial^2 g}{\partial c^2}, \quad \frac{\partial^2 g}{\partial c^2} = \frac{\partial \tilde{\mu}}{\partial c}. \end{aligned} \quad (2.5)$$

Strictly speaking, the reduced chemical potential tends to minus infinity near pure A and tends to plus infinity near pure B.

The velocity of each interface in the laboratory reference frame between two neighboring phases is determined by the step of fluxes (in the same reference frame) at this interface. If one neglects the change of atomic volume during transformation, the equation for the interface velocity is

$$\frac{dX_{i-1,i}}{dt} = \frac{\Omega J_B^{(i)}(X_{i-1,i} + 0) - \Omega J_B^{(i-1)}(X_{i-1,i} - 0)}{c_L^{(i)} - c_R^{(i-1)}}. \quad (2.6)$$

Eq. (2.6) immediately follows from the conservation of matter (in the reference frame of the moving interface the incoming and outgoing fluxes, found using Galilei

rule, are equal, since the interface is a 2D object and has no space to accumulate any component:

$$\Omega J_B^{(i)}(X_{i-1,i} + 0) - c_L^{(i)} \frac{dX_{i-1,i}}{dt} = \Omega J_B^{(i-1)}(X_{i-1,i} - 0) - c_R^{(i-1)} \frac{dX_{i-1,i}}{dt}.$$

In general, the problem of solving diffusion equations in each of the phase regions with interfaces, moving according to Eq. (2.6), is a very complicated Stephan problem [45]. Luckily for a description of reactive diffusion, in most real cases one can use a steady-state approximation for fluxes in all growing intermediate phase layers. This approximation is valid for any phase layer with narrow concentration range. One can prove this statement rigorously [46], but here we describe only an idea. Indeed, since homogeneity interval of the intermediate phase is narrow, concentration “has no way out” and it keeps itself almost constant (close to stoichiometry) over the whole phase layer. That’s why the time derivative of concentration is small, and so the flux divergence is close to zero:

$$\frac{\partial c}{\partial t} = -\text{div}(\Omega J_B), \quad \frac{\partial c}{\partial t} \approx 0 \Rightarrow \text{div}(\Omega J_B) \approx 0.$$

In one-dimensional case (diffusion couple) the divergence is simply equal to diffusion coordinate derivative. The derivative being equal to zero implies that the flux density almost doesn’t change within the whole phase layer. In particular, it is the same at the left and at the right interface of the same phase (but, of course, different in other phase layers and varying with time):

$$\frac{\partial}{\partial x} \Omega J_B \approx 0 \Rightarrow \Omega J_B(x) \approx \text{const} \Rightarrow \Omega J_B^{(i)}(X_{i-1,i} + 0) \approx \Omega J_B^{(i)}(X_{i,i+1} - 0) = \Omega J_B^{(i)}. \quad (2.7)$$

This means that the product of interdiffusion coefficient and concentration gradient is nearly equal everywhere inside the phase:

$$\tilde{D} \frac{\partial c}{\partial x} \approx \text{const over } x.$$

Still, this doesn’t imply that concentration gradient is equal everywhere, as interdiffusion coefficient may considerably change even at little deviations from stoichiometry (especially in phases of B2-type, for example, NiAl). Hence, it’s generally incorrect to claim that concentration profile inside the phase is linear. Let’s make elementary transformations. If a certain value is constant, it can be taken both inside and outside the integral sign. We’ll take it inside it:

$$\Omega J^{(i)} = -\tilde{D} \frac{\partial c}{\partial x} \approx \text{const} \equiv -\tilde{D} \frac{\partial c}{\partial x} \frac{\int_{X_L^{(i)}}^{X_R^{(i)}} dx}{\int_{X_L^{(i)}}^{X_R^{(i)}} dx} = -\frac{\int_{X_L^{(i)}}^{X_R^{(i)}} \tilde{D}(c(x)) \frac{\partial c}{\partial x} dx}{X_R^{(i)} - X_L^{(i)}} = -\frac{\int_{c_L^{(i)}}^{c_R^{(i)}} \tilde{D}(c) dc}{\Delta X^{(i)}}. \quad (2.8)$$

The value $\int_{c_L^{(i)}}^{c_R^{(i)}} \tilde{D}(c) dc$ is called Wagner's integral coefficient and is often written as

$$\int_{c_L^{(i)}}^{c_R^{(i)}} \tilde{D}(c) dc \equiv D^{(i)} \Delta c^{(i)}. \quad (2.9)$$

Here $D^{(i)} = \frac{1}{\Delta c^{(i)}} \int_{c_L^{(i)}}^{c_R^{(i)}} \tilde{D}(c) dc$ is an effective interdiffusion coefficient averaged over the phase. The kinetics of solid state reactions is always determined by the product of effective diffusivity and the homogeneity zone width (i.e., the integral coefficient). And this is good, because homogeneity zone width in many phases is so narrow that it seems almost impossible to measure it experimentally. Wagner's integral coefficient can be transformed using Darken's relation, expressing interdiffusion coefficient in a binary system with diffusion coefficients of tracers and the second derivative of Gibbs potential (per one atom) with respect to concentration (Eq. (2.5)) as

$$\begin{aligned} D^{(i)} \Delta c^{(i)} &= \int_{c_L^{(i)}}^{c_R^{(i)}} \tilde{D}(c) dc = \int_{c_L^{(i)}}^{c_R^{(i)}} (c_A D_B^* + c_B D_A^*) \frac{c_A c_B}{kT} \frac{\partial^2 g}{\partial c^2} dc = \\ &= ((1 - c^{(i)}) \bar{D}_{Bi}^* + c^{(i)} \bar{D}_{Ai}^*) \frac{(1 - c^{(i)}) c^{(i)}}{kT} \int_{c_L^{(i)}}^{c_R^{(i)}} \frac{\partial^2 g}{\partial c^2} dc = \\ &= \bar{D}_i^* \frac{(1 - c^{(i)}) c^{(i)}}{kT} \left(\left. \frac{\partial g}{\partial c} \right|_{iR} - \left. \frac{\partial g}{\partial c} \right|_{iL} \right). \end{aligned} \quad (2.10)$$

Here $\bar{D}_i^* = (1 - c^{(i)}) \bar{D}_{Bi}^* + c^{(i)} \bar{D}_{Ai}^*$ is the average combination of tracer diffusivities over the i th phase.

Derivatives of Gibbs free energy over concentration taken at the tangent points of common tangents can be represented in the following way (see Fig. 2.14):

$$\left. \frac{\partial g}{\partial c} \right|_{iR} \approx \frac{g^{(i+1)} - g^{(i)}}{c^{(i+1)} - c^{(i)}}, \quad \left. \frac{\partial g}{\partial c} \right|_{iL} \approx \frac{g^{(i)} - g^{(i-1)}}{c^{(i)} - c^{(i-1)}}. \quad (2.11)$$

Anyone can easily check that

$$\frac{g^{(i+1)} - g^{(i)}}{c^{(i+1)} - c^{(i)}} - \frac{g^{(i)} - g^{(i-1)}}{c^{(i)} - c^{(i-1)}} = \frac{(c^{(i+1)} - c^{(i-1)})}{(c^{(i+1)} - c^{(i)})(c^{(i)} - c^{(i-1)})} \Delta g_i(i+1, i-1 \rightarrow i). \quad (2.12)$$

Here $\Delta g_i(i+1, i-1 \rightarrow i)$ is a driving force (per atom) of reaction $(i+1) + (i-1) \rightarrow i$. Geometrically it is a vertical interval between $g^{(i)}$ (the bottom of the $g(c)$ -curve for the i th phase) and common tangent connecting the $(i-1)$ th phase and $(i+1)$ th phase. Combining Eqs. (2.10)–(2.12), one gets

$$D^{(i)} \Delta c^{(i)} = \bar{D}_i^* \frac{(1 - c^{(i)}) c^{(i)} (c^{(i+1)} - c^{(i-1)})}{(c^{(i+1)} - c^{(i)})(c^{(i)} - c^{(i-1)})} \frac{\Delta g_i(i+1, i-1 \rightarrow i)}{kT}. \quad (2.13)$$

Unfortunately, one cannot write something similar for marginal phases $i = 0$ and $i = N + 1$ (solutions of B in A and of A in B). Flux cannot be treated as steady-state in marginal solutions because it tends to zero at “infinity.” If the concentration range of a solution is narrow, one can treat interdiffusivity within the solution as constant and corresponding concentration profile as an error function. We will not describe this case here. Instead, we will consider cases when the solubilities of marginal solutions are tending to zero and corresponding fluxes are also tending to zero. In this case, the phase growth kinetics is determined by the set of ordinary differential equations. We will write these equations taking into account that left and right concentrations for each phase homogeneity range, $c_L^{(i)} \propto c_R^{(i)}$, can be taken as equal to stoichiometric value $c^{(i)}$ in all cases except when we need to use their difference (in the nominator of the flux):

$$\begin{aligned}\frac{dX_{0,1}}{dt} &= \frac{1}{c^{(1)} - 0} \left(0 - \frac{D^{(1)} \Delta c^{(1)}}{X_{1,2} - X_{0,1}} \right) \\ \frac{dX_{i-1,i}}{dt} &= \frac{1}{c^{(i)} - c^{(i-1)}} \left(\frac{D^{(i-1)} \Delta c^{(i-1)}}{X_{i-1,i} - X_{i-2,i-1}} - \frac{D^{(i)} \Delta c^{(i)}}{X_{i,i+1} - X_{i-1,i}} \right), \quad i = 2, \dots, N \\ \frac{dX_{N,N+1}}{dt} &= \frac{1}{1 - c^{(N)}} \left(\frac{D^{(N)} \Delta c^{(N)}}{X_{N,N+1} - X_{N-1,N}} - 0 \right).\end{aligned}\quad (2.14)$$

2.2.2 The Standard Model for Single Intermediate Phase ($N = 1$)

First consider the case of one phase 1 layer growth with narrow concentration interval during annealing of a sample couple containing almost mutually insoluble materials A, B (let A component be on the left, and B component on the right). Thus, we'll neglect interdiffusion fluxes in the initial components of diffusion couple ($c^{(0)} \approx 0$, $c^{(2)} \approx 1$). Thereby we consider all A atoms, which “managed to diffuse” to the 1/B boundary, to react with B atoms and not to go further, growing the phase “on the right”. In the same way, B atoms, which “managed to diffuse” to the A/1 boundary, react with A and grow the phase “on the left”. Let's neglect the molar volume changes at intermetallic formation, as thus right away disregard those effects that are connected with stresses, arising at phase boundaries.

Wagner diffusivity in this case is $D^{(1)} \Delta c^{(1)} = \bar{D}_1^* \frac{\Delta g_1(B,A \rightarrow 1)}{kT}$.

Thus, the growth rate of the single intermediate phase is determined by the mobility of atoms in it (tracer diffusivities) and by thermodynamic driving force of phase formation. As we can see, the “elusive” homogeneity interval itself is of little importance for us. In such a way, the product of the density of B flux through phase layer and atomic volume (that is, “the flux density of the volume transferred by B atoms”) equals to

$$\Omega J_B^{(1)} = - \frac{D^{(1)} \Delta c^{(1)}}{\Delta X^{(i)}}. \quad (2.15)$$

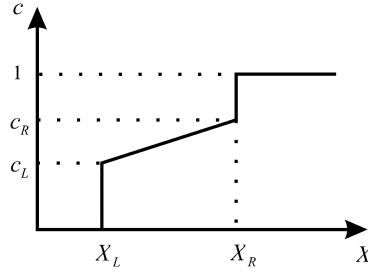


Figure 2.15 Concentration profile at one phase growth between insoluble components.

Now apply the flux balance conditions (2.6) for each of two moving interfaces (see also Fig. 2.15):

$$\begin{aligned} (1 - c_R) \frac{dx_R}{dt} &= \frac{D_1 \Delta c_1}{\Delta x_1} \\ c_L \frac{dx_L}{dt} &= - \frac{D_1 \Delta c_1}{\Delta x_1} \end{aligned} \quad (2.16)$$

From these equations one can easily derive the differential equation for the phase thickness $\Delta x(t)$,

$$\frac{d\Delta x}{dt} = \frac{a}{\Delta x(t)}, \quad (2.17)$$

where

$$a = \frac{1 - \Delta c_1}{(1 - c_R)c_L} D_1 \Delta c_1 \approx \frac{D_1 \Delta c_1}{c_1(1 - c_1)}. \quad (2.18)$$

And this gives the well-known parabolic law of phase growth

$$(\Delta x)^2 = (\Delta x_0)^2 + \frac{2D_1 \Delta c_1}{c_1(1 - c_1)} t. \quad (2.19)$$

If the thickness of the layer already considerably exceeds the initial thickness (the latter is taken right after the nucleation and lateral growth with formation of primary continuous layer) then

$$\Delta x \approx \sqrt{\frac{2D_1 \Delta c_1}{c_1(1 - c_1)} t} = \sqrt{\frac{\bar{D}_1^*}{c^{(1)}(1 - c^{(1)})} \frac{\Delta g_1(B, A \rightarrow 1)}{kT} t}. \quad (2.20)$$

Once more, in the case of single growing phase layer, its growth rate is determined by the mobility of tracer atoms multiplied by the thermodynamic stimulus of the phase formation.

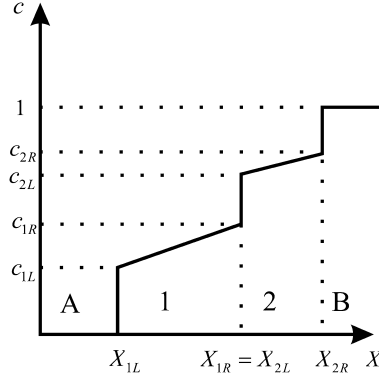


Figure 2.16 Concentration profile at two phases growing between insoluble components.

2.2.3 The Standard Model for the Case of Two Intermediate Phases ($N = 2$)

Now, let's examine the case of two phases, 1 and 2, growing between two mutually insoluble metals. Here we again make the assumption of **constant** fluxes over the thickness of each phase (see also Fig. 2.16):

$$\Omega J_B^{(1)} = -\frac{D_1 \Delta c_1}{\Delta x_1}; \quad \Omega J_B^{(2)} = -\frac{D_2 \Delta c_2}{\Delta x_2}. \quad (2.21)$$

Equations of balance of particle number at interfaces have the following form:

$$\begin{aligned} (1 - c_R^{(2)}) \frac{dx_{2R}}{dt} &= \frac{D_2 \Delta c_2}{\Delta x_2}, \\ (c_L^{(2)} - c_R^{(1)}) \frac{dx_{2L}}{dt} &= -\frac{D_2 \Delta c_2}{\Delta x_2} + \frac{D_1 \Delta c_1}{\Delta x_1}, \\ (c_L^{(1)} - 0) \frac{dx_{1L}}{dt} &= -\frac{D_1 \Delta c_1}{\Delta x_1}. \end{aligned} \quad (2.22)$$

It's quite easy to obtain the system of differential equations for phase thicknesses from Eq. (2.22), namely

$$\begin{aligned} \frac{d\Delta x_1}{dt} &= a_{11} \frac{D_1 \Delta c_1}{\Delta x_1} + a_{12} \frac{D_2 \Delta c_2}{\Delta x_2}, \\ \frac{d\Delta x_2}{dt} &= a_{21} \frac{D_1 \Delta c_1}{\Delta x_1} + a_{22} \frac{D_2 \Delta c_2}{\Delta x_2}. \end{aligned} \quad (2.23)$$

Here

$$a_{ik} = \begin{pmatrix} \frac{c^{(2)}}{c^{(1)}} & -1 \\ -1 & \frac{1-c^{(1)}}{1-c^{(2)}} \end{pmatrix} \frac{1}{c^{(2)} - c^{(1)}}. \quad (2.24)$$

The set of Eqs. (2.23) has parabolic solutions as well, $\Delta x_1 = k_1 t^{1/2}$, $\Delta x_2 = k_2 t^{1/2}$,

$$\frac{k_2}{k_1} = \frac{r - 1 + \sqrt{(r - 1)^2 + 4r \frac{c^{(2)}}{c^{(1)}} \frac{1-c^{(1)}}{1-c^{(2)}}}}{2 \frac{c^{(2)}}{c^{(1)}}}, \quad r \equiv \frac{D^{(2)} \Delta c^{(2)}}{D^{(1)} \Delta c^{(1)}}.$$

If Wagner diffusivity of the second phase is much lower, $r \ll 1$, then it gives

$$k_1 \approx \sqrt{\frac{2D^{(1)} \Delta c^{(1)}}{c^{(1)}(1 - c^{(1)})}}, \quad k_2 \approx \frac{1 - c^{(1)}}{1 - c^{(2)}} \sqrt{\frac{2D^{(1)} \Delta c^{(1)}}{c^{(1)}(1 - c^{(1)})}} \frac{D^{(2)} \Delta c^{(2)}}{D^{(1)} \Delta c^{(1)}}. \quad (2.25)$$

The latter equation demonstrates that kinetic suppression of the second phase proceeds not only at nucleation stage but also at the growth stage: phase 2 grows slower than it could in the absence of phase 1.

2.3 FLUX-DRIVEN RIPENING OF Cu_6Sn_5 SCALLOPS DURING REACTION OF CU SUBSTRATE WITH LIQUID TIN-BASED SOLDER

As mentioned in Section 2.1, the theory of Flux-Driven Ripening (FDR) is actually a kinetic theory of soldering. It was first suggested in 2002 [10,11]. It introduced the concept of non-conservative ripening proceeding simultaneously with reactive growth due to diffusion via a system of liquid channels of molten solder between grains of growing phase.

Historically, the initial version of this theory was applied to the eutectic SnPb solder. It has a melting point of 183°C, pure Sn melts at 237°C so the solder reaction (soldering) typically occurs at 200–250°C. The typical duration of soldering reaction is from a few seconds to a few minutes. In these reactions, Cu_6Sn_5 and Cu_3Sn intermetallic compounds (IMCs) are formed at the interfaces. Actually, these compounds provide the bonds joining copper with solder in the solid state. In the case of reaction with liquid solder, the Cu_6Sn_5 compound is the first and main growing phase which has scallop-type morphology. The channel between neighboring scallops plays a major role in reaction kinetics. The mean size of the scallops can increase to several microns after a few minutes of reaction. Good joining means the formation of scallops of about micron size. Big size of scallops leads to decreasing mechanical strength of the joint. Thus, control of the scallops mean size and even size distribution is crucial for the reliability of the solder joints. As in usual grain growth or ripening, the number of remaining scallops decreases and their mean size correspondingly increases (Fig. 2.1). The mean

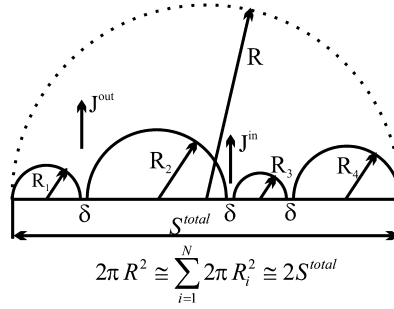


Figure 2.17 Schematic diagram of a cross-section of an array of scallops on Cu. J_{in} is an influx from the substrate into melt via channels (serving for the growth of scallops), J_{out} is an outflux of copper which was not used for building up the intermetallic compound. For small solder bumps, this outflux quickly tends to zero after their saturation.

lateral size of scallops, as well as mean height, were found to obey an approximately $t^{1/3}$ time dependence. The number of scallops decreases with time t as $t^{-2/3}$. The activation energy of the scallops growth in the temperature interval from 200 to 240°C is within the interval 0.2–0.3 eV/atom. On the other hand, the copper-rich phase Cu_3Sn is a thin layer and its growth is very slow.

The situation changes drastically if copper interacts with solid tin, instead of liquid tin. In this case (solid state aging) both phases grow simultaneously with similar growth rates, and Cu_6Sn_5 compound forms a continuous layer, instead of an array of scallops.

Beautiful illustration of this fact was made by Hodaj and Liashenko [12] who used the known property of liquid tin – ability of deep and long overcooling without crystallization. They managed to make a direct comparison of copper reaction with solid tin at 222°C and with supercooled liquid tin at the SAME temperature. Reaction with liquid tin proceeds much faster, and in this case, mainly the phase Cu_6Sn_5 with scallop-like morphology is growing. It proves that in reaction with liquid solder quite different mechanism is realized. Namely, it is (i) a formation of liquid channels between scallops due to full wetting of grain boundaries in Cu_6Sn_5 by liquid solder (reason of wetting is thermodynamic: one typical large-angle grain boundary between two grains of η -phase Cu_6Sn_5 is less favorable than two interfaces grain/liquid solder, $\gamma_{\eta/\eta} > 2\lambda_{\eta/\text{molten solder}}$), (ii) fast diffusion of copper into reaction zone via these liquid channels, (iii) redistribution of the incoming flux of copper into melt between scallops. Fig. 2.17 shows a schematic diagram of a cross-section of an array of hemispherical Cu_6Sn_5 scallops grown on Cu, represented by the solid curves. As we just mentioned, there exist liquid channels between scallops, reaching at first the Cu surface and later the Cu_3Sn surface. The width of the channel “ δ ” (a few nanometers in the narrowest place) is typically small compared to the radius of scallops. The channels serve as rapid diffusion paths for Cu to go into the molten solder to grow the scallops. In [13] we predicted for the first time the

width of the channel as $\delta = \frac{(\gamma_{\eta/\eta} - 2\gamma_{\eta/\text{molten solder}})}{\Delta g_{\text{solder} \rightarrow \eta}} \Omega$. Typically it is 1–3 nm. Further, for the sake of simplicity, we will represent the scallops as hemispheres. This assumption reflects the experimental observations during first few minutes of reflow. On the total interfacial area “ S^{total} ” of the Cu substrate, the total surface area between all hemispherical scallops and molten solder is just twice “ S^{total} .” Indeed, the area of each hemisphere, $2\pi R^2$, is just twice the area of the substrate under this hemisphere, πR^2 . Here we neglect the problem of close packing – this problem is not that serious due to scattering of sizes when small hemispheres may fill the space between large hemispheres. Applying the just mentioned relationship to each scallop and summing over all scallops, one obtains $S^{\text{Cu/Sn}} = \sum 2\pi R_i^2 = 2 \sum \pi R_i^2 = 2S^{\text{total}}$. Thus, during the growth of total volume, the total surface area of the scallops is not changing while they remain hemispherical (or just conserve the constant aspect ratio). Here, we ignore the cross-sectional area of the channels on the interface since δ is very small. In our modeling, we skip the very early stage of liquid droplet saturation with copper. After this, all the in-flux of Cu from the Cu substrate is used for the growth of the scallops. Also, we suppose that the interfacial diffusion of Cu along the scallop/Cu or scallop/Cu₃Sn interface is not the rate-limiting factor of the scallop growth. Similar to usual ripening processes, in soldering reaction, the larger scallops grow at the expense of smaller scallops. Yet, there are two important constraints. The first constraint is that the interface of reaction is constant. The second is conservation of mass, in which all the in-flux of Cu is used for the scallop growth. The growth of the mean scallop size means that the number of channels between scallops decreases. Therefore, the in-flux of Cu needed for the growth also decreases. We will start with a simplified model of monosized scallop growth.

2.3.1 Simplified Model of Monosized Hemispheres

Strictly speaking, monosize distribution in our system is unrealistic and contradicts the ripening since all scallops just cannot grow simultaneously remaining hemispherical. So the growth of some scallops is possible only if some of neighboring scallops are shrinking. Therefore, the initial monosize distribution, in reality, should be definitely transformed into a polysize distribution. The monosize model is applicable only for an estimate of average values. The constraint of constant total interface area gives

$$N\pi R^2 \cong S^{\text{total}} = \text{const}, \quad (2.26)$$

where N is the number of scallops. The cross-sectional area of channels at the bottom for the supply of Cu from the substrate (free section) is

$$S^{\text{free}} = N2\pi R \frac{\delta}{2} = \frac{\delta}{R} S^{\text{total}}. \quad (2.27)$$

Here δ is the channel width. So the cross-sectional area of channels decreasing during the reaction is inversely proportional to the mean size. Here we do not take into account

the possible input of triple joints of channels (it has been done recently in [12]). The total volume of the forming compound is equal to

$$V_i = N \frac{2\pi}{3} R^3 = \frac{2}{3} S^{total} R. \quad (2.28)$$

During first minutes of scallop growth, the nucleation and growth of Cu_3Sn are suppressed [47,48]. So, for simplicity, we will neglect the growth of Cu_3Sn layer between the copper substrate and Cu_6Sn_5 . Then, assuming that all copper atoms diffusing along channels from the substrate are used for construction of the growing compound scallops, conservation law gives

$$n_i c_i \frac{dV_i}{dt} = J^{in} S^{free}. \quad (2.29)$$

Here n_i is atomic density in the compound, i.e., the number of atoms per unit volume, and c_i is an atomic fraction of Cu in the compound, which is 6/11 in Cu_6Sn_5 . The in-flux is taken approximately as

$$J^{in} \approx n D \frac{c^b - c^e}{R}. \quad (2.30)$$

Here n is atomic density or a number of atoms per unit volume in the melt or molten solder, $c^e = c^{\eta/melt}$ is an equilibrium concentration (atomic fraction) of copper in solder at the planar interface $\text{Cu}_6\text{Sn}_5/\text{solder}$, $c^b = c^{Cu/melt}$ is an equilibrium concentration of Cu in solder at the interface Cu/liquid solder at the channel's bottom, or at the interface $\text{Cu}_3\text{Sn/liquid solder}$ at the channel's bottom (see Fig. 2.18).

Substituting Eqs. (2.28) and (2.30) into the balance equation (2.29), one gets

$$n_i c_i \frac{2}{3} S^{total} \frac{dR}{dt} = n D \frac{c^b - c^e}{R} \left(\frac{\delta}{R} S^{total} \right), \quad (2.31)$$

which immediately gives

$$R^3 = kt, \quad k = \frac{9}{2} \frac{n}{n_i} \frac{D(c^b - c^e)\delta}{c_i}. \quad (2.32)$$

Note that the expression for the rate constant does not contain surface tension n , despite the “ripening-like” time law.

If we take $\frac{n}{n_i} \approx 1$, $c_i = \frac{6}{11}$, $D \approx 10^{-5} \frac{\text{cm}^2}{\text{s}}$, $\delta \approx 5 \cdot 10^{-7} \text{ cm}$, $c^b - c^e \approx 0.01$,

$$n/n_i \approx 1, \quad c_i = 6/11, \quad D \approx 10^{-5} \text{ cm}^2/\text{s}, \quad \delta \approx 2.5 \cdot 10^{-7} \text{ cm}, \quad c^b - c^e \approx 0.01.$$

Here the concentration c^b is taken for the equilibrium of melt with the Cu_3Sn_1 phase, and the rate constant is $k \approx 2 \cdot 10^{-13} \frac{\text{cm}^3}{\text{s}}$. For example, for an annealing time $t = 300 \text{ s}$, it gives $R \approx 4 \cdot 10^{-4} \text{ cm}$, which agrees very well with experimental data.

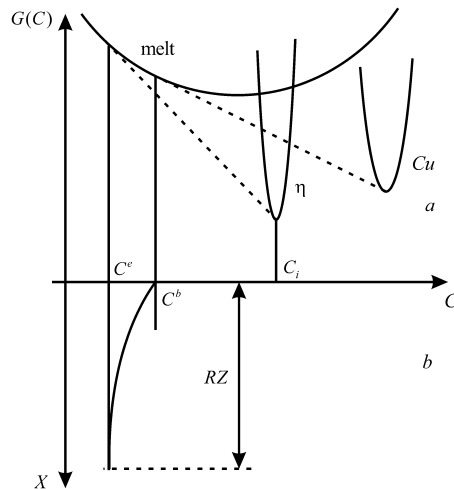


Figure 2.18 Schematic dependence of Gibbs free energy versus composition. Cu quasi-equilibrium concentration in the melt in the vicinity of the substrate (C^b), in the intermetallic compound Cu_6Sn_5 or η -phase (C_i), and in the melt for stable equilibrium with planar η -phase (C^e). RZ means “Reaction Zone”.

2.3.2 Theoretical Prediction of Liquid Channel Width

It would be very important to make theoretical predictions for the width of channels. Obviously, the channel cannot be too wide, otherwise, a driving force of reaction will fill the existing gap by the η -phase growing grains. On the other hand, the channel width cannot be zero because then two compound/liquid interfaces will convert into one boundary between two solid grains, and consequently the energy will increase due to the GB-wetting condition $\gamma_{\eta\eta} > 2\gamma_{\eta/l}$.

Let us consider the channel of width δ , dividing the two parallel walls of η -compound grains, based on the substrate of ε -phase. (In case of absence of the ε -phase, one should consider copper instead of this phase.) The bottom of the channel presents the contact of the liquid tin-based solution and ε -phase so that in usual free-contact one might expect the emergence of η -phase. Yet, it should mean simultaneously the increase of surface energy. It means that we actually have the nucleation problem – competition of bulk and surface terms. The only peculiarity is that the nucleus now is the island of η -phase containing grain-boundary instead of two preexisting η -phase/liquid interfaces.

Nucleation of the compound island within the interface can be “homogeneous” – “kissing” of grains somewhere at an arbitrary point contact of two walls with formation of the disk of η -phase. Nucleation can be (with higher probability) “heterogeneous” – formation of η -phase island (semicylindrical or rectangular “sheet” of η -phase) at the base of ε -phase bottom. The second possibility has higher probability due to the presence of copper necessary to form a “sheet” of η -phase from the tin-based liquid.

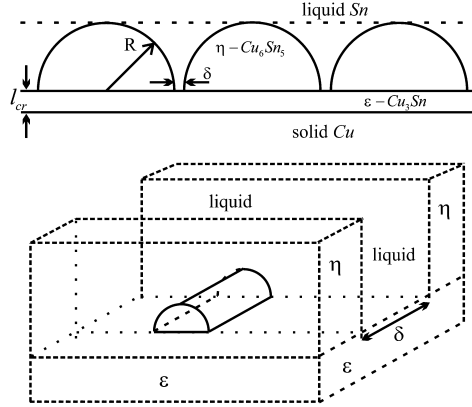


Figure 2.19 Schematic presentation of the emerging of the semicylindrical η -phase island between two parallel η -phase walls (belonging to neighboring scallops) above the ε -phase.

Consider a semidisc of radius R and thickness δ at the bottom of the channel. The semidisc consists of two semidisks of thicknesses $\delta_1, \delta_2, \delta_1 + \delta_2 = \delta$, being the “continuations” of the two neighboring grains (see Fig. 2.19).

The change of Gibbs free energy due to formation of the semidisc is equal to

$$\Delta G(R, \delta) = \left(-\frac{\Delta g_{\varepsilon+solder \rightarrow \eta}}{\Omega} \right) \cdot \delta \cdot \frac{1}{2} \pi R^2 + (\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}) \cdot \frac{1}{2} \pi R^2 + \gamma_{\eta/liquid} \cdot \pi R \cdot \delta + (\gamma_{\eta/\varepsilon} - \gamma_{\varepsilon/liquid}) \cdot 2R \cdot \delta. \quad (2.33)$$

The first term is a “bulk” one. The second term corresponds to change from two solid/liquid interfaces to one grain-boundary. The third term corresponds to a side semicircle. The last, fourth term, corresponds to a change of bottom rectangular side interface from liquid/ ε to η / ε . Simple transformations give:

$$\Delta G(R, \delta) = \left(\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid} - \frac{\Delta g_{\varepsilon+solder \rightarrow \eta}}{\Omega} \delta \right) \cdot \frac{1}{2} \pi R^2 + \left(\frac{\pi}{2} \gamma_{\eta/liquid} + \gamma_{\eta/\varepsilon} - \gamma_{\varepsilon/liquid} \right) \cdot \delta \cdot 2R. \quad (2.34)$$

One can easily see that the R -dependence of Gibbs free energy

(i) should have typical barrier type at $\delta > \frac{\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}}{\Delta g_{\varepsilon+solder \rightarrow \eta}} \Omega$

or

(ii) should be monotonically increasing at $\delta < \frac{\gamma_{\eta/\eta} - 2\gamma_{\eta/liquid}}{\Delta g_{\varepsilon+solder \rightarrow \eta}} \Omega$.

Thus, there exists some “critical” channel width, under which the further filling of the liquid channel by eta-phase becomes impossible:

$$\delta^* = \frac{\gamma_{\eta/\eta} - 2\gamma_{\eta/\text{liquid}}}{\Delta g_{\varepsilon + \text{solder} \rightarrow \eta}} \Omega. \quad (2.35)$$

If $\delta > \delta^*$ then nucleation is not even needed, and the channel will proceed, becoming narrower by normal movement of walls till the width reaches the mentioned critical value.

Thus, our model predicts the width of the liquid channels.

2.3.3 Account of Size Distribution – Basic Equations

We introduce $f(t, R)$ as the size distribution function. The total number of grains is equal to

$$N(t) = \int_0^\infty f(t, R) dR. \quad (2.36)$$

The total area of all scallops bottom is

$$\sum_{i=1}^N \pi R_i^2 = \int_0^\infty \pi R^2 f(t, R) dR = S^{\text{total}} - S^{\text{free}} \cong S^{\text{total}} = \text{const}. \quad (2.37)$$

The total free surface area of channels for copper supply is

$$S^{\text{free}} = \int_0^\infty \frac{\delta}{2} 2\pi R f(t, R) dR. \quad (2.38)$$

The total volume of the compound phase is

$$V_i = \sum_{i=1}^N \frac{2}{3} \pi R_i^3 = \int_0^\infty \frac{2}{3} \pi R^3 f(t, R) dR. \quad (2.39)$$

Conservation of number of copper atoms gives:

$$\begin{aligned} n_i c_i \frac{d}{dt} \int_0^\infty \frac{2}{3} \pi R^3 f(t, R) dR &= nD \frac{\Delta c}{\frac{\int R f(t, R) dR}{\int f dR}} \delta \int_0^\infty \pi R f(t, R) dR \\ &= \pi n D \Delta c \delta \int_0^\infty f(t, R) dR. \end{aligned} \quad (2.40)$$

Since scallops grow or shrink atom by atom, the distribution function should satisfy the continuity equation in the size space:

$$\frac{\partial f}{\partial t} = - \frac{\partial}{\partial R} (f u_R). \quad (2.41)$$

Here the velocity in the size space, u_R , is simply the growth rate of scallops with radius R , $u_R = \frac{dR}{dt}$, and is determined by the flux density on (or out of) each individual scallop:

$$\frac{dR}{dt} \cong \frac{-j(R)}{n_i c_i}. \quad (2.42)$$

In LSW theory each grain is taken as spherical. It is surrounded by infinite supersaturated solid solution. The expressions for local flux $j(R)$ and the size change $\frac{dR}{dt}$ are usually found as a quasistationary solution of a diffusion problem in infinite space around a spherical grain with fixed supersaturation $< c > -c^e$ at infinity: $u_R = \frac{dR}{dt} = \frac{n}{n_i} \frac{D}{c_i} \frac{< c > - (c^e + \alpha/R)}{R}$. In our case, the scallops are very close, they almost touch each other. In this sense one can try to interpret the situation as the grain growth, but under conditions of constant surface and increasing total volume. Thus, the classical equations for ripening in our case are not valid. In Flux-Driven Ripening, the transport of copper through the liquid channels is a rate-controlling step. Indeed, **ripening (under the constraint of the constant surface area) is possible only in case of volume growth, and volume growth is possible only in case of incoming flux**. Under the condition of the constant surface area, the rate of ripening will be determined by the incoming flux, and this flux will be redistributed among scallops. (Some of the scallops will grow and others will shrink.) In the case of zero incoming flux, the ripening among the scallops becomes classical, i.e., the volume is conserved. Experimentally, such behavior can be observed in the reaction between molten solder and a thin film of Cu after the film is consumed.

According to general principles of nonequilibrium thermodynamics, the flux on (out of) each scallop should be proportional to the difference between the average chemical potential of copper μ in reaction zone. We take μ to be the same everywhere in the reaction zone – mean-field approximation. The chemical potential at the curved interface “scallop-melt” is equal to $\mu_\infty + \frac{\beta}{R}$, here $\beta = 2\gamma\Omega$:

$$-j(R) = L \left(\mu - \mu_\infty - \frac{\beta}{R} \right), \quad \frac{dR}{dt} = \frac{L}{n_i c_i} \left(\mu - \mu_\infty - \frac{\beta}{R} \right). \quad (2.43)$$

Here parameters L , μ can be determined consistently from two constraints – of constant surface and mass conservation. The first constraint of constant surface gives

$$\frac{dS_{total}}{dt} = 0 = \frac{d}{dt} \sum 2\pi R_i^2 = \sum 4\pi R_i \frac{dR_i}{dt} = \frac{4\pi L}{n_i c_i} \left((\mu - \mu_\infty) \sum R_i - \beta N \right),$$

yielding

$$\mu - \mu_\infty = \frac{\beta}{< R >}. \quad (2.44)$$

Conservation law implies

$$\frac{1}{2} \frac{n}{n_i} \delta \frac{D \Delta c}{c_i} = \frac{\sum R_i^2 \frac{dR_i}{dt}}{N} = \frac{L}{n_i c_i N} \sum R_i^2 \left(\frac{\beta}{\langle R \rangle} - \frac{\beta}{R_i} \right) = \frac{L \beta}{n_i c_i} \frac{\langle R^2 \rangle - \langle R \rangle^2}{\langle R \rangle}, \quad (2.45)$$

which gives the product of two parameters:

$$L \beta = n_i c_i \frac{k}{9} \frac{\langle R \rangle}{\langle R^2 \rangle - \langle R \rangle^2}, \quad u_R = \frac{dR}{dt} = \frac{k}{9} \frac{1}{\langle R^2 \rangle - \langle R \rangle^2} \left(1 - \frac{\langle R \rangle}{R} \right). \quad (2.46)$$

Hence, in our approximation (mean-field), the basic equation for the distribution function is

$$\frac{\partial f}{\partial t} = - \frac{k}{9} \frac{\langle R \rangle}{\langle R^2 \rangle - \langle R \rangle^2} \frac{\partial}{\partial R} \left(f \left(\frac{1}{\langle R \rangle} - \frac{1}{R} \right) \right). \quad (2.47)$$

Here the rate coefficient k is determined by value of the incoming flux proportional to the channel width:

$$\langle R^3 \rangle = kt, \quad k = \frac{9}{2} \frac{n}{n_i} \frac{D(c^b - c^c) \delta}{c_i}. \quad (2.48)$$

Eqs. (2.47)–(2.48) are the main equations for distribution function in our Flux-Driven Ripening theory. It contains the unknown parameter of average radius, which is, in our case, equal to the critical radius. It means that only scallops with R greater than $\langle R \rangle(t)$ can grow at the moment t . Size distribution appears to be similar to grain size distribution in grain growth derived by Hillert:

$$g(u) = \text{const} \cdot \frac{u}{(2-u)^4} \exp\left(-\frac{4}{2-u}\right), \quad u = \frac{R}{\langle R \rangle}.$$

So the time law for mean size in Flux-Driven Ripening during the soldering reaction is similar to Ostwald ripening (described by the classic LSW-theory). Yet, the rate of ripening is determined by the width of liquid channels instead of surface tension. (Of course, strictly speaking, the channel width may depend on surface tensions, as discussed above.) On the other hand, the size distribution is practically identical with classical Hillert model for the grain growth. It is important to remember that ripening in FDR (in copper/liquid solder reaction) is non-conservative, the volume is growing, interface area remaining approximately constant. If our Eq. (2.35) for the channel width is reasonable, we can predict the ripening rate and growth rate in soldering.

2.4 FLUX-DRIVEN LAMELLAR PRECIPITATION OF Cu_6Sn_5 INTO POROUS Cu_3Sn STRUCTURE

2.4.1 General Remarks

At high temperature, the metastable alloys decompose via nucleation of isolated precipitates inside the parent phase, with subsequent growth and ripening. It is well-known that at relatively low temperatures, when the bulk diffusion is frozen but grain boundary and interface diffusion are not frozen, nature finds an alternative way to decompose the thermodynamically unstable system. This low-temperature process is usually called cellular decomposition (if initial and resulting phases are solid solutions) or eutectoid transformation (if initial and resulting phases are compounds or pure materials). The understanding and theory of this process, as an alternative to bulk diffusion mechanism, was developed by Turnbull [49], Hillert [50], and John Cahn [51]. Recently, it was discovered that similar process can proceed in an open system under the condition of outgoing fluxes [18]. Namely, as we will see below, the components in this process are not just redistributed along the moving interface (as in normal cellular precipitation in a closed system), but one of the components is “sucked out” outside from the moving interface through the just formed lamellar structure. Therefore, it seems natural to develop the Cahn’s theory into the Theory of Flux-Driven Cellular Precipitation (or Flux-Driven Eutectoid Transformation).

Let “i” be a binary compound with a narrow range of homogeneity. Let by some reason (selective oxidation, surface diffusion to external sink, radiation influence, etc.) some number of atoms of one of the components (B) are extracted leaving vacancies behind. Let the vacancy sinks at dislocations be not too efficient – it means that the time of relaxation of the vacancy concentration to the equilibrium level may be longer than the time of new structure nucleation. As a result, the compound will find itself simultaneously (i) supersaturated with vacancies and (ii) depleted with B (or supersaturated with A) – deviated from stoichiometry. The first reason should lead to void nucleation. The second reason should lead to precipitation (nucleation) of the phase “j”, “next” in the direction of decreasing B (richer in A). For example, let us consider compound Cu_6Sn_5 , from which some Sn atoms are sucked out by fast surface diffusion of tin to react with copper walls (or, maybe, with some components of surrounding flux). If compound Cu_6Sn_5 loses Sn, it becomes supersaturated by copper, therefore it should precipitate the particles of the phase nearest at the phase diagram from the copper side. This phase is Cu_3Sn – so, the Cu_3Sn particles should precipitate. On the other hand, if extraction of tin is related to the formation of extra vacancies, they should gather into voids. Thus, compound Cu_6Sn_5 should simultaneously demonstrate the precipitation of Cu_3Sn phase and of voids. If the sucking out of B continues, then both voids and precipitates of new phase should grow along the outgoing flux of B.

So, on the one hand, our work is just some modification of the classical Turnbull’s and Cahn’s approach to eutectoid transformation for the case of the open decomposing

system. The main difference is the change of boundary conditions due to the existence of outgoing flux. The other peculiarity is that one of the emerging phases is just “emptiness” (hollow channels). Actually, we observe decomposition of the pseudo-ternary system copper–tin–vacancies under external outflux of tin. On the other hand, this section describes the recently discovered new morphology of the intermetallic Cu_3Sn .

At first (in Section 2.4.2), we will review shortly the main experimental observations. Then, (in Section 2.4.3) we will present the discussion of possible thermodynamic reasons of newly discovered morphology, then follow the basic equations and boundary conditions of the Flux-Driven Precipitation theory (Section 2.4.4).

2.4.2 Experimental Observations

It is well-known that the growth of Cu_3Sn phase layer in the process of reactive diffusion between Cu and Sn or between copper and Cu_6Sn_5 -phase leads to the formation of Kirkendall voids in the vicinity of Cu/ Cu_3Sn moving interface [52]. It happens (i) because copper is the main diffusant across growing Cu_3Sn phase layer, generating the back flux of vacancies to the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface and (ii) because the vacancy sinks at dislocations near interface do not work properly, enabling supersaturation by vacancies and voids formation. Recently, nanotwinned copper was used to form the contact with solder [48]. In this case, voiding can be almost suppressed, due to numerous vacancy sinks at the twin boundaries. Moreover, our present section is not about Kirkendall voids formation at the interface Cu/ Cu_3Sn during reactive growth of Cu_3Sn phase. This effect is known and, in principle, its nature and kinetics are clear. Instead, our chapter treats the process which starts later: Imagine the layer of tin-based solder (with thickness of 15–30 microns) between two copper rods. If solder is molten, its reaction with copper goes very fast and in about one minute all solder is consumed by the fast growing phase Cu_6Sn_5 . If annealing continues, after this the solid state aging of the sandwich Cu– Cu_6Sn_5 –Cu leads to the growth of two thin Cu_3Sn layers. They grow normally up to several microns thickness each. If copper is not nanotwinned, simultaneously with compound growth the chain of Kirkendall voids along both Cu/ Cu_3Sn interfaces appears. After this, the new phenomenon starts: one can observe the formation of much more porous Cu_3Sn with different morphology (Fig. 2.3). This morphology resembles the picture of cellular precipitation, or, even more, eutectoid decomposition with essential difference – the second phase in the lamellar structure is here just “emptiness” (net of interconnected voids – empty channels). According to experimental data [19], a region of such porous structure inside starts from the sides and propagates in almost steady-state regime until full disappearance of Cu_6Sn_5 . Clearly, tin is going out due to some driving force. Most probably, it is a driving force of Cu_3Sn formation at the sides of the sample due to surface diffusion of tin to the side walls of copper rods. It looks like the presence of surrounding flux (gumboil) somehow helps tin approach the side walls of copper rods, but the full picture is not yet clear in this respect. It is possible that the

surrounding flux (gumboil) contains some components reacting with tin. One thing is clear – for some reason tin is being sucked out via the sides of remaining Cu_6Sn_5 layer.

First, we consider shortly the list of possible explanations of the above-described phenomenon.

2.4.3 Thermodynamic Analysis of Possible Transformations

At first, let us understand that it is possible for Cu_6Sn_5 to be decomposed into Cu_3Sn and Sn,



which later diffuses out, leaving the empty channels. Fig. 2.20 below shows the Gibbs free energies (from left to right) of (i) pure copper, (ii) Cu_3Sn phase, (iii) Cu_6Sn_5 phase, and (iv) pure solid tin (in which copper is almost insoluble).

We can see that in both cases (523 and 423 K) the decomposition of η -phase (Cu_6Sn_5) into ε -phase (Cu_3Sn) and tin is thermodynamically **unfavorable** – Gibbs free

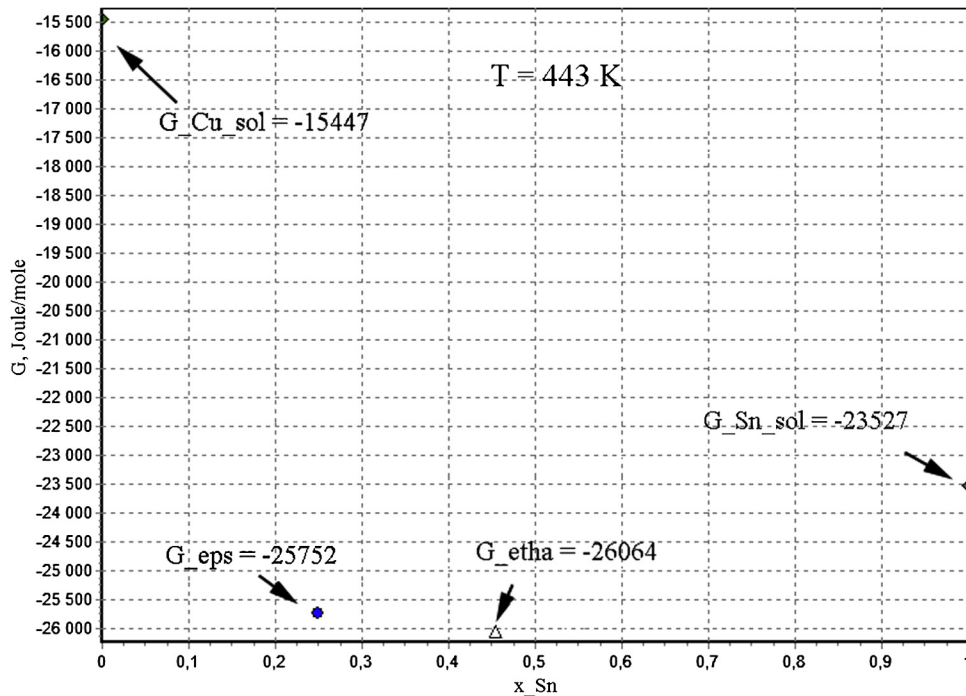


Figure 2.20 Gibbs free energies (in joules per mole) of initial components and of two intermediate phases at 423 K (solid tin).

energy of Cu_6Sn_5 is situated lower than the common tangent of Cu_3Sn and Sn :

$$\Delta g_{\text{Cu}_6\text{Sn}_5 \rightarrow 2\text{Cu}_3\text{Sn} + 3\text{Sn}} = +852 \text{ J/mole.} \quad (2.50)$$

Thus, **direct** decomposition of Cu_6Sn_5 into Cu_3Sn plus pure Sn is not favorable. Yet, one can imagine the reaction



as consisting of the following two steps:



During the first step, 3 moles of tin atoms may be deducted from one mole of Cu_6Sn_5 -phase not in the form of bulk tin phase (which is thermodynamically unfavorable, as we have just demonstrated above), but in the form of surface atoms at the free surface of Cu_3Sn phase in the hollow channels.

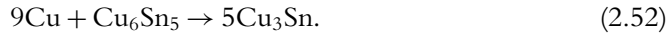
One should also take into account the volume change and stress accumulation during the growth of continuous Cu_3Sn layer in the reaction of Cu with Cu_6Sn_5 . It is related to the non-conservation of volume during the reaction. Indeed, let us evaluate the change of volume in reaction $9\text{Cu} + \text{Cu}_6\text{Sn}_5 \rightarrow 5\text{Cu}_3\text{Sn}$:

Volume per atom of Cu_3Sn is $\Omega(\varepsilon) = 1.46 \cdot 10^{-29} \text{ m}^3/\text{atom}$,

Volume per atom of Cu_6Sn_5 is $\Omega(\eta) = 1.80 \cdot 10^{-29} \text{ m}^3/\text{atom}$,

Volume per atom of Cu is $\Omega(\text{Cu}) = 1.19 \cdot 10^{-29} \text{ m}^3/\text{atom}$.

Reaction of Cu_3Sn formation from Cu reaction with Cu_6Sn_5 is



The volume of the left-hand side in Eq. (2.52) is $9\Omega(\text{Cu}) + 11\Omega(\eta) = 30.51 \cdot 10^{-29} \text{ m}^3$.

The volume of the right-hand side in Eq. (2.52) is $5 \cdot 4 \cdot \Omega(\varepsilon) = 29.20 \cdot 10^{-29} \text{ m}^3$.

Relative change of volume per atom is negative and equal to

$$\frac{\Delta\Omega}{\Omega(\varepsilon)} = \frac{(29.20 - 30.51)10^{-29}}{1.46 \cdot 10^{-29}} \approx -0.045.$$

Even if all this volume change were to go to void formation without any relaxation, the void fraction would not exceed 4.5%. This is much less than one observes in the porous zone. So the volume change during the reaction cannot be responsible for the observed amount of voids in porous Cu_3Sn . Alternatively, voids formation can be well

explained by the extraction (out-diffusion) of tin atoms from Cu_6Sn_5 . Note that in the case of rigidly constrained sides of the sample the volume change of minus 4.5% would mean significant tensile stresses of a few gigapascals. Such tensile stresses are not sufficient to provide the observed amount of porosity, but they can assist in nucleation of voids.

Currently, we can see only one reasonable explanation of the second-type morphology of porosity in Cu_3Sn (porous, sponge-like percolating matrix of Cu_3Sn containing an array of interconnected voids). We believe that this net of interconnected voids forms the percolating cluster, making possible the migration of tin along the surfaces of voids to react with copper sides (and, maybe, with other reagents in underfill). Tin, of course, is not lost – it goes to the external (side) surface of copper, inducing the reaction with copper and formation of additional side layer of intermetallic. At this moment we cannot exclude other possible reagents, sucking tin out from Cu_6Sn_5 . The extraction of tin by its surface outdiffusion leads to gradual conversion of the phase Cu_6Sn_5 into two-phase zone. This growing zone consists of colonies of the lamellar structures: a Cu_3Sn layer of some width a is followed by an empty channel of width b , and this $a + b$ structure is periodically repeated.

One can find the fractions $a/(a + b)$ and $b/(a + b)$ of crystalline Cu_3Sn and of voids from the reaction: $\text{Cu}_6\text{Sn}_5 - 3\text{Sn} \rightarrow 2\text{Cu}_3\text{Sn}$.

If 3 moles of tin are extracted, then molar volume 118.72 cm^3 of Cu_6Sn_5 converts into two molar volumes of Cu_3Sn : $2 * 35.01 \text{ cm}^3 = 70.02 \text{ cm}^3$.

The rest is empty (void): $118.72 - 2 * 35.01$.

Thus, void fraction should be (if one neglects the relaxation effects)

$$b/(a + b) = 1 - 70.02/118.72 = 0.41. \text{ Respectively, } a/(a + b) = 0.59.$$

So, if the volume of tin, which has gone, is not relaxed, then the porous Cu_3Sn should contain about 40% of voids.

In the case of equal atomic volumes, the ratio b/a would be 3/8: Cu_6Sn_5 has 11 atoms, 3 atoms of Sn go and are replaced by 3 vacancies, 8 atoms go for construction of 2 molecules of Cu_3Sn . So, the void corresponds to the volume of 3 atoms which had been extracted. Then, $2\text{Cu}_3\text{Sn}$ corresponds to a new phase volume, containing 8 atoms. If all atomic volumes are approximated as the same, then the ratio must be

$$b/a = 3/8. \tag{2.53}$$

This very approximation will be used below.

2.4.4 Kinetic Model of the Eutectoid-Like Porous Zone Formation in Open System

In the following, we will concentrate on the behavior and conservation of tin, but it is impossible to describe the process without an account of copper diffusion along the

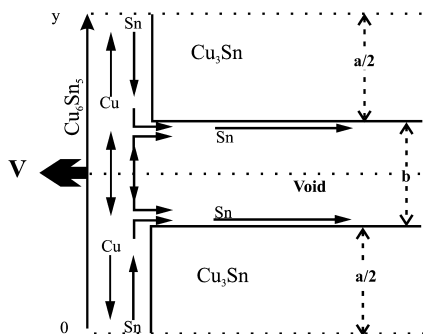


Figure 2.21 Scheme of lamellar zone formation by outdiffusion of tin.

moving interface, “leaving place” for empty channels. So far we will treat the channels as planar and interface as planar as well – we will take it as a constraint. Let V be the velocity, with which the interface between Cu_6Sn_5 and lamellar structure “ Cu_3Sn + lamellar voids” moves from the initial side inside the remaining phase Cu_6Sn_5 (see Fig. 2.21).

In our model tin first migrates to the surfaces of hollow channels (“corridors”) (I) via an interface of length a between Cu_6Sn_5 and Cu_3Sn phases, and simultaneously (II) via an interface of length b between Cu_6Sn_5 and a hollow “corridor”. After this, tin migrates along the walls of the corridor to react with copper.

For better clarity, we will describe the directions and magnitudes of Cu interface fluxes, with respect to Sn fluxes. Let us make the simple calculation (assuming all atomic volumes the same): One mole of Cu_6Sn_5 loses 3 moles of Sn and is converted into 2 moles of Cu_3Sn and void (“3 moles of vacancies”). We divide one mole of Cu_6Sn_5 into two parts: “left” contains $8/11$ mole of Cu_6Sn_5 and is followed by two moles of Cu_3Sn . The “right” part contains $3/11$ mole of Cu_6Sn_5 and is followed by Void (empty channel) (see Fig. 2.22).

It means that $8/11 \cdot 6 = 48/11$ moles of Cu atoms in the non-converted matrix of Cu_6Sn_5 are followed by 6 moles of Cu atoms in the column of Cu_3Sn , and for this, the left side should **get** (by interface diffusion) $6 - 48/11 = 18/11$ additional moles of copper atoms. On the other hand, $8/11 \cdot 5 = 40/11$ moles of Sn atoms in the unconverted matrix of Cu_6Sn_5 are followed by 2 moles of Sn atoms in the column of Cu_3Sn , and for this, the same left part should lose $40/11 - 2 = 18/11$ moles of Sn atoms. Thus, during the reaction, the “left” part just exchanges $18/11$ moles of Sn atoms to the same quantity of Cu atoms.

The “right” part **loses both** copper and tin – $18/11$ moles of copper (going to the left part to construct Cu_3Sn) and $15/11$ moles of tin (diffusing outside along the walls of mentioned “corridor”), which fully corresponds to the stoichiometry of Cu_6Sn_5 phase.

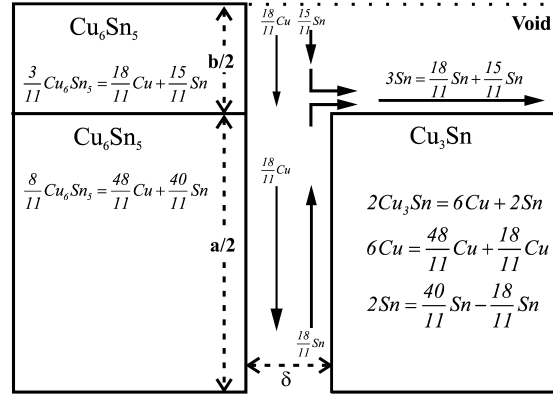


Figure 2.22 Scheme of components redistribution along the interface in FDP.

Thus, in the “right” part of interface the fluxes of copper and tin are not opposite, but instead codirected, and their ratio corresponds to the ratio of molar fractions (Fig. 2.22).

Now we discuss the driving forces generating the flux directions shown in Fig. 2.22. For Sn the driving force seems evident – it is a low tin chemical potential after interaction with side copper – in other words, it is the driving force of already mentioned reaction $\text{Cu}_6\text{Sn}_5 + 9\text{Cu} \rightarrow 5\text{Cu}_3\text{Sn}$ (and, maybe, other reaction with underfill). In our model, this reaction is realized by interface diffusion along $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ and then by surface diffusion of tin along percolating cluster of free surfaces of Cu_3Sn . In the “left” part of Fig. 2.22, the copper flux along interface **must** be opposite and equal in absolute value to the tin flux along the same interface (to provide conservation of volume, if one neglects the difference of atomic volumes). Equality of absolute magnitudes and opposite directions of Cu and tin interface fluxes in the “left” part – along the η/ε interphase interface – can be realized by various mechanisms (interface Kirkendall effect, interfacial backstress (“osmotic pressure”), but here we will not go into details.

In the “right” part the fluxes should be codirected and proportional to stoichiometric fractions, to provide the full disappearance of material ahead of the propagating void channel. The thermodynamic reason is the following: sucking out of tin from Cu_6Sn_5 decreases its concentration in this compound and, simultaneously, increases the concentration of copper, which means also an increase of copper chemical potential. So, copper migrates along the slope of its chemical potential, to the edge of the void channel.

We will formulate and solve equations of tin diffusion along the two interfaces – $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ (“left” part) and $\text{Cu}_6\text{Sn}_5/\text{void}$ (“right” part). In both cases, we will neglect segregation effects (for simplicity) – otherwise, one should take interface fluxes as proportional to the chemical potential gradient, instead of a concentration gradient. Accounting for segregation is obvious, but it needs additional thermodynamic information about interface $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ and about free surfaces of Cu_6Sn_5 and of Cu_3Sn .

I. $|y| < a/2$. Diffusion of tin along interface $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ – the “left” part

Diffusion of tin along the moving interface in its own reference frame with an account of side fluxes is described similarly to the diffusion at the moving front of cellular precipitation:

$$\frac{\partial n_{\text{Sn}}^{\text{int } \eta/\varepsilon}}{\partial t} = D_{\text{Sn}}^{\text{int } \eta/\varepsilon} \frac{\partial^2 n_{\text{Sn}}^{\text{int } \eta/\varepsilon}}{\partial y^2} + \frac{V}{\delta} (n^\eta c_{\text{Sn}}^\eta - n_{\text{Sn}}^{\text{int } \eta/\varepsilon}(y)). \quad (2.54)$$

As usual, we further assume the steady-state approximation

$$D_{\text{Sn}}^{\text{int } \eta/\varepsilon} \frac{\partial^2 n_{\text{Sn}}^{\text{int } \eta/\varepsilon}}{\partial y^2} \approx \frac{V}{\delta} (n_{\text{Sn}}^{\text{int } \eta/\varepsilon}(y) - n^\eta c_{\text{Sn}}^\eta). \quad (2.55)$$

If y is counted from the center of interval, a , then the solution should be symmetric:

$$\begin{aligned} n_{\text{Sn}}^{\text{int } \eta/\varepsilon}(y) &= A_L \cdot \cos h\left(\frac{y}{\lambda_L}\right) + B_L \\ \lambda_L &= \sqrt{\frac{D_{\text{Sn}}^{\text{int } \eta/\varepsilon} \delta}{V}}. \end{aligned} \quad (2.56)$$

Constant A_L can be found from the conservation condition for tin in a -band:

$$-D_{\text{Sn}}^{\text{int } \eta/\varepsilon} \frac{\partial n_{\text{Sn}}^{\text{int } \eta/\varepsilon}}{\partial y} \bigg|_{y=a/2} \cdot \delta \cdot W \cdot t = (n^\eta c_{\text{Sn}}^\eta - n^\varepsilon c_{\text{Sn}}^\varepsilon) V t \frac{a}{2} W, \quad (2.57)$$

or

$$-\frac{A_L}{\lambda_L} \cdot \sinh \frac{a}{2\lambda_L} = \frac{Va}{2D_{\text{Sn}}^{\eta/\varepsilon} \delta} (n^\eta c_{\text{Sn}}^\eta - n^\varepsilon c_{\text{Sn}}^\varepsilon),$$

so that

$$A_L = -\frac{(a/2\lambda_L)}{\sinh(a/2\lambda_L)} (n^\eta c_{\text{Sn}}^\eta - n^\varepsilon c_{\text{Sn}}^\varepsilon). \quad (2.58)$$

The most “dangerous” (oversimplified) assumption is that at the center of the future Cu_3Sn ($y = 0$) the concentration at interface $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ should coincide with a concentration of Cu_6Sn_5 . This condition gives us the second constant B_L :

$$n^\eta c_{\text{Sn}}^\eta = A_L \cdot \cos h\left(\frac{0}{\lambda_L}\right) + B_L = A_L + B_L \Rightarrow B_L = n^\eta c_{\text{Sn}}^\eta - A_L. \quad (2.59)$$

Without such (or similar) condition one should solve the optimization problem for fastest growth velocity.

II. Diffusion of tin along the Cu_6Sn_5 /void interface

Diffusion of tin along the moving interface in its own reference frame with an account of side fluxes is described similarly to the diffusion at the moving front of cellular precipitation:

$$\frac{\partial n_{Sn}^{\text{int } \eta/\text{void}}}{\partial t} = D_{Sn}^{\text{int } \eta/\text{void}} \frac{\partial^2 n_{Sn}^{\text{int } \eta/\text{void}}}{\partial \gamma^2} + \frac{V}{\delta} (n^\eta c_{Sn}^\eta - n_{Sn}^{\text{int } \eta/\text{void}}(\gamma)). \quad (2.60)$$

Steady-state approximation is

$$D_{Sn}^{\text{int } \eta/\text{void}} \frac{\partial^2 n_{Sn}^{\text{int } \eta/\text{void}}}{\partial \gamma^2} \approx \frac{V}{\delta} (n_{Sn}^{\text{int } \eta/\text{void}}(\gamma) - n^\eta c_{Sn}^\eta). \quad (2.61)$$

If γ is counted from the center of interval, b , then the solution should be symmetric:

$$\begin{aligned} n_{Sn}^{\text{int } \eta/\text{void}}(\gamma) &= A_R \cdot \cosh\left(\frac{\gamma}{\lambda_R}\right) + B_R, \\ \lambda_R &= \sqrt{\frac{D_{Sn}^{\text{int } \eta/\text{void}} \delta}{V}}. \end{aligned} \quad (2.62)$$

Constant A_R can be found from the conservation condition for tin in a b -band:

$$-D_{Sn}^{\text{int } \eta/\text{void}} \frac{\partial n_{Sn}^{\text{int } \eta/\text{void}}}{\partial \gamma} \Big|_{\gamma=(a+b)/2+b/2} \cdot \delta \cdot W \cdot t = (n^\eta c_{Sn}^\eta - 0) V t \frac{b}{2} W, \quad (2.63)$$

so that

$$A_R = -\frac{(b/2\lambda_R)}{\sinh(b/2\lambda_R)} (n^\eta c_{Sn}^\eta). \quad (2.64)$$

By analogy with Eq. (2.59), we suppose that at the center of the future void ($\gamma = (a+b)/2$) the concentration should coincide with a concentration of Cu_6Sn_5 . This condition gives us the second constant B_R :

$$n^\eta c_{Sn}^\eta = A_R \cdot \cosh\left(\frac{0}{\lambda}\right) + B_R = A_R + B_R \Rightarrow B_R = n^\eta c_{Sn}^\eta - A_R. \quad (2.65)$$

A natural constraint is the continuity of tin concentration along interface, including the border between “left” and “right” parts:

$$A_L \cdot \left(\cosh\left(\frac{a}{2\lambda_L}\right) - 1 \right) = A_R \cdot \left(\cosh\left(\frac{b}{2\lambda_R}\right) - 1 \right) \quad (2.66)$$

$$\begin{aligned} \frac{(a/2\lambda_L)}{\sinh(a/2\lambda_L)} (n^\eta c_{Sn}^\eta - n^\varepsilon c_{Sn}^\varepsilon) \cdot \left(\cosh\left(\frac{a}{2\lambda_L}\right) - 1 \right) = \\ = \frac{(b/2\lambda_R)}{\sinh(b/2\lambda_R)} (n^\eta c_{Sn}^\eta) \cdot \left(\cosh\left(\frac{b}{2\lambda_R}\right) - 1 \right). \end{aligned} \quad (2.67)$$

We already know that assuming all atomic volumes as approximately the same, the ratio b/a in our case should be equal $3/8$, we can express b in terms of a and get one transcendent algebraic equation for one unknown a :

$$\frac{\sinh\left(\frac{3}{8}a/2\lambda_R\right)}{\sinh(a/2\lambda_L)} \frac{\cosh\left(\frac{a}{2\lambda_L}\right) - 1}{\cosh\left(\frac{3}{8}\frac{a}{2\lambda_R}\right) - 1} = \frac{n^\eta c_{Sn}^\eta}{n^\eta c_{Sn}^\eta - n^\varepsilon c_{Sn}^\varepsilon}. \quad (2.68)$$

Taking approximately $n^\eta \approx n^\varepsilon$ (since in this section we already assumed all atomic volumes the same) and introducing dimensionless unknown and dimensionless parameter

$$x \equiv \frac{a}{2\lambda_L}, \quad p \equiv \frac{3}{8} \frac{\lambda_L}{\lambda_R} = \frac{3}{8} \sqrt{\frac{D^{\text{int } \eta/\varepsilon}}{D^{\text{int } \eta/\text{vacuum}}}}, \quad (2.69)$$

one gets the final equation

$$\frac{\sinh(px)}{\sinh(x)} \frac{\cosh(x) - 1}{\cosh(px) - 1} = \frac{c_{Sn}^\eta}{c_{Sn}^\eta - c_{Sn}^\varepsilon} = \frac{20}{9}. \quad (2.70)$$

In case $p \equiv \frac{3}{8}$, ($\frac{D^{\text{int } \eta/\varepsilon}}{D^{\text{int } \eta/\text{vacuum}}} = 1$) Eq. (2.47) has a numerical solution $x \approx 1.9$, so that

$$\begin{aligned} a \approx 2 \cdot 1.9\lambda_L = 3.8 \sqrt{\frac{D^{\text{int } \eta/\varepsilon} \delta}{V}} \approx 3.8 \sqrt{\frac{10^{-13} \frac{\text{m}^2}{\text{s}} 10^{-9} \text{ m}}{10^{-9} \frac{\text{m}}{\text{s}}}} \approx 1.3 \cdot 10^{-6} \text{ m}, \\ b = \frac{3}{8}a \approx 0.43 \cdot 10^{-6} \text{ m}. \end{aligned} \quad (2.71)$$

Here we took (so far) the velocity from experimental observations, but very soon below we will be able to estimate it theoretically (and it will indeed match this order of magnitude). If one looks at the experimental pictures, our rough estimates appear very reasonable.

Now comes the main question – how to find the velocity V of moving transformation front? In the classic works on cellular precipitation in a closed system, this question (conjugate with the question of the optimal period of lamellar structure) is difficult and leads to using the semiempirical principle of the maximum release rate of Gibbs free energy or to similar hypotheses. In our case of the open system, it seems easier to answer this question than in the classic discontinuous precipitation theory. The reason is that (i) in our case the transformation is complete, and (ii) fluxes along interfaces and along the free surface are linked and related to the external driving force of reaction.

So, in our case velocity is not chosen by the system among a variety of possibilities, but instead is determined unambiguously by the external driving force, sucking out tin and generating the precipitation process.

The total outflux of tin from the square area $W * W$ is equal to

$$\begin{aligned}
 J_{Sn}^{total} &\approx \frac{W}{a+b} \cdot W \cdot \delta \cdot \left(-D_{Sn}^{\text{int } \eta/\varepsilon} \frac{\partial n_{Sn}^{\text{int } \eta/\varepsilon}}{\partial y} \Big|_{y=a/2} - D_{Sn}^{\text{int } \eta/\text{void}} \frac{\partial n_{Sn}^{\text{int } \eta/\text{void}}}{\partial y} \Big|_{y=(a+b)/2+b/2} \right) \approx \\
 &\approx \frac{W^2 V}{a+b} \cdot (a(n^\eta c_{Sn}^\eta - n^\varepsilon c_{Sn}^\varepsilon) + b(n^\eta c_{Sn}^\eta - 0)) = \\
 &= W^2 V \cdot \left(n^\eta c_{Sn}^\eta - \frac{a}{a+b} n^\varepsilon c_{Sn}^\varepsilon \right) \approx n W^2 V \cdot \left(\frac{5}{11} - \frac{8}{11} \frac{1}{4} \right) = \frac{3}{11} n W^2 V. \quad (2.72)
 \end{aligned}$$

To estimate the velocity of the transformation front, one should equate the just evaluated total flux through some square area $W * W$ of the side surface of decomposing alloy to the total diffusion side flux through both sides of each of $W/(a+b)$ lamellae. Total flux has the structure of product of the mobility D/kT , thermodynamic driving force, effective area of the easy diffusion paths via the net of free surfaces of the lamellar structure:

$$J_{Sn}^{total} \sim 2 \frac{W}{a+b} n W \delta \frac{(D_{Sn}^{surf})^*}{l} \frac{\Delta g}{kT} \sim \frac{3}{11} n W^2 V. \quad (2.73)$$

Thus,

$$V \sim \frac{22}{3} \frac{\delta (D_{Sn}^{surf})^*}{l(a+b)} \frac{\Delta g}{kT} \sim 7 \frac{\delta}{l(a+b)} (D_{Sn}^{surf})^* \frac{\Delta g}{kT}. \quad (2.74)$$

Eq. (2.74) so far cannot be used for direct estimation of velocity V since lamellar sizes a and b also depend on V . Therefore, let us substitute Eq. (2.71) into Eq. (2.74):

$$V \sim 7 \frac{\delta}{l \cdot 3.8 \sqrt{\frac{D_{Sn}^{\text{int } \eta/\varepsilon} \delta}{V} \frac{11}{8}}} (D_{Sn}^{surf})^* \frac{\Delta g}{kT} \approx \sqrt{V} \cdot \frac{1.4}{l} \sqrt{\frac{\delta}{D_{Sn}^{\text{int } \eta/\varepsilon}}} (D_{Sn}^{surf})^* \frac{\Delta g}{kT},$$

so that

$$V \sim 2 \frac{\delta (D_{Sn}^{surf})^*}{l^2 D_{Sn}^{\text{int } \eta/\varepsilon}} \left(\frac{\Delta g}{kT} \right)^2. \quad (2.75)$$

Eq. (2.75) is our theoretical prediction of the precipitation front velocity V .

The driving force per atom of Cu_3Sn formation from Cu and Cu_6Sn_5 is about $\Delta g \approx 0.75 \cdot 10^{-20} \text{ J}$, $\frac{\Delta g}{kT} \approx 1$ at $T = 523 \text{ K}$.

We take the characteristic width of porous zone and distance from it to Cu as about 50 microns.

Let us try to evaluate the surface diffusivity of tin at the surface of Cu_3Sn using the empirical rule $(D^{surf})^* \sim 10^{-4} \frac{\text{m}^2}{\text{s}} \cdot \exp(-8.9 \frac{T^{melt}}{T})$.

According to equilibrium phase diagram, phase Cu_3Sn decomposes before reaching melting but not far from it at a temperature of about 950 K.

Thus, $(D^{surf})^* \sim 10^{-4} \frac{\text{m}^2}{\text{s}} \cdot \exp(-8.9 \frac{950}{523}) \sim 10^{-11} \frac{\text{m}^2}{\text{s}}$. It is 100 times less than for diffusion in the melt, but ten times larger than the bulk diffusion before melting.

If one takes $(D_{Sn}^{surf})^* \sim 10^{-11} \frac{\text{m}^2}{\text{s}}$, then

$$V \sim 2 \frac{10^{-9} (10^{-11})^2}{(5 \cdot 10^{-5})^2 10^{-13}} \cdot 1 \sim 0.8 \cdot 10^{-9} \frac{\text{m}}{\text{s}}.$$

Fifteen hours of annealing after the start of pores formation may give the thickness of porous layer of about $L = Vt \sim 8 \cdot 10^{-10} \frac{\text{m}}{\text{s}} \cdot 0.5 \cdot 10^5 \text{ s} = 40 \cdot 10^{-6} \text{ m} = 40 \text{ microns}$.

That is also a very reasonable correspondence to the experimental picture.

In this section, we discussed the new mechanism of the recently discovered new morphology – porous Cu_3Sn compound with the lamellar structure of crystalline and void phases. We treat this process as flux-driven discontinuous decomposition $\text{Cu}_6\text{Sn}_5 - 3\text{Cu} \rightarrow 2\text{Cu}_3\text{Sn} + \text{Voids}$, generated by the outflux of tin from the system by surface diffusion along the external surface and along the percolating net of newborn empty channels. New theory gives reasonable predictions of lamellar structure sizes (Eq. (2.71)) and of propagation velocity (Eq. (2.75)).

2.5 FLUX-DRIVEN NUCLEATION DURING REACTIVE DIFFUSION

2.5.1 General Remarks

Reactive diffusion in thin-film couples demonstrates sequential phase formation, instead of simultaneous growth. It means that, contrary to the bulk case, in thin film case and in nanosystems some phases are suppressed so that they may have no chance to appear at all. To predict the time-dependent observed phase spectrum of such a system, we do not need absolute values of nucleation periods, but instead their ratios. This task appeared to be complicated, and so far was solved only partially.

Classical nucleation in terms of attachment and detachment frequencies.

At first, we shortly remind the classical nucleation theory by considering the formation of a spherical nucleus of an IMC in an initially homogeneous supersaturated solution of B in A. We assume that nature “takes care” of stoichiometry (atomic fraction C_i of B in IMC remains constant). Gibbs potential of parent phase with one embryo/nucleus depends on its size (number of atoms n) as

$$\Delta G(n) = -n\Delta g + \gamma \cdot 4\pi r_0^2 n^{2/3} \quad (2.76)$$

($r_0 \equiv (3\Omega/(4\pi))^{1/3}$, Ω is atomic volume, γ denotes the interfacial energy per unit area).

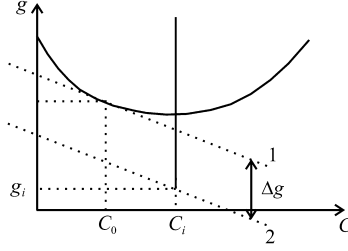


Figure 2.23 Rule of parallel tangents.

The bulk driving force per atom Δg is determined by the so-called “rule of parallel tangents” (not to confuse with common tangent) (see Fig. 2.23).

Critical size and nucleation barrier are found from extremum condition

$$n_{cr} = \frac{4\pi}{3\Omega} \left(\frac{2\gamma\Omega}{\Delta g} \right)^3, \quad G^* = \frac{4\pi\gamma}{3} \left(\frac{2\gamma\Omega}{\Delta g} \right)^2. \quad (2.77)$$

Overcoming the nucleation barrier is a stochastic process consisting of random attachments and detachments of atoms, ν_+ , ν_- being the frequencies of these events. Their combinations $\bar{\nu} = (\nu_+ + \nu_-)/2$, $\Delta\nu = \nu_+ - \nu_-$ are often used. The first combination is a diffusivity (rate of the random walk) of clusters in the size space, the second combination is a drift velocity of clusters: for subcritical clusters $\Delta\nu < 0$, for the overcritical nucleus $\Delta\nu > 0$. The flux of clusters in the size space is given by a combination of the diffusion and drift terms:

$$j(n) = \Delta\nu \cdot f(n) - \bar{\nu} \frac{\partial f}{\partial n}, \quad (2.78)$$

with $f(n)$ being the number of clusters (per unit volume) containing n atoms. In equilibrium, this flux is zero and f is a Boltzmann distribution,

$$f_{eq}(n) = \text{const} \cdot \exp(-\Delta G(n)/kT). \quad (2.79)$$

Substituting equilibrium distribution into zero flux condition, one gets interrelation between the drift and diffusion terms in size space, which is identical with Nernst–Einstein relation between mobility and diffusivity in usual space:

$$\Delta\nu(n) = -\frac{\bar{\nu}(n)}{kT} \frac{\partial \Delta G}{\partial n}. \quad (2.80)$$

It is well-known [4] that in the case of diffusion-controlled nucleation in a closed system, the drift term not far from the critical size ($|\delta n| \equiv |n - n_{cr}| \ll n_{cr}$) is

$$\Delta\nu^{\text{internal}} \cong \frac{4\pi D\alpha}{c_1\Omega} \left(\left(\frac{n}{n_{cr}} \right)^{1/3} - 1 \right) \cong \frac{4\pi D\alpha}{3c_1\Omega n_{cr}} \delta n, \quad \alpha = \frac{2\gamma\Omega}{kT} c_{eq}, \quad (2.81)$$

and the diffusion term in size space is

$$\bar{v}(n) = 3 \frac{c_{eq} D}{c_1 r_0^2} n^{1/3}, \quad (2.82)$$

where D is the diffusion coefficient of B in the dilute solution. If nucleation is interface controlled, then $\bar{v}(n)$ is proportional to $n^{2/3}$ instead of $n^{1/3}$ [4].

2.5.2 External Flux Divergence in Open System – Idea of Flux-Driven Nucleation (FDN)

External fluxes may assist nucleation (FAN) if their divergence is negative, and may suppress nucleation (FSN) if divergence is positive. Divergence means imbalance of outgoing and incoming fluxes at the surface of elemental volume divided by the size of this volume. If divergence of monomers is negative, incoming flux is larger than the outgoing one. So, in this case, the flux divergence should help the growth of even subcritical embryo.

If nucleation proceeds in the field of external fluxes with nonzero divergence, the drift term in the size space is changed to

$$\Delta v^{total} \cong \Delta v^{internal} + \left. \frac{dn}{dt} \right|^{external} = \Delta v^{internal} + \Delta v^{external}. \quad (2.83)$$

From a kinetic point of view, the ability of precipitate to grow or shrink (to be overcritical or subcritical) is determined by the sign of the drift velocity. In the case of a closed system, thermodynamic and kinetic approaches give the same result – zero drift corresponds to vanishing Gibbs potential derivative. If the system has a global distribution of fluxes, thermodynamic and kinetic approaches give different results [48]: a thermodynamically unstable embryo may survive and grow, if the second term on the right side of Eq. (2.83) is positive and larger than the absolute value of the negative first term ($\Delta v^{internal}$) – Flux-Assisted Nucleation (FAN), nucleation barrier decreased. Conversely, if the second term in Eq. (2.85) is negative then even “thermodynamically viable” nuclei can be suppressed – Flux-Suppressed Nucleation (FSN), nucleation barrier increased. In general, we will call this situation FDN (Flux-Driven Nucleation). To remain formally in the framework of the standard Fokker–Planck scheme, it is convenient to introduce an **effective Gibbs potential**. A change of this effective potential takes into account the additional “external” shift term. In a standard case (when the external flux divergence in usual space is zero), the equilibrium distribution of clusters in size space is given by Eq. (2.81) and corresponds to zero flux in the size space. If the flux divergence in usual space is not zero, then the condition of zero flux in size space

leads to another distribution, $f_0(n) \neq f_{eq}(n)$,

$$\frac{\Delta v^{total}}{\bar{v}} = \frac{\partial \ln f_0}{\partial n}, \quad \frac{\Delta v^{internal}}{\bar{v}} = \frac{\partial \ln f_{eq}}{\partial n}. \quad (2.84)$$

Combining Eqs. in (2.84), one gets

$$\frac{\partial \ln(f_0/f_{eq})}{\partial n} = \frac{\Delta v^{total} - \Delta v^{internal}}{\bar{v}} = \frac{\Delta v^{external}}{\bar{v}}. \quad (2.85)$$

If the external drift term vanishes at size n tending to zero (and we will treat only such examples), one can conclude that external influence for n tending to zero, should be negligible, so that $\lim_{n \rightarrow 0} (f_0/f_{eq}) = 1$, and respectively $\lim_{n \rightarrow 0} \ln(f_0/f_{eq}) = 0$. Then

$$\ln(f_0/f_{eq}) = \int_0^n \frac{\Delta v^{external}(n')}{\bar{v}(n')} dn', \quad f_0(n) = f_{eq}(n) \exp\left(\int_0^n \frac{\Delta v^{external}(n')}{\bar{v}(n')} dn'\right). \quad (2.86)$$

Taking into account Eq. (2.79), we can represent zero-flux distribution as

$$f_0(n) = \text{const} \cdot \exp(-\Delta G^{eff}(n)/kT), \quad (2.87)$$

with newly introduced **effective Gibbs potential change** [29]

$$\Delta G^{eff}(n) = \Delta G(n) - kT \int_0^n \frac{\Delta v^{external}(n')}{\bar{v}(n')} dn'. \quad (2.88)$$

Obviously, the maximum of effective Gibbs potential change corresponds to zero drift – unstable equilibrium, and should be treated as the effective nucleation barrier. Below, we consider two examples of FDN – suppression of IMC formation and acceleration of Kirkendall/Frenkel void formation.

2.5.3 Nucleation and Growth of Single Intermediate Phase at α/β Meta-Equilibrium Interface

Let us consider the interface of two phases, L and R, which are in metastable equilibrium with each other – for example, weak solution of B in A and of A in B. Metastable equilibrium means that the common tangent links $g_L(c)$ and $g_R(c)$ directly, without account of the intermediate phase “I” before the formation of this phase (see Fig. 2.24).

It is well known (see, for example, [9] and Section 2.2) that the growth rate of the compound i layer of thickness ΔX_i with almost stoichiometric composition c_i within narrow interval Δc_i , growing between practically insoluble components, is equal to

$$\frac{d\Delta X_i}{dt} = \frac{1}{c_i(1-c_i)} \frac{D_i \Delta c_i}{\Delta X_i + \lambda_i}. \quad (2.89)$$

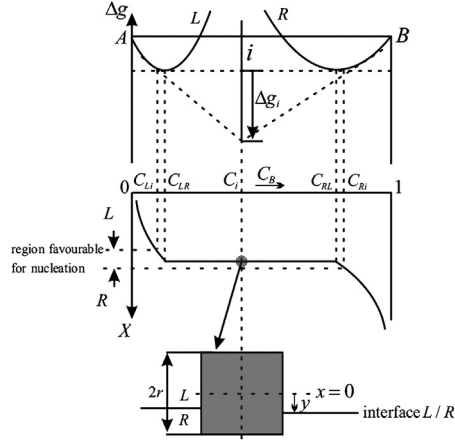


Figure 2.24 Thermodynamic and spatial schemes of IMC nucleation between two **homogeneous** (zero gradients) phases, L and R , which are in metastable equilibrium with each other. The thermodynamic driving force of IMC formation is determined by the difference between the common tangent of metastable phases and Gibbs free energy of i th phase. External flux is zero.

Characteristic length λ_i accounts for interface barriers. It is related to the finite time needed by an atom to overcome barriers. Less known is the interpretation of the product $D_i \Delta c_i$ of mean interdiffusivity and equilibrium phase concentration range. Actually, one should write $D_i \Delta c_i = \int_{c_{iL}}^{c_{iR}} \tilde{D}(c) dc$ (Wagner diffusivity) with the Darken interdiffusion coefficient [9]

$$\tilde{D}(c) = (cD_A^* + (1-c)D_B^*) \frac{c(1-c)}{kT} \frac{\partial^2 g}{\partial c^2}, \quad (2.90)$$

where g is Gibbs free energy per atom, varying to a little extent inside the phase, but its first derivative $\partial g / \partial c$ typically changing drastically so that the second derivative $\partial^2 g / \partial c^2$ becomes large (correlating with the outstanding stability of IMC). Simple transformations (using common tangent rule) give:

$$\begin{aligned} \int_{c_L}^{c_R} \tilde{D}(c) dc &= \overline{D_j^*} \frac{c_j(1-c_j)}{kT} \left(\left. \frac{\partial g}{\partial c} \right|_{i,B} - \left. \frac{\partial g}{\partial c} \right|_{i,A} \right) = \overline{D_j^*} \frac{c_j(1-c_j)}{kT} \left(\frac{g_B - g_j}{1-c_j} - \frac{g_j - g_A}{c_j - 0} \right) = \\ &= \overline{D_j^*} \frac{\Delta g_j(A+B \rightarrow j)}{kT}. \end{aligned} \quad (2.91)$$

Here D_j^* – a combination of tracer diffusion coefficients averaged over the phase, $\overline{D_j^*} \equiv cD_A^* + (1-c)D_B^*$, $\Delta g_i(A+B \rightarrow i)$ – is a thermodynamic driving force (per one atom) of IMC formation. So, the growth rate can be written as some effective mobility times the

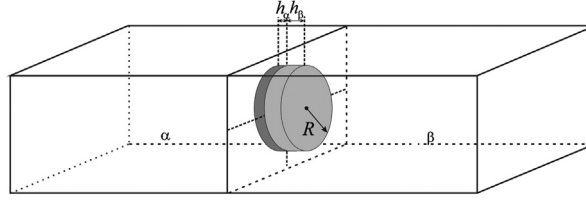


Figure 2.25 Nucleus of intermediate phase (compound) “i” emerging at the interface of two parent phases, α , β , in metastable equilibrium between them.

driving force:

$$\frac{d\Delta X_i}{dt} = \frac{1}{c_i(1-c_i)} \frac{\overline{D}_i^*}{\Delta X_i + \lambda_i} \frac{\Delta g_i(A+B \rightarrow i)}{kT}. \quad (2.92)$$

We will reorganize Eq. (2.92) into a form suitable for nucleation theory. Let S_j be the area of interfaces i/A and i/B, so that $n = S_j \Delta X_j / \Omega$ is the number of atoms of IMC. On the other hand, for far overcritical volumes of IMC (when one can neglect surface energy),

$$\Delta g_j(A+B \rightarrow j) = -\partial G / \partial n. \quad (2.93)$$

Then the rate of uptake of atoms into the growing IMC phase is

$$\frac{dn}{dt} = \left(\frac{\overline{D}_i^* / \Omega}{c_i(1-c_i)} \frac{S_i}{\Delta X_i + \lambda_i} \right) \left(-\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \bar{v}_i \cdot \left(-\frac{1}{kT} \frac{\partial G}{\partial n} \right) = \Delta v. \quad (2.94)$$

The coefficient

$$\bar{v}_i \equiv \left(\frac{\overline{D}_i^* / \Omega}{c_i(1-c_i)} \frac{S_i}{\Delta X_i + \lambda_i} \right) \quad (2.95)$$

can be successfully used as an average attachment/detachment frequency in Fokker–Planck approach.

Now consider the initial stage of IMC formation – its nucleation, which appears most probably at the interface. If solubilities of A in B and of B in A can be neglected, the only interdiffusion inside newly born nucleus determines the rate of its growth or elimination. For the sake of simplicity, we take the nucleus shape to be disc-like with radius R and thickness $h = h_\alpha + h_\beta$. The aspect ratio $\varphi = h/R$ should be optimized (see Fig. 2.25).

The Gibbs free energy change due to nucleation of such disc-like precipitate is

$$\Delta G(n, \varphi) = -n\Delta g_i + W^{surf}(n, \varphi), \quad (2.96)$$

$$W^{surf}(n, \varphi) = (\gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha\beta})\pi R^2 + (\gamma_{\alpha i}h_\alpha + \gamma_{\beta i}h_\beta)2\pi R, \quad (2.97)$$

$$h_\alpha = \frac{c_\beta - c_i}{c_\beta - c_\alpha} h, \quad h_\beta = \frac{c_i - c_\alpha}{c_\beta - c_\alpha} h \quad (\text{from conservation of matter}), \quad (2.98)$$

$$R = (\Omega/\pi)^{1/3} n^{1/3} \varphi^{-1/3}, \quad R\varphi = h = (\Omega/\pi)^{1/3} n^{1/3} \varphi^{2/3}. \quad (2.99)$$

Optimization of surface energy gives

$$\varphi_{opt} = \frac{\gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha\beta}}{\frac{c_\beta - c_i}{c_\beta - c_\alpha} \gamma_{\alpha i} + \frac{c_i - c_\alpha}{c_\beta - c_\alpha} \gamma_{\beta i}} \equiv \frac{\Delta\gamma}{\gamma_i}, \quad \Delta\gamma \equiv \gamma_{\alpha i} + \gamma_{\beta i} - \gamma_{\alpha\beta}, \quad \gamma_i \equiv \frac{c_\beta - c_i}{c_\beta - c_\alpha} \gamma_{\alpha i} + \frac{c_i - c_\alpha}{c_\beta - c_\alpha} \gamma_{\beta i}, \quad (2.100)$$

$$W^{surf}(n, \varphi_{opt}) = \tilde{\gamma} s_0 n^{2/3}, \quad \tilde{\gamma} = (\Delta\gamma \gamma_i^2)^{1/3}, \quad s_0 = 3(\pi \Omega^2)^{1/3}. \quad (2.101)$$

Thus, the drift in the size space can be written by analogy with Eq. (2.94) additionally accounting for the surface term in Gibbs energy,

$$-\frac{\partial \Delta G}{\partial n} = \Delta g_i - \frac{\partial W^{surf}(n, \varphi_{opt})}{\partial n} = \Delta g_i - 2(\pi \Delta\gamma \gamma_i^2 \Omega^2)^{1/3} n^{-1/3}, \quad (2.102)$$

$$\Delta v = \bar{v}_i \cdot \left(\frac{\Delta g_i}{kT} - \frac{2(\pi \Delta\gamma \gamma_i^2 \Omega^2)^{1/3}}{kT n^{1/3}} \right). \quad (2.103)$$

The critical size is found from zero conditions for drift or for derivative of Gibbs free energy:

$$n_{cr} = (2\tilde{\gamma} s_0 / (3\Delta g))^{3/2}. \quad (2.104)$$

At diffusion-controlled nucleation ($\lambda_i = 0$),

$$\bar{v}_i \equiv \frac{\bar{D}_i^*}{c_i(1 - c_i)\Omega} \frac{S_i}{\Delta X_i + 0} = \left(\frac{\bar{D}_i^*}{c_i(1 - c_i)} \left(\frac{\pi}{\Omega} \right)^{2/3} \left(\frac{\gamma_i}{\Delta\gamma} \right)^{4/3} \right) n^{1/3}. \quad (2.105)$$

2.5.4 Nucleation of Single IMC at an Interface in Competition With Diffusion in Neighboring Solid Solutions

Formation of marginal solid solutions competes with an intermediate phase and decreases the phase growth rate. Accounting for Eq. (2.91) and flux balance at the moving interfaces yields

$$\frac{d\Delta X_i}{dt} = \left(\frac{\bar{D}_i^*}{c_i(1 - c_i)} \frac{1}{\Delta X_i} \right) \left(\frac{\Delta g_i}{kT} - \frac{2(\pi \Delta\gamma \cdot \gamma_i^2 \Omega^2)^{1/3}}{kT n^{1/3}} \right) - \frac{1}{1 - c_i} \sqrt{\frac{D_\beta}{\pi t}} c_{A\beta}^{eq} - \frac{1}{c_i} \sqrt{\frac{D_\alpha}{\pi t}} c_{B\alpha}^{eq}. \quad (2.106)$$

Thus, in our case an additional drift in size space due to flux divergence at interfaces is

$$\Delta v^{ext} = \frac{\pi R_{optimized}^2}{\Omega} \left(-\frac{1}{1-c_i} \sqrt{\frac{D_\beta}{\pi t}} c_{A\beta}^{eq} - \frac{1}{c_i} \sqrt{\frac{D_\alpha}{\pi t}} c_{B\alpha}^{eq} \right). \quad (2.107)$$

Thus, the effective Gibbs free energy barrier is

$$\begin{aligned} \Delta G^{eff}(n) = & -n\Delta g + \tilde{\gamma} \cdot s_0 n^{2/3} \\ & + \frac{3kT}{4\pi^{1/3}} \left(\frac{\Delta\gamma}{\gamma} \right)^{2/3} \left(c_i \sqrt{\frac{D_\beta}{\bar{D}_i^*}} c_{A\beta}^{eq} + (1-c_i) \sqrt{\frac{D_\alpha}{\bar{D}_i^*}} c_{B\alpha}^{eq} \right) \frac{\Omega^{1/3}}{\sqrt{\pi \bar{D}_i^* t}} n^{4/3}. \end{aligned} \quad (2.108)$$

One may represent it in the form

$$\begin{aligned} \frac{\Delta G^{eff}(n)}{kT} = & -a_3 x + a_2 x^2 + a_4 \sqrt{\frac{\tau_0}{t}} x^4, \\ x \equiv & n^{1/3}, \quad \tau_0 \equiv \frac{\Omega^{2/3}}{\pi \bar{D}_i^*}, \quad a_3 = \Delta g/kT, \quad a_2 = \tilde{\gamma} \cdot s_0/kT, \\ a_4 = & \frac{3}{4\pi^{1/3}} \left(\frac{\Delta\gamma}{\gamma} \right)^{2/3} \left(c_i \sqrt{\frac{D_\beta}{\bar{D}_i^*}} c_{A\beta}^{eq} + (1-c_i) \sqrt{\frac{D_\alpha}{\bar{D}_i^*}} c_{B\alpha}^{eq} \right). \end{aligned} \quad (2.109)$$

Eqs. (2.108) and (2.109) for effective nucleation barrier contain a positive term proportional to the fourth power of size (actually, $n^{4/3}$) and inversely proportional to the square root of time. For very small times (case (a)) this term is the main, making nucleation barrier infinitely high and the probability of nucleation tending to zero. Case (b) corresponds to the possibility of the metastable nucleus. In case (c) thermodynamics eventually wins and nuclei of IMC grow and form a continuous layer (see Fig. 2.26).

Transition from case (a) to case (b) corresponds to simultaneous zero first derivative and zero second derivative of Gibbs energy with respect to x :

$$\begin{cases} -3a_3 x_*^2 + 2a_2 x_* + 4a_4 \sqrt{\frac{\tau_0}{t^*}} x_*^3 = 0, \\ -6a_3 x_* + 2a_2 + 12a_4 \sqrt{\frac{\tau_0}{t^*}} x_*^2 = 0. \end{cases} \quad (2.110)$$

This set of two algebraic equations with two unknowns, t^* and x_* , is easily solved as

$$x_* = \frac{4a_2}{3a_3}, \quad t^* = \tau_0 \left(\frac{32a_2 a_4}{9a_3^2} \right)^2. \quad (2.111)$$

For $t < t^*$, the nucleation of intermediate phase is totally kinetically suppressed by the external fluxes.

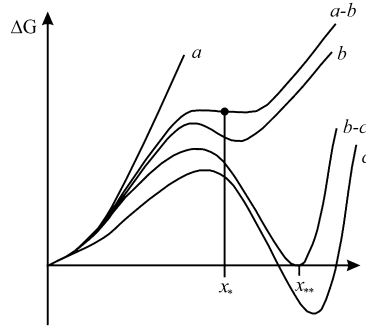


Figure 2.26 Dependence of Gibbs free energy on the size of embryo/nucleus between two growing parent solutions (B in A and A in B) for three cases: (a) early stage – external fluxes in the parent phases (marginal solutions) kinetically suppress the embryo of emerging compound, (a–b) crossover from (a) to (b), when the local minimum appears – first and second derivatives are simultaneously equal to zero; (b) transient stage when the metastable nucleus of IMC is possible, (b–c) crossover from regime (b) to regime (c) when the second minimum becomes global – first derivative and function itself are equal to zero, curve touches the abscissa; and (c) late stage when the neighboring phases cannot suppress nucleation anymore.

Transition from case (b) to case (c) corresponds to simultaneous zero first derivative and zero change of Gibbs energy both with respect to x :

$$\begin{cases} -3a_3x_{**}^2 + 2a_2x_{**} + 4a_4\sqrt{\frac{\tau_0}{t^{**}}}x_{**}^3 = 0, \\ -a_3x_{**}^3 + a_2x_{**}^2 + a_4\sqrt{\frac{\tau_0}{t^{**}}}x_{**}^4 = 0. \end{cases} \quad (2.112)$$

This set of two algebraic equations with two unknowns, t^{**} and x_{**} , is easily solved as

$$x_{**} = \frac{2a_2}{a_3}, \quad t^{**} = \tau_0 \left(\frac{4a_2a_4}{a_3^2} \right)^2. \quad (2.113)$$

For $t > t^{**}$, the nucleation of intermediate phase is not suppressed by the external fluxes, so that nuclei can grow and form a continuous phase layer. Analysis of Eq. (2.113) shows that the minimal time of suppression corresponds to the phase with the maximal product of self-diffusivity inside phase and squared driving force of compound formation, $\bar{D}_i^* \cdot (\Delta g_i)^2$ (if one neglects the differences in surface tensions). Such a phase may be expected as the first phase to form in the contact zone.

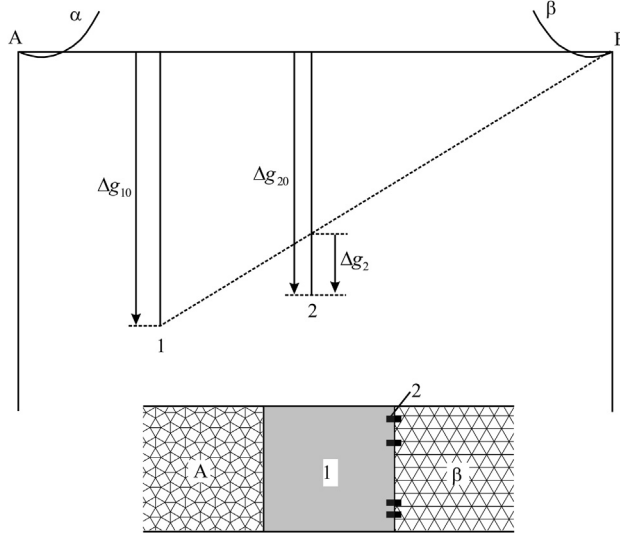


Figure 2.27 Scheme of IMC 2 nucleation between the growing layer of IMC 1 and one of the parent phases β (weak solution of A in B). $\Delta g_{10} = \Delta g_{\alpha+\beta \rightarrow 1}$ is a driving force of IMC 1 formation directly from parent phases, $\Delta g_{20} = \Delta g_{\alpha+\beta \rightarrow 2}$ is a driving force of IMC 2 formation directly from parent phases, $\Delta g_2 = \Delta g_{1+\beta \rightarrow 2}$ is a driving force of IMC 1 formation directly from parent phases.

2.5.5 Flux-Driven Nucleation of the Second IMC at the Interface to Pure B

Before formulating the main kinetic equation, note that the driving force to form the second IMC by reaction of the first and B is less than that of the direct formation from almost pure A and B (see Fig. 2.27).

Therefore, the formula for Wagner diffusivity differs from Eq. (2.68):

$$\begin{aligned} \int_{c_L}^{c_R} \tilde{D}(c) dc &= \overline{D}_2^* \frac{c_2(1-c_2)}{kT} \left(\frac{g_B - g_2}{1-c_2} - \frac{g_2 - g_1}{c_2 - c_1} \right) \\ &= \overline{D}_2^* \frac{c_2(1-c_1)}{c_2 - c_1} \frac{\Delta g_2(1+B \rightarrow 2)}{kT}. \end{aligned} \quad (2.114)$$

For the nucleation of IMC 2 between already growing layer of IMC 1 and pure B, one may use known growth equations [9] with modified driving force:

$$\frac{d\Delta X_2}{dt} = \frac{(1-c_1)^2 c_2}{(c_2 - c_1)^2 (1-c_2)} \frac{D_2^*}{\Delta x_2} \left(\frac{\Delta g_{1+B \rightarrow 2}}{kT} - \frac{2}{3} \tilde{\gamma} s_0 n_2^{-1/3} \right) - \frac{1}{c_2 - c_1} \frac{D_1 \Delta c_1}{\Delta x_1}. \quad (2.115)$$

In terms of number of atoms in the disc-like nucleus, the kinetic equations are:

$$\Delta v_2 = \frac{dn_2}{dt} = \frac{S_2 d\Delta X_2}{\Omega dt} = \tilde{v}_2 \left(\frac{\Delta g_{1+B \rightarrow 2}}{kT} - \frac{2\tilde{\gamma} s_0 n_2^{-1/3}}{3kT} \right) - \frac{D_1 \Delta c_1}{\Delta x_1} \frac{(\pi/\Omega)^{1/3}}{c_2 - c_1} \left(\frac{\gamma_i}{\Delta \gamma} \right)^{2/3} n_2^{2/3} \quad (2.116)$$

where

$$\bar{v}_2 = \frac{(1 - c_1)^2 c_2}{(c_2 - c_1)^2 (1 - c_2)} \left(\frac{\pi}{\Omega} \right)^{2/3} \left(\frac{\gamma_i}{\Delta\gamma} \right)^{4/3} D_2^* n_2^{1/3}. \quad (2.117)$$

Thus,

$$-kT \frac{\Delta v_2}{\bar{v}_2} = -\Delta g_{1+B \rightarrow 2} + \frac{2\tilde{\gamma}s_0}{3n_2^{1/3}} + kT \frac{\left(\frac{\Omega}{\pi}\right)^{1/3} D_1 \Delta c_1}{D_2^* \Delta X_1} \frac{(1 - c_2)(c_2 - c_1) \left(\frac{\Delta\gamma}{\gamma_i}\right)^{2/3}}{(1 - c_1)^2 c_2} n_2^{1/3}. \quad (2.118)$$

So, we can now construct an effective Gibbs nucleation barrier:

$$\begin{aligned} \Delta G^{\text{eff}}(n_2) &= \Delta G(n_2) - kT \int_0^n \frac{\Delta v_2^{\text{external}}(n')}{\bar{v}_2(n')} dn' = \\ &= -\Delta g_{1+B \rightarrow 2} x^3 + \tilde{\gamma}s_0 x^2 + kT \frac{(\Omega/\pi)^{1/3} D_1 \Delta c_1}{D_2^* \Delta X_1} \frac{3(1 - c_2)(c_2 - c_1) \left(\frac{\Delta\gamma}{\gamma_i}\right)^{2/3}}{4(1 - c_1)^2 c_2} x^4. \end{aligned} \quad (2.119)$$

It can be represented in the following form:

$$\begin{aligned} \frac{\Delta G^{\text{eff}}(n)}{kT} &= -a_3 x + a_2 x^2 + b_4 \frac{(\Omega/\pi)^{1/3}}{\Delta X_1} x^4, \\ x &\equiv n^{1/3}, \quad l_0 \equiv (\Omega/\pi)^{1/3}, \quad a_3 = \Delta g/kT, \quad a_2 = \tilde{\gamma} \cdot s_0/kT, \\ b_4 &= \frac{D_1 \Delta c_1}{D_2} \left(\frac{\Delta\gamma}{\gamma} \right)^{2/3} \frac{3(1 - c_2)(c_2 - c_1)}{4(1 - c_1)^2 c_1}. \end{aligned} \quad (2.120)$$

Note that Eq. (2.120) is formally similar to the dependence obtained in [26] in the frame of nucleation thermodynamics at the interface in the sharp concentration gradient – it also contains the fourth power of linear size, in addition to standard third and second powers, but now it depends on diffusivities ratio (see also [53]). Here the last term has the positive sign, meaning additional height of nucleation barrier (Flux-Suppressed Nucleation) (see Fig. 2.28).

Algebra analogous to Eqs. (2.112)–(2.115) shows that nucleation of IMC 2 becomes kinetically possible when the suppressing phase layer becomes sufficiently thick:

$$\Delta X_1 > \Delta X_1^{\text{crossover}} = \frac{\bar{D}_1^* \Delta g_{A+B \rightarrow 1}}{\bar{D}_2^* (\Delta g_{1+B \rightarrow 2})^2} \left(\frac{\Omega}{\pi} \right)^{1/3} \frac{(1 - c_2)(c_2 - c_1) 8\tilde{\gamma}s_0 (\Delta\gamma/\gamma_i)^{2/3}}{3(1 - c_1)^2 c_2}. \quad (2.121)$$

Eq. (2.121) evidently can give cross-over thickness of the suppressing phase on the order of tens or hundreds of nanometers. Indeed, for reasonable parameters, $D_1^*/D_2^* = 10$, $c_1 = 1/3$, $c_2 = 1/2$, $\Omega = 10^{-29} \text{ m}^3$, $\Delta g|_{A+B \rightarrow 1} = 10^{-19} \text{ J/atom}$, $\Delta g|_{1+B \rightarrow 2} = 2 \cdot 10^{-20} \text{ J/atom}$, $\gamma_i = 1 \text{ J/m}^2$, $\Delta\gamma = 0.5 \text{ J/m}^2$, one gets $\Delta X_1^{\text{crossover}} \approx 150 \text{ nm}$.

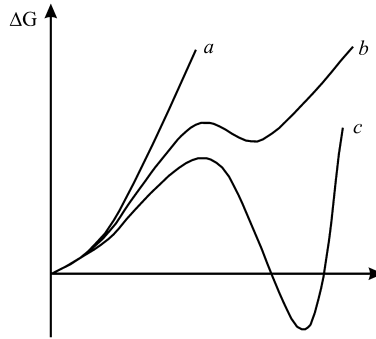


Figure 2.28 Dependence of Gibbs free energy on the size of embryo/nucleus between already growing layer of compound 1 and one of marginal parent solutions (A in B) for three cases: (a) early stage – external flux in the competitive phase 1 kinetically suppresses the embryo of emerging compound 2; (b) transient stage when the metastable nucleus of IMC 2 becomes possible; and (c) late stage when the neighboring phases cannot suppress nucleation anymore.

Thus, the divergence of external fluxes in the nucleation region introduces additional positive or negative drift terms in Fokker–Planck equation for nucleus migration in the size space. These additional drift terms can be described in the framework of the so-called effective nucleation barrier, which is usually time-dependent and may furthermore depend on the ratio of diffusion characteristics. At the initial stage of reactive diffusion, this effective nucleation barrier may appear to be infinite. This means full suppression of nucleation by the external fluxes.

2.6 SUMMARY

We made a short review of 15 flux-driven transformations in an open system. Four of them were analyzed in detail – Standard Multiphase Growth, Flux-Driven Ripening, Flux-Driven Growth (case of discontinuous decomposition into compound+voids) and Flux-Driven Nucleation. We could see that the external fluxes drastically change the main properties of all three stages of the phase transformation.

In the nucleation problem, one should distinguish thermodynamically critical and kinetically critical nuclei: thermodynamically critical nucleus corresponds to the saddle point of Gibbs free energy surface, whereas kinetically critical nucleus corresponds to zero drift in size space, and due to the divergence of external fluxes point of zero drift does not coincide with the above-mentioned saddle point.

In the growth problem, the most interesting seems to be the simultaneous growth of compound and void lamellae due to sucking out of one of the components via the side boundaries of the real system.

In the ripening problem, the divergence of external fluxes in reaction zone and constraints on the surface totally change the behavior of new phase volume, surface and of size distributions.

About half of the mentioned flux-driven transformations, so far, have not being described properly. It is a real challenge for theoreticians, as well as for modeling community.

REFERENCES

- [1] J.W. Christian, *The Theory of Transformations in Metals and Alloys*, Newnes, 2002.
- [2] P. Bellon, G. Martin, Irradiation-induced formation of metastable phases: a master-equation approach, *Physical Review B* 38 (4) (1988) 2570.
- [3] P. Pochet, P. Bellon, L. Chaffron, G. Martin, Phase transformations under ball milling: theory versus experiment, in: *Materials Science Forum*, in: Trans Tech Publications, vol. 225, 1996, pp. 207–216.
- [4] J. Schmelzer (Ed.), *Nucleation Theory and Applications*, Wiley–VCH, Weinheim, 2005.
- [5] P. Shewmon, *Diffusion in solids*, in: The Minerals, Metals & Materials Society, *Diffusion in Solids*, second edition, Retroactive Coverage, United States, 1989, p. 246.
- [6] J.W. Cahn, The kinetics of cellular segregation reactions, *Acta Metallurgica* 7 (1) (1959) 18–28.
- [7] I.M. Lifshitz, V.V. Slyozov, The kinetics of precipitation from supersaturated solid solutions, *Journal of Physics and Chemistry of Solids* 19 (1–2) (1961) 35–50;
I.M. Lifshitz, V.V. Slyozov, On kinetics of diffusion decay of oversaturated solid solutions, *JETP* 35 (2) (1958) 479–492.
- [8] C. Wagner, Ostwald ripening theory, *Ber. Bunsenges. Phys. Chem.* 65 (1961) 581–591.
- [9] A.M. Gusak, et al., *Diffusion-Controlled Solid State Reactions: in Alloys, Thin-Films, and Nanosystems*, John Wiley & Sons, 2010.
- [10] A.M. Gusak, K.N. Tu, Kinetic theory of flux-driven ripening, *Physical Review B* 66 (11) (2002) 115403.
- [11] K.N. Tu, A.M. Gusak, M. Li, Physics and materials challenges for lead-free solders, *Journal of Applied Physics* 93 (3) (2003) 1335–1353.
- [12] O.Y. Liashenko, F. Hodaj, Differences in the interfacial reaction between Cu substrate and metastable supercooled liquid Sn–Cu solder or solid Sn–Cu solder at 222°C: experimental results versus theoretical model calculations, *Acta Materialia* 99 (2015) 106–118.
- [13] A.M. Gusak, O.Y. Liashenko, F. Hodaj, Models of phase formation, growth and competition, *Cherkasy University Bulletin: Physical and Mathematical Sciences* 269 (16) (2013) 3–18.
- [14] X. Rui, Y. Tang, O.I. Malyi, A. Gusak, Y. Zhang, Z. Niu, Q. Yan, Ambient dissolution–recrystallization towards large-scale preparation of V₂O₅ nanobelts for high-energy battery applications, *Nano Energy* 22 (2016) 583–593.
- [15] G. Wulff, *Zeitschrift für Kristallographie und Mineralogie* 34 (5/6) (1901) 449–530.
- [16] A. Gusak, R. Kozubski, D. Tyshchenko, Grain growth in open systems, in: *Diffusion Foundations*, in: Trans Tech Publications, vol. 5, 2015, pp. 229–244.
- [17] K.N. Tu, A.M. Gusak, I. Sobchenko, Linear rate of grain growth in thin films during deposition, *Physical Review B* 67 (24) (2003) 245408.
- [18] I. Panchenko, K. Croes, I. De Wolf, J. De Messemaeker, E. Beyne, K.J. Wolter, Degradation of Cu₆Sn₅ intermetallic compound by pore formation in solid–liquid interdiffusion Cu/Sn microbump interconnects, *Microelectronic Engineering* 117 (2014) 26–34.
- [19] A.M. Gusak, C. Chen, K.N. Tu, Flux-driven cellular precipitation in open system to form porous Cu₃Sn, *Philosophical Magazine* 96 (13) (2016) 1318–1331.

- [20] Aditya Kumar, Effects of Interfacial Reactions and Electromigration on the Cu/Electroless Ni–P/Sn–3.5Ag Solder Joint Strength, PhD thesis, Nanyang Technological University, Singapore, 2008.
- [21] U. Gösele, K.N. Tu, Growth kinetics of planar binary diffusion couples: “thin-film case” versus “bulk cases”, *Journal of Applied Physics* 53 (4) (1982) 3252–3260.
- [22] A.M. Gusak, K.P. Gurov, The kinetics of phase formation in the diffusion zone during interdiffusion. General theory, *Fiz. Met. Metalloved.* 53 (5) (1982) 842–847.
- [23] A.M. Gusak, K.P. Gurov, in: *Solid State Phenomena*, 1992, pp. 23–24, 117–122.
- [24] A.M. Gusak, Peculiarities of nucleation in the field of a concentration gradient of the binary-system, *Ukrainian Journal of Physics* 35 (5) (1990) 725–729.
- [25] P.J. Desre, A.R. Yavari, Suppression of crystal nucleation in amorphous layers with sharp concentration gradients, *Physical Review Letters* 64 (13) (1990) 1533.
- [26] F. Hodaj, A.M. Gusak, Suppression of intermediate phase nucleation in binary couples with metastable solubility, *Acta Materialia* 52 (14) (2004) 4305–4315.
- [27] M.O. Pasichnyy, G. Schmitz, A.M. Gusak, V. Vovk, Application of the critical gradient concept to the nucleation of the first-product phase in Co/Al thin films, *Physical Review B* 72 (1) (2005) 014118.
- [28] M. Ibrahim, Z. Balogh-Michels, P. Stender, D. Baither, G. Schmitz, Nucleation controlled the reaction of Cu₃Si in the field of a sharp concentration gradient, *Acta Materialia* 112 (2016) 315–325.
- [29] A.M. Gusak, F. Hodaj, G. Schmitz, Flux-driven nucleation at interfaces during reactive diffusion, *Philosophical Magazine Letters* 91 (9) (2011) 610–620.
- [30] K.N. Tu, A.M. Gusak, *Kinetics in Nanoscale Materials*, John Wiley & Sons, 2014.
- [31] A.O. Kovalchuk, A.M. Gusak, K.N. Tu, Theory of repeating nucleation in point contact reactions between nanowires, *Nano Letters* 10 (12) (2010) 4799–4806.
- [32] W. Tang, S.T. Picraux, J.Y. Huang, A.M. Gusak, K.N. Tu, S.A. Dayeh, Nucleation and atomic layer reaction in nickel silicide for defect-engineered Si nanochannels, *Nano Letters* 13 (6) (2013) 2748–2753.
- [33] A.M. Gusak, A.O. Kovalchuk, Oscillatory regime of ordering during interdiffusion, *Physical Review B* 58 (5) (1998) 2551.
- [34] Z. Erdélyi, D.L. Beke, A. Taranovskyy, Dissolution and off-stoichiometric formation of compound layers in solid state reactions, *Applied Physics Letters* 92 (13) (2008) 133110.
- [35] Z. Erdélyi, M. Pasichnyy, V. Bezpalchuk, J.J. Tomán, B. Gajdics, A.M. Gusak, Stochastic kinetic mean-field model, *Computer Physics Communications* 204 (2016) 31–37.
- [36] V.V. Turlo, A.M. Gusak, K.N. Tu, Model of phase separation and of morphology evolution in two-phase alloy, *Philosophical Magazine* 93 (16) (2013) 2013–2025.
- [37] A.M. Gusak, T.V. Zaporozhets, K.N. Tu, U. Gösele, Kinetic analysis of the instability of hollow nanoparticles, *Philosophical Magazine* 85 (36) (2005) 4445–4464.
- [38] A.M. Gusak, T.V. Zaporozhets, Hollow nanoshell formation and collapse in binary solid solutions with large range of solubility, *Journal of Physics: Condensed Matter* 21 (41) (2009) 415303.
- [39] A.M. Gusak, K.N. Tu, Interaction between the Kirkendall effect and the inverse Kirkendall effect in nanoscale particles, *Acta Materialia* 57 (11) (2009) 3367–3373.
- [40] M.J.H. Van Dal, A.M. Gusak, C. Cserhati, A.A. Kodentsov, F.J.J. Van Loo, Microstructural stability of the Kirkendall plane in solid-state diffusion, *Physical Review Letters* 86 (15) (2001) 3352.
- [41] M.J.H. Van Dal, A.M. Gusak, C. Cserhádi, A.A. Kodentsov, F.J.J. Van Loo, Spatio-temporal instabilities of the Kirkendall marker planes during interdiffusion in β' -AuZn, *Philosophical Magazine A* 82 (5) (2002) 943–954.
- [42] A. Gusak, M. Danielewski, A. Korbel, M. Bochniak, N. Storozhuk, Elementary model of severe plastic deformation by KoBo process, *Journal of Applied Physics* 115 (3) (2014) 034905.
- [43] A.T. Wu, A.M. Gusak, K.N. Tu, C.R. Kao, Electromigration-induced grain rotation in anisotropic conducting beta tin, *Applied Physics Letters* 86 (24) (2005) 241902.
- [44] J.R. Lloyd, Electromigration induced resistance decrease in Sn conductors, *Journal of Applied Physics* 94 (10) (2003) 6483–6486.

- [45] G.V. Kidson, Some aspects of the growth of diffusion layers in binary systems, *Journal of Nuclear Materials* 3 (1) (1961) 21–29.
- [46] A.M. Gusak, M.V. Yarmolenko, A simple way of describing the diffusion phase growth in cylindrical and spherical samples, *Journal of Applied Physics* 73 (10) (1993) 4881–4884.
- [47] O. Liashenko, A.M. Gusak, F. Hodaj, Phase growth competition in solid/liquid reactions between copper or Cu_3Sn compound and liquid tin-based solder, *Journal of Materials Science: Materials in Electronics* 25 (10) (2014) 4664–4672.
- [48] A. Gusak, F. Hodaj, O. Liashenko, Criteria of kinetic suppression of lateral growth of intermediate phases, *Philosophical Magazine Letters* 95 (2) (2015) 110–121, <http://dx.doi.org/10.1080/09500839.2015.1020350>.
- [49] D. Turnbull, Theory of cellular precipitation, *Acta Metallurgica* 3 (1) (1955) 55–63.
- [50] M. Hillert, On theories of growth during discontinuous precipitation, *Metal. Trans.* 3 (1972) 2729–2741, <http://dx.doi.org/10.1007/BF02652840>.
- [51] J.W. Cahn, The kinetics of cellular segregation reactions, *Acta Met.* 7 (1959) 18.
- [52] W.L. Chiu, C.M. Liu, Y.S. Huang, C. Chen, Formation of nearly void-free Cu_3Sn intermetallic joints using nanotwinned Cu metallization, *Applied Physics Letters* 104 (17) (2014) 171902.
- [53] A.M. Gusak, F. Hodaj, A.O. Bogatyrev, Kinetics of nucleation in the concentration gradient, *Journal of Physics: Condensed Matter* 13 (12) (2001) 2767.

CHAPTER 3

Thermodynamic-Kinetic Method on Microstructural Evolutions in Electronics

Tomi Laurila^{*}, Alope Paul[†], Hongqun Dong^{*}, Vesa Vuorinen^{*}

^{*}School of Electrical Engineering, Aalto University, Finland

[†]Indian Institute of Science, Bangalore, India

3.1 INTRODUCTION

In order to have a better understanding of the basic characteristics of microsystems under different environmental conditions, more attention must be paid to the chemical compatibility between dissimilar materials found at various levels of devices [1]. When two materials are in contact, interdiffusion, chemical reactions, etc., can take place across the interface. The energetic prerequisites of different phenomena, which can take place at the interface, can be evaluated by thermodynamics. When this information is supplemented by diffusion-kinetic considerations, development of the reaction layers as a function of time can be assessed. This is the very essence of the thermodynamic-kinetic (T-K) method. In this chapter the basics of the T-K-method and a few practical examples of its utilization will be presented.

3.2 THERMODYNAMIC EVALUATION OF PHASE EQUILIBRIA

In many cases one is interested in equilibria under constant pressure, and therefore the Gibbs free energy is the expedient thermodynamic function. In order to quantitatively assess the energetics of the system under investigation, analytical expressions for the free energy functions of all phases present in that system must be derived. The thermodynamic models used in the description of the Gibbs free energy of different phases are important, since successful and reliable calculation relies on the appropriate choice of model for each phase appearing in the system. The data that can be fed in to the thermodynamic assessment of a system under consideration include, but are not limited to a wide variety of experimental and theoretical information, such as thermochemical data, activity data from electrochemical experiments, measurements of equilibrium vapor pressures, microstructural observations, and results from atomistic calculations [2,3], for instance. In this chapter we will not consider the mathematical structure of the models used to describe various phases or the technical details of the assessment procedure in

any detail, as there are several reviews available in the literature [2,3]. On the contrary, our focus will be on the exploitation of the critically assessed thermodynamic data in the analyses of the evolution of the reaction zone between dissimilar materials as well as on highlighting examples of how the obtained data can be represented with the help of relatively simple diagrams.

After the models for the phases have been constructed and the available experimental and theoretical (such as from first principles calculations) data has been fitted into them, the phase equilibria are determined by summing together the Gibbs (free) energies of individual phases and then minimizing this total Gibbs free energy of the n -component system under investigation at constant temperature and pressure:

$$G_{tot} = \sum_{\phi} \sum_i (\mu_i^{\phi} n_i^{\phi}) = \sum_{\phi} \gamma^{\phi} \sum_{i=1}^n \left(x_i \mu_i^{\circ} + RT \sum_i x_i \ln x_i + G_m^E \right) \quad (3.1)$$

where γ is the relative amount of a phase ϕ , R is the universal gas constant, T temperature (in Kelvin), and x_i is a mole fraction of component i in the system. The parameters μ_i° in Eq. (3.1) represent the partial molar Gibbs energies or chemical potentials of the pure components and are taken either from available databanks or from the literature. It is important to realize that as only relative values of thermodynamic functions can be calculated, a fixed reference state has to be established for each element or species to make thermodynamic results quantitative. The choice of the reference state is generally arbitrary as long as the fixed state is consistently utilized throughout the whole analysis. The reference state can then be conveniently defined to be zero and all other possible states of the element can be compared against this self-chosen “origin” to obtain their relative stabilities. Unfortunately, the reference states used in the literature data are not always unambiguously stated [3–5] and thus caution is recommended when assessment work is carried out.

The total Gibbs energy of the system can be expressed with the help of chemical potentials as follows (see also in Eq. (3.1) above):

$$G_{tot} = \sum_{\phi} \sum_i (\mu_i^{\phi} n_i^{\phi}) \quad (3.2)$$

which are related to the activities of the components as follows:

$$\mu_i^{\phi} \equiv \mu_i^{\circ}(T) + RT \ln a_i \quad (3.3)$$

where $a_i = \gamma_i x_i$ and γ_i is the activity coefficient. Differences in the chemical potentials of individual species inside and between dissimilar phases are the driving forces for diffusion of elements in any given system under investigation. It should be noted that Eq. (3.2) provides a very important connection between component and system level properties.

3.2.1 Different Types of Equilibria

The chemical potential (or activity) of component i will have the same value in all the phases (where it has access) that exist in complete mutual equilibrium. Consequently, the driving force for the diffusion of component i will be zero if the system is under complete equilibrium. However, during reactions taking place between different materials, the equilibrium is generally established only at the interfaces. This means that despite the fact that the activity of a given component has the same value at the immediate interface, activity gradients exist inside the adjoining phases. These gradients, together with diffusivities, dictate the movement of species in different phases inside the reaction zone.

The equilibrium states especially important for us are: (i) complete thermodynamic equilibrium; (ii) local thermodynamic equilibrium, and (iii) metastable equilibrium. Also the partial equilibrium, in which the equilibrium condition is fulfilled only with respect to some of the species, is frequently met.

(i) Complete Equilibrium

As stated above, when the system's total Gibbs free energy has reached its global minimum value, the system is in mechanical, thermal, and chemical equilibrium with its surroundings [6]:

$$dG = 0 \text{ and } G \text{ in global minimum or} \quad (3.4)$$

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\phi.$$

Thus, when complete equilibrium prevails the chemical potentials of all species ($i = A, B, C, \text{ etc.}$) are equal in all phases ($\alpha, \beta, \dots, \phi$) that are accessible to the species and there are no gradients inside the phases. Consequently, complete (or global) thermodynamic equilibria are seldom met in practical applications.

(ii) Local Equilibrium

Local equilibrium implicates that the equality of chemical potentials of species is established only at the interfaces between dissimilar phases, the thermodynamic functions are continuous across the interfaces and the compositions at the phase boundaries can be obtained from the systems equilibrium temperature composition diagram. Consequently, the local equilibrium between the α -phase and β -phase at the interphase can be defined as follows [6]:

$$\mu_i^\alpha = \mu_i^\beta,$$

$$\begin{aligned} \mu_i^\alpha &= {}^0\mu_i^\alpha + RT \ln a_i^\alpha = {}^0\mu_i^\alpha + RT \ln x_i^\alpha + RT \ln \gamma_i^\alpha, \\ \mu_i^\beta &= {}^0\mu_i^\beta + RT \ln a_i^\beta = {}^0\mu_i^\beta + RT \ln x_i^\beta + RT \ln \gamma_i^\beta, \end{aligned} \quad (3.5)$$

where ${}^0\mu_i$ is the chemical potential of pure i in the standard state, μ_i^j the chemical potential of component i in phase j , a_i^j the activity of component i in phase j , x_i^j the mole fraction of component i in phase j , γ_i^j the activity coefficient of component i in phase j , R is the gas constant, and T the temperature. The concept of local equilibrium is of central importance when interphasial reactions are analyzed utilizing the so-called diffusion couple approach [7–9]. Specifically, if local equilibrium can be assumed to prevail in the system, the reaction products formed between components in a binary system can be predicted by using the relevant phase diagram. After annealing for a sufficiently long time at a certain temperature, all the thermodynamically stable phases of the system at that particular temperature (and only them) must exist as layers between the end members. In a binary system only single-phase regions can be formed and the interfaces between these phases must be macroscopically planar under constant pressure and temperature as dictated by the Gibbs phase rule. For instance, if pure fcc-Cu is in contact with liquid Sn at 250°C the intermetallic compounds that will be formed in the reaction zone can be directly seen from the corresponding phase diagram (see Fig. 3.1, dashed–dotted line). From the critically assessed thermodynamic description of the system, more information can be obtained by utilizing the Gibbs free energy diagram (see Fig. 3.2), where the molar Gibbs energy curves of the solution phases fcc (α), bct (β), and Liquid (Liq) are presented as g^α , g^β , and g^{Liq} , respectively. As intermetallic compounds Cu_6Sn_5 (η) and Cu_3Sn (ε) have a narrow homogeneity range, they have been modeled as stoichiometric line compounds. The β -Sn with body-centered tetragonal and α -Cu with face-centered cubic structure have been defined as the reference states for the pure Sn and Cu, respectively. Consequently, the stability of all other structures possible in the system will be compared to this “zero-level” shown by a line connecting the above reference states across the composition range. The energy changing along this line would correspond to a purely mechanical mixture of Cu and Sn without any chemical intermixing. The local equilibria at the interfaces I, II, and III, marked with dashed, dotted, and dashed–dotted lines, respectively, are $\mu_{\text{Sn}}^{\text{Liq}} = \mu_{\text{Sn}}^\eta$ and $\mu_{\text{Cu}}^{\text{Liq}} = \mu_{\text{Cu}}^\eta$, $\mu_{\text{Sn}}^\eta = \mu_{\text{Sn}}^\varepsilon$ and $\mu_{\text{Cu}}^\eta = \mu_{\text{Cu}}^\varepsilon$ as well as $\mu_{\text{Sn}}^\varepsilon = \mu_{\text{Sn}}^\alpha$ and $\mu_{\text{Cu}}^\varepsilon = \mu_{\text{Cu}}^\alpha$.

Two intermetallic compounds [Cu_6Sn_5 (η) and Cu_3Sn (ε)] are grown after 64 min annealing at 250°C as shown in Fig. 3.3(A). Note that the local equilibrium between Sn and Cu changes as a function of temperature. If the temperature is raised to 500°C (see Fig. 3.1, dashed contact line), Cu_6Sn_5 is not stable anymore, and liquid Sn comes into direct equilibrium with Cu_3Sn , which can also be experimentally verified (see Fig. 3.3(B)). Another phase (δ) becomes stable and can be observed between Cu_3Sn and Cu. The Gibbs free energy diagram at 500°C for the Cu–Sn system is presented in Fig. 3.4. One can clearly observe from Fig. 3.4 that, for example, the Gibbs energy of η -phase is now above the common tangent line connecting liquid Sn and ε -phase (hence the direct equilibrium between ε -phase and liquid Sn is established). The interfacial compositions (such as $x_{\text{Cu}}^{\text{Liq}|\varepsilon}$ and $x_{\text{Cu}}^{\delta|\alpha}$), corresponding to this equilibrium are easily

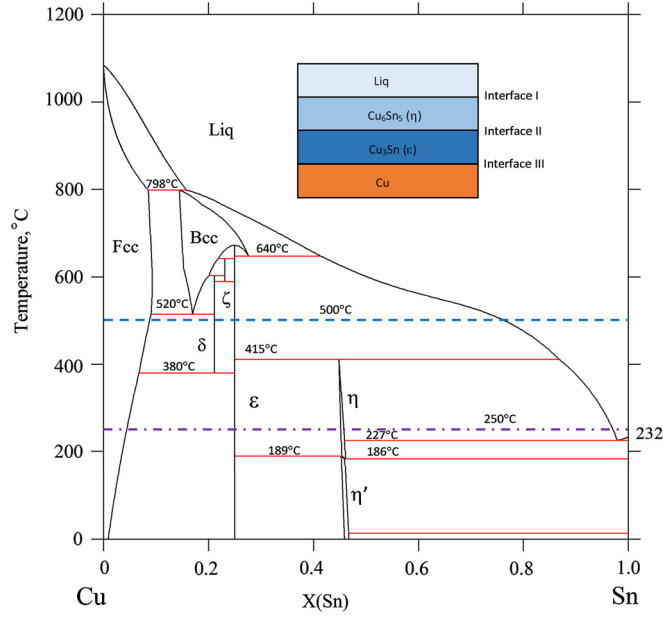


Figure 3.1 Binary Cu–Sn phase diagram with two temperatures of interest superimposed.

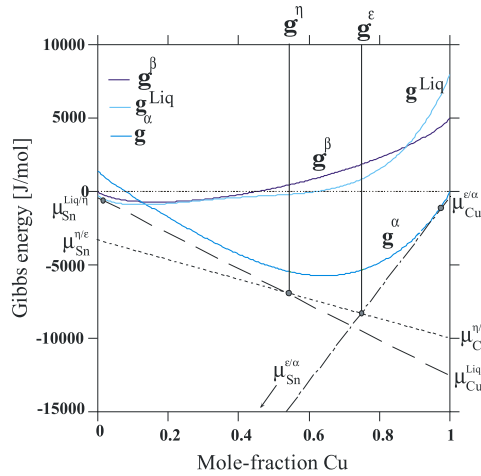


Figure 3.2 Sn–Cu molar Gibbs free energy diagram as 235°C.

derived from the diagram. Moreover, the driving forces for diffusion can be readily obtained from the Gibbs energy diagrams. In Fig. 3.4, $\Delta\mu_{Cu}^I$ represents the driving force for a pure Cu atom to diffuse through the δ - and ϵ -phases to the liquid/ ϵ -interface to react with Sn atom, as will be discussed in more detail later on.

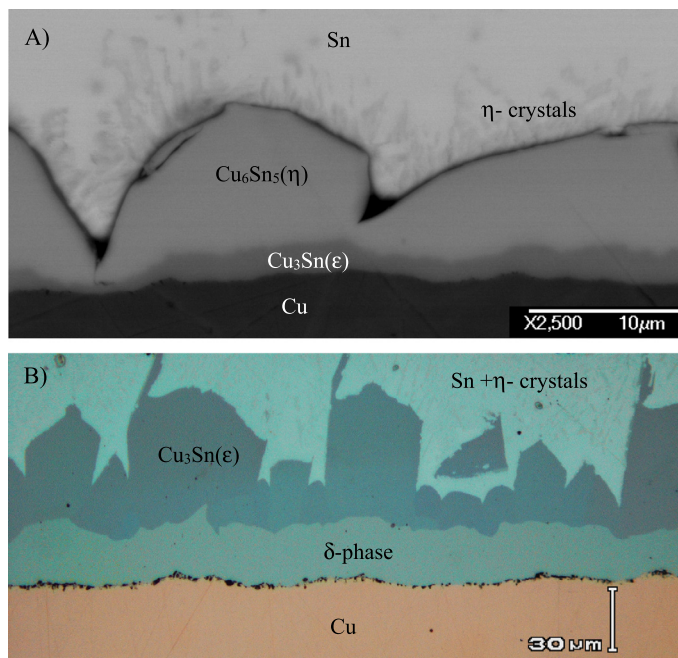


Figure 3.3 Micrographs from Cu–Sn binary reaction couple at (A) 235°C (SEM) and (B) at 500°C (optical).

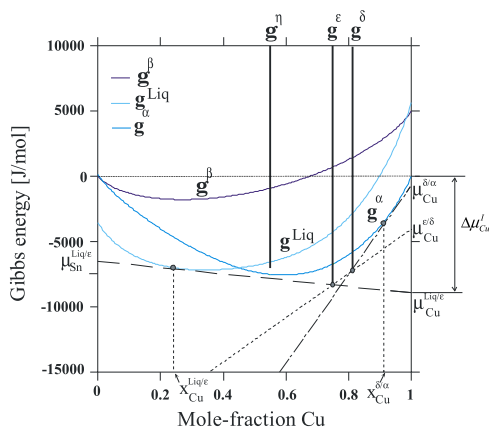


Figure 3.4 Sn–Cu molar Gibbs free energy diagram at 500°C.

(iii) Metastable Equilibrium

Metastable equilibrium can be defined as a local minimum of the total Gibbs energy of the system and it can be complete, local, or partial. Out of these, the local metastable

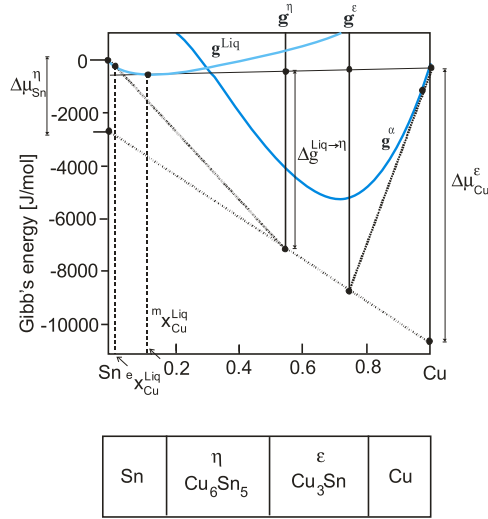


Figure 3.5 Sn–Cu molar Gibbs free energy diagram as 235°C showing driving forces for diffusion.

equilibrium concept will be used frequently in the thermodynamic–kinetic method. In order to leave the metastable state and reach the global equilibrium, some activation (e.g., thermal energy) must be brought into the system. Quite frequently one or more intermetallic compounds are missing from the reaction zone between two materials even though they are thermodynamically stable. Thus, these interfaces are in local metastable equilibrium. Another commonly encountered situation can occur during rapid interfacial reactions when one of the reacting materials is in a liquid state. Under these circumstances, during the few first seconds, the solid material exists in local metastable equilibrium with the liquid which contains a certain amount of dissolved metal atoms, before the intermetallic compound(s) is formed at the interface. This situation is readily rationalized with the help of Gibbs energy diagrams, as shown in the next section.

3.2.2 Different Thermodynamic Diagram Types

Here we will present some of the thermodynamic property diagrams that are encountered when utilizing thermodynamic–kinetic method. It is assumed that the reader is familiar with the typical temperature composition diagrams [10] and our focus will be on somewhat less frequently used diagram types [11–13].

Molar Gibbs Energy Diagrams

The molar Gibbs energy diagrams are extremely helpful when analyzing interfacial phenomena. A much more detailed presentation about the properties, usage, etc., of these diagrams can be found from [13]. Fig. 3.5 exhibits the molar Gibbs free energy diagram

of the binary Cu–Sn system calculated at 235°C. For instance, the equilibrium solubility of fcc-Cu to a liquid solder (L), which is ${}^eX_{Cu}^L$ is given by the common tangent drawn on the curves g_{bin}^L and g^η . The equilibrium solubility is the amount of Cu that can be dissolved to liquid solder infinitely slowly before the η -phase comes into local equilibrium with the liquid. However, as the driving force is zero at this point (equilibrium, no supersaturation), the formation of the η -phase does not occur with this composition. In real applications, the dissolution of fcc-Cu does not take place infinitely slow and, consequently, the equilibrium solubility is generally exceeded. However, there is an upper limit for the maximum value of the solubility of fcc-Cu to liquid Sn, which can also be determined from Fig. 3.5. As higher amount of fcc-Cu dissolve into liquid a situation is eventually faced where the dissolution of even more Cu would lead to the precipitation of pure metallic fcc-Cu out of the supersaturated melt. This corresponds to the common tangent construction between the solder and pure fcc-Cu (Fig. 3.5). The upper value of Cu that can be dissolved into liquid solder at any rate, i.e., the metastable solubility ${}^mX_{Cu}^L$ is given by the tangent point on the liquid curve at this metastable equilibrium. Also the driving force for the formation of the η -phase has risen to its maximum (shown in the diagram as $\Delta g_m^{L \rightarrow \eta}$ in Fig. 3.5), when this value has been reached. The metastable solubility is directly related to the dissolution rate of a given metal to a particular solder and thus it gives important insights about the kinetics of intermetallic compounds formation between different metallizations and solders. It is to be noted that in many cases the value of metastable solubility is around 2–3 times the equilibrium solubility [4].

Next we will give a brief example of how the above stated approach can be used to estimate the thickness of a intermetallic (IMC) layer to be formed in a given solid/liquid reaction couple. The following discussion follows closely that of presented by Rönkä et al. [11]. Under the assumption of a metastable local equilibrium, the motion of the interface between a conductor metal and a liquid can be estimated for a semiinfinite planar geometry. From standard solutions of diffusion equations for a moving boundary, the position of the interface is given by $z(t)$ with $z > 0$ defined in the liquid as [11]:

$$z(t) = 2\lambda(\tilde{D}_L t)^{1/2} \quad (3.6)$$

where t is time and $\tilde{D}_L$ is the interdiffusion coefficient in the liquid (typically in the order of 10^{-5} cm²/s). In the solid state the diffusion is negligible compared to the liquid state, and so λ can be extracted from the relation [11]

$$\lambda\sqrt{\pi}\left(\frac{X_M^S}{\nu^S} - \frac{{}^mX_M^S}{\nu^L}\right) = \frac{\left(\frac{X_M^L}{\nu^L} - \frac{{}^mX_M^L}{\nu^L}\right)}{1 - \operatorname{erf}(\lambda)} e^{-\lambda^2} \quad (3.7)$$

where X_M^L and $X_{M\infty}^S$ are the atomic fractions of the conductor metal in the liquid and in the solid far away from the interface, ${}^mX_M^L$ is the metastable solubility of the conductor

Table 3.1 The layer thickness of the intermetallics formed by immersing pure conductor metals into the eutectic Sn₂₆Pb solder at 230°C for 10 and 100 seconds under RMA flux

Conductor metal	Intermetallic	Thickness/ μm	
		10 s	100 s
Ni	Ni ₃ Sn ₄	indistinguishable	indistinguishable
Cu	Cu ₆ Sn ₅	0.5	1.0
Au	AuSn ₄ + Pb	10	10
Pd on Cu	PdSn ₄	4	40

metal in the liquid solder, and ν^S and ν^L are the solid and liquid molar volumes. As can be seen in Eq. (3.7), the dissolution rate essentially depends only on the metastable solubility of the conductor metal in the molten solder.

In many cases the metastable solubility cannot be calculated with high enough accuracy as the thermodynamic functions are typically optimized to fit the experimental data only in the stable region. As a consequence, much too high values for metastable solubilities can be obtained [5]. In such a case stable equilibrium solubility (obtained from the corresponding phase diagram for instance) can be used in the calculations, perhaps multiplied by 2–3 to estimate the metastable one. In fact, all the calculations done so far [11] show that the dissolution rate strongly depends on the solubility of conductor metal in the molten solder. Therefore, as stated above, for many purposes the knowledge of the phase diagram of a solder/conductor system is adequate for determining the relative qualitative dissolution rates in function of temperature and solder composition despite the limited kinetic data available.

To give a few examples of actual systems, the measured layer thicknesses of some intermetallic compounds formed by immersing pure conductor metals into the eutectic Sn₂₆Pb solder at 230°C for 10 and 100 seconds have been presented in Table 3.1. The thickness of Ni₃Sn₄ intermetallic on nickel was indistinguishable even after 100 seconds immersion time. On copper, a Cu₆Sn₅ intermetallic layer with thickness of 0.5 μm was formed after 10 seconds and the thickness after 100 seconds reached 1 μm . A thick layer of palladium was also plated on copper substrate. After 10 seconds immersion a 4 μm -thick layer of PdSn₄ intermetallic was found, which grew further up to 40 μm in 100 seconds. In the case of copper and palladium a homogeneous intermetallic layers were found. On the other hand, the gold sample formed a 10 μm -thick AuSn₄ intermetallic layer already in 10 seconds, after which the thickness stayed unchanged. It was also noticeable that the AuSn₄ layer was not homogeneous but contained some lead-rich areas. Furthermore, while nickel, copper, and palladium samples preserved their original thickness, gold wire was continuously getting thinner due to the ongoing dissolution [11].

A general sequence of events that occur in a given solid/liquid reaction couple can be described as follows [5]: (i) immediately after the metallurgical contact of liquid

to the solid, the contacted material (typically metal) starts to dissolve into the liquid. Initially, the rate of dissolution is high, particularly if the liquid is not predoped with the metal in question. After a short period of time the layer of the melt that is immediately adjacent to the contacted metal becomes saturated with the dissolved metal. (ii) In principle, at the local equilibrium solubility, the solid IMC starts to form by chemical reaction in this part of melt, although metastable supersaturation usually occurs. The formation of the IMC takes the metal solute out of the saturated solder and causes some further dissolution of the contacted metal. (iii) After the temperature starts to decrease (during cooling stage) additional reaction layer forms out of the supersaturated melt by solidification. In the case of Cu the dissolution is essentially stopped after the formation of intermetallic layer Cu_6Sn_5 . When the Cu_6Sn_5 -layer is formed, the driving force for the dissolution of Cu disappears since a local stable equilibrium between the Cu_6Sn_5 intermetallic compound and molten solder.

The Au sample, however, behaved differently. It is more likely that the majority of the AuSn_4 layer was formed during cooling of the sample, and so the dissolution of the Au wire could continue without disturbance during the whole immersion time [11]. Also the lead-rich precipitates in the AuSn_4 layer supported this assumption. Hence, there is also a connection between the stability of the first IMC layer that becomes in contact with the melt and the thickness of the same IMC that is formed during the liquid/solid contact. This can be understood readily as follows: as the stability of Ni_3Sn_4 is much higher than that of Cu_6Sn_5 , the solubility of fcc-Ni to molten solder must be much less than that of fcc-Cu. Thus, the local equilibrium with the first IMC forming in the system is encountered with less amount of solid dissolved into liquid in the case of Ni-Sn than in Cu-Sn. Accordingly, there is also much less material in the liquid in the case of Ni-Sn that can be used to form the intermetallic layer in question than in Cu-Sn case. More detailed explanation of these issues can be found in [12].

The common tangent construction can be used to extract the driving forces for diffusion of Cu through Cu_3Sn and Sn through Cu_6Sn_5 as shown in Fig. 3.5. Here $\Delta\mu_{\text{Cu}}^\varepsilon$ is the chemical potential difference of Cu between interfaces $\text{Cu}_3\text{Sn}/\text{Cu}$ and $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$, which drives the diffusion of Cu through Cu_3Sn . Likewise, the chemical potential difference $\Delta\mu_{\text{Sn}}^\eta$ of Sn between the interfaces $\text{Sn}/\text{Cu}_6\text{Sn}_5$ and $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ drives the diffusion of Sn through the Cu_6Sn_5 layer. With a similar tangent construction, the driving forces for the diffusion of Cu through the η and ε phases can be determined.

The changes in the stabilities of the η and ε phases will obviously change also the values of $\Delta\mu_{\text{Sn}}^\eta$ and $\Delta\mu_{\text{Cu}}^\varepsilon$, and accordingly increase or decrease the driving forces for diffusion of these components. This is shown in Fig. 3.6, which gives a section taken from the molar Gibbs energy diagram at 150°C for the ternary Cu-Ni-Sn system. It is important to realize that the Gibbs energy diagram shown in Fig. 3.6 is not, in fact, a binary one, but it is an isopleth (in other words, a vertical section) out of a 3 dimensional

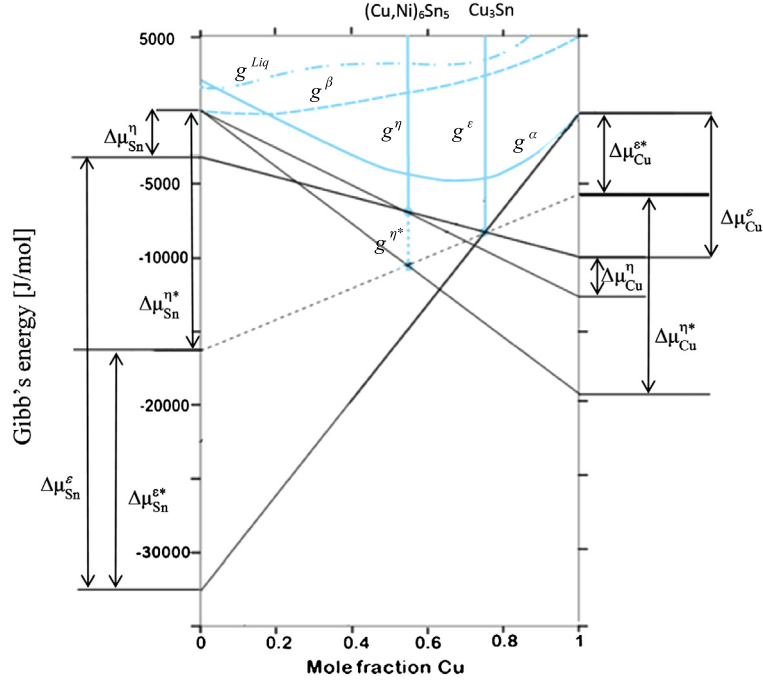


Figure 3.6 Isoleth from a ternary Cu–Ni–Sn molar Gibbs free energy diagram at 150°C.

ternary Cu–Ni–Sn diagram. As the tie-lines in ternary systems are not usually in the plane of the vertical sections [12], the free energy values must be obtained along the diffusion paths (following the tie-lines) as done here. More details about this procedure can be found, for example, in [4,12]. While continuing our analysis, it is important to note that in Cu_6Sn_5 both Sn and Cu are known to diffuse while in Cu_3Sn it is Cu that is the main diffusing species [14,15]. From Fig. 3.6 one can see that when, for example, 10 at.% Ni is added to $(\text{Cu,Ni})_6\text{Sn}_5$ its stability will increase as shown experimentally [16] and by utilizing atomistic calculations [17]. The chemical potentials (and thereby activities) of the species at the Sn/ $(\text{Cu,Ni})_6\text{Sn}_5$ and $\text{Cu}_3\text{Sn}/\text{Cu}$ interfaces are affected by these changes in such a way that the driving force for Sn diffusion through $(\text{Cu,Ni})_6\text{Sn}_5$ increases from $\Delta\mu_{\text{Sn}}^{\eta}$ to $\Delta\mu_{\text{Sn}}^{\eta*}$ (almost 4 times $\Delta\mu_{\text{Sn}}$), whereas the driving force for diffusion of Cu through Cu_3Sn decreases from $\Delta\mu_{\text{Cu}}^{\epsilon}$ to $\Delta\mu_{\text{Cu}}^{\epsilon*}$ (about 3/5 $\Delta\mu_{\text{Cu}}$). As shown by the changes in the chemical potential differences (from $\Delta\mu_{\text{Sn}}^{\epsilon}$ to $\Delta\mu_{\text{Sn}}^{\epsilon*}$ and $\Delta\mu_{\text{Cu}}^{\eta}$ to $\Delta\mu_{\text{Cu}}^{\eta*}$) in Fig. 3.6, the driving force for diffusion of Sn over Cu_3Sn decreases and diffusion of Cu through Cu_6Sn_5 increases in comparison to the binary case. Since the diffusion flux is linearly proportional to the driving force, the material flux can be expected to grow over (Cu_6Sn_5) and to decrease over Cu_3Sn . When combined with the diffusion kinetic data from the system [18] this information can be used to calculate

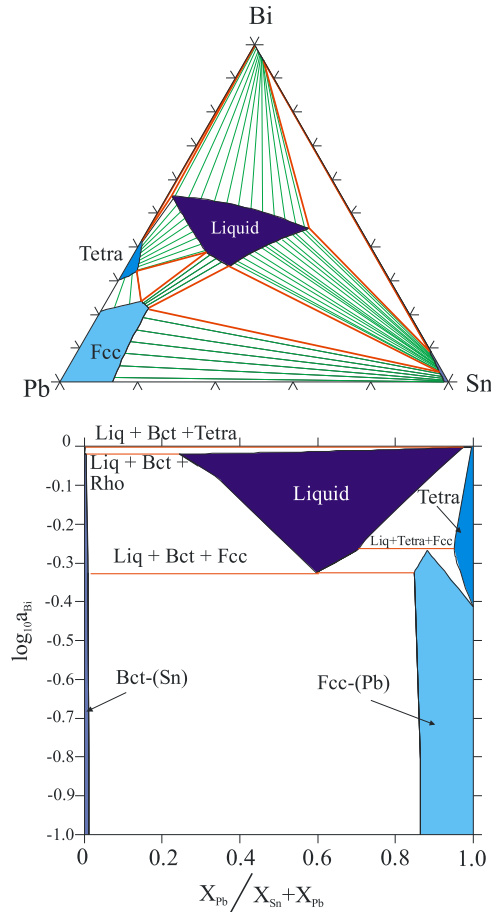


Figure 3.7 Isothermal section from the Bi–Pb–Sn ternary system at 120°C and the corresponding activity diagram (showing the activity of Bi) at 120°C.

changes in the intrinsic fluxes of Sn and Cu inside the intermetallic compounds, for instance. It is to be noted that different types of driving forces, such as stress gradients or electrical gradients (electromigration), can also be tackled with the approach outlined above.

Activity Diagrams

The activity diagram shown on the right-hand side of Fig. 3.7 is yet another type of stability diagram. Here the thermodynamic potential of interest of one of the components is plotted as a function of the relative atomic fractions of the other two components under constant temperature and pressure conditions. The construction of such diagrams

naturally requires activity data, which can be obtained from the assessed thermodynamic data. During the calculations, the activities of the stoichiometric compounds at equilibrium are regarded to be one. As the precision of the calculations is highly dependent on the accuracy and consistency of the thermodynamic data used, great care should be exercised when using data from different sources.

The binary systems (Sn–Bi, Sn–Pb, and Pb–Bi) are represented by the edges of the diagram shown in Fig. 3.7. The ternary phase relations are represented by the inside of the diagram. The stoichiometric single-phase regions are represented as vertical lines, one phase regions with extensive solubility as well as two-phase regions as areas and three phase equilibria as horizontal lines. Tie-lines are also valid inside the two-phase regions in these diagrams. Accordingly, the diffusion path of a given component (see below) should cross the two phase regions along a tie-line and not to cross it. To guide the eye identical phase regions in the ternary isothermal section and in the corresponding activity diagram (defined at the same temperature) are identified with the same color in Fig. 3.7. In the isothermal section the three phase equilibria are shown as red triangles and in the activity diagram they appear as red horizontal lines. As will be explained later on, if one wants to investigate the odds of diffusion of certain elements in a given reaction layer structure in a multicomponent system, activity diagrams for all the diffusing species must be calculated.

Diffusion Couples and the Diffusion Path

Formal diffusion kinetic frame is introduced in Section 3.3, but here we will nevertheless discuss about the extremely important related concepts of diffusion couple and diffusion path. Especially the latter concept is very much of thermodynamic origin. In a given binary system the interaction between components and the resulting interfacial reaction products can be predicted by using only the relevant phase diagram. At a certain temperature after sufficiently long time, all the thermodynamically stable phases of the system at that particular temperature (and only them) must exist as layers between the end members. Following the chemical potential point of view as explained in Chapter 1 of Volume 1, only single-phase homogeneous regions can be formed in a binary system, and the concentrations at the interfaces between the phases can be read directly from the phase diagram (Fig. 3.8).

If certain stable phases are absent in the reaction zone, it can be caused either by problems in nucleation or by the so called “kinetic” stability, which is described in detail in [19]. If there are no nucleation problems hindering the phase formation and the diffusion can be taken to be the rate-limiting step, the resulting phase layer sequence is determined by the corresponding phase diagram. Generally, in a given binary system one can also say something about the evolution of the system as a function of time, if the interdiffusion coefficients (see Section 3.3) in all the growing phases are known. However, when higher order systems such as ternary or quaternary ones are considered,

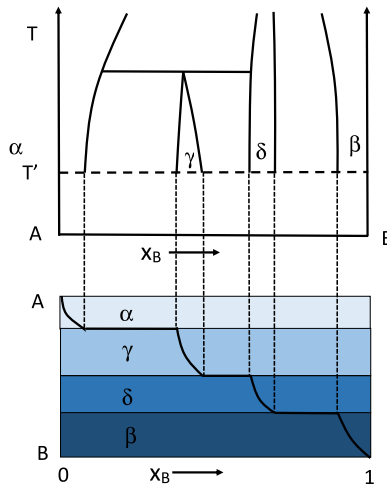


Figure 3.8 Schematic binary phase diagram and the corresponding reaction structure at T_0 (redrawn from [9]).

the prediction of the reaction layers becomes highly difficult. This stems from the fact that, for example, in a ternary system the formation of two-phase regions and curved interfaces can take place as enabled by the additional degree of freedom. This means that theoretically many different phase sequences are possible and the final structure cannot, typically, be predicted directly from the phase diagram. In addition, the concentration and activity gradients are not necessarily pointing to the same direction in ternary system as generally is the case in binary ones. This enables, for example, the so-called “up-hill” diffusion, where diffusion of one component takes place against its concentration (but not activity) gradient.

When the mass transport through the bulk is the rate-limiting step, phase transformation will be diffusion controlled. Then the boundary conditions governing the diffusion rates can be estimated by taking that whenever two phases meet at a given interface, their compositions right at this interface are those (or very close to) required by the equilibrium phase diagram, and the thermodynamic potentials are continuous across the interface. This is the local equilibrium approximation [3] as discussed to some depth above. If the local equilibrium can be assumed to prevail in the system, it is possible to use the phase diagram of the system coupled with a few simple rules to predict possible or at least to rule out impossible reaction sequences in ternary systems. The first rule ensures that the mass-balance, which requires that material cannot be created or destroyed during reaction, is fulfilled. Accordingly, the diffusion path, which is a line in the ternary isotherm, representing the locus of the average compositions parallel to the original interface through the diffusion zone [20–22], must cross at least once the straight line connecting the end members of the diffusion couple. The system will fol-

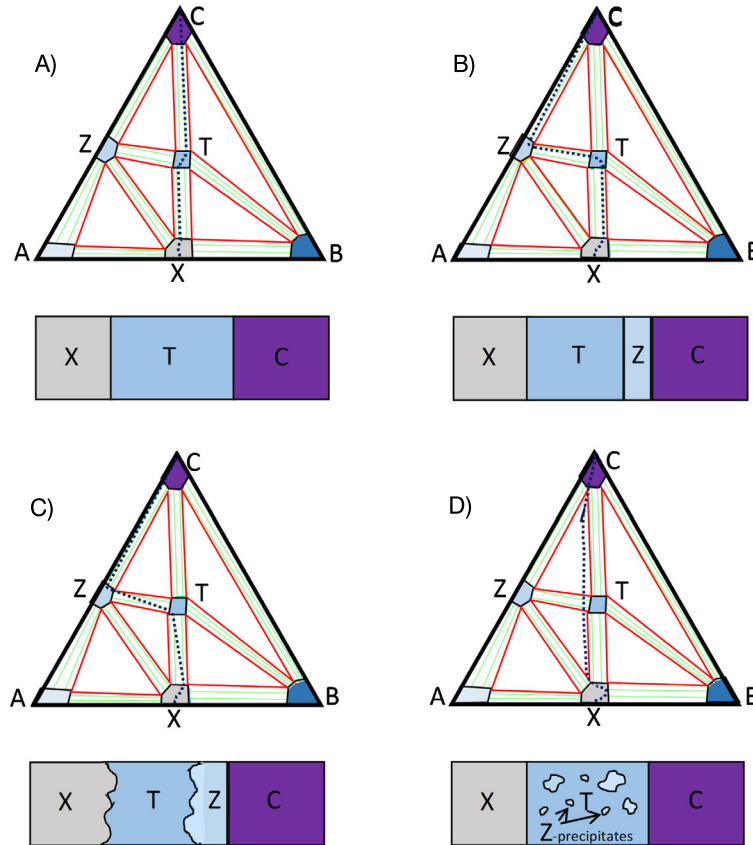


Figure 3.9 Examples of possible morphologies for the reaction layer in a diffusion couple X/C. The corresponding diffusion paths are plotted on the isotherms (redrawn from [9]).

low only one unique reproducible diffusion path during the reaction. Kirkaldy et al. have presented a few principles that the diffusion path must follow [22–24].

The diffusion path concept can be visualized with the help of Fig. 3.9, which shows the hypothetical A–B–C phase diagram with two binary compounds X and Z and the ternary compound T [9]. In Fig. 3.9 four diffusion paths with the corresponding morphologies of the diffusion zone, for the diffusion couple C versus X, are given. In all of them the mass-balance requirement is fulfilled. Mass-balance considerations also provide constraints about the relative thicknesses of the various reaction layers such as T and Z in Fig. 3.9(B) as follows. Specifically, the Z-phase has to be much thinner than the T-phase. This is because the Z-phase is much further from the contact-line (e.g., average composition) than the T-phase. Not only the relative thicknesses, but also the total thickness of the diffusion layer is related to the diffusion path. For example,

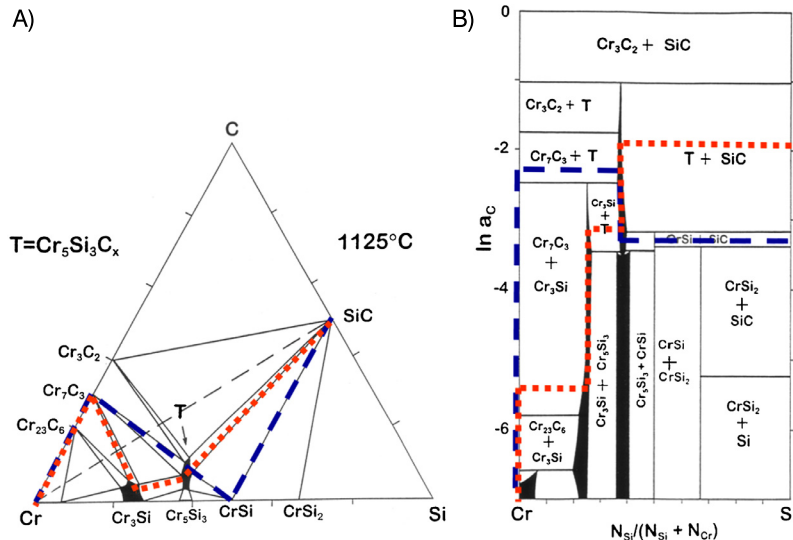


Figure 3.10 Isothermal section from the Cr–Si–C system at 1125°C and the corresponding activity diagram for carbon (redrawn from [25]).

if the diffusion is very slow in the Z-phase and fast in the T-phase, then the total layer width for Figs. 3.9, (B) or (C), must be smaller than in the case of Fig. 3.9(D). In the first example, the continuous Z-layer acts as a kind of diffusion barrier, whereas in the second case the faster diffusion in the T-phase governs the total layer thickness, which is probably only little hindered by the discontinuous Z-particles. One must realize that diffusion path corresponds only to a topological distribution of phases in space.

To predict the diffusion path or to exclude impossible ones with the help of the mass-balance requirement alone is an immensely difficult task. Therefore, van Loo et al. [9] proposed another restriction, which is based on the thermodynamic driving force behind the diffusion phenomenon. This rule states that an element cannot diffuse intrinsically against its own activity gradient. This is easy to understand as if this were to take place, atoms should transport from low to high chemical potential area. From the basic thermodynamics we know that this kind of process that does not spontaneously occur in nature. By calculating the chemical activities of components as functions of the relative atomic fractions of the elements, and taking into account the above mentioned mass-balance considerations, the sequence of compounds formed during the reaction can often be predicted, as can be seen from the following examples.

An example is shown in Fig. 3.10, which is redrawn from [25]. It shows the isothermal section from the Cr–Si–C system at 1398 K (Fig. 3.10(A)). Two hypothetical diffusion paths that both fulfill the mass-balance requirement are superimposed on the isothermal section. From Fig. 3.10(B) it is evident that only the reaction sequence

SiC/Cr₅Si₃C_x/Cr₃Si/Cr₇C₃/Cr₂₃C₆/Cr can form by diffusion of carbon in the system. This is because in the reaction layer sequence SiC/CrSi/Cr₅Si₃C_x/Cr₇C₃/Cr₂₃C₆/Cr, carbon should diffuse against its activity gradient (thus its gradient in chemical potential) to reach the Cr₅Si₃C_x + Cr₇C₃ two phase region from CrSi.

It should be noted that the assumption of local equilibrium, which is necessary for the above treatment, is not self-evident, especially when dimensions of the reaction couple are small (diffusion barriers, nanoparticles, etc.). The reactions at the interfaces need to be fast enough with respect to diffusion so that all the atoms arriving to the reaction region are used immediately for the local equilibrium to prevail. Subsequently, the rate-determining step in the phase growth is diffusion. However, with very thin layers or small nanoparticles this requirement may not be always fulfilled. This stems from the special conditions prevailing during thin film reactions: (a) relatively low reaction temperatures, (b) small dimensions, (c) high density of short-circuit diffusion paths, (d) relatively large stresses incorporated in thin films, (e) relatively high concentration of impurities, (f) metastable structures, (g) large gradients, and so on. Based on these conditions, it appears evident that global thermodynamic equilibrium is practically never met in thin film systems. However, the local equilibrium is generally attained at interfaces quite rapidly and can therefore still be expected to prevail in most cases as shown by experimental results [18]. Thus, it is argued that the procedure presented above provides a feasible analysis method also for thin film reactions, as there is no fundamental difference between thin film and bulk reaction couples.

3.3 KINETIC CONSIDERATIONS

The driving force for interdiffusion is the difference in concentration (or more precisely, in chemical potential) inside a phase. Typically, diffusion kinetic analyses are based on the standard solutions of Fick's laws under given initial and boundary conditions. In the case of the steady state material flow, i.e., when the concentration remains constant with time, Fick's first law states that the flux of element *i* (*J_i*) is directly proportional to the product of the diffusion coefficient (*D*) and the concentration gradient of an element *i* [7]:

$$J_i = -D_i \frac{\partial C_i}{\partial x}. \quad (3.8)$$

For non-steady state diffusion, in which the concentration varies with distance and time, Fick's second law is applied [7]:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial J_i}{\partial x} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_i}{\partial x} \right). \quad (3.9)$$

Thus, at constant temperature the rate of change of concentration is equal to the diffusivity times the rate of change of the concentration gradient. If the interdiffusion

constant in Eq. (3.9) is not concentration dependent, the equation can be solved with standard textbook methods (see [18] and references therein). However, when the interdiffusion coefficient is concentration dependent, other methods are required, such as Boltzmann–Matano or Sauer–Freise analysis [18]. Both methods require there to be a significant (measurable) composition difference within a phase under investigation. However, if the system includes phases that have narrow homogeneity ranges (like many intermetallic compounds in solder interconnections), the above-mentioned analyses are not applicable and the method derived by Wagner [18,26] needs to be utilized instead.

The total Gibbs energy of the system, as shown in Eq. (3.1), can be expressed as a function of chemical potentials, which are related to the activities of the components according to Eq. (3.3) (which is reproduced here for convenience) as follows [18]:

$$\mu_i^\phi \equiv \mu_i^0(T) + RT \ln a_i. \quad (3.10)$$

Since the chemical potential of a component i will have the same value in all the equilibrated phases, the difference in activity of a component (i.e., the driving force for its diffusion) will vanish at equilibrium. A fundamental condition is that no atom can diffuse intrinsically against its own activity gradient as discussed above and in [9]. If a maximum is found experimentally in the activity profile of a component, the intrinsic movement of the other components causes it. This condition is used as a criterion when thermodynamic prerequisites for the diffusion of certain species in a given reaction sequence is rationalized with the help of activity diagrams (Fig. 3.7). In addition, the thermodynamic data obtained from the simulations can be utilized also in quantitative diffusion flux calculations as shown next.

The intrinsic flux of a component A in, for instance, an A–B binary alloy will be written in terms of gradient in chemical potential [18]:

$$J_A = -L_{AA} \frac{d\mu_A}{dx} = -M_A C_A \frac{d\mu_A}{dx} \quad (3.11)$$

where L_{AA} is the phenomenological constant and M_A is called the atomic mobility of A. The chemical potential of A, μ_A , can be written in terms of activity, a_A , as shown in Eq. (3.3). Substituting Eq. (3.3) into Eq. (3.11) and noting that $dN_A = (V_m^2/V_B)dC_A$ [27] and $C_A = N_A/V_m$, one obtains

$$J_A = -M_A RT \frac{V_m}{V_B} \left(\frac{\partial \ln a_A}{\partial \ln N_A} \right) \frac{dC_A}{dx}, \quad (3.12)$$

with $\frac{d \ln a_A}{d \ln N_A} = \frac{d \ln a_B}{d \ln N_B}$ being the *thermodynamic factor* (a_A and a_B are the chemical activities of components, and mole fraction is now denoted by N_i). The standard state is generally the pure element (Raoultian) reference state. In a binary system there is only one thermodynamic factor, but this is not the case in ternary systems or if the vacancy

concentration in a binary case deviates from its equilibrium value. In the latter case chemical potential of vacancies is no longer zero and the binary system turns effectively to a ternary one.

The mobility of A, M_A , can be experimentally determined from a tracer experiment. If one deposits an “infinitely” thin layer of a radioactive isotope of A on the surface of an homogeneous A–B alloy, the activity as a function of the distance in the diffusion direction after annealing can be measured using the sectioning technique. By applying the method of Gruzin [28], in which it is assumed that the atoms A and isotopes A^* move identically, a so-called *tracer diffusion coefficient* D_A^* can be derived. The Nernst–Einstein relation directly connects the tracer diffusion coefficient to the atomic mobility:

$$D_i^* = M_i R T. \quad (3.13)$$

When we now take Fick’s law, Eqs. (3.12) and (3.13), we arrive at a general relation between the intrinsic and tracer diffusion coefficients:

$$D_A = D_A^* \frac{V_m}{V_B} \left(\frac{\partial \ln a_A}{\partial \ln N_A} \right). \quad (3.14)$$

Similar relations can be written for component B in a binary system. Note here that these discussed ternary and multicomponent systems are more complex, and interested readers are pointed to [18] for further insights. If the pertinent thermodynamic data are available (see Eq. (3.14)), the tracer diffusion coefficients can be used for calculation of intrinsic diffusivities. At this point, it is appropriate to remember that when we calculated the phase and stability diagrams for the system under investigation we had this thermodynamic data. By proceeding this way, we can utilize tracer diffusion coefficients that often are available in the literature to obtain intrinsic diffusion coefficients. This will greatly reduce the amount of experiments otherwise necessary when reactive phase growth in a specific system is studied. It is to be noted here that while marker experiments can be used to determine intrinsic diffusion coefficients (D_i ’s) (needed in the thermodynamic–kinetic analysis) they can be only determined at Kirkendall-plane (i.e., at one composition). Thus, when investigating a phase with extensive solubility range, many diffusion couples and/or multifoil experiments must be carried out to determine the D_i ’s over the chosen concentration range. On the other hand, when thermodynamically assessed data on the system is available, the D_i ’s can be calculated with the help of Eq. (3.14).

In many cases, the phase under investigation grows with almost no solubility range and it is not possible to determine the vanishingly small concentration gradient. Accordingly, calculation of the interdiffusion coefficient becomes impossible. To circumvent this problem, Wagner [26] introduced the integrated diffusion coefficient ($\tilde{D}_{\text{int}}$), which

can be expressed in terms of composition of i as

$$\tilde{D}_{\text{int}} = \int_{N'_i}^{N''_i} \tilde{D} dN_i = \tilde{D} \Delta N_i \quad (3.15)$$

where $\tilde{D}$ (m^2/s) is the interdiffusion coefficient, N_i is the composition of i and $\Delta N_i = N''_i - N'_i$ is the (narrow) homogeneity range of the product phase.

Further, interdiffusion coefficient, $\tilde{D}$, is related to the tracer diffusion coefficient of the species, D_A^* and D_B^* , by

$$\tilde{D} = (N_A D_B^* + N_B D_A^*) W \left(\frac{d \ln a_B}{d \ln N_B} \right) \quad (3.16)$$

where N_A and N_B are the compositions of A and B in the AB-phase, $\frac{d \ln a_B}{d \ln N_B}$ is the thermodynamic factor, a_B is the activity of the element B, and W is the vacancy wind effect and can be in most cases considered as one [18]. By substituting Eq. (3.16) into Eq. (3.15) and following standard utilization of common tangent construction in Gibbs energy diagrams [13,18], we obtain

$$\tilde{D}_{\text{int}} = \int_I^{\text{II}} (N_A D_B^* + N_B D_A^*) N_B d \ln a_B = (N_A D_B^* + N_B D_A^*) N_B [\ln a_B^{\text{I}} - \ln a_B^{\text{II}}], \quad (3.17)$$

where I and II represent the interfaces from which the product phase grows.

Further following Eq. (3.17) and from the standard thermodynamic relation (Eq. (3.3)), we can write

$$\tilde{D}_{\text{int}} = (N_A D_B^* + N_B D_A^*) \frac{N_B (\mu_B^{\text{II}} - \mu_B^{\text{I}})}{RT} = -(N_A D_B^* + N_B D_A^*) \frac{N_B \Delta \mu_B^o}{RT}, \quad (3.18)$$

where μ_B is the chemical potential of B, $\Delta \mu_B^o$ is the driving force for the diffusion of B. The values of $\Delta \mu_B^o$ under different ambient conditions can be calculated from the appropriate data. For derivation of the above relations, the readers are referred to [18]. For estimation of the data based on experimental results following the relations above, Chapter 3 in Volume 1 can be followed.

A Physicochemical Approach to Explain the Morphological Evolution in an Interdiffusion Zone

In many cases when a product phase grows by reactive diffusion, a characteristic morphology develops in that particular layer. For example, three incremental diffusion couples from Co–Si [18], Ni–Si [25], and Ni–Al [18] systems along with their microstructures are shown in Fig. 3.11. It can be seen that when there is a Kirkendall marker plane present inside a phase, a duplex morphology is always accompanying it.

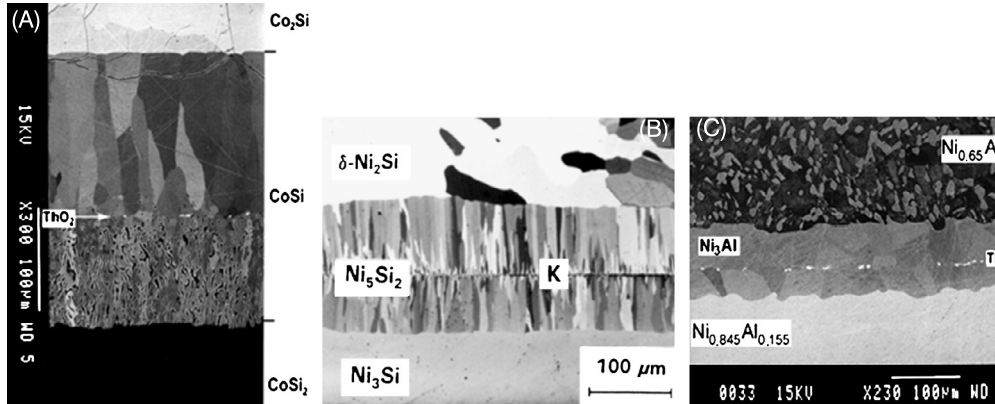


Figure 3.11 Micrographs showing the microstructures and position of Kirkendall planes in different systems (Figs. 3.11, (A) and (C), from [18]; Fig. 3.11 (B) from [25]).

All that has been stated above indicates that the reactive phase layer growth depends heavily on the properties of the particular interface where it grows. In reactive diffusion, the product phase layers are grown because there are chemical reactions taking place at the interfaces where the diffusing components participate. Thus, even though one can use the phenomenological approach outlined above to investigate the thickness evolution of growing reaction layers, if morphological evolution in the interdiffusion zone is to be investigated, the reactions at the reaction interfaces must be taken into account. However, it is important to realize that despite their importance the interfacial reactions are not typically the rate controlling process in the examples discussed below. This is because in these the diffusions of components through the product phase take much longer than the reactions at the interface, especially after the initial steps of the phase growth. However, there are many examples, specifically in thin film condition, where the growth of the phase may be reaction controlled [18]. In addition, if one is to understand the morphological features of the reaction zone, the physicochemical approach must be used. For the following examples (Section 3.5), diffusion is always considered as the rate controlling process. The equivalence of the physicochemical approach and the phenomenological relations discussed above are shown in [18]. Readers are also suggested to familiarize themselves with Chapter 4 in Volume 2.

3.4 THERMODYNAMIC-KINETIC METHOD

In Sections 3.2 and 3.3 of this chapter the two very fundamental fields, energetics and kinetics, were briefly introduced. It will be shown next that both of these building blocks are needed when reactive phase growth is investigated. Thus, during the phase growth, at a very general level, one can always identify two factors that are involved,

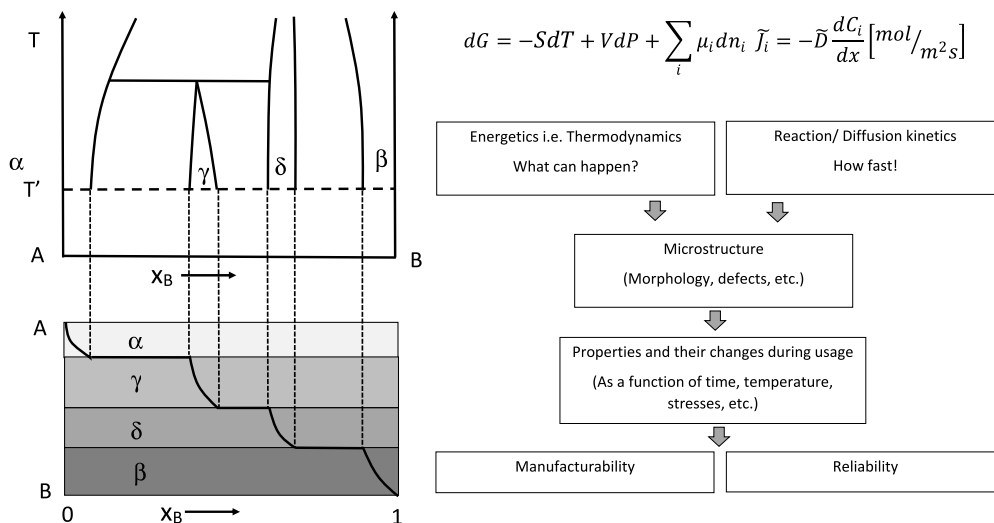


Figure 3.12 Schematic presentation of the thermodynamic-kinetic method.

namely the thermodynamic driving force ΔG and the kinetic “factor” K . Thus, a product of the two contributing factors $\Delta\mu^*K$ can be taken to phenomenologically describe phase growth at this most general level. While looking at this very generic expression, an infinite number of combinations may be thought of, but three different cases that really stand out are: (i) very large driving force ($\Delta\mu$) but very sluggish kinetics (K), which will lead to slow or no growth of the phase in question, (ii) very low driving force ($\Delta\mu$) but very facile kinetics (K), which again can lead to slow or no growth, and (iii) both factors are large enough so that the phase growth is feasible. Thus, it is evident, even with these very elementary considerations, that if one only looks at the energetic or kinetic part alone, the analysis may become very erroneous. This combination of “what can happen” and “how fast it will happen” is at the very heart of the thermodynamic-kinetic method (Fig. 3.12). It combines these two “pillars” into a solid foundation that can be used for many different applications as will be shown in Section 3.5. In addition, both quantitative thermodynamic and diffusion kinetic data can be readily utilized within the “machinery” of method as the thermodynamic-kinetic method provides clear guidelines what thermodynamic quantities or diffusion coefficients must be used, for instance. To provide a few connections between thermodynamics and diffusion kinetics one lists, for example, the following: (i) using the Gibbs free energy diagrams, provide the driving forces for diffusion to calculate integrated diffusion coefficient based on the tracer diffusion data (Eq. (3.18)), (ii) calculate intrinsic diffusion coefficients by utilizing the activity data, (iii) investigate the effect of alloying elements on the driving forces for diffusion by using Gibbs energy diagrams, and (iv) rationalize how the aforementioned changes

affect the reactions and dissociation at different interfaces with the use of the physicochemical approach, and so forth. Some of the ways to use thermodynamic-kinetic method are shown in Section 3.5. It is naturally self-evident, however, that many other possibilities also exist.

3.5 UTILIZATION OF THE T-K METHOD IN MICROSYSTEMS TECHNOLOGY

In this chapter, several examples where the thermodynamic-kinetic approach introduced in Section 3.4 is utilized to study different cases dealing with interfacial reactions will be presented. The examples show how powerful the thermodynamic-kinetic method is in rationalizing the formation of reaction layer sequences, effect of impurities or alloying elements on the reactions, and so on. Since the approach is completely general, the only limitation in its application is the lack of relevant thermodynamic and kinetic data. Nevertheless, even without proper data the method can be used as an aid to one's reasoning to provide general guidelines. This is seen in some of the cases where the proper data is not available, but the method still provides considerable insight to the problem at hand.

In many applications, the functional structures in MEMS devices need hermetical encapsulations so that they remain protected against moisture, dust particles, various gases, or different loads. Solid Liquid Interdiffusion (SLID) [or Transient Liquid-Phase (TLP)] bonding, a metallic seal bonding method, is considered to be one of the most promising and attractive encapsulation methods in terms of MEMS packaging for industrial use [29–33]. The method makes use of the phenomena where high-melting-point phases are formed by diffusion in the presence of a liquid at low temperatures [34]. At least one low-melting-point metal and one high-melting-point metal, which can react with one another and form intermetallic compound (IMC) phases, are involved in an SLID process. Au–Sn couple is one of the metal combinations, among many possible candidate systems material systems, which shows significant potential for applications [35–39]. However, it is known that Au will react strongly with Sn even at room temperature [40]. Accordingly, if the entire Sn layer is consumed, the bonding process will become more challenging to control. Thus, the solid-state reactions at low temperatures are extremely important limitations in terms of storing the deposited wafers and selecting the subsequent processing steps after Sn deposition during the production phase.

Interfacial reactions in an Au–Sn system in solid-state have been extensively investigated, especially in thin-film diffusion couples [41–45]. With the Sn layer plated after the Au layer, the first phase formed in the reaction between solid Sn and Au is typically AuSn₄. Almost simultaneously, the formation of AuSn takes place with slightly slower kinetics [45]. The formation of the AuSn₂ phase takes place after the decomposition of initial AuSn and AuSn₄ phases. Ni and Cu metallizations are commonly used with

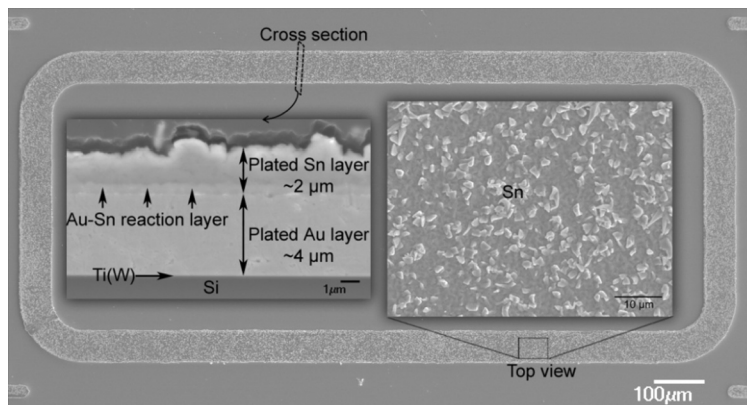


Figure 3.13 The cross-section and surface view of the test sample.

Au–Sn solders and therefore in addition to Au–Sn binary system we must consider at least the ternary Au–Cu–Sn and Au–Ni–Sn systems.

In the following, we will first examine the temperature-dependence of the reaction layer growth between Au and Sn, using experimental methods [46]. Sn/Au diffusion couples were prepared using electroplating and then annealed separately at 298 and 333 K. The two temperatures represent the possible temperatures for storage at room temperature or the other processes needed after Sn plating, such as etching. The growth behavior of the intermetallic compound layers formed during annealing was observed using a metallographic method. Based on the observations, the process of the growth of compound layers will be discussed. After completing with the Au–Sn system, we will proceed to analyze the reactions in the ternary Au–Cu–Sn [47] and Au–Ni–Sn [48] systems and show how the thermodynamic-kinetic method provides valuable information also in these cases.

3.5.1 Binary Au–Sn System

Fig. 3.13 shows the cross-section/surface view of the test sample (cap wafer). Standard single-side-polished 150 mm silicon wafers were used to prepare the samples. A thin titanium–tungsten layer and a gold layer were sputtered, respectively, as the adhesion layer and the seed layer. Then, the seal rings were electroplated to the resist openings on the wafers, using the Neutronex 309 from Enthone for the Au bath and Solderon BP from Rohm & Haas for the Sn bath. The dimension of the plated ring was $1576\ \mu\text{m} \times 783\ \mu\text{m}$, with the width being $60\ \mu\text{m}$. The target thicknesses of the gold and tin electroplating were 4 and $2\ \mu\text{m}$, respectively. Here we use the unbonded cap wafer to study the Au–Sn solid state reaction kinetics. All the samples do not experience any SLID bonding process before the tests. All of the plated cap wafers were diced into small

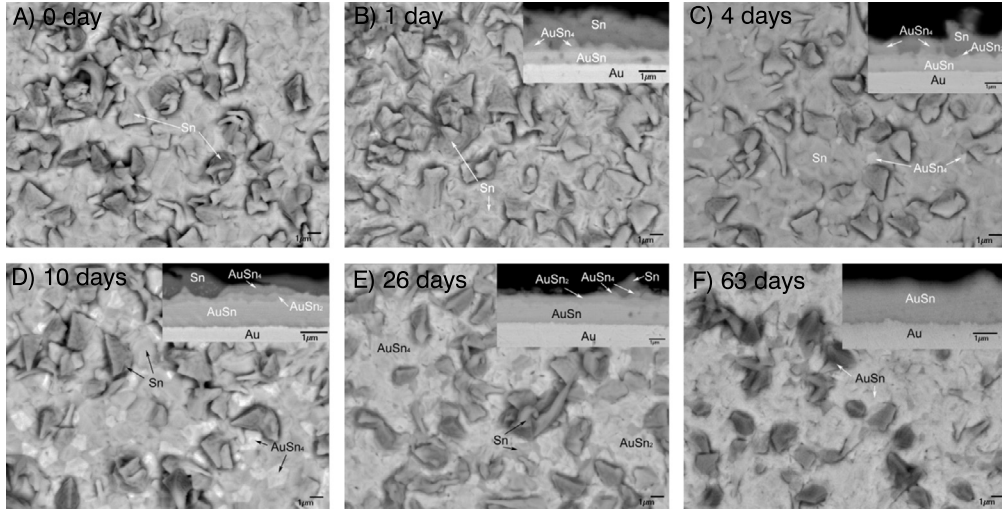


Figure 3.14 Surface and the corresponding cross-section microstructure of Au–Sn couple stored at room temperature after 0, 1, 4, 10, 26, and 63 days.

chips with dimensions of 10 mm × 10 mm. The chips were stored at room temperature (including the time required to prepare the sample for the SEM). Two of these chips, one for the surface view and the other for the cross-section view, were inspected after 1, 2, 4, 7, 10, 17, 26, and 63 days. In addition, 14 samples were annealed in the Heracles Oven at a stable temperature of 60°C, and, similarly, two of the chips were selected separately after an annealing time of 1, 4, 9, 16, 25, 36, and 49 hours. All the chips for the cross-sectional samples were molded with epoxy (Struers, Epo Fix) and cured at room temperature for 24 hours. During the curing phase, the temperature of the molding epoxy increased only a few degrees above room temperature. Therefore, the curing process during molding can also be considered as room temperature storage, and the 24 hours needed for molding was counted as a part of the total storage time.

Room Temperature Storage

Fig. 3.14 shows the typical surface and corresponding cross-section micrographs of the samples stored at room temperature (298 K) after several days. Due to the amount of time, 24 h, used to prepare the cross-section sample, the cross-section image of the as-plated reference sample is not available. However, the top-view samples could be taken immediately after the plating. Thus in Fig. 3.14(A) only top-view micrographs from the samples are shown. Figs. 3.14(B)–(F) show both the top and the cross-sectional views from the samples. Fig. 3.14(A) exemplifies that only Sn could be found on the surface of the reference samples. The color change in the image was generated based on the height difference on the surface of the samples. After a storage time of 1 day, the

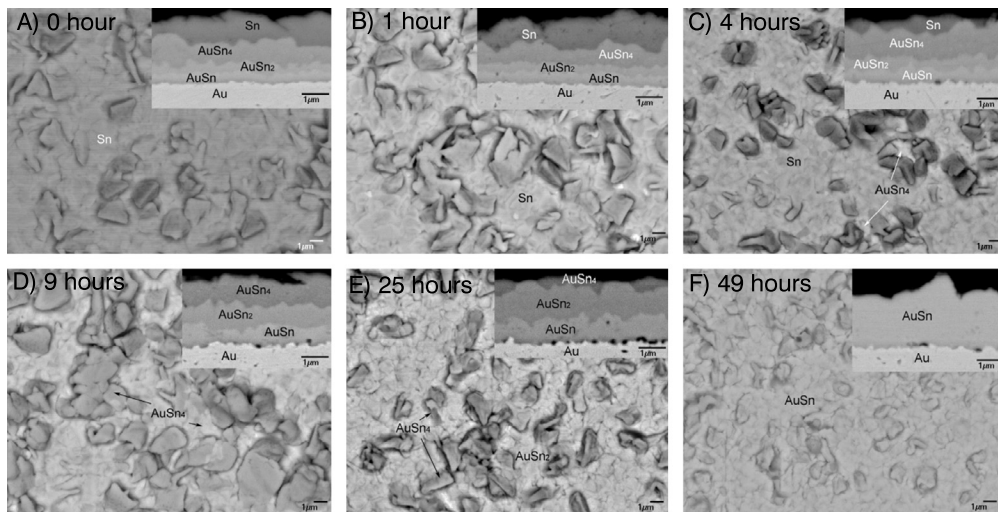


Figure 3.15 Surface and the corresponding cross-section microstructure of Au–Sn couple stored at 60°C after 0, 1, 4, 9, 25, and 49 hours.

cross-section image shows a continuous AuSn layer at the Au interface and discontinuous scallop-shaped AuSn₄ on top of AuSn. Again, only Sn could be detected on the surface (Fig. 3.14(B)). When the storage time was increased to 4 days (Fig. 3.14(C)), a continuous layer of AuSn₂ could be observed between AuSn and AuSn₄ scallops. Both the surface and cross-section images show that the Sn layer becomes thinner, and a small amount of AuSn₄ can be detected in the surface view. When the storage time was increased, the thickness of IMC layers increased and that of Sn layer decreased steadily. More and more AuSn₄ grains became exposed on the sample surface after 10 days, as shown in Fig. 3.14(D). After 26 days, most of the Sn had been consumed, as shown in Fig. 3.14(E). During the storage period, AuSn retained its layered structure and its thickness increased steadily with time. Likewise, AuSn₄ retained its scallop-shaped structure. AuSn₂ layer appeared between the AuSn layer and AuSn₄ grains after 4 days of storage and its thickness increased with the storage time. Although the Au₅Sn phase is stable at lower temperatures, it was not detected in the case of the room temperature storage within the resolution limits of SEM. If the storage time was increased to 63 days, all Sn was ultimately transformed into AuSn, as shown in Fig. 3.14(F).

Annealing at 60°C

The growth of the IMCs at 60°C was quite similar to their growth at room temperature but at a much faster rate. The typical SEM images of the reference sample and the ones annealed for 1, 4, 9, 25, and 49 hours are shown in Fig. 3.15. The order of the intermetallic layers on the Au side was AuSn, AuSn₂, and AuSn₄. A layer of pure Sn

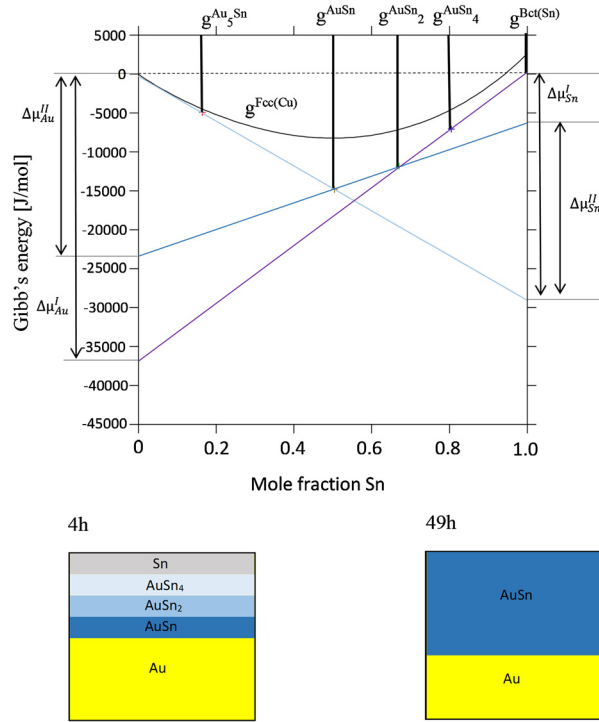


Figure 3.16 Au–Sn molar Gibbs free energy diagram at 60°C.

existed on top of the AuSn_4 layer. During annealing, the thickness of the Sn layer decreased quite quickly, and no Sn existed in the layered structure after 9 hours of annealing. The thickness of the AuSn_4 layer increased as the Sn layer decreased. After the Sn was totally consumed, the AuSn_4 layer became the resource of Sn atoms for the growth of the other two IMC layers. Thus, it can be seen from Fig. 3.15(E) that growth of AuSn_2 and AuSn layers has continued at the expense of AuSn_4 . When the annealing time was long enough, such as 49 hours in our set of experiments (Fig. 3.15), both the AuSn_4 and AuSn_2 layers vanished and AuSn was the only IMC left in the structure. Further changes are not expected to occur since the reaction kinetics for the Au-rich compounds are much lower.

The reaction sequence for the formation of interfacial intermetallic compounds during aging can be rationalized with the help of a thermodynamic-kinetic approach. Fig. 3.16 shows the Gibbs energy diagram for the Au–Sn system at 60°C. The stabilities of the phases as well as the driving forces for diffusion can be obtained with the calculated free-energy diagram by using $\text{Au}(\text{Fcc})$ and $\beta\text{-Sn}$ as reference states for Au and Sn, respectively. It should be noted that the high temperature phases (β , ζ) as well as $\alpha\text{-Sn}$ have been excluded from the figure because these phases were not observed

experimentally. In addition, the β -Sn phase is considered as pure Sn since the solubility of Au is quite low. In Fig. 3.16 the common tangent lines represent the local equilibria at the Au|AuSn, AuSn|AuSn₂, and AuSn₄|Sn interfaces. Based on the differences in the chemical potentials of the elements across the IMC layers, the driving forces for diffusion and chemical reactions can be obtained. The chemical potentials of the diffusing species are read from the tangent line and y -axis intersection points. For example, the chemical potentials of Sn and Au at the Sn|AuSn₄ interface are about 0 (i.e., unit activity) and -39 kJ/mol, respectively. Therefore, $\Delta\mu_{Au}(I)$ represents the free energy change when Au is diffused from the Au|AuSn interface to the AuSn₄|Sn interface, whereas $\Delta\mu_{Sn}(I)$ represents the free energy change when Sn moves in the opposite direction. The driving forces for diffusion of Au and Sn are approximately -38 and -30 kJ/mol, respectively. This situation corresponded to the structure after 4 hours of aging at 60°C . Since we have a limited amount of Sn available for further reactions, the local equilibria will be changed as a function of time. The same chemical potential differences, after the total consumption of the Sn and AuSn₄ layers, are indicated by $\Delta\mu_{Au}(II)$ and $\Delta\mu_{Sn}(II)$. Thus, the driving forces for Au and Sn have been decreased to approximate -25 and -24 kJ/mol, respectively. Finally, as in the case after 49 hours of annealing, all other intermetallics, except for AuSn, had been consumed by the reaction and the driving forces have practically ceased to exist. Therefore, this structure proved to be very stable against further changes during the aging process.

Fig. 3.17 the same sequence of events for the room temperature annealing. As can be seen from the figure the main difference between the situation at 60°C and at room temperature (RT) is that AuSn₄ should not be stable at RT as shown by the molar Gibbs free energy diagram in Fig. 3.17. However, experimentally we can clearly detect a thin AuSn₄ layer between AuSn₂ and Sn layers (Fig. 3.14). Thus, in this case the Sn/AuSn₄ and AuSn₄/AuSn₂ interfaces provide an example of metastable local equilibrium (Section 3.2.2). As can be seen from Fig. 3.14, the AuSn₄ phase does not form a layer as it does at 60°C , but is present only as local “precipitates.” The formation of the metastable AuSn₄ is likely to be associated with the high diffusion flux in that phase when compared to the other Au–Sn intermetallic compounds [5,19]. However, as it is metastable at room temperature the AuSn₄ will disappear from the reaction zone as the equilibrium state is approached.

Annealing at -70°C

Based on the results above, it is evident that in the Au/Sn couple reaction layer growth proceeds rather quickly at room temperature range. This will have an effect on two important points in terms of designing the SLID bonding process. First, it will affect the feasible storage time of the electroplated wafers before bonding. As mentioned above, SLID bonding requires an adequate amount of liquid Sn to be present during the bonding process. At the same time, the thickness of the plated Sn is also limited by

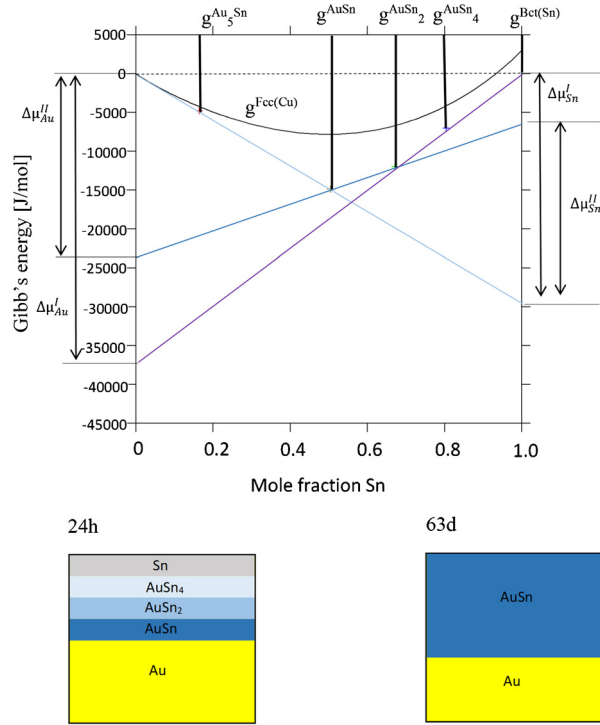


Figure 3.17 Au–Sn molar Gibbs free energy diagram at room temperature.

the amount of Au on the wafers, which means that the thickness of the Sn cannot be increased just to obtain enough liquid. Thus, it becomes quite important to maintain the Sn in an unreacted form during storage. At room temperature, the storage time should be less than one week with plating thicknesses currently being used, in order to ensure that enough unreacted Sn is still available in the seal ring to be melted to liquid. One solution for achieving a longer storage time is to keep the wafers at lower temperatures. We proceeded to store the as-plated samples at -70°C for 25 days. We could not find, through SEM observation, any obvious morphological change or fracture caused by the transformation of β -Sn to α -Sn (i.e., tin pest) on the surface image of these stored samples. The surface and cross-section micrograph is shown in Fig. 3.18. The microstructure looks quite similar to the one stored for 1 day at room temperature (shown in Fig. 3.14(B)). There was still plenty of Sn left in the ring structure. This low temperature storage might be one of the best choices to keep the wafer “fresh.” The second effect will be on the manufacturing steps after the plating. The results of the annealing at low temperatures show that elevating the processing temperature to just 60°C can significantly accelerate the solid-state reactions between Au and Sn. Any heating

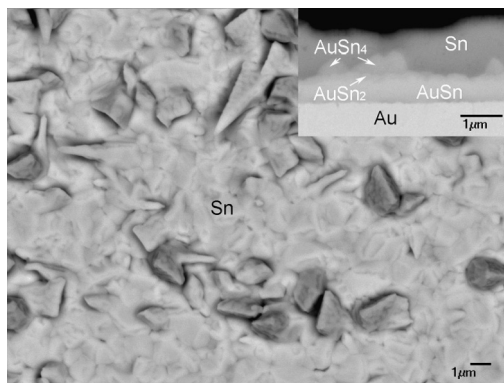


Figure 3.18 Surface and cross-section micrograph of the samples stored at -70°C for 25 days. No $\alpha\text{-Sn}$ (i.e., tin pest) phase is found on either the surface or cross-section.

steps after plating can cause this kind of problem and should be limited to a very short amount of time.

The following conclusions can be made based on the above shown experimental results and thermodynamic-kinetic analyses. The IMC layers, which consisted of AuSn , AuSn_2 , and AuSn_4 , formed at the Au/Sn interface of the diffusion couple already at room temperature. The ratios of the thicknesses of the AuSn , AuSn_2 , and AuSn_4 layers were approximately equal to 4:1:1 and 1:1:2.5 at $T = 298$ and 333 K, respectively. In order to solve the problem of the solid-state reaction so that SLID bonding can be used for industrial purposes, storing electroplated wafers at a lower temperature than 203 K is recommended. It is also advisable to carry out the electroplating as one of the last processing steps before SLID bonding when considering the fast solid-state reaction rate at $T = 333$ K.

3.5.2 Au–Cu–Sn Ternary System

The reaction couples used to investigate the reaction zone formed in the Au-Cu-Sn system were manufactured by placing a $100\text{ }\mu\text{m}$ thick near eutectic $\text{Au}_{80}/\text{Sn}_{20}$ (wt.%) [$\text{Au}_{70.7}/\text{Sn}_{29.7}$ (at.%), Goodfellow Ltd.] alloy foil between etched (1 min in dilute HCl +Methanol solution) 0.5 mm thick Cu foils (99,99+, Goodfellow Ltd.). The sandwich structures were subsequently soldered at 320°C for 100 and 2500 s at air furnace by utilizing RMA (Rosin Mildly Activated) flux and water quenching. After the soldering for 100 s at 320°C a number of samples were annealed at 150°C in a forced convection oven (Heraeus Instruments UT6) for 6600 hours.

Fig. 3.19 shows the overall microstructure of the solid $\text{Cu}|\text{liquid Au-20wt.\%Sn}$ sandwich joint after soldering at 320°C for 100 and 2500 s and subsequent water quenching. As can be seen from Fig. 3.19(A), there is an uneven layer of Au_5Sn formed

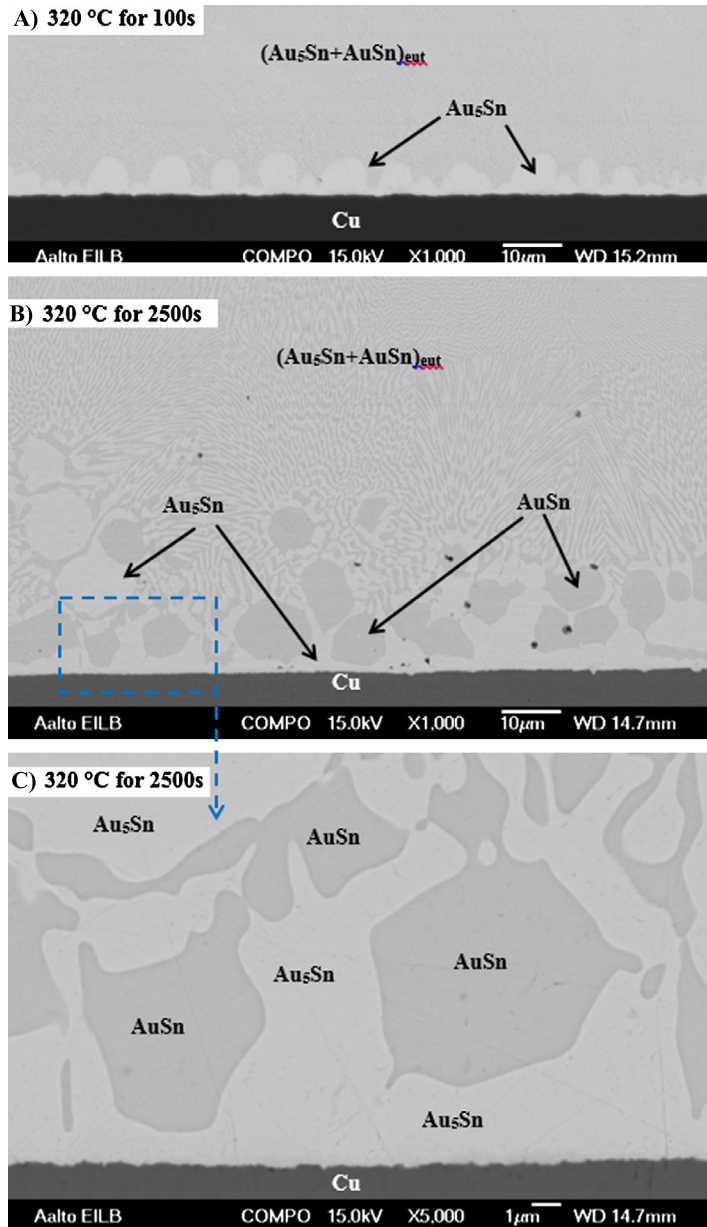


Figure 3.19 Cu|Au₈₀Sn₂₀ (wt.%) interfacial microstructure after soldering at 320°C for (A) 100 s; (B) and (C) 2500 s.

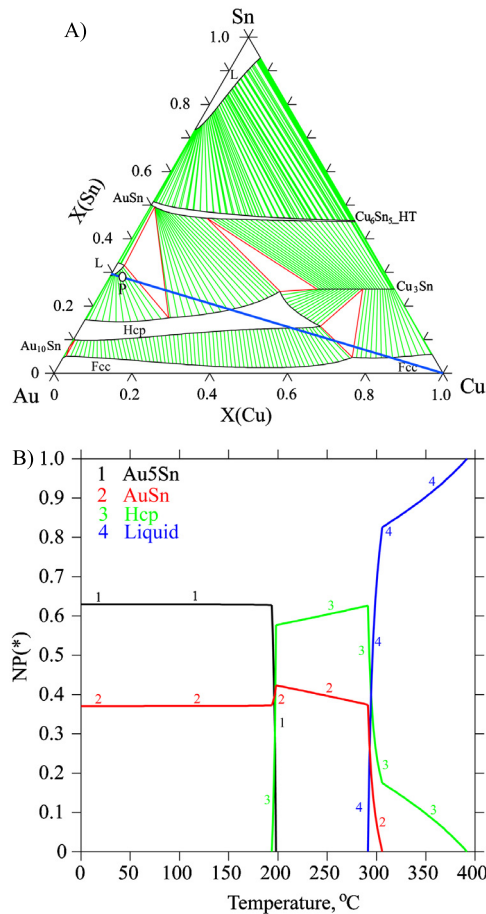


Figure 3.20 (A) Metastable isothermal section at 320°C (i.e., the ordered and ternary phases are excluded from the calculation) together with the contact line corresponding to the liquid $\text{AuSn}_{\text{eut}}|\text{Cu}$ diffusion couple, and (B) the relative amount of phases during cooling with nominal composition of $\text{Au}_{28.6}\text{at.}\% \text{ 4at.}\% \text{ Cu}$, marked with P).

between the eutectic $\text{Au}_5\text{Sn} + \text{AuSn}$ and Cu during cooling. After the longer 2500 s annealing (see Fig. 3.19, (B) and (C)) coarsening of AuSn phase is also seen close to the interface. It seems obvious that this interfacial microstructure is metastable due to high dissolution rate of Cu, i.e., Cu dissolves in the liquid, but neither Sn nor Au diffuses into solid Cu. Au_5Sn is not stable at 320°C, therefore, during cooling the hcp phase is formed first together with AuSn phase and then Hcp transformed into Au_5Sn . Close ($<5 \mu\text{m}$) to the interface the Cu content of the Au_5Sn , detected with EDS, was up to 10 at.%. The formation of the observed microstructures can be rationalized with the help of metastable diagrams.

Fig. 3.20(A) shows the metastable isothermal section at 320°C together with the contact line between the original AuSn eutectic alloy composition and the Cu-substrate. This diagram was calculated by suspending the formation of the ordered fcc phases as well as all the ternary phases. As can be seen from Fig. 3.20(A), when Cu dissolves to liquid Au–20wt.%Sn alloy, the local nominal composition enters rapidly to the liquid+hcp two-phase area, indicating that the hcp phase must be the first solid phase to form. The scallop like structures (Au_5Sn) observed at the interface in Fig. 3.19(A) can be formed from supersaturated melt either (i) isothermally or (ii) immediately when cooling starts. With longer reaction time (2500 s at 320°C) more Cu will dissolve into the liquid and thus the local nominal composition moves towards Cu along the contact line. The solidification of this interfacial region can be described with the s.c. NP diagram shown in Fig. 3.20(B) where the relative amount of phases are shown as a function of temperature. The metastable solubility is generally considered to be two to three times larger than the equilibrium solubility. Here it is assumed that the local nominal composition of the liquid reaches Cu content of 4 at.% (indicated with point P in Fig. 3.20(A)) and the subsequent cooling occurs via the following reaction sequence: (i) Firstly, hcp-phase (see line 3 in Fig. 3.20(B)) reaches the equilibrium with the liquid phase, then (ii) at about 300°C the AuSn phase (line 2 in Fig. 3.20(B)) becomes stable. The relative amount of liquid (line 4 in Fig. 3.20(B)) continues to decrease until the temperature reaches about 290°C. (iii) After that the structure is composed of hcp phase and AuSn phase (line 2) with about 60/40 ratio. (iv) Finally, slightly below 200°C, Au_5Sn (line 1 in Fig. 3.20(B)) becomes stable and hcp turns to be unstable and thus the final microstructure is composed of Au_5Sn and AuSn phases as observed from Figs. 3.19, (B) and (C).

After making the sandwich joint at 320°C for 100 s, the solid state Cu | Au–20wt.%Sn diffusion couples were annealed at 150°C. Fig. 3.21 shows the microstructure of the sample after annealing for 6600 hours. As shown in Fig. 3.21(B), the interfacial microstructure is composed of Cu/ Cu_3Au / CuAu /(Au,Cu) $_5\text{Sn}$ with isolated precipitates of AuSn/($\text{Au}_5\text{Sn}+\text{AuSn}$)_{eut} layers from the bottom to top. When comparing Figs. 3.19(A) and 3.19(B) to Fig. 3.21(A), it is obvious that the eutectic $\text{Au}_5\text{Sn}+\text{AuSn}$ has coarsened during the annealing. The continuous interfacial layer of (Au,Cu) $_5\text{Sn}$ contains about 15 at.% Cu dissolved into Au sublattice. As can be seen from Figs. 3.21(B) and 3.21(C), small AuSn precipitates were observed inside the (Au,Cu) $_5\text{Sn}$ layer. The AuCu_3 phase formed between Cu and AuCu (see Fig. 3.21(C)) was too thin to be analyzed quantitatively.

Table 3.2 lists the calculated ternary solubilities for the binary compounds using the present thermodynamic assessment, as well as the values reported in the literature [16, 19] and the experimental results from this work. By comparing with these calculated and measured data, the present calculation fit well with the experimentally determined results, with a deviation less than 4%. Two isothermal sections (at 360 and 200°C) were

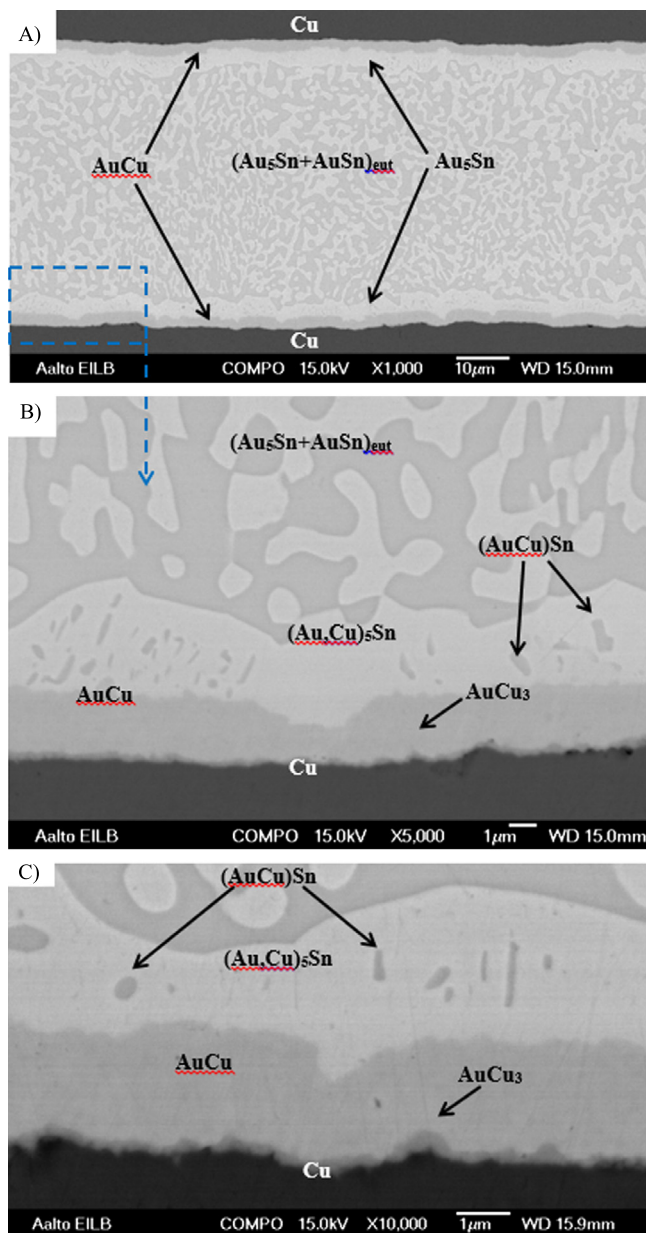


Figure 3.21 Microstructure from the Au-20wt.%Sn/Cu diffusion couple after annealing at 150°C for 6600 hours.

Table 3.2 Composition ranges of compounds, with comparison between calculated results and experimentally determined values

Temperature (°C)	Phase	Composition	Reference
150	Au ₅ Sn	~16 at.% of Cu 15.50 at.% of Cu	Experimental result, [48] Assessed, [48]
	AuCu	~3 at.% of Sn 2.96 at.% of Sn	Experimental result, [48] Assessed, [48]
	Hcp AuCu ₃	1.99 at.% of Sn 11.04 at.% of Sn	Assessed, [48] Assessed, [48]
	B	Au _{30.3} Cu _{49.7} Sn ₂₀ –Au _{25.7} Cu _{54.3} Sn ₂₀	Assessed, [48]
	Cu ₆ Sn ₅ _LT	0.75 at.% of Au	Assessed, [48]
200	Hcp	28 at.% of Cu 19 at.% of Cu 27.76 at.% of Cu	[57] Assessed, [55] Assessed, [48]
	NiAs	Complete solid solubility between AuSn and Cu ₆ Sn ₅ _HT Complete solid solubility between AuSn and Cu ₆ Sn ₅ _HT Complete solid solubility between AuSn and Cu ₆ Sn ₅ _HT	[55] Assessed, [55] Assessed, [48]
	A	Au ₄₆ Cu ₃₄ Sn ₂₀ –Au ₄₃ Cu ₃₇ Sn ₂₀ Au ₄₅ Cu ₃₅ Sn ₂₀ –Au ₄₃ Cu ₃₇ Sn ₂₀ Au _{46.99} Cu _{33.01} Sn ₂₀ –Au _{42.17} Cu _{37.83} Sn ₂₀	[55] Assessed, [55] Assessed, [48]
	B	Au ₃₅ Cu ₄₅ Sn ₂₀ –Au ₂₀ Cu ₆₀ Sn ₂₀ Au ₃₂ Cu ₄₈ Sn ₂₀ –Au ₁₇ Cu ₆₃ Sn ₂₀ Au _{34.98} Cu _{45.02} Sn ₂₀ –Au _{18.92} Cu _{61.08} Sn ₂₀	[57] Assessed, [58] Assessed, [48]
	C	Au ₃₄ Cu ₃₃ Sn ₃₃ –Au ₃₂ Cu ₃₅ Sn ₃₃ Au ₃₄ Cu ₃₃ Sn ₃₃ –Au ₃₃ Cu ₃₄ Sn ₃₃ Au _{33.9} Cu _{32.8} Sn _{33.3} –Au ₄₃ Cu _{35.1} Sn _{33.3}	[57] Assessed, [58] Assessed, [48]
	Cu ₃ Sn	10 at.% of Au No Au solubility 9.67 at.% of Au	[57] Assessed, [58] Assessed, [48]
	Au ₃ Cu	1.53 at.% of Au	Assessed, [48]
	AuCu	2.47 at.% of Au	Assessed, [48]
	AuCu ₃	4.90 at.% of Au	Assessed, [48]

continued on next page

subsequently calculated (Fig. 3.22(A)–(B)) with the experimental points superimposed on the isothermal section. As shown in Fig. 3.22(A)–(B), the present thermodynamic description can reproduce the measured phase equilibria, except for the tie-line between A and C compounds at 360°C. In this work, the tie-line between A and C compound was replaced by the one between the B and AuSn–Cu₆Sn₅ solution phase. However, the present result is considered to be reasonable as it is possible that the tie-line between A and C was, in fact, a result from nonequilibrium condition, as reported by Karlsen et al. They stated that, “*phase B has the character of the a low-temperature phase relative to A*” [49] and “*on the Au-rich side of phase B, where long annealing periods are needed to get rid of the last traces of phase A*” [50]. On the other hand, in order to the tie-line between phases A and C to be achieved, dramatic decrease in the homogeneity range

Table 3.2 (continued)

Tempera- ture (°C)	Phase	Composition	Reference
360	Hcp	~47 at.% of Cu 19 at.% of Cu 45.15 at.% of Cu	[56] Assessed Assessed, [48]
	NiAs	Complete solid solubility between AuSn and Cu ₆ Sn ₅ HT Complete solid solubility between AuSn and Cu ₆ Sn ₅ HT Complete solid solubility between AuSn and Cu ₆ Sn ₅ HT	Assessed Assessed, [48]
	A	Au ₄₂ Cu ₃₈ Sn ₂₀ –Au ₄₇ Cu ₃₃ Sn ₂₀ Au ₄₃ Cu ₃₇ Sn ₂₀ –Au ₄₉ Cu ₃₁ Sn ₂₀ Au ₄₃ Cu ₃₇ Sn ₂₀ –Au ₄₅ Cu ₃₅ Sn ₂₀ Au _{42.1} Cu _{37.9} Sn ₂₀ –Au _{47.8} Cu _{32.2} Sn ₂₀	[56] [55] Assessed, [58] Assessed, [48]
	B	Au ₁₁ Cu ₆₉ Sn ₂₀ –Au ₃₈ Cu ₄₂ Sn ₂₀ Au ₁₂ Cu ₆₈ Sn ₂₀ –Au ₃₆ Cu ₄₄ Sn ₂₀ Au ₁₇ Cu ₆₃ Sn ₂₀ –Au ₃₂ Cu ₄₈ Sn ₂₀ Au _{11.9} Cu _{68.1} Sn ₂₀ –Au _{38.2} Cu _{41.8} Sn ₂₀	[56] [55] Assessed, [58] Assessed, [48]
	C	Au _{33.0} Cu _{33.7} Sn _{33.3} –Au _{37.0} Cu _{29.7} Sn _{33.3} Au _{33.0} Cu _{33.7} Sn _{33.3} –Au _{37.0} Cu _{29.7} Sn _{33.3} Au ₃₃ Cu ₃₄ Sn ₃₃ –Au ₃₄ Cu ₃₃ Sn ₃₃ Au _{33.5} Cu _{33.2} Sn _{33.3} –Au _{37.7} Cu _{29.0} Sn _{33.3}	[56] [55] Assessed, [58] Assessed, [48]
	Cu ₃ Sn	12 at.% of Au No Au solubility 11.56 at.% of Au	[56] Assessed, [58] Assessed, [48]
	AuCu AuCu ₃	1.02 at.% of Au 1.58 at.% of Au	Assessed, [48] Assessed, [48]

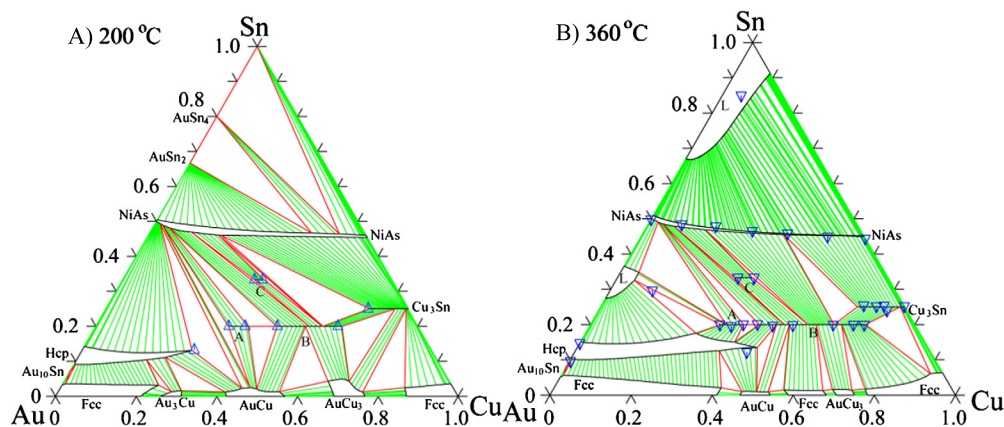


Figure 3.22 Calculated isothermal sections of Au–Cu–Sn system, with experimental points superimposed (A) isothermal section at 200°C; (B) isothermal section at 360°C.

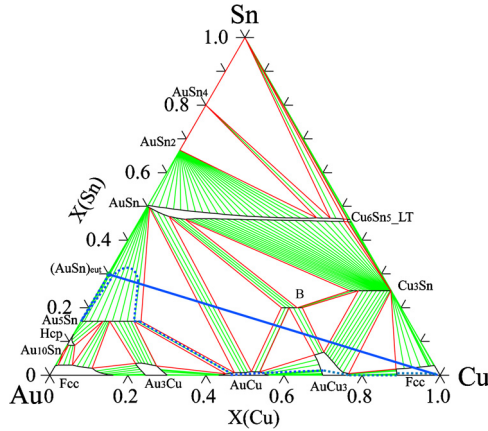


Figure 3.23 Isothermal section of Au–Cu–Sn phase diagram at 150°C with diffusion path superimposed. The end points of solid blue line represent the starting contact composition; and the observed diffusion path is shown as a dotted line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

of B at the Au-rich side would have to take place. This kind of procedure was in fact undertaken in [51]. However, here the phase B was formed at low temperature through a solid-state reaction, and it still showed a wide homogeneity range (Table 3.2). Therefore, it strongly indicates that the detected composition range of B compound is correct and not a metastable kinetically frozen situation.

The isothermal section at 150°C is shown in Fig. 3.23. As illustrated in the figure, only ternary compound B appears. This is consistent with the result shown in [52] where only phase B was detected at 170°C.

After verifying that the calculated isothermal section at 150°C was acceptable, the virtual diffusion path describing the experimentally observed reaction layer sequence was superimposed on this isothermal section as shown in Fig. 3.23. The diffusion path starts from the Cu corner, takes a tie-line connecting Cu and AuCu₃ and moves along that to the AuCu₃ phase. It was experimentally observed that there is Sn dissolved in AuCu₃ phase, and therefore the diffusion path moves upwards (towards increasing Sn content) inside the AuCu₃ one phase field. After that the diffusion path takes a tie-line connecting AuCu₃ and AuCu and proceeds to the AuCu one phase field. From there the diffusion path takes another tie-line and travels along it to the Au₅Sn phase. In order to fulfill the mass balance, it will then proceed into the two phase area (Au,Cu)₅Sn + AuSn by crossing the tie-lines at a certain angle (and also goes to the other side of the contact line) and then turns back to (Au,Cu)₅Sn. This part of the path corresponds to the AuSn precipitates inside the (Au,Cu)₅Sn, as shown in Fig. 3.21. Finally, the diffusion path will proceed along the binary Au–Sn edge to the other end of the contact line (eutectic Au₅Sn + AuSn).

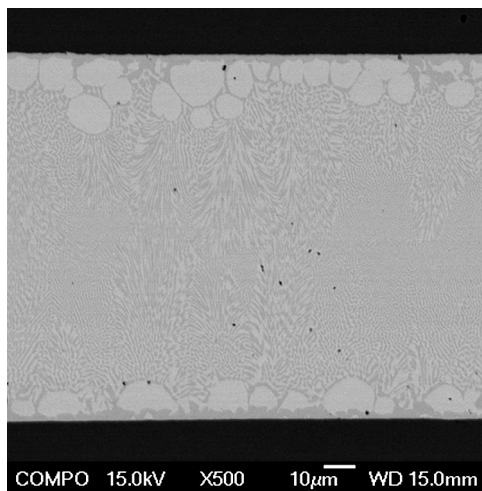


Figure 3.24 Ni|Au80Sn20 interfacial microstructure after soldering at 320°C for 100 s.

3.5.3 Au–Ni–Sn System

The microstructural characteristics of the Au–20wt.%Sn | Ni reaction couples were studied by SEM/EDX analysis. Fig. 3.24 shows the microstructure of the as-solidified sandwich joint (i.e., soldered at 320°C for 100 s), with a higher magnification image inserted on the left side of the graph. As expected from the Au–Sn binary phase system, the Au–20wt.%Sn solder matrix is composed of a two-phase microstructure: the bright constituent ζ' -phase and the dark constituent δ -phase. Between the Ni layer and the solder, two reaction products have been formed. According to the EDX analysis, Ni is present in both of the products; moreover, the Ni contents in these compounds are on the increase towards the Ni layer. The composition of these two compounds near the Ni side are approximately 47.5at.%Au–47.8at.%Sn–4.7at.%Ni and 82.6at.%Au–15.3at.%Sn–2.1at.%Ni. The ratios of the atom percentages of (Au+Ni) to these of Sn are 52.2:47.8 and 84.7:15.3 (i.e., $\sim 1:1$ and 5:1, respectively) and suggest that the reaction products are (Au,Ni)Sn and (Au,Ni)₅Sn. In the following text, these compounds are denoted as $\delta(\text{Ni})$ and $\zeta'(\text{Ni})$, respectively. In Fig. 3.24, the irregular while continuous dark layer formed against Ni is the $\delta(\text{Ni})$ compound, which has an average thickness of about 2.2 μm . Between the $\delta(\text{Ni})$ and (AuSn)_{eut} the bright scallops were identified as $\zeta'(\text{Ni})$ phase. However, the (Ni,Au)₃Sn₂ compound which is the equilibrium product at the interface was not observed for the as-soldered sample zone. During soldering, the Ni atoms from the Ni layer continuously dissolve into the molten solder until local metastable equilibria is reached. The local nominal composition moves towards Ni along the contact line of the end members (the blue line in Fig. 3.25(top)). When the composition of the solder (the point “n” in Fig. 3.25, (top) and (middle))

close to the Ni layer enters the liquid + $\zeta(\text{Ni})$ two-phase area, the liquid becomes in local equilibria with $\zeta(\text{Ni})$. Therefore, based on the mass balance requirement it is plausible to assume that the $\zeta(\text{Ni})$ phase becomes in local metastable equilibria with Ni. Assuming that the Ni content reaches the point “n” after a given soldering time, the phases that formed during solidification can be represented by the vertical dotted arrow and the sequence is: $\text{L} + \zeta(\text{Ni}) \rightarrow \text{L} + \zeta(\text{Ni}) + \delta(\text{Ni}) \rightarrow \zeta(\text{Ni}) + \delta(\text{Ni}) + (\text{Ni, Au})_3\text{Sn}_2 \rightarrow \zeta'(\text{Ni}) + \delta(\text{Ni}) + (\text{Ni, Au})_3\text{Sn}_2$. Based on the observed Ni content of the $\zeta'(\text{Ni})$ alloy (i.e., ~ 2 at.%) the reaction sequence during cooling can be rationalized with the help of Fig. 3.25(middle). The $\delta(\text{Ni})$ and $\zeta(\text{Ni})$ phases are nucleated from liquid and, therefore, can grow to observable thickness. On the other hand, the formation of $(\text{Ni, Au})_3\text{Sn}_2$ requires solid state diffusion and thus it cannot be observed within the resolution limits of SEM. It is to be emphasized that the short soldering time (100 s) and rapid cooling may not enable the formation of complete local equilibria.

Fig. 3.26 shows the interfacial microstructure of the samples aged at 150°C for 1200, 2500, and 4600 hours. The microstructure has evolved markedly during the annealing. The growth of the $\zeta'(\text{Ni})$ grains towards the coarse solder matrix is evident. According to the EDX analysis, Ni contents in $\delta(\text{Ni})$ and $\zeta'(\text{Ni})$ were around 3 and 3.5 at.% for the samples annealed at 150°C . In addition, compared with the microstructure of the as-soldered samples, two more continuous layers, namely Ni_3Sn_2 and Ni_3Sn , were formed between the Ni layer and the irregular $\delta(\text{Ni})$ layer. In the Ni_3Sn_2 layer, up to around 32 at.% Ni was substituted by Au in the Ni-sublattice at the solder side. Thus, in the following discussion it will be denoted as $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ with $0 \leq x < 0.582$. The ternary solubility of Au in the Ni_3Sn phase could not be precisely measured owing to the small thickness of the Ni_3Sn interlayer. Fig. 3.26(A) shows the microstructure of the sample after being annealed at 150°C for 1200 hours. The thickness of the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ and Ni_3Sn layers were around 0.9 and 0.2 μm , respectively. Here the average thickness of the $\delta(\text{Ni})$ layer slightly decreased to around 1 μm and this layer was even seen to disappear in a few locations. Eventually, the microstructure of the samples annealed for 1200 hours was found to be composed of $\text{Ni}/\text{Ni}_3\text{Sn}/(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2/\delta(\text{Ni})/(\delta + \zeta')_{\text{eutectic}}$ from bottom to top in Fig. 3.26(A). Figs. 3.26, (B) and (C), illustrate the interfacial microstructures of samples aged at 150°C for 2500 and 4600 hours, respectively. During these annealing periods, the thicknesses of the Ni_3Sn and $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ layers continued to increase as a function of increasing annealing time. For instance, the thicknesses of the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ and Ni_3Sn layers reached up to ~ 1.9 and 0.3 μm , respectively, for samples experiencing 4600 hours of annealing. In addition, the local equilibria between the $\delta(\text{Ni})$ and $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ layers continuously diminished with the increase of the annealing time. On the other hand, the fraction local contacts between $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ and $\zeta'(\text{Ni})$ increased (Figs. 3.26, (B) and (C)). Consequently, at this stage the structure of the interfacial reaction layer for the diffusion couples consisted of $\text{Ni}/\text{Ni}_3\text{Sn}/(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2/\delta(\text{Ni})$ or $\zeta'(\text{Ni})/(\delta + \zeta)_{\text{eutectic}}$. As mentioned earlier, the

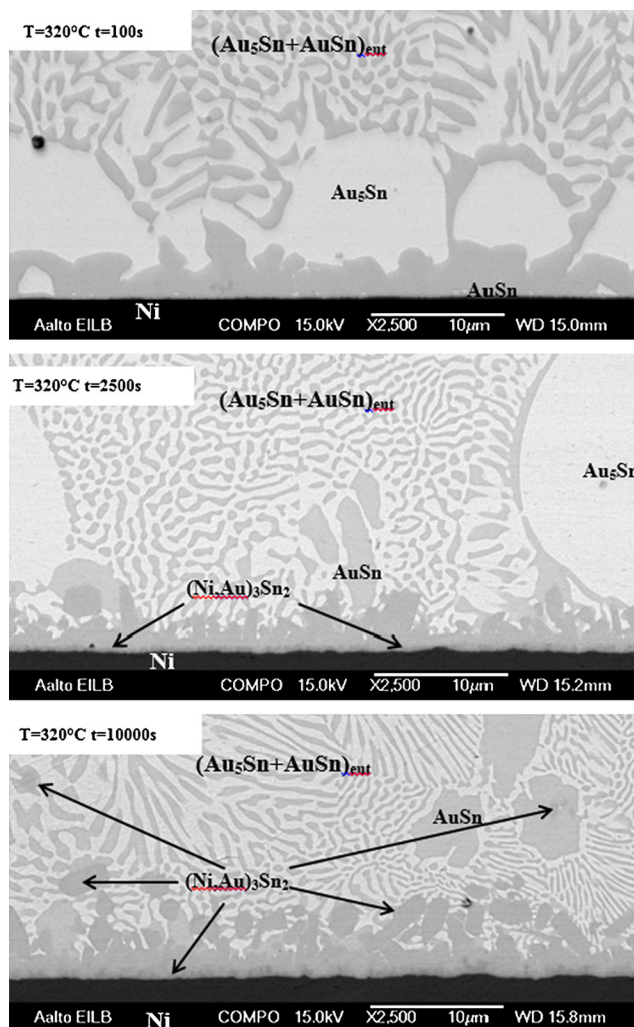


Figure 3.25 Ni/Au80Sn20 interfacial microstructure after soldering and keeping at 320°C for: (Upper) 100 s; (middle) 2500 s; and (bottom) 10000 s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

$\delta(\text{Ni})$ phase on top of the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ layer was gradually replaced by $\zeta'(\text{Ni})$, with a longer annealing time. It is suggested that the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2/\delta(\text{Ni})$ interface would be completely transformed to the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2/\zeta'(\text{Ni})$ interface, after a longer isothermal aging at 150°C. Thus, the reaction sequence of the Au–20wt.%Sn|Ni diffusion couple at 150°C is proposed as $\text{Ni}/\text{Ni}_3\text{Sn}/(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2/\zeta'(\text{Ni})/(\delta + \zeta')_{\text{eutectic}}$. The schematic of the diffusion path (the dotted line in Fig. 3.27) is superimposed on the calculated 150°C isothermal section of the Au–Ni–Sn system.

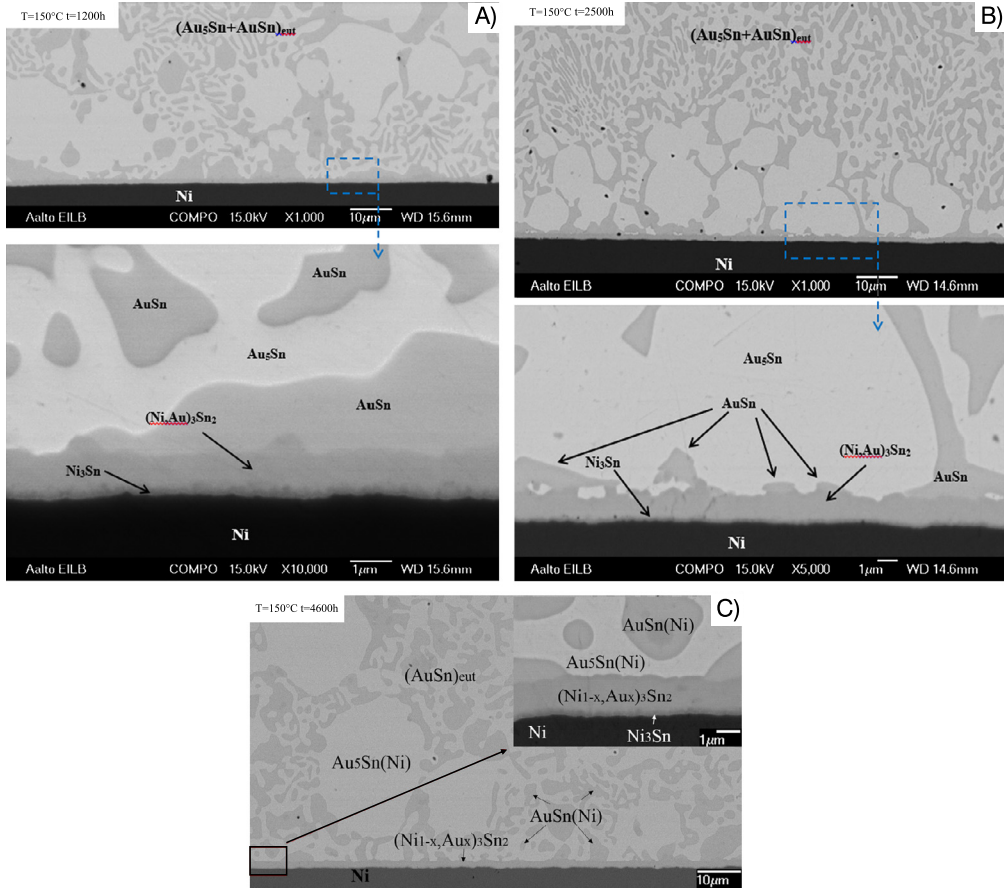


Figure 3.26 The microstructure of Au–20wt.%Sn/Ni diffusion couple after annealing at 150°C for (A) 1200 hours, (B) 2500 hours, and (C) 4600 hours.

The diffusion path starts from the Ni corner towards the Ni_3Sn phase along the binary Ni–Sn edge of the diagram. After reaching Ni_3Sn , it will continue to move inside the single phase area to $(\text{Ni,Au})_3\text{Sn}_2$ where approximate 1.6 at.% Au is dissolved [53]. The diffusion path then proceeds towards $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ along one of the tie-lines, as shown in Fig. 3.27. The path moves inside the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ single-phase field towards $\zeta'(\text{Ni})$ instead of $\delta'(\text{Ni})$ or the three phase field (i.e., the tie-triangle area in Fig. 3.27). As shown in Fig. 3.26(C), several locations could be found where three phases are in contact, namely $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$, $\delta(\text{Ni})$, and $\zeta'(\text{Ni})$. These locations correspond to the corner of the tie-triangle for the given three-phase equilibrium. However, according to the Gibbs phase rule, once temperature and pressure are fixed, only two-phase areas can be formed in the diffusion couple, since the concentration (activity) differences

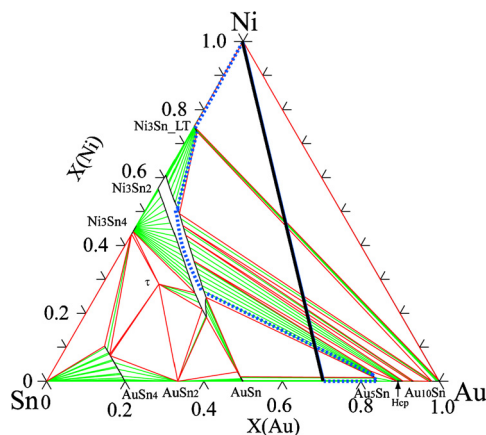


Figure 3.27 Isothermal section of Au–Ni–Sn phase diagram at 150°C with diffusion path superimposed. The end points of solid black line represent the starting contact composition; and the observed diffusion path is shown as a dotted line.

that are needed to drive the diffusion require the remaining degree of freedom. In the present case, there are three-phase contact points rather than regions, which indicate that the diffusion path hits the corner of the three-phase tie-triangle only at some points. At these local three-phase contact points, diffusion cannot proceed owing to the absence of activity differences. On the other hand, the global diffusion path (where only two-phase regions are present) proceeds to $\zeta'(\text{Ni})$ by taking one of the tie-lines in the corresponding two-phase field. After reaching $\zeta'(\text{Ni})$, the path must move to the Ni-free ζ' phase and then return to the original nominal composition along the binary Au–Sn edge, in order to fulfill the mass-balance requirement.

For the purpose of rationalizing the observed interfacial reaction sequence in the diffusion couple (Au–20wt.%Sn|Ni), activity diagrams were calculated, as well as the driving forces for the diffusion of the three species over the phases in the proposed reaction sequence. Fig. 3.28 illustrates the calculated activity diagrams for all the three species at 150°C. The predicted diffusion path together with the end member compositions of the reaction couple were superimposed on these diagrams. As shown in Fig. 3.28, all three elements can intrinsically diffuse in the proposed reaction sequence as the predicted structure can be formed without any of the elements having to diffuse against their own activity gradients (without the diffusion path moving upwards in the activity diagrams). The results derived above are further supported by the calculated chemical-potential gradient along the reaction path (Table 3.3). The values show that starting from the Ni layer towards the solder matrix, the chemical potential of Ni becomes more negative, while those of Sn and Au change in the opposite direction. Thus, all elements can move along their lowering chemical potentials as required if the intrin-

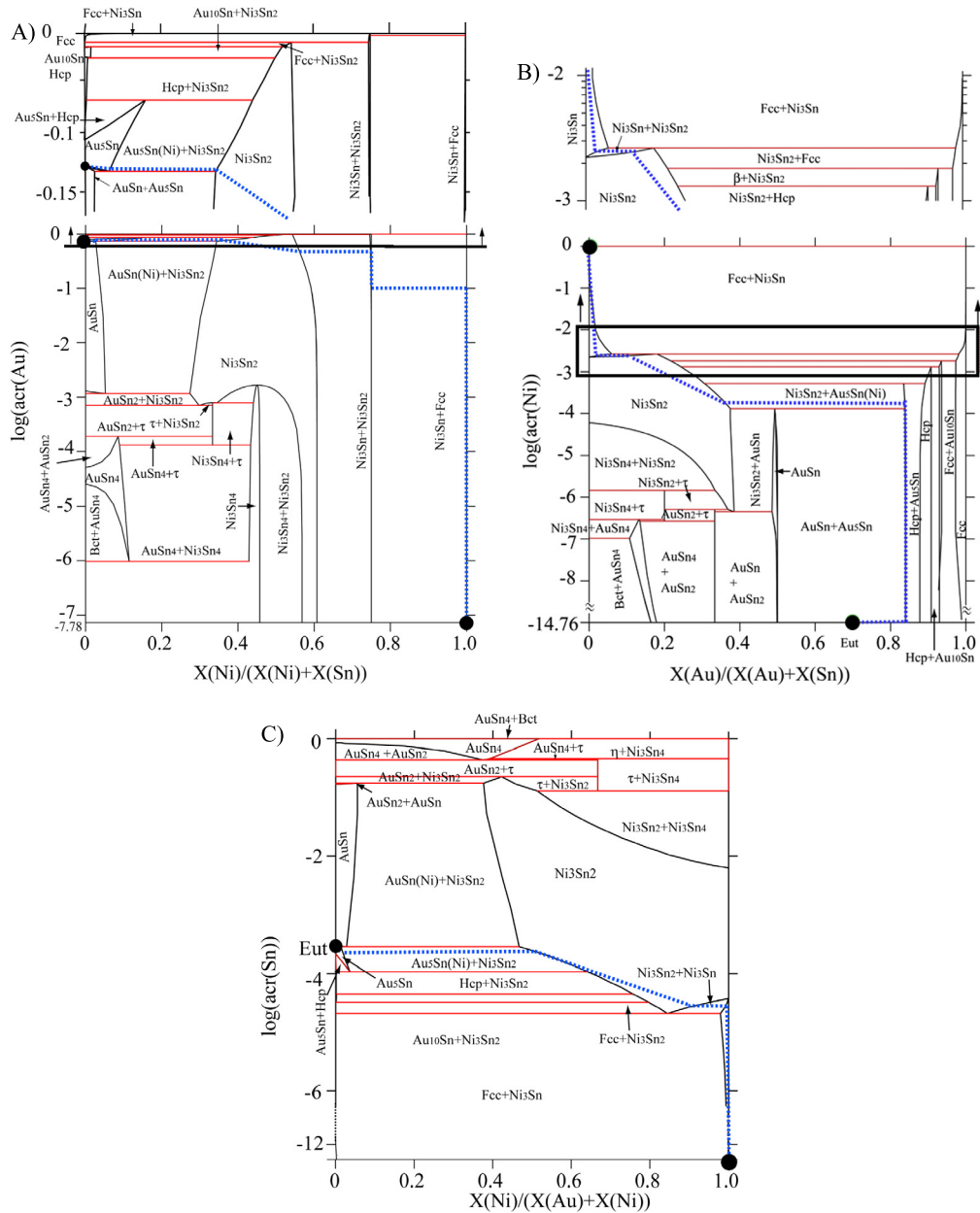


Figure 3.28 Calculated activity diagrams for (A) Au, (B) Ni, and (C) Sn at 150°C with superimposed diffusion path.

Table 3.3 Calculated values of chemical potentials of different species at various interfaces of the reaction couple

Interface	x (Au)	X (Ni)	μ_{Au}	μ_{Ni}	μ_{Sn}
Eutectic/Au ₅ Sn	0.707	2.67E-04	-1053.3	-45145.9	-28601.3
(Au,Ni) ₅ Sn/(Ni _{1-x} Au _x) ₃ Sn ₂	0.285	0.25	-1062.2	-31154.8	-28829.1
(Ni _{1-x} Au _x) ₃ Sn ₂ /Ni ₃ Sn	7.73E-02	0.513	-1238.3	-20987.1	-37491
Ni ₃ Sn/Ni	4.31E-06	0.756	-8100.8	-2.6727E-02	-102287.1

Reference states: Au (fcc), Ni (fcc), and Sn (bct). The composition of the elements was selected from the tie-lines of the corresponding two-phase fields.

sic diffusion of a given species is to take place [18]. Thus, based on the thermodynamic analysis, all the species in the system, namely Au, Ni, and Sn, can diffuse intrinsically in the proposed reaction sequence.

Hence, the evolution of the microstructure in the diffusion couple annealed at 150°C can be explained as follows: (i) when the samples were soldered at 320°C, the Ni atoms dissolved into the molten solder matrix. This contributes to the solubility of Ni in the $\delta(\text{Ni})$ and $\zeta'(\text{Ni})$ compounds. (ii) During solidification and following isothermal annealing, the intermetallic compounds evolved with the aging time. The thickness of $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ increasing linearly with the square root of aging time indicates that the growth of the $(\text{Ni}_{1-x}\text{Au}_x)_3\text{Sn}_2$ layer was diffusion controlled. Similar growth behavior of Ni₃Sn has been reported in [54]. The $\delta(\text{Ni})$ continuous layer gradually disappearing on the interface could also be associated with the diffusion and the interfacial reactions in the couple in question.

CONCLUSIONS

Based on what has been shown it is evident that the thermodynamic-kinetic method can be used to rationalize the evolution of interfacial reaction zone in many types of systems. One of the strengths of the method is clearly in its generality. Metal-metal reaction couples or phase formation between inorganic materials are by no means the only applications that the thermodynamic-kinetic method can be used in. Biological applications, for example, provide no fundamental problems, as long as there is adequate data available. However, as was seen above, even when there is very little or practically no data about the system under investigation, this method can be used as an aid for rationalizing as shown above. The method is, of course, not intended to be used in isolation from the experiments. In order to acquire knowledge about the morphology and distribution of phases inside the reaction zone experimental investigations are needed, for example, by Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). The main motivation to use the thermodynamic-kinetic method stems from the fact that by its help, it is possible to avoid the so called “trial-and-error” approach that easily leads to confusing and even completely erroneous results.

REFERENCES

- [1] J. Kivilahti, The chemical modeling of electronic materials and interconnections, *JOM – J. Minerals Metal. Mater. Soc.* 54 (2002) 52.
- [2] H. Lukas, S. Fries, B. Sundman, *Computational Thermodynamics: The Calphad Method*, Cambridge University Press, ISBN 978-0-521-86811-2, 2007, 313 pages.
- [3] M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations*, Cambridge Press, 1998.
- [4] T. Laurila, V. Vuorinen, M. Paulasto-Kröckel, Impurity and alloying effects on interfacial reaction layers in lead-free soldering, *Materials Science and Engineering – R* R68 (2010) 1–38.
- [5] T. Laurila, V. Vuorinen, J.K. Kivilahti, Interfacial reactions between lead-free solders and common base materials, *Materials Science and Engineering – R* R49 (1–2) (2005) 1–60.
- [6] N.A. Gokcen, *Thermodynamics*, Techscience Incorporated, 1975.
- [7] J. Philibert, *Atom Movements: Diffusion and Mass Transport in Solids*, Les Editions de Physique, 1991.
- [8] T. Laurila, J. Molarius, Reactive phase formation in thin film metal/metal and metal/silicon diffusion couples, *Critical Reviews in Solid State and Materials Science* 28 (2003) 185.
- [9] F.J.J. van Loo, Multiphase diffusion in binary and ternary solid-state systems, *Prog. Solid St. Chem.* 20 (1990) 47.
- [10] F.N. Rhines, *Phase Diagrams in Metallurgy – Their Development and Applications*, McGraw-Hill, 1956.
- [11] K.J. Rönkä, F.J.J. van Loo, J.K. Kivilahti, A diffusion-kinetic model for predicting solder/conductor interactions in high density interconnections, *Metallurgical and Materials Transactions A* 29A (1998) 2951–2956.
- [12] V. Vuorinen, H. Yu, T. Laurila, J.K. Kivilahti, Formation of the intermetallic compound between liquid Sn and different CuNi_x metallizations, *Journal of Electronics Materials* 37 (6) (2008) 792–805.
- [13] M. Hillert, in: H. Aaronson (Ed.), *Lectures on the Theory of Phase Transformations*, AIME, 1975.
- [14] A. Paul, *The Kirkendall Effect in Solid State Diffusion*, Doctoral Dissertation, Technical, University of Eindhoven, 2004.
- [15] A. Paul, C. Ghosh, W.J. Boettinger, Diffusion parameters and growth mechanism of phases in the Cu–Sn system, *Metallurgical and Materials Transactions A* 42A (2011) 952–963.
- [16] V. Vuorinen, T. Laurila, T. Mattila, E. Heikinheimo, J.K. Kivilahti, Solid-state reactions between Cu (Ni) alloys and Sn, *J. Electron. Mater.* 36 (10) (2007) 1355.
- [17] K. Nogita, T. Nishimura, Nickel-stabilized hexagonal (Cu,Ni)₆Sn₅ in Sn–Cu–Ni lead-free solder alloys, *Scr. Mater.* 59 (2008) 191.
- [18] A. Paul, T. Laurila, V. Vuorinen, S. Divinsky, *Thermodynamics, Diffusion and the Kirkendall Effect in Solids*, Springer, ISBN 978-3-3190-7460-3, 2014, 548 pages.
- [19] T. Laurila, J. Molarius, Reactive phase formation in thin film metal/metal and metal/silicon diffusion couples, *Critical Reviews in Solid State and Materials Science* 28 (2003) 185.
- [20] P. Shewmon, *Diffusion in Solids*, 2nd edition, TMS, 1989.
- [21] J.S. Kirkaldy, D.J. Young, *Diffusion in the Condensed State*, The Institute of Metals, UK, 1987.
- [22] J.S. Kirkaldy, Diffusion in multicomponent metallic systems, *Can. J. Phys.* 36 (1958) 899.
- [23] J.S. Kirkaldy, L.C. Brown, Diffusion behaviour in ternary, multiphase systems, *Can. Met. Q.* 2 (1963) 89.
- [24] D. Coates, J.S. Kirkaldy, Phase interface stability in isothermal ternary systems, in: *Proc. Second Internat. Conf. on Crystal Growth*, North-Holland Publishing, Amsterdam, 1968, pp. 549–554.
- [25] A.A. Kodentsov, M.J.H. van Dal, C. Cserhati, F.J.J. van Loo, Reactive phase formation in binary and ternary silicide systems, in: L. Miglio, F. d’Heurle (Eds.), *Silicides: Fundamentals and Applications*, World Scientific, Singapore, 2000.
- [26] C. Wagner, The evaluation of data obtained with diffusion couples of binary single-phase and multiphase systems, *Acta Metall.* 17 (1969) 99.

- [27] L.E. Trimble, D. Finn, A. Cosgarea Jr., A mathematical analysis of diffusion coefficients in binary systems, *Acta Met.* 13 (1965) 501.
- [28] P.L. Gruzin, Self-diffusion in gamma iron, *Dokl. Akad. Nauk S.S.S.R.* 86 (1952) 289.
- [29] E. Suhir, Y. Lee, C. Wong, *Micro- and Opto-Electronic Materials and Structures: Physics, Mechanics, Design, Reliability, Packaging: Volume I: Materials Physics-Materials Mechanics. Volume II: Physical Design-Reliability and Packaging*, Springer, 2007.
- [30] R. Tummala, M. Swaminathan, *System on Package: Miniaturization of the Entire System*, McGraw-Hill Professional, 2008.
- [31] A.L. Hartzell, M.G. Da Silva, H.R. Shea, *MEMS Reliability*, Springer, 2011.
- [32] M. Esashi, Wafer level packaging of MEMS, *J. Micromech. Microengineering* 18 (7) (2008) 073001.
- [33] W. Reinert, P. Merz, Metallic alloy seal bonding, in: V. Lindroos, M. Tilli, A. Lehto, T. Motooka (Eds.), *Handbook of Silicon Based MEMS Materials and Technologies*, William Andrew Publishing, Boston, 2010, pp. 533–542, Chapter 34, <http://dx.doi.org/10.1016/B978-0-8155-1594-4.00034-6>.
- [34] L. Bernstein, Semiconductor joining by the solid-liquid-interdiffusion (SLID) process: I. The systems Ag–In, Au–In, and Cu–In, *Journal of the Electrochemical Society* 113 (12) (1966) 1282–1288.
- [35] T.A. Tollefsen, A. Larsson, O.M. Løvvik, K. Aasmundtveit, Au–Sn SLID bonding—properties and possibilities, *Metallurgical and Materials Transactions B* 43 (2) (2012) 397–405.
- [36] G.S. Matijasevic, C.C. Lee, C.Y. Wang, Au–Sn alloy phase diagram and properties related to its use as a bonding medium, *Thin Solid Films* 223 (2) (1993) 276–287.
- [37] C.C. Lee, C.Y. Wang, G. Matijasevic, Advances in bonding technology for electronic packaging, *Journal of Electronic Packaging* 115 (2) (1993) 201–207.
- [38] R.W. Johnson, Cai Wang, Yi Liu, J.D. Scofield, Power device packaging technologies for extreme environments, *IEEE Transactions on Electronics Packaging Manufacturing* 30 (3) (2007) 182–193.
- [39] K. Wang, K. Aasmundtveit, H. Jakobsen, Surface evolution and bonding properties of electroplated Au/Sn/Au, in: 2nd 2008 Electronics System-Integration Technology Conference, 2008 ESTC, 2008, pp. 1131–1134.
- [40] C. Chang, T.A. Callcott, E.T. Arakawa, Diffusion of Au into Sn thin films studied by the attenuated total reflection method, *J. Appl. Phys.* 53 (11) (1982) 7362–7366, <http://dx.doi.org/10.1063/1.330103>.
- [41] S. Nakahara, R.J. McCoy, Kirkendall void formation in thin-film diffusion couples, *Appl. Phys. Lett.* 37 (1) (1980) 42–44, <http://dx.doi.org/10.1063/1.91696>.
- [42] L. Buene, Interdiffusion and phase formation at room temperature in evaporated gold–tin films, *Thin Solid Films* 47 (2) (1977) 159–166.
- [43] L. Buene, S.T. Jacobsen, Room temperature interdiffusion in evaporated Au–Sn films, *Phys Scripta* 18 (6) (1978) 397.
- [44] B. Hugsted, L. Buene, T. Finstad, O. Lønsjø, T. Olsen, Interdiffusion and phase formation in Au/Sn thin film couples with special emphasis on substrate temperature during condensation, *Thin Solid Films* 98 (2) (1982) 81–94.
- [45] S. Nakahara, R.J. McCoy, L. Buene, J.M. Vandenberg, Room temperature interdiffusion studies of Au/Sn thin film couples, *Thin Solid Films* 84 (2) (1981) 185–196.
- [46] H. Xu, V. Vuorinen, H. Dong, M. Paulasto-Kröckel, Solid-state reaction of electroplated thin film Au/Sn couple at low temperatures, *Journal of Alloys and Compounds* 619 (2015) 325–331.
- [47] D. Hong, V. Vuorinen, X.M. Tao, T. Laurila, M. Paulasto-Kröckel, Thermodynamic reassessment of Au–Cu–Sn ternary system, *Journal of Alloys and Compounds* 588 (2014) 449–460.
- [48] H.Q. Dong, V. Vuorinen, X.W. Liu, T. Laurila, J. Li, M. Paulasto-Kröckel, Microstructural evolution and mechanical properties of Au–20wt.%Sn/Ni interconnection, *Journal of Electronic Materials* 45 (1) (2016) 566–575.
- [49] O.B. Karlsen, A. Kjekshus, C. Romming, E. Rost, *Acta Chemica Scandinavica* 46 (1992) 1076.
- [50] O.B. Karlsen, A. Kjekshus, E. Roest, *Acta Chemica Scandinavica* 46 (1992) 147.

- [51] Y.W.A. Sentosa, Thermodynamic Assessment of the Au–Cu–Sn Ternary System, Master Thesis, National Taiwan University of Science and Technology, 2007.
- [52] J.F. Roeder, Phase Equilibria and Compound Formation in the Au–Cu–Sn System at Low Temperature, PhD Thesis, Lehigh University, 1988.
- [53] J.W. Morris Jr., H.L. Reynolds, Advances in Electronic Packaging, ASME, 1997, pp. 1529–1534, EEP-vol. 19–2.
- [54] H.G. Song, J.P. Ahn, J.W. Morris Jr., Journal of Electronic Materials 30 (2001) 1083–1087.
- [55] X.J. Liu, M. Kinaka, Y. Takaku, I. Ohnuma, R. Kainuma, K. Ishida, Journal of Electronic Materials 34 (2005) 670.
- [56] A. Dębski, W. Gąsior, Z. Moser, R. Major, Journal of Alloys and Compounds 491 (2010) 173.
- [57] C. Schmetterer, H. Flandorfer, K.W. Richter, U. Saeed, M. Kauffman, P. Roussel, H. Ipser, Intermetallics 15 (2007) 869.
- [58] A.Zemanova.A. Kroupa, A. Dinsdale, Monatshefte für Chemie – Chemical Monthly 143 (2012) 1255.

CHAPTER 4

Microstructural Evolution by Reaction–Diffusion: Bulk, Thin Film, and Nanomaterials

Aloke Paul

Indian Institute of Science, Bangalore, India

Ever since the first report of solid state diffusion in 1889, this field has witnessed significant growth in terms of laying down the fundamentals and mechanisms of diffusion. Most of the developments are oriented towards relating composition dependent diffusion coefficients with defects and driving forces. One of the most important inventions of the last decade in the field of solid state diffusion is the discovery of previously unknown phenomenon related to Kirkendall effect [1]. Inert particles used at the bonding interface of dissimilar materials subjected to interdiffusion can mostly be found in one plane (or composition), namely the stable Kirkendall marker plane. However, now we know that, under a certain condition, these inert particles might spread over a wide region, leading to unstable Kirkendall marker plane [2,3]. There can also be situations when markers split into more than one plane, leading to bifurcation or trifurcation of Kirkendall marker plane [3–8]. These findings led to the better understanding of phenomenological diffusion process based on which many new theoretical models were developed by different groups. One of such examples is the development of a physico-chemical model that relates the microstructural evolution of the interdiffusion zone with relative mobilities of the components [4,8–10]. Utilizing this model, it is now possible to analyze the growth mechanism of phases based on quantitative or qualitative analysis just by examining the diffusion-controlled microstructural evolution between dissimilar materials. This is important for the analysis of materials in various applications where inert particles cannot be used to quantify the relative mobilities of the species. In the beginning, mathematics behind this model is introduced by considering a single phase layer in an interdiffusion zone, following which the analysis is extended to multiphase growth.

4.1 MATHEMATICAL FORMULATIONS FOR ESTIMATION OF THE DIFFUSION COEFFICIENTS UTILIZING PHYSICOCHEMICAL MODEL

As explained in Chapter 3 of Volume 1, diffusion coefficients are directly estimated from the composition profile that is developed in an interdiffusion zone after confirming the

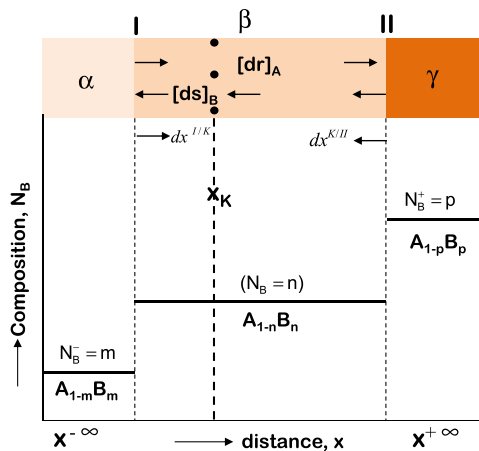


Figure 4.1 A schematic representation of the diffusion couple explaining the physicochemical approach.

parabolic growth of a phase layer. The relations do not consider the microstructural evolution in an interdiffusion zone. However, as explained in the proceeding sections, we know that interdiffusion zone grows with a characteristic microstructure depending on the relative mobilities of the components and therefore the location of Kirkendall marker plane. The concept behind Kirkendall marker plane is explained in detail in Chapter 3 of Volume 1. In this section, the physicochemical model is explained, which combines the reaction–dissociation process at different interfaces and diffusion rates of the components through the product phase [4,9]. To confirm the veracity of the model, it is first necessary to show that by this method also we estimate exactly the same values of the diffusion coefficients when conventional methods are followed, along with an added advantage that one can explain/predict the microstructure of an interdiffusion zone based on this model.

Suppose, we make a diffusion couple of compounds $\alpha(A_{1-m}B_m)$ and $\gamma(A_{1-p}B_p)$ so that $\beta(A_{1-n}B_n)$ grows in an interdiffusion zone, as shown in Fig. 4.1. As explained in Chapter 1 of Volume 1, phase mixtures do not grow in an interdiffusion zone of a binary system because of thermodynamic reasons. m , n and p are the mole fractions of B in different compounds such that $m < n < p$. Considering the normal downhill diffusion process, A should be dissociated from the A-rich α phase to produce the product phase β at the interface I. The dissociated component then diffuses through the product phase and reacts with the B-rich γ phase at the interface II to produce the β phase. The diffusion direction of B is opposite of that of A, i.e., from B-rich γ phase to the A-rich α phase. Therefore, the γ phase dissociates at the interface II to produce component B and the β phase. The dissociated component then diffuses through the product phase and reacts with α to produce β at the interface I. The total amounts

of diffusing components A and B depend on the diffusion rates of these components through the product phase and the annealing time at a particular temperature. For the sake of derivation of the relations for the estimation of these diffusion coefficients, we assume that $[dr]_A$ mol/m² of component A crosses Kirkendall marker plane in the short annealing time dt . Similarly $[ds]_B$ mol/m² of component B crosses the marker plane in the same period of time. The location of Kirkendall marker plane is denoted as x_K . It must be clear from the discussion above that the thicknesses of the product phase that is grown in the left- and right-hand side of Kirkendall marker plane are due to the reaction and dissociation at the interface I and II, respectively. Therefore, the thicknesses of different sublayers of the product phase grown from two different interfaces should be related to the mole fractions produced by the reaction–dissociation with the help of molar volume as follows:

At interface I:

$$(\text{Dissociation of A}) \quad \frac{n}{n-m} dr A_{1-m} B_m (\alpha \text{ phase}) \rightarrow dr[A]_d + \frac{m}{n-m} dr A_{1-n} B_n (\beta \text{ phase}),$$

$$(\text{Reaction of B}) \quad \frac{1-n}{n-m} ds A_{1-m} B_m (\alpha \text{ phase}) + ds[B]_d \rightarrow \frac{1-m}{n-m} ds A_{1-n} B_n (\beta \text{ phase}).$$

At interface II:

$$(\text{Reaction of A}) \quad \frac{n}{p-n} dr A_{1-p} B_p (\gamma \text{ phase}) + dr[A]_d \rightarrow \frac{p}{p-n} dr A_{1-n} B_n (\beta \text{ phase}),$$

$$(\text{Dissociation of B}) \quad \frac{1-n}{p-n} ds A_{1-p} B_p (\gamma \text{ phase}) \rightarrow ds[B]_d + \frac{1-p}{p-n} ds A_{1-n} B_n (\beta \text{ phase}).$$

The β phase that is produced at interface I is $\frac{1}{n-m}[m dr + (1-m) ds]$ mol/m² and that at interface II is $\frac{1}{p-n}[p dr + (1-p) ds]$ mol/m². These can be related to the thickness of the sublayers on different sides of Kirkendall marker plane by multiplying the mole fractions with the molar volume of the product phase v_m . Considering that the thicknesses of the product phase grown from interfaces I and II during annealing time dt are $dx^{I/K}$ and $dx^{K/II}$, respectively, we can write

$$\frac{1}{n-m}[m dr + (1-m) ds] v_m = dx^{I/K}, \quad (4.1a)$$

$$\frac{1}{p-n}[p dr + (1-p) ds] v_m = dx^{K/II}. \quad (4.1b)$$

For the sake of similar derivation of the relations for the estimation of the diffusion coefficients as explained in Chapter 3 of Volume 1, we write the compositions of different

parts of the diffusion couple as follows: mole fractions of component B of the left- and right-hand sides of the unaffected end-members of the diffusion couple are $m = N_B^-$ and $p = N_B^+$, respectively, and the mole fraction of the product phase is $n = N_B$. Therefore, Eqs. (4.1a) and (4.1b) can be rewritten as

$$N_B^- dr + (1 - N_B^-) ds = \frac{N_B - N_B^-}{v_m} dx^{I/K}, \quad (4.2a)$$

$$N_B^+ dr + (1 - N_B^+) ds = \frac{N_B^+ - N_B}{v_m} dx^{K/II}. \quad (4.2b)$$

To estimate the diffusion parameters, we need to integrate the above relations for total annealing time t such that

$$\begin{aligned} N_B^- \int_0^r dr + (1 - N_B^-) \int_0^s ds &= \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx, \\ N_B^- r + (1 - N_B^-) s &= \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx, \end{aligned} \quad (4.3a)$$

$$\begin{aligned} N_B^+ \int_0^r dr + (1 - N_B^+) \int_0^s ds &= \int_{x_K}^{x^{+\infty}} \frac{N_B^+ - N_B}{v_m} dx, \\ N_B^+ r + (1 - N_B^+) s &= \int_{x_K}^{x^{+\infty}} \frac{N_B^+ - N_B}{v_m} dx. \end{aligned} \quad (4.3b)$$

Note here that the diffusing flux at zero annealing time is zero.

Since r and s are related to the diffusion rates of components A and B, we need to write the relations with respect to these for the estimation of the diffusion rates of the components. Multiplying Eq. (4.3a) by $(1 - N_B^+)$ and Eq. (4.3b) by $(1 - N_B^-)$ and then subtracting, we get

$$\begin{aligned} &N_B^- (1 - N_B^+) r - N_B^+ (1 - N_B^-) r \\ &= (1 - N_B^+) \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx - (1 - N_B^-) \int_{x_K}^{x^{+\infty}} \frac{N_B^+ - N_B}{v_m} dx, \\ r &= - \left[(1 - N_B^+) \int_{x^-}^{x_K} \frac{N_B - N_B^-}{N_B^+ - N_B^-} \frac{1}{v_m} dx - (1 - N_B^-) \int_{x_K}^{x^{+\infty}} \frac{N_B^+ - N_B}{N_B^+ - N_B^-} \frac{1}{v_m} dx \right]. \end{aligned}$$

Utilizing the composition normalizing variable introduced by Sauer–Freise [11], $Y_B = \frac{N_B - N_B^-}{N_B^+ - N_B^-}$ such that $1 - Y_B = \frac{N_B^+ - N_B}{N_B^+ - N_B^-}$, we can write

$$r = - \left[(1 - N_B^+) \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - (1 - N_B^-) \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx \right],$$

$$r = - \left[N_A^+ \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - N_A^- \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx \right], \quad (4.4a)$$

since $N_A^+ + N_B^+ = 1$.

Multiplying Eq. (4.3a) by N_B^- and Eq. (4.3b) by N_B^+ and then subtracting, we get

$$N_B^+ (1 - N_B^-) s - N_B^- (1 - N_B^+) s = N_B^+ \int_{x^-}^{x_K} \frac{N_B - N_B^-}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{v_m} dx,$$

$$s = N_B^+ \int_{x^-}^{x_K} \frac{N_B - N_B^-}{N_B^+ - N_B^-} \frac{1}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{N_B^+ - N_B}{N_B^+ - N_B^-} \frac{1}{v_m} dx,$$

$$s = N_B^+ \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx. \quad (4.4b)$$

Next, the intrinsic flux of component A, J_A , and the intrinsic flux of component B, J_B , should be related to r and s . The intrinsic fluxes crossing Kirkendall marker plane at which we determine these parameters, are inversely proportional to $t^{1/2}$. Further, a positive sign for the flux of A should be considered since A diffuses from left to right and a negative sign should be considered for the flux of B since it diffuses from right to left. Therefore, we can write

$$r = \int_0^r dr = \int_0^t J_A dt = \int_0^t \frac{k}{t^{1/2}} dt = \frac{kt^{1/2}}{1/2} = 2tJ_A = -2tD_A \frac{\partial C_A}{\partial x}, \quad (4.5a)$$

$$s = \int_0^s ds = - \int_0^t J_B dt = - \int_0^t \frac{k}{t^{1/2}} dt = -2tJ_B = 2tD_B \frac{\partial C_B}{\partial x}, \quad (4.5b)$$

where k is the proportionality constant. Following Fick's first law of diffusion, $J_i = -D_i \frac{\partial C_i}{\partial x}$. Combining Eqs. (4.4) and (4.5), we can write

$$D_A = \frac{1}{2t} \left(\frac{\partial x}{\partial C_A} \right) \left[N_A^+ \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - N_A^- \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx \right], \quad (4.6a)$$

$$D_B = \frac{1}{2t} \left(\frac{\partial x}{\partial C_B} \right) \left[N_B^+ \int_{x^-}^{x_K} \frac{Y_B}{v_m} dx - N_B^- \int_{x_K}^{x^+} \frac{1 - Y_B}{v_m} dx \right]. \quad (4.6b)$$

Note that these are the same relations of intrinsic diffusion coefficients derived by van Loo [12] following the conventional route, i.e., directly from the composition profiles without considering dissociation–reactions at the interfaces. From the standard thermodynamic relations $\partial C_A = (\frac{\bar{v}_B}{\bar{v}_m})\partial N_A$, $\partial C_B = (\frac{\bar{v}_A}{\bar{v}_m})\partial N_B$, $\partial N_A + \partial N_B = 0$ [1], the ratios of intrinsic diffusivities (or fluxes) can be written as

$$\frac{\bar{v}_A D_B}{\bar{v}_B D_A} = \frac{s}{r}. \quad (4.7)$$

Therefore, by determining the values of r and s following the physicochemical approach, one can straightaway determine the ratio of diffusivities. It should be noted at this point that partial molar volumes of the components in a line compound or a compound with a narrow homogeneity range cannot be estimated since composition-dependent lattice parameter data are not available. In general, lattice parameter data at the stoichiometric composition are known. Therefore, it is common practice that we consider partial molar volumes as equal to the molar volumes, although these values could be much different. The tracer diffusion coefficients and the intrinsic diffusion coefficients are related by (see Chapter 3 in Volume 1)

$$D_A = \frac{\nu_m}{\bar{v}_B} D_A^* \frac{d \ln a_A}{d \ln N_A} = \frac{\nu_m}{\bar{v}_B} D_A^* \Phi, \quad (4.8a)$$

$$D_B = \frac{\nu_m}{\bar{v}_A} D_B^* \frac{d \ln a_B}{d \ln N_B} = \frac{\nu_m}{\bar{v}_A} D_B^* \Phi, \quad (4.8b)$$

where D_i^* is the tracer diffusion coefficient of component i . Φ is the thermodynamic factor and according to the Gibbs–Duhem relation in a binary system $\Phi = \frac{d \ln a_A}{d \ln N_A} = \frac{d \ln a_B}{d \ln N_B}$ [1].

Comparing Eqs. (4.7) and (4.8), we can write

$$\frac{D_B^*}{D_A^*} = \frac{s}{r}. \quad (4.9)$$

Therefore, by neglecting the partial molar volumes, we actually measure the ratio of the tracer diffusivities. Note that tracer diffusivities are the diffusivities in the absence of thermodynamic driving forces and are related to the self-diffusion coefficients (D_S^i) by $D_i^* = f_i D_S^i$, where f_i is the correlation factor of component i .

Next, we need to write the relations for interdiffusion and integrated interdiffusion coefficients with respect to r and s . As shown in Chapter 3 of Volume 1, interdiffusion coefficient, $\tilde{D}$, and the intrinsic diffusion coefficients, D_i , are related by

$$\tilde{D} = C_A \bar{v}_A D_B + C_B \bar{v}_B D_A, \quad (4.10)$$

since $N_B + N_A = 1$, $dN_B + dN_A = 0$, $C_i = \frac{N_i}{v_m}$, and utilizing the standard thermodynamic relations $\partial C_A = (\frac{\bar{v}_B}{v_m})\partial N_A$ and $\partial C_B = (\frac{\bar{v}_A}{v_m})\partial N_B$, we can write Eq. (4.10) with respect to r and s with the help of Eqs. (4.5a) and (4.5b) as

$$\begin{aligned}\tilde{D} &= C_A \bar{v}_A \frac{s}{2t} \frac{\partial x}{\partial C_B} - C_B \bar{v}_B \frac{r}{2t} \frac{\partial x}{\partial C_A}, \\ \tilde{D} &= \frac{N_A}{v_m} \bar{v}_A \frac{s}{2t} \frac{\partial x}{\partial N_B} \frac{v_m^2}{\bar{v}_A} - \frac{N_B}{v_m} \bar{v}_B \frac{r}{2t} \frac{\partial x}{\partial N_A} \frac{v_m^2}{\bar{v}_B}, \\ \tilde{D} &= \frac{v_m}{2t} \frac{\partial x}{\partial N_B} [N_B r + N_A s].\end{aligned}\quad (4.11)$$

We cannot estimate the interdiffusion coefficient in a compound with very narrow homogeneity range since we cannot estimate very small concentration gradient from the measured composition profile. Therefore, it should be expressed with respect to the integrated interdiffusion coefficient, which is defined as the interdiffusion coefficient integrated over the unknown composition range of the phase and expressed as

$$\tilde{D}_{\text{int}}^\beta = \int_{N_B^I}^{N_B^{II}} \tilde{D} dN_B = \int_{x_\beta^I}^{x_\beta^{II}} \frac{v_m}{2t} [N_B r + N_A s] dx = \frac{v_m^\beta}{2t} [N_B^\beta r + N_A^\beta s] \Delta x_\beta. \quad (4.12)$$

The unknown composition range of the β phase is $\Delta N_B^\beta = N_B^{II} - N_B^I$. The thickness of the phase layer is $\Delta x_\beta = x_\beta^{II} - x_\beta^I$. The average molar volume of the phase v_m^β and the composition N_B^β can be considered as constant. During the fixed annealing time of t , fixed amount of fluxes, r and s , transfer through Kirkendall marker plane.

It should be noted at this point that, since the derivation of intrinsic diffusion coefficients give the same relations as derived following the conventional route, the values estimated for interdiffusion coefficients following the physicochemical approach (Eq. (4.11)) and the relations derived by Wagner [13] or Sauer–Freise [11] as expressed in Eq. (4.13) (see Chapter 3 in Volume 1) will give the same values:

$$\tilde{D}(Y_B^*) = \frac{v_m^*}{2t(dY_B/dx)_{x^*}} \left[(1 - Y_B^*) \int_{x^*}^{x^*} \frac{Y_B}{v_m} dx + Y_B^* \int_{x^*}^{x^*+\infty} \frac{(1 - Y_B)}{v_m} dx \right]. \quad (4.13)$$

In fact, by substituting Eqs. (4.4a) and (4.4b) into Eq. (4.11), one can easily derive the relation expressed in Eq. (4.13) by following a few simple steps.

Similarly, integrated interdiffusion coefficients estimated from Eq. (4.12) will give the same value when following the relation derived by Wagner [13] that is expressed as

(see Chapter 3 of Volume 1 for the calculation procedure)

$$\begin{aligned} \tilde{D}_{\text{int}}^{\beta} = & \frac{(N_B^{\beta} - N_B^{-})(N_B^{+} - N_B^{\beta})}{N_B^{+} - N_B^{-}} \frac{(\Delta x_{\beta})^2}{2t} + \\ & \frac{\Delta x_{\beta}}{2t} \times \left[\frac{(N_B^{+} - N_B^{\beta}) \sum_{i=2}^{\beta-1} \frac{\nu_m^{\beta}}{\nu_i^{\beta}} (N_B^i - N_B^{-}) \Delta x_i + (N_B^{\beta} - N_B^{-}) \sum_{i=\beta+1}^{n-1} \frac{\nu_m^{\beta}}{\nu_i^{\beta}} (N_B^{+} - N_B^i) \Delta x_i}{N_B^{+} - N_B^{-}} \right]. \end{aligned} \quad (4.14)$$

As explained in Chapter 3 of Volume 1, the values of diffusion coefficients by following the conventional route are directly estimated from the compositions profiles. On the other hand, reaction–dissociation equations at the interfaces are considered in a physicochemical approach for the estimation of the same values. This has an added advantage in understanding the microstructology of the interdiffusion zone. In an interdiffusion zone, when a new phase layer β grows between two phases α and γ end-members, it has to nucleate for the growth by reaction–dissociation from interfaces I and II. In most material systems, nucleation barrier is reasonably high and therefore, after nucleation at the very initial stage, components simply join the existing grains after diffusion through the phase layer, leading to the continuous growth of the existing grains. Since the growth occurs from two different interfaces on either side of Kirkendall marker plane, a duplex morphology will be found when the marker plane is located in the middle of the product phase, as shown in a couple of examples in Fig. 4.2 [4,14]. It should be noted here that the analysis above is true only in the case of diffusion-controlled parabolic growth of the product phase, which can be established by a linear fit when time-dependent experimental data are plotted with respect to $(\Delta x_{\beta})^2$ vs. $2t$. This means that, although we discussed grain morphology above, we are not considering here the nucleation or reaction controlled process. This further means that we are considering the system in which reaction–dissociation process is fast enough such that the slow rate of diffusion of components through the phase layer controls the growth rate of the product phase.

4.2 ESTIMATION OF THE DIFFUSION PARAMETERS FOLLOWING PHYSICOCHEMICAL APPROACH

The analysis above explains that we estimate the same value of diffusion parameters when we follow the conventional route (i.e., directly from the composition profile) or the physicochemical approach. Now, we consider an example based on the experimental results to explain the steps one should follow in a physicochemical approach.

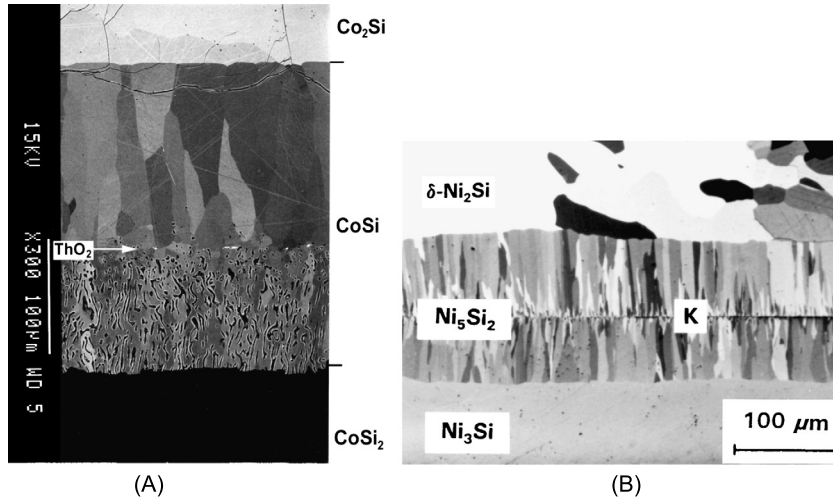


Figure 4.2 Growth of the product phase (A) CoSi in a $\text{Co}_2\text{Si}/\text{CoSi}_2$ diffusion couple annealed at 1000°C for 49 hours [4] and (B) Ni_5Si_2 in $\text{Ni}_2\text{Si}/\text{Ni}_3\text{Si}$ annealed at 800°C for 25 hours [14] diffusion couple with duplex morphology showing the growth of different sublayers from different interfaces.

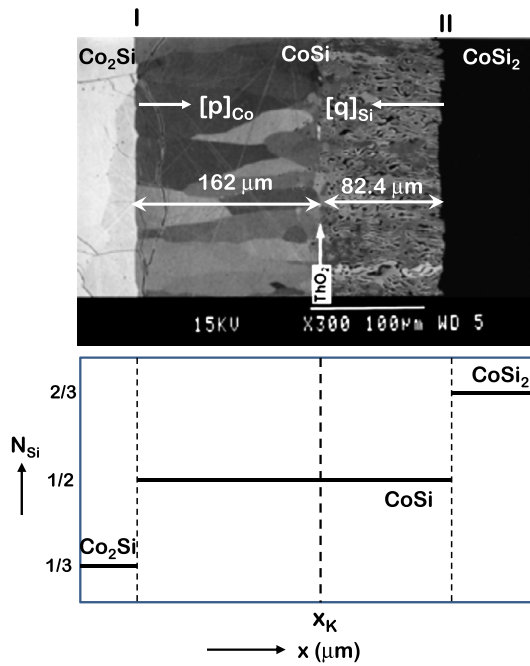


Figure 4.3 A schematic representation of the diffusion of components in a couple of $\text{Co}_2\text{Si}/\text{CoSi}_2$ in which CoSi is grown at the interface when annealed at 1100°C for 49 hours.

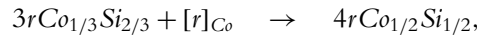
4.2.1 Growth of a Single Product Phase in an Interdiffusion Zone Between Two Other Compounds

Let us consider the growth of CoSi in a diffusion couple of Co₂Si/CoSi₂ that was annealed at 1100°C for 49 hours, as shown in Fig. 4.3. For the growth of the product phase, Co dissociates from the Co-rich Co₂Si phase at the interface I to produce the CoSi phase. Co then diffuses to the interface II and react with CoSi₂ to produce the same CoSi phase. Similarly, Si dissociates from the Si-rich CoSi₂ phase at interface II to produce CoSi. The dissociated Si diffuses to interface I and reacts with Co₂Si to produce CoSi. If we consider that the total diffusing amounts of components Co and Si are r and s mole/m² during the annealing time $t = 49$ hours, the reaction–dissociation at two interfaces can be written as

Interface I (Co₂Si/CoSi):



Interface II (CoSi/CoSi₂):



The total amount in moles of the product phases produced by the reaction–dissociation above can be related to the thickness of the sublayers on different sides of the marker plane utilizing the molar volume data calculated from known lattice parameter as

$$(2r + 4s)\nu_m^{\text{CoSi}} = \Delta x_{\text{CoSi}}^I, \quad (4.15a)$$

$$(4r + 2s)\nu_m^{\text{CoSi}} = \Delta x_{\text{CoSi}}^{II}. \quad (4.15b)$$

The thicknesses of the sublayers are mentioned in Fig. 4.3 as $\Delta x_{\text{CoSi}}^I = 162$ and $\Delta x_{\text{CoSi}}^{II} = 82.4$ μm. The actual length of $\Delta x_{\text{CoSi}}^{II}$ is 107 μm; however, it is reduced by 23% because of the presence of Kirkendall voids which are sometime (in some product phases) produced by supersaturated vacancies. The molar volume of the CoSi product phase is $\nu_m^{\text{CoSi}} = 6.6 \times 10^{-6}$ m³/mol [4]. Using these values, we estimate the values of r and s as 0.07 and 6.1 mol/m², respectively. The same values of r and s can also be estimated directly by solving the relations expressed in Eq. (4.3):

$$N_{\text{Si}}^- r + (1 - N_{\text{Si}}^-) s = \int_{x^-}^{x_K} \frac{N_{\text{Si}} - N_{\text{Si}}^-}{\nu_m^{\text{CoSi}}} dx = \frac{N_{\text{Si}}^{\text{CoSi}} - N_{\text{Si}}^-}{\nu_m^{\text{CoSi}}} \int_{x^-}^{x_K} dx = \frac{N_{\text{Si}}^{\text{CoSi}} - N_{\text{Si}}^-}{\nu_m^{\text{CoSi}}} \Delta x_{\text{CoSi}}^I,$$

$$N_{Si}^+ r + (1 - N_{Si}^+) s = \int_{x_K}^{x^{+\infty}} \frac{N_{Si}^+ - N_{Si}}{\nu_m^{CoSi}} dx = \frac{N_{Si}^+ - N_{Si}^{CoSi}}{\nu_m^{CoSi}} \int_{x_K}^{x^{+\infty}} dx = \frac{N_{Si}^+ - N_{Si}^{CoSi}}{\nu_m^{CoSi}} \Delta x_{CoSi}^I,$$

where $N_{Si}^- = 1/3$, $N_{Si}^+ = 2/3$, and $N_{Si}^{CoSi} = 1/2$. The following diffusion parameters can be estimated utilizing the relations expressed in Eqs. (4.9) and (4.12):

$$\frac{D_{Si}^*}{D_{Co}^*} = \frac{s}{r} = \frac{6.1}{0.07} = 87,$$

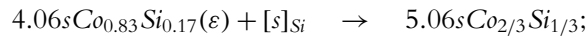
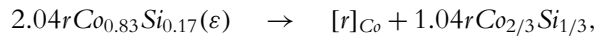
$$\begin{aligned} \tilde{D}_{int}^{CoSi} &= \frac{\nu_m^{CoSi}}{2t} [N_{Si}^{CoSi} r + N_{Co}^{CoSi} s] \Delta x_{\beta} \\ &= \frac{6.60 \times 10^{-6}}{2 \times 49 \times 60 \times 60} \left[\frac{1}{2} \times 0.07 + \frac{1}{2} \times 6.1 \right] (162 + 82.4) \times 10^{-6} \\ &= 1.41 \times 10^{-14} \text{ m}^2/\text{s}. \end{aligned}$$

It must be apparent from the reaction–dissociation equations that the product grows differently from two different interfaces, leading to duplex morphology.

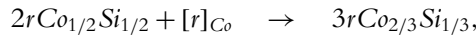
4.2.2 Growth of a Single Product Phase in an Interdiffusion Zone Between Two End-Members of a Diffusion Couple With Phase Mixture

As shown in Fig. 4.4, the product phase Co_2Si grows in a diffusion couple of $\text{Co}_{0.81}\text{Si}_{0.19}$ and $\text{Co}_{0.52}\text{Si}_{0.48}$. According to the Co–Si phase diagram [15], the end-member $\text{Co}_{0.81}\text{Si}_{0.19}$ is a phase mixture of ε -Co(Si) solid solution with a composition of $\text{Co}_{0.83}\text{Si}_{0.17}$ at 1100°C and Co_2Si . The alloy $\text{Co}_{0.52}\text{Si}_{0.48}$ is a mixture of Co_2Si and CoSi . Since the product phase is Co_2Si , the same phase from the end-members of the diffusion couple will join directly, depending on the amounts (that can be found by the lever rule) of ε -Co(Si) solid solution in one end-member and CoSi in another end-member which are consumed by the reaction dissociation process. The reaction–dissociation equations at the interfaces can be written as [8]

Interface I:



Interface II:



$$(1.3r + 5.6s)v_m^{Co_2Si} = \Delta x_{Co_2Si}^I \quad (4.16a)$$

A similar procedure needs to be followed for the growth of the product phase from interface II. $(3r + 3s)$ moles of Co_2Si are grown by the reaction and dissociation processes. At the same time, some amount is added directly. Since $(2r + 4s)$ moles of $CoSi$ are consumed, following the lever rule, the number of moles of the Co_2Si phase from the alloy $Co_{0.52}Si_{0.48}$ that will be directly added can be written as $\frac{0.5-0.48}{0.48-1/3} \times (2r + 4s) = 0.136 \times (2r + 4s)$. Therefore, the sublayer thickness of Co_2Si that is grown from interface II can be written as

$$[(3r + 3s) + 0.136(2r + 4s)]v_m^{Co_2Si} = \Delta x_{Co_2Si}^{II} \quad (4.16b)$$

$$(3.3r + 3.5s)v_m^{Co_2Si} = \Delta x_{Co_2Si}^{II}$$

The thicknesses of the sublayers, as mentioned in Fig. 4.4, are $\Delta x_{Co_2Si}^I = 147 \mu m$ and $\Delta x_{Co_2Si}^{II} = 309 \mu m$. Using the molar volume value of Co_2Si , that is, $v_m^{Co_2Si} = 6.56 \times 10^{-6} m^3/mol$, the values of r and s are estimated as 13.3 and 0.915, respectively. The integrated diffusion coefficient and the ratio of the tracer diffusion coefficients are estimated from Eqs. (4.9) and (4.12) for an annealing time of 100 hours as

$$\frac{D_{Si}^*}{D_{Co}^*} = \frac{s}{r} = 0.07,$$

$$\begin{aligned} \tilde{D}_{int}^{Co_2Si} &= \frac{v_m^{Co_2Si}}{2t} [N_{Si}^{Co_2Si} r + N_{Co}^{Co_2Si} s] \Delta x_{Co_2Si} \\ &= \frac{6.56 \times 10^{-6}}{2 \times 100 \times 60 \times 60} \left[\frac{1}{3} \times 13.3 + \frac{2}{3} \times 0.915 \right] (147 + 309) \times 10^{-6} \\ &= 2.1 \times 10^{-14} m^2/s. \end{aligned}$$

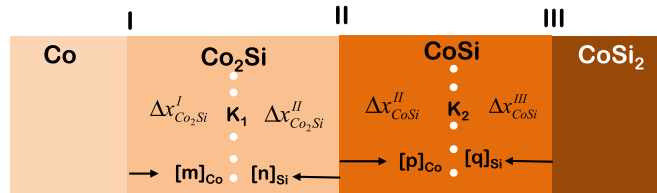
4.2.3 Simultaneous Growth of the Product Phases in an Interdiffusion Zone and the Use of Physicochemical Approach

The reaction–diffusion process is complicated when more than one phase grows in an interdiffusion zone. Instead of estimating the diffusion parameters from the thickness of the product phase, we shall treat it just the opposite. Utilizing the previously estimated integrated diffusion coefficients of the product phases and the ratios of diffusivities of the components in these phases, we shall estimate the thicknesses of the sublayers and predict the microstructure one should expect. With this aim, we consider two different systems, explaining the difference in microstructural evolution.

First, let us consider the Co–Si system in which two phases Co_2Si and $CoSi$ grow between Co and $CoSi_2$. The data required for the analysis are given in Table 4.1 which were measured at $1100^\circ C$ [4]. A schematic diagram in Fig. 4.5 describes the diffusion

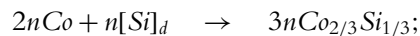
Table 4.1 Integrated diffusion coefficients and ratio of tracer diffusivities of Si and Co at 1100°C along with the molar volumes of Co₂Si and CoSi [4]

	Phases	
	Co ₂ Si	CoSi
$\tilde{D}_{\text{int}}$ [m ² /s]	$(1.5 \pm 0.5) \times 10^{-14}$	$(4.6 \pm 0.3) \times 10^{-14}$
$\frac{D_{\text{Si}}^*}{D_{\text{Co}}^*} = \left(\frac{\bar{v}_{\text{Co}} D_{\text{Si}}}{\bar{v}_{\text{Si}} D_{\text{Co}}} \right)$	0.06 ± 0.025	35 ± 15
v_m [m ³ .mole ⁻¹]	6.56×10^{-6}	6.60×10^{-6}

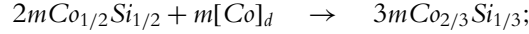
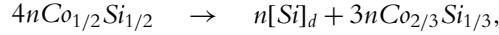
**Figure 4.5** A schematic diagram describing the diffusion of components in a Co/CoSi₂ diffusion couple.

of components and growth of the phases. From the latest finding on Kirkendall effect, we know that all the phases might have a Kirkendall plane, which should be considered initially for the analysis [4]. We consider that the total amounts of Co and Si that cross Kirkendall marker plane in the Co₂Si phase, which can be related to the intrinsic diffusion coefficients of the components, are $[m]_{\text{Co}}$ and $[n]_{\text{Si}}$ mole/m², respectively. At the same annealing time, the total amounts of Co and Si that cross Kirkendall marker plane in the CoSi phase contributing to the growth of the same phase are $[p]_{\text{Co}}$ and $[q]_{\text{Si}}$ mole/m², respectively. Co₂Si phase grows at interface I because of the reaction of Co with the diffused Si after dissociation at interface II. At interface II, Co₂Si grows because of the dissociation of Si from the CoSi phase and also the reaction of Co with CoSi after diffusing from interface I. On the other side, at interface II, CoSi grows because of the dissociation of Co from Co₂Si and also because of the reaction of Si with the same phase after diffusion from interface III. The dissociated Co at interface II diffuses through the CoSi product phase to react with CoSi₂ for the production of CoSi. At the same time, Si dissociates from the CoSi₂ phase at interface III to yield the CoSi product phase. It must be clear from the description above that the phases grow from interfaces I and III depending on the diffusion rates of the components. On the other hand, the growth process is complicated at interface II. At this interface, both product phases grow by consuming the other phase and also get consumed because of growth of the other phase. Reaction–dissociation equations can be written as

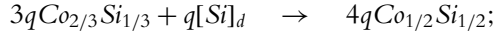
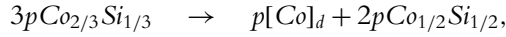
Interface I:



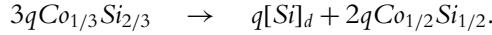
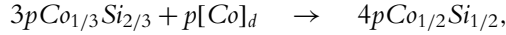
Interface II (Co₂Si – side):



Interface II (CoSi side):



Interface III:



The reaction equations written above indicate that for every mole of diffused component, the amount of Co₂Si produced at interface I is $3n$ moles and that at interface II is $(3m + 3n)$ moles. However, at the same time $(3p + 3q)$ moles of Co₂Si are consumed at interface II. At the same interface II, $(2p + 4q)$ moles of CoSi are produced and $(4n + 2m)$ moles get consumed. $(4p + 2q)$ moles of CoSi are produced at interface III. Considering the molar volume of the phases, the numbers of moles of the product phases are related to the thicknesses of the sublayers by

$$\begin{aligned} v_m^{\text{Co}_2\text{Si}} \times 3n &= \Delta x_{\text{Co}_2\text{Si}}^I, \\ v_m^{\text{Co}_2\text{Si}} \times (3m + 3n - 3p - 3q) &= \Delta x_{\text{Co}_2\text{Si}}^{II}, \\ v_m^{\text{CoSi}} \times (2p + 4q - 4n - 2m) &= \Delta x_{\text{CoSi}}^{II}, \\ v_m^{\text{CoSi}} \times (4p + 2q) &= \Delta x_{\text{CoSi}}^{III}. \end{aligned} \quad (4.17a)$$

The integrated diffusion coefficients can be expressed as [9]

$$\begin{aligned} \tilde{D}_{\text{int}}^{\text{Co}_2\text{Si}} &= \frac{v_m^{\text{Co}_2\text{Si}}}{2t} [N_{\text{Si}}^{\text{Co}_2\text{Si}} m + N_{\text{Co}}^{\text{Co}_2\text{Si}} n] (\Delta x_{\text{Co}_2\text{Si}}^I + \Delta x_{\text{Co}_2\text{Si}}^{II}), \\ \tilde{D}_{\text{int}}^{\text{CoSi}} &= \frac{v_m^{\text{CoSi}}}{2t} [N_{\text{Si}}^{\text{CoSi}} p + N_{\text{Co}}^{\text{CoSi}} q] (\Delta x_{\text{CoSi}}^{II} + \Delta x_{\text{CoSi}}^{III}). \end{aligned} \quad (4.17b)$$

The ratio of the diffusivities can be expressed as

$$\begin{aligned} \left. \frac{D_{\text{Si}}^*}{D_{\text{Co}}^*} \right|_{\text{Co}_2\text{Si}} &= \left. \frac{\bar{v}_{\text{Co}} D_{\text{Si}}}{\bar{v}_{\text{Si}} D_{\text{Co}}} \right|_{\text{Co}_2\text{Si}} = \frac{n}{m}, \\ \left. \frac{D_{\text{Si}}^*}{D_{\text{Co}}^*} \right|_{\text{CoSi}} &= \left. \frac{\bar{v}_{\text{Co}} D_{\text{Si}}}{\bar{v}_{\text{Si}} D_{\text{Co}}} \right|_{\text{CoSi}} = \frac{q}{p}. \end{aligned} \quad (4.17c)$$

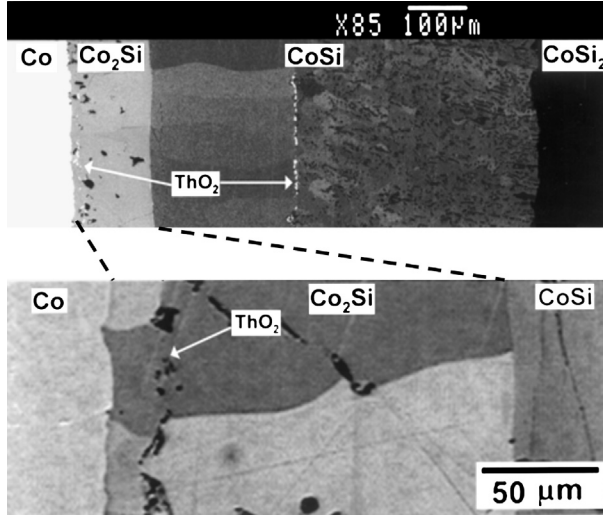


Figure 4.6 Interdiffusion zone of a Co/CoSi₂ diffusion couple annealed at 1100°C for 100 hours [4].

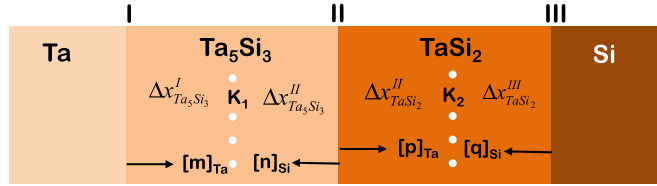


Figure 4.7 A schematic representation of the diffusion of components in a Ta/Si diffusion couple.

Using the data as listed in Table 4.1, the different parameters are estimated, after solving Eqs. (4.17) and using the annealing time of 100 hours, as

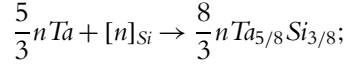
$$\begin{aligned}\Delta x_{Co_2Si}^I &= 32 \mu\text{m}, & \Delta x_{Co_2Si}^{II} &= 133 \mu\text{m}, & \Delta x_{CoSi}^{II} &= 168.5 \mu\text{m}, \\ \Delta x_{CoSi}^{III} &= 294.5 \mu\text{m}, \\ m &= 26.8, & n &= 1.6, & p &= 0.6, & \text{and} & q &= 21.0 \text{ mol/m}^2.\end{aligned}$$

The most important fact to be noted here is that all the sublayers, especially adjacent to interface II, have positive values despite being consumed by the other phase during growth. This indicates that we should find Kirkendall marker plane in both phases, as is indeed found experimentally. This is the reason for finding a duplex morphology in both phases, as shown in Fig. 4.6.

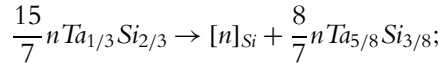
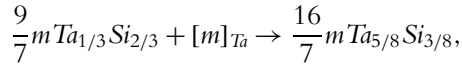
Next, we consider the Ta–Si system to show another situation. Ta–Si system has four intermetallic compounds, however, only two phases (TaSi₂ and Ta₅Si₃) grow in the interdiffusion zone when annealed at 1250°C for 9 hours because of very slow growth

kinetics of the other phases [16]. The schematic representation of the growth process is explained in Fig. 4.7. Following a similar line of discussion, as already explained above for the growth of the phases in the interdiffusion zone, the reaction–dissociation equations at the interfaces can be written as

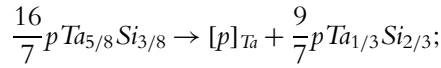
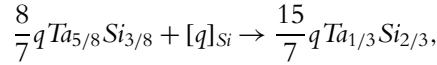
Interface I:



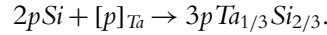
Interface II (Ta₅Si₃ side):



Interface II (TaSi₂ side):



Interface III:



The following sublayer thicknesses with respect to reaction–dissociation equations written above can be written as:

$$\begin{aligned} \frac{8}{3}n \times v_m^{Ta_5Si_3} &= \Delta x_{Ta_5Si_3}^I, \\ \left[\left(\frac{16}{7}m + \frac{8}{7}n \right) - \left(\frac{16}{7}p + \frac{8}{7}q \right) \right] \times v_m^{Ta_5Si_3} &= \Delta x_{Ta_5Si_3}^{II}, \\ \left[\left(\frac{15}{7}q + \frac{9}{7}p \right) - \left(\frac{15}{7}n + \frac{9}{7}m \right) \right] \times v_m^{TaSi_2} &= \Delta x_{TaSi_2}^{II}, \\ 3p \times v_m^{TaSi_2} &= \Delta x_{TaSi_2}^{III}. \end{aligned} \quad (4.18a)$$

The diffusion parameters can be expressed as

$$\begin{aligned} \tilde{D}_{\text{int}}^{Ta_5Si_3} &= \frac{v_m^{Ta_5Si_3}}{2t} [N_{Ta}^{Ta_5Si_3} n + N_{Si}^{Ta_5Si_3} m] (\Delta x_{Ta_5Si_3}^I + \Delta x_{Ta_5Si_3}^{II}), \\ \tilde{D}_{\text{int}}^{TaSi_2} &= \frac{v_m^{TaSi_2}}{2t} [N_{Ta}^{TaSi_2} q + N_{Si}^{TaSi_2} p] (\Delta x_{TaSi_2}^{II} + \Delta x_{TaSi_2}^{III}), \end{aligned} \quad (4.18b)$$

Table 4.2 Integrated diffusion coefficients and ratios of diffusivities of the components at 1250°C along with the data of molar volumes of Ta₅Si₃ and TaSi₂

	Phase	
	Ta ₅ Si ₃	TaSi ₂
$\tilde{D}_{\text{int}}$ [m ² /s]	1.41×10^{-16}	5.02×10^{-14}
$\frac{D_{\text{Si}}^*}{D_{\text{Ta}}^*} = \left(\frac{\bar{v}_{\text{Ta}} D_{\text{Si}}}{\bar{v}_{\text{Si}} D_{\text{Ta}}} \right)$	5.8	1.1
v_m [m ³ ·mole ⁻¹]	9.48×10^{-6}	8.71×10^{-6}

$$\left. \frac{D_{\text{Si}}^*}{D_{\text{Ta}}^*} \right|_{\text{Ta}_5\text{Si}_3} = \frac{n}{m}, \quad (4.18c)$$

$$\left. \frac{D_{\text{Si}}^*}{D_{\text{Ta}}^*} \right|_{\text{TaSi}_2} = \frac{q}{p}.$$

We solve for the unknown values using data listed in Table 4.2 for 9 hours as

$$\Delta x_{\text{Ta}_5\text{Si}_3}^I = 64.07, \quad \Delta x_{\text{Ta}_5\text{Si}_3}^{II} = -63.52, \quad \Delta x_{\text{TaSi}_2}^{II} = 42.7$$

$$\text{and } \Delta x_{\text{TaSi}_2}^{III} = 78.15 \mu\text{m},$$

$$m = 0.437, \quad n = 2.535, \quad p = 2.99, \quad \text{and } q = 3.29 \text{ mol/m}^2.$$

The main difference compared to the Co–Si system discussed above is that one of the sublayers $\Delta x_{\text{Ta}_5\text{Si}_3}^{II}$ has a negative value. It indicates that this sublayer is consumed completely along with a large part of the $\Delta x_{\text{Ta}_5\text{Si}_3}^I$ such that the total thickness of the Ta₅Si₃ phase is $\Delta x_{\text{Ta}_5\text{Si}_3}^I + \Delta x_{\text{Ta}_5\text{Si}_3}^{II} = 0.55 \mu\text{m}$. This further means that a uniform morphology is expected in this phase. On the other hand, both sublayers of TaSi₂ have positive values, and a duplex morphology is expected in this phase. This is indeed found in the Ta/Si diffusion couple, as shown in Fig. 4.8.

4.3 EVOLUTION OF MICROSTRUCTURE DEPENDING ON THE LOCATION OF KIRKENDALL MARKER PLANE

Based on the explanations given in previous sections, we can explain/predict different types of morphologies depending on the location of Kirkendall plane, which is controlled by the relative mobilities of the components. Different locations of Kirkendall marker plane in an interdiffusion zone of a binary system with two phase layers is considered. The developed understanding can be easily extended to single or multiphase and multicomponent systems. As shown in Fig. 4.9, four different examples can be found, depending on relative mobilities of the components and whether end-members of the diffusion couple are prepared from pure components or an alloy.

Suppose two phases, $\alpha\text{-A}_{1-m}\text{B}_m$ and $\beta\text{-A}_{1-n}\text{B}_n$, have grown in the interdiffusion zone of an imaginary diffusion couple made from pure components A and B. In a

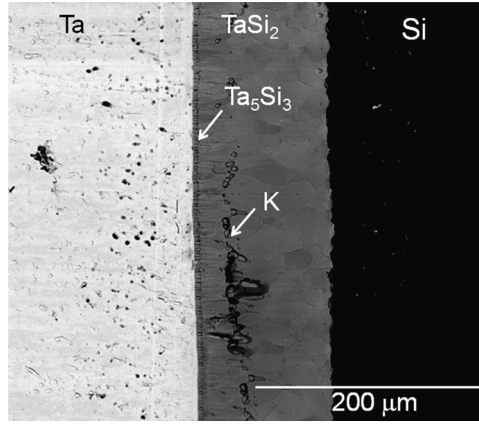


Figure 4.8 A diffusion couple of Ta/Si annealed at 1250°C for 9 hours [16].

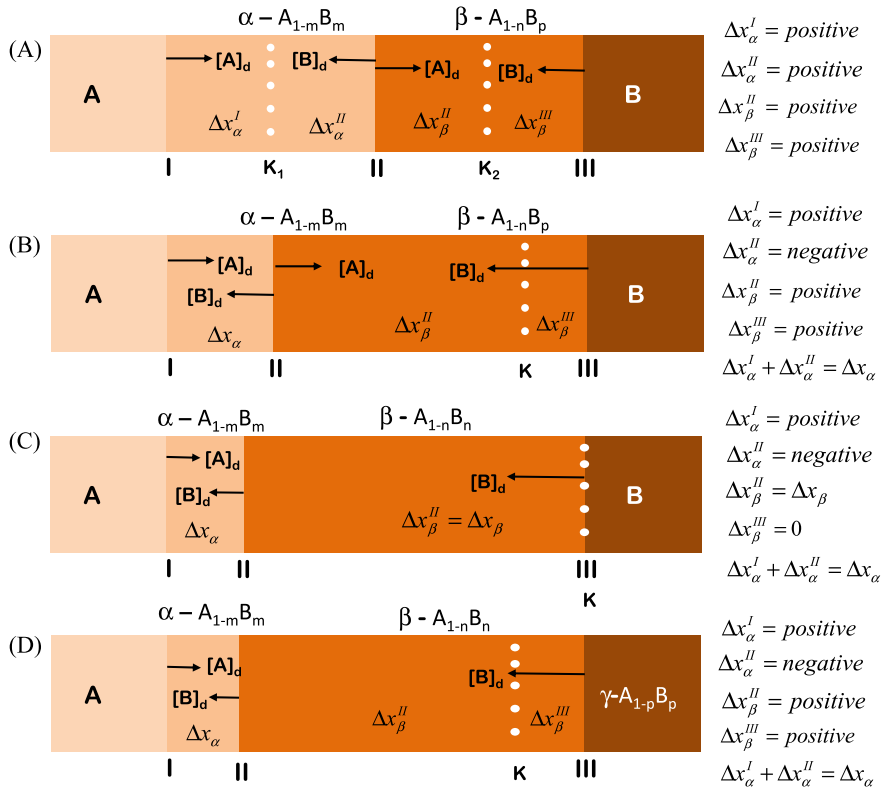


Figure 4.9 Imaginary interdiffusion zone with different situations depending on relative mobilities of the components and end-member compositions.

special case, as shown in Fig. 4.9A, the marker planes can be present in both phases such that inert particles placed at the initial bonding interface bifurcates into two different planes. Therefore, the thickness of all the sublayers will be positive, and duplex morphologies are expected in both phases. Experimental evidence is already shown in Fig. 4.6. In most other examples, a single marker plane is found in the whole interdiffusion zone, as illustrated in Figs. 4.9(B)–(D). Different situations might emerge, depending on the relative mobilities of the components and end-member compositions. As shown in Fig. 4.9(B), suppose that in the β -phase B has higher diffusion rate than A. Therefore, the location of Kirkendall marker plane in the β -phase is expected to be towards the end-member B. This further indicates that the growth rate of the same phase is higher from interface II compared to the growth from interface III. Since the growth rate of β is higher at interface II, this will consume the α -phase at a higher rate that would otherwise grow from the same interface. It could lead to complete consumption of Δx_{α}^{II} along with some part of Δx_{α}^I . If the thicknesses of the sublayers are estimated from the diffusion coefficients, Δx_{α}^{II} will have a negative value in this situation. A similar situation was found in the Ta–Si system as shown in Fig. 4.8. Therefore, the β -phase will have a duplex morphology since it grows from both interfaces, whereas the α -phase will have a single grain morphology since it grows from one interface only. There can be another situation as shown in Fig. 4.9(C), in which the β -phase might grow because of diffusion of B only such that the diffusion rate of A is negligible. Therefore, $\Delta x_{\beta}^{III} = 0$ and $\Delta x_{\beta}^{II} = \Delta x_{\beta}$. In this case also the growth rate of the β -phase at interface II might be so high such that it consumes part of the α -phase sublayer that would grow otherwise from the same interface. Along with that, a part of the α -phase that grows from interface I is also consumed. Since the whole thickness of the β -phase is grown from interface II and the α -phase from interface I, both these phases will have uniform morphology. Similar diffusion rates through the phases, however, will create different morphological evolution if the end-members are made of an alloy or compound instead of pure components, as shown in Fig. 4.9(D). Let us consider that α and β grows between A and compound γ -A_{1-p}B_p. When component B dissociates from γ , it will produce the β -phase at interface III. Therefore, although B has a much higher diffusion rate compared to A in β , this phase will have a duplex morphology, unlike in the previous case.

4.4 A FEW EXAMPLES OF MORPHOLOGICAL EVOLUTIONS AND INDICATIONS OF DIFFUSION RATES OF COMPONENTS

Based on the description given in the previous sections, it must be clear that morphological evolution mainly depends on the growth from different interfaces depending on relative mobilities of the components, irrespective of the diffusion mechanisms such as lattice or grain boundary and dimension of the material systems such as bulk, thin film,

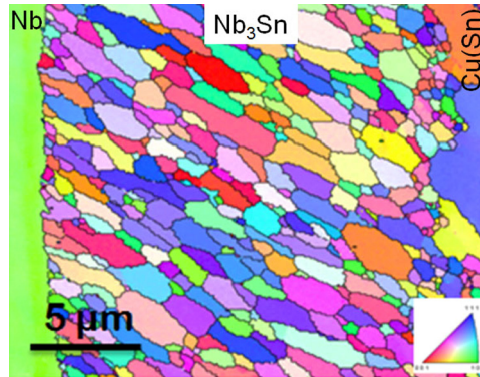


Figure 4.10 Interdiffusion zone of an Nb/Cu(Sn) diffusion couple in which Nb₃Sn is grown as the product phase.

or nanomaterials. In general, nucleation barrier for a new compound in the interdiffusion zone is high, and diffusing components join the already nucleated grain at very initial stage. Therefore, in most systems, as shown in the microstructures in Co–Si and Ta–Si systems, long grains are found from one interface to another or Kirkendall marker plane, depending on the location of the marker plane in a particular phase. However, there are a few systems, in which grain nucleate repeatedly. As shown in Fig. 4.10, when Nb was coupled with Cu(Sn) bronze alloy for the growth of Nb₃Sn superconductor intermetallic compound, Kirkendall marker plane was located at the Nb₃Sn/Cu(Sn) interface, indicating that the phase is grown by the diffusion of Sn through the product phase and by reaction with Nb at the Nb/Nb₃Sn interface. It is evident that the interdiffusion zone comprises small grains instead of continuous grains across the interdiffusion zone, indicating the ease of nucleation. Similar behavior was noticed for the growth of the product phase in the Ni/Sn system.

The physicochemical model is applicable for the growth of phases in both metallic and nonmetallic systems as long as the diffusion controlled process prevails. The microstructural evolution of a product phase might indicate the diffusion mechanism of components in which inert particles are not used to detect the location of Kirkendall marker plane. In fact, suitable markers are not possible to incorporate in thin films or nanomaterials. Too small particles might not act as suitable Kirkendall markers and could be dragged by the grain boundaries [17]. High-resolution electron microscopes could be very handy in this regard which can reveal the microstructure at nanoscale. One such example is shown in Fig. 4.11(A) [18], where an Al₂O₃ layer has grown on Zr-doped β -NiAl bond coat between the bond coat and yttria stabilized zirconia (YSZ). Al₂O₃ is a preferred oxidation resistant layer because of the very low diffusion rate of oxygen through this phase. This product phase has grown with columnar gains across the interdiffusion zone by the diffusion of Al, indicating the location of the marker plane at

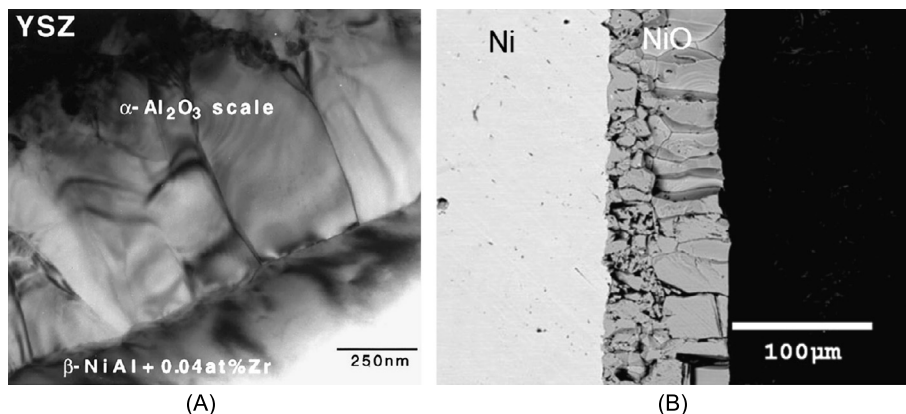


Figure 4.11 (A) TEM bright field image of the Al_2O_3 scale that is grown on Zr-doped β -NiAl after annealing at 1200°C for 2 hours [18] and (B) growth of NiO on Ni substrate at 1200°C for 9 hours.

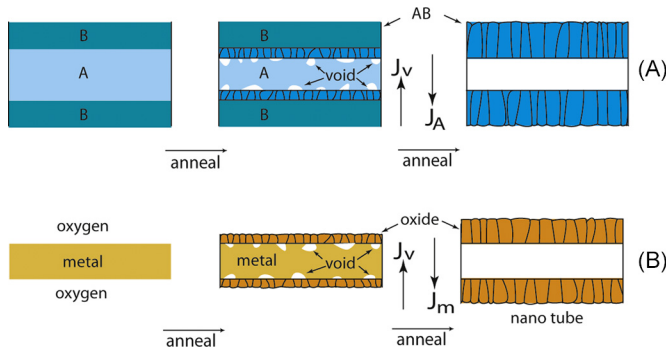


Figure 4.12 Formation of nanotube between (A) A–B and (B) metal–oxygen is explained.

the $\text{Al}_2\text{O}_3/\beta$ -NiAl. In most oxides, lattice diffusion of oxygen is negligible, and one should expect a similar microstructure. However, a duplex morphology is found in an NiO layer, as shown in Fig. 4.11(B) during oxidation of Ni indicating diffusion of both Ni and O. The outer layer consists of longer columnar grains that are grown from NiO/oxygen interface by the diffusion of Ni. The other sublayer grows at the Ni/NiO interface because of diffusion of oxygen. Studies indicate that oxygen could diffuse via grain boundaries in this phase [19].

Formation of voids due to Kirkendall effect during diffusion-controlled growth of a product phase between two dissimilar materials is a major concern in many applications. On the other hand, utilizing this adverse side of Kirkendall effect, nanoporous materials and nanotubes are being produced. Numerous studies have been published that described production of these nanomaterials utilizing this concept. These can be broadly

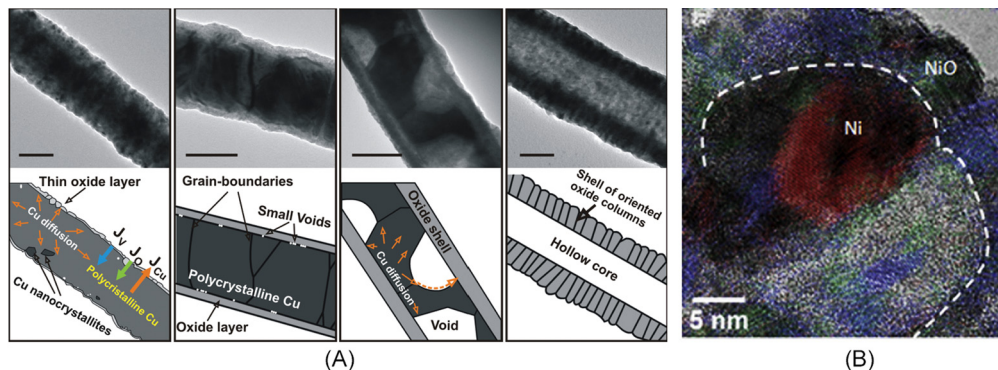


Figure 4.13 (A) Growth of Cu-oxide with an oriented microstructure by Kirkendall effect [20] and (B) growth of NiO with an oriented microstructure [21]. A dotted line is drawn to guide the interface between Ni and NiO.

divided into two types. In one type, nanorod/wire of material A is coated with another material B such that a compound of AB is produced at the interface by solid-state diffusion. In the formation of nanotubes, as shown in Fig. 4.12(A), materials are chosen such that A has a much higher diffusion rate compared to the negligible diffusion rate of B through the AB product phase. Further, the amounts of A and B are chosen such that both are consumed completely to produce a single-phase product layer. In another type, as shown in Fig. 4.12(B), nanorods/wires of material A are oxidized such that an oxide nanotubes are grown after complete consumption of A. Therefore, in both cases, the core material diffuses out through the product phase to react with another material at the AB/B or oxide/oxygen interface for growth of the product phase. In the latter example, an oriented microstructural growth of the product phase is reported during the production of the Cu-oxide layer from Cu nanowires [20], as shown in Fig. 4.13(A). A similar feature is clearly seen in a high-resolution transmission electron micrograph of an NiO layer during the production of nanoporous structure from Ni nanoparticles [21], as shown in Fig. 4.13(B). Based on the discussion in this chapter, we know that this is rather expected in a diffusion-controlled growth process.

REFERENCES

- [1] A. Paul, T. Laurila, V. Vuorinen, S. Divinski, *Thermodynamics, Diffusion and the Kirkendall Effect in Solids*, Springer, Heidelberg, Germany, 2014.
- [2] M.J.H. van Dal, M.C.L.P. Pleumeekers, A.A. Kodentsov, F.J.J. van Loo, Intrinsic diffusion and Kirkendall effect in Ni–Pd and Fe–Pd solid solutions, *Acta Materialia* 48 (2000) 385–396.
- [3] M.J.H. van Dal, A.M. Gusak, C. Cserháti, A.A. Kodentsov, F.J.J. van Loo, Spatio-temporal instabilities of the Kirkendall marker planes during interdiffusion in β' -AuZn, *Philosophical Magazine A* 82 (2002) 943–954.

- [4] A. Paul, M.J.H. van Dal, A.A. Kodentsov, F.J.J. van Loo, The Kirkendall effect in multiphase diffusion, *Acta Materialia* 52 (2004) 623–630.
- [5] A. Paul, A.A. Kodentsov, F.J.J. van Loo, Bifurcation of the Kirkendall plane during interdiffusion in the intermetallic compound β -NiAl, *Acta Materialia* 52 (2004) 4041–4048.
- [6] A. Paul, A.A. Kodentsov, F.J.J. van Loo, Intermetallic growth and Kirkendall effect manifestations in Cu/Sn and Au/Sn diffusion couples, *Zeitschrift für Metallkunde* 95 (2004) 913–920.
- [7] A.A. Kodentsov, A. Paul, F.J.J. van Loo, Bifurcation of the Kirkendall plane and patterning in reactive diffusion, *Zeitschrift für Metallkunde* 95 (2004) 258–260.
- [8] A. Paul, A.A. Kodentsov, F.J.J. Van Loo, Physico-chemical analysis of compound growth in a diffusion couple with two-phase end-members, *Intermetallics* 14 (2006) 1428–1432.
- [9] C. Ghosh, A. Paul, A physico-chemical approach in binary solid-state interdiffusion, *Acta Materialia* 55 (2007) 1927–1939.
- [10] C. Ghosh, A. Paul, Different phenomenological theories and their abilities to describe the interdiffusion process in a binary system during multiphase growth, *Acta Materialia* 57 (2009) 493–502.
- [11] F. Sauer, V. Freise, Diffusion in binären gemischen mit Volumenänderung, *Zeitschrift für Elektrochemie* 66 (1962) 353–363.
- [12] F.J.J. van Loo, On the determination of diffusion coefficients in a binary metal system, *Acta Metallurgica* 18 (1970) 1107–1111.
- [13] C. Wagner, The evaluation of data obtained with diffusion couples of binary single-phase and multi-player systems, *Acta Metallurgica* 17 (1969) 99–107.
- [14] J.H. Gülpen, A.A. Kodentsov, F.J.J. van Loo, Growth of silicides in Ni–Si and Ni–SiC bulk diffusion couples, *Zeitschrift für Metallkunde* 86 (1995) 530–539.
- [15] K. Ishida, T. Nishizawa, M.E. Schlesinger, *Journal of Phase Equilibria* 12 (1991) 578–586.
- [16] S. Roy, A. Paul, Growth mechanism of tantalum silicides by interdiffusion, *Philosophical Magazine* 92 (2012) 4215–4229.
- [17] G.J. van Gorp, W.F. van der Weg, D. Sigurd, Interactions in the Co/Si thin-film system. II. Diffusion-marker experiments, *Journal of Applied Physics* 49 (1978) 4011–4020.
- [18] B.A. Pint, I.G. Wright, W.Y. Lee, Y. Zhang, K. Prüßner, K.B. Alexander, Substrate and bond coat compositions: factors affecting alumina scale adhesion, *Materials Science and Engineering A* 245 (1998) 201–211.
- [19] R. Peraldi, D. Monceau, B. Pieraggi, Correlations between growth kinetics and microstructure for scales formed by high-temperature oxidation of pure nickel. II. Growth kinetics, *Oxidation of Metals* 58 (2002) 275–295.
- [20] A.A. El Mel, Marie Buffière, P.Y. Tessier, S. Konstantinidis, W. Xu, I. Wathuthanthri, C.H. Choi, C. Bittencourt, R. Snyders, Highly ordered hollow oxide nanostructures: the Kirkendall effect at the nanoscale, *Small* 9 (2013) 2838–2843.
- [21] J.G. Railsback, A.C. Jhonston-Peck, J. Wang, J.B. Tracy, Size-dependent nanoscale Kirkendall effect during the oxidation of nickel nanoparticles, *ACS Nano* 4 (2010) 1913–1920.

CHAPTER 5

Electromigration in Metallic Materials and Its Role in Whiskering

Praveen Kumar

Indian Institute of Science, Bangalore, India

5.1 INTRODUCTION TO ELECTROMIGRATION

Transfer of mass and energy is at the heart of many physical and chemical processes that form the backbone of the modern science and technology. Transport studies help in understanding these processes and reveal the underlying physics that governs the process dynamics. In this context, electromigration is basically an electric field driven diffusion controlled transport phenomenon [1–5], wherein metal atoms (or atoms in a conductor) are pushed in the opposite direction of the applied electric field [5–7], or sometimes along the direction of electric field, e.g., in the case of liquid Ga, Sn, etc. [8–10]. On application of an electric potential across a conductor, electrons start flowing from the cathode to the anode; during this process they collide with the metal atoms/ions and transfer their momentum (partially or completely) to the colliding atoms/ions. In general, at low current densities, or equivalently small electric field, the total momentum transferred from all the colliding electrons to an ion/atom is not sufficient to “transport” the atom from its current position to the next. However, above a critical current density, e.g., $>10^4$ A/cm² for several solid metals, the probability of displacing an atom out of its original site to a new equilibrium site becomes significant. So, the atoms get pushed towards the anode by the force of the flowing electrons; this force is called the *electron wind force*. In addition, since metals are usually stable in cationic or positively charged states, they get electrostatically attracted due to Coulomb force towards the negative electrode (i.e., cathode). This force is called the *direct force*. So, the electromigration force is the net resultant of these two opposing forces. Atoms move in the direction of the dominating, or the higher of the two forces; we will present a quantitative description of electromigration driven mass transport in Section 5.1.1. It should be noted that the “form” of the metallic material does not change due to electromigration and such material transport is not driven by chemical reaction. Hence, the motion of ions in an electrolytic bath, during corrosion, etc., is not classified as *classical* electromigration. In this chapter, we focus only on the classical electromigration.

The phenomenon of atomic movement under electromigration force is schematically shown in Fig. 5.1(A). As mentioned earlier, in case of electromigration in most solid metals, the wind force is generally larger than the direct force [6,11,12], thereby

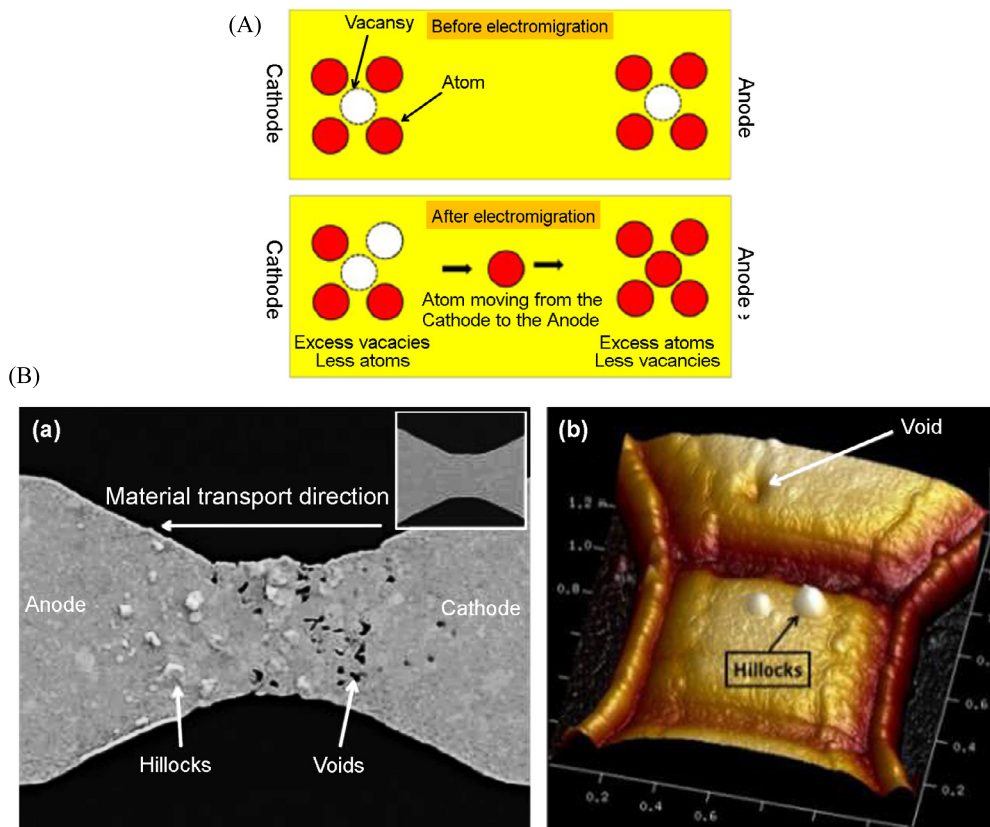


Figure 5.1 (A) A schematic diagram of the electromigration driven atomic transport process. (B) A micrograph obtained using scanning electron microscope (SEM) (left image) and 3D profile obtained using an atomic force microscope (AFM) (right image) of metal lines, showing formation of voids and hillocks due to electromigration [19]. The inset in the left image of (B) shows a low magnification image of the as-fabricated sample.

atoms in solid metallic materials move from the cathode to the anode region, i.e., in the direction opposite to the electric field. Through such mass transport, tensile stresses are generated at the cathode and hence voids are created in nearby regions, as the atoms leave their sites. These transported atoms occupy new sites near the anode, generating compressive stress and eventually creating material pile up or hillocks as well as whiskers in the vicinity of the anode. As an example, Fig. 5.1(B) shows micrographs of voids and hillocks created by electromigration in a metal line.

As the voids and hillocks (or whiskers) grow with time in the conductor, electromigration may lead to damage in microelectronic devices by resulting in an open circuit and a short circuit near the cathode and the anode, respectively. Therefore, electromi-

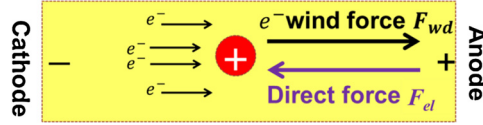


Figure 5.2 Schematic illustration of the two electromigration forces, namely wind force and direct force, acting on a positively charged metal ion.

gration in the current carrying thin film structures has been a major reliability issue since the advent of the modern microelectronics. Therefore, a major objective of electromigration research for a long time has aptly been to increase reliability of interconnects by minimizing electromigration. This led to the proposal as well as implementation of several innovative solutions, such as minor alloying [13,14], transition to interconnects with high melting temperatures (such as adoption of Cu interconnects in place of Al interconnects) [15,16], improvement in thermal management [17,18], etc., to alleviate the damaging effects of electromigration over the intended life-span of a microelectronics or micro-electro-mechanical system (MEMS) products; we will discuss more about them in Section 5.3. In such efforts, the main goal has been to reduce the effective diffusivity of the material. Next, quantitative models for electromigration and the critical role of diffusion in controlling the extent of electromigration will be highlighted.

5.1.1 Fundamental Governing Equations for Electromigration

Using the primary diffusive mass transport equation, i.e., the Fick's law, the Boltzmann statistics, and force of electromigration, we will derive the expression for the velocity of the material flow driven by electromigration. From above discussion and Fig. 5.2, it can be inferred that the force of electromigration ($\vec{F}_{EM}$) is basically the resultant of two opposing forces, i.e., the electron wind force ($\vec{F}_{wd}$) and the direct force ($\vec{F}_{el}$). These forces are directly proportional to the applied external electric field. Thus, the resultant electromigration force can be written as

$$\vec{F}_{EM} = \vec{F}_{el} + \vec{F}_{wd} = Z_{el}e\vec{E} - Z_{wd}e\vec{E} = Z^*e\vec{E} \quad (5.1)$$

where Z_{el} is the electrostatic charge number, which is often taken to be the nominal valency [6], Z_{wd} is the charge number due to the electron wind, e and $\vec{E}$ are the free electron charge and the applied electric field, respectively. Since direct force is in the direction of electric field, Z_{el} is generally taken as a positive number. Hence, Z_{wd} is negative as the wind force is opposite to the electric field. Z^* is the effective charge number, which combines the effects of both the electron wind force and the direct force. If Z^* is positive, then the material transport direction is in the direction of the electric field, whereas if Z^* is negative, then the material transport occurs in the opposite direction of the electric field (i.e., in direction of electron flow).

Since the chemical potential gradient, $\vec{\nabla}U$, is the driving force for the mass flux, we can write the following for the case of electromigration:

$$-\vec{\nabla}U = \vec{F}_{EM}. \quad (5.2)$$

Now, using Eq. (5.2) and taking concentration $c(x) = \Omega^{-1}$ where Ω is the atomic volume for a pure metal, we get the following expression for the electromigration driven mass flux:

$$J_D = -\frac{Dc(x)}{kT} \vec{\nabla}U = D \frac{F_{EM}}{\Omega kT} \quad (5.3)$$

where D is diffusivity, k is Boltzmann constant, and T is the absolute temperature. Therefore, the velocity of material flow, v , or drift velocity of atoms due to electromigration, is given as

$$v = \Omega J_D = \frac{DF_{EM}}{kT}. \quad (5.4)$$

And finally, inserting Eq. (5.1) into Eq. (5.4), we get

$$v = \frac{D}{kT} Z^* e E. \quad (5.5)$$

Now, if electric field (E) is written as ρj , where ρ is the electrical resistivity and j is the current density, in Eq. (5.5), we get the following expression for the drift velocity:

$$v = \frac{D}{kT} Z^* e \rho j. \quad (5.6)$$

Since diffusivity is given by the following expression:

$$D = D_0 e^{-\frac{Q}{RT}} \quad (5.7)$$

where D_0 is the frequency factor, Q is the activation energy, and R is the molar gas constant, Eq. (5.6) can be rewritten as follows in terms of experimental conditions of temperature and current density:

$$v = \frac{D_0}{kT} e^{-\frac{Q}{RT}} Z^* e \rho j. \quad (5.8)$$

Besides measuring the electromigration induced drift velocity of atoms, it is also important to develop “life models”, predicting the time required before an interconnect can be declared unusable due to the accumulation of electromigration damages. A few experimental set-ups and models are available for predicting the median time to failure (MTTF) of a conductor susceptible to electromigration induced damages (see Section 5.1.2). More often, these models are based on monitoring an increase in the

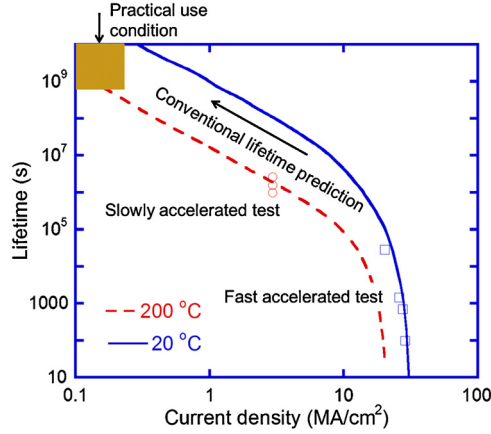


Figure 5.3 Interconnect lifetime data (reproduced from [20]) at accelerated test condition scaled up to service condition using Black's equation for $n = 2$ [20,21].

electrical resistance of the conductor by a certain amount, such as 2%, 10%, etc. Black's equation [3], given as

$$t_{50} = aj^{-n} \exp(Q/kT), \quad (5.9)$$

is also based on resistance monitoring and is generally used to scale the test data to the service condition. Here, t_{50} is MTTF, a is a constant, Q is the activation energy, and n is an exponent usually taken as 2. Fig. 5.3 shows experimental MTTF data and its match with Black's equation (i.e., Eq. (5.9)) using $n = 2$. As shown in Fig. 5.3, Black's equation with $n = 2$ aptly describes the electromigration induced failure in the thin film interconnects. Interestingly, Fig. 5.3 shows extrapolation of the test data to the service or practical conditions using the electromigration parameters obtained through experiments performed in lab; next, accordingly, we will describe the philosophy of conducting electromigration tests in lab.

5.1.2 Performing Electromigration Experiments in Lab

As described above, electromigration is a major reliability issue associated with current carrying metal lines. So, the assessment of electromigration induced damages is necessary for ascertaining the reliability of metallic interconnects. However, under usual service conditions, electromigration tests will need to be run for very long time (around thousands of hours) as it is a very slow process. Therefore, we need to increase the current density or the temperature to accelerate the process in the lab scale experiments; these experiments performed under lab conditions are, thereby, aptly called accelerated electromigration tests.

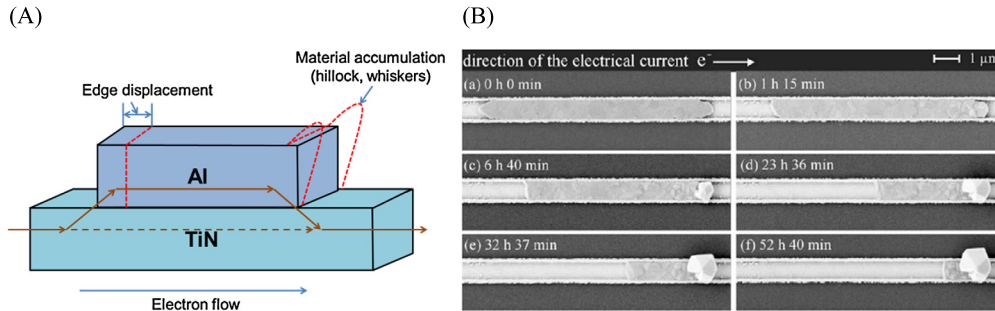


Figure 5.4 (A) Schematic illustration of Blech structure used for studying electromigration induced drift in thin film structures: This particular example shows drift of Al strip on TiN substrate driven by electromigration [adopted from [20]]. (B) Time-lapse micrographs showing evolution of extent of depletion zone at the cathode and material accumulation (or hillock) at the anode [24].

In a conventional electromigration experiment, j and T are externally applied or controlled to ensue electromigration, drift velocity (v) is measured and the rest of the terms in Eqs. (5.8) and (5.9) are assumed to be constant for a particular metal under particular experimental conditions. It should be noted that electrical resistivity of a metallic conductor is a function of temperature and the above expression (i.e., Eq. (5.8)) should be modified to account for the effect of temperature on the electrical resistivity. However, since this variation is often linear, the electrical resistivity can be assumed to be constant throughout an experiment, especially if ΔT remains very small (usually $<50^\circ\text{C}$). Interestingly, such a condition generally prevails in most of thin film structures, particularly when the current density is kept below 10^6 A/cm^2 [22].

Fig. 5.4(A) shows a schematic of Blech's sample for conducting electromigration induced drift experiment [7]; this particular sample structure is widely used for studying electromigration in thin films. Blech structure also represents the real interconnects, which are often placed on top of an substrate, e.g., SiO_2 , etc., with an interlayer in-between and have several sharp bends, and wherein the electrons enter and leave the thin film interconnects from and to the interlayer, respectively, resulting in current crowding at the ends. The particular experimental system employed by Blech in the classic studies on electromigration consisted of a thin Al strip on TiN substrate [7]. Since Al (or any other pure metal, e.g., Cu, Ag, etc.) provides a low resistive path in the sample as compared to the very thin interlayer (which are often TaN, TiN, W, etc.), most of the current flows through the Al metal film (see Fig. 5.4(A) where the dotted arrow represents a minor current path). On application of high density current, Al (or metal) atoms drift towards the anode due to the electromigration force. In this process, voids and hillocks or whiskers grow at the cathode and the anode, respectively. Fig. 5.4(B) clearly shows the formation as well as the evolution of voids and hillock in Cu thin film lines with continued electromigration. It should be noted that electromigration induced

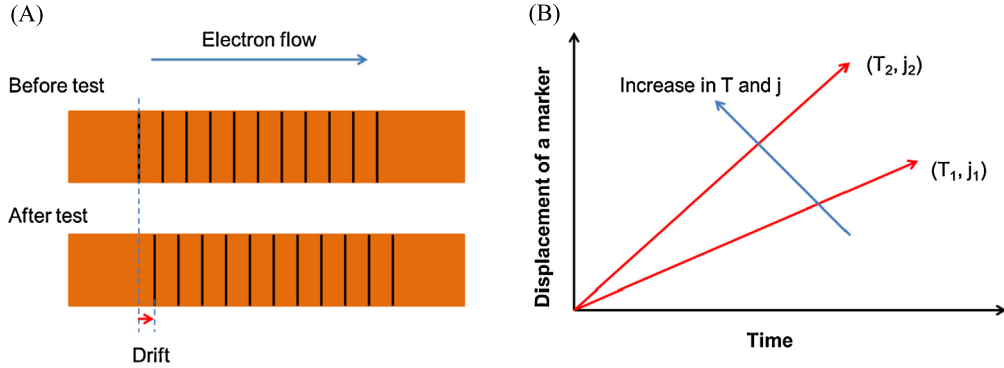


Figure 5.5 A schematic illustration of (A) experimental setup for studying electromigration induced drift in thin metal wires, and (B) time–displacement data obtained at constant temperature and current density.

drift in Blech structure is affected by the choice of the substrate or the interlayer, and it is also affected by the current crowding and hence temperature rise at the both ends of the test metal film [23] (see Section 5.1.7 for more details).

Some of the classic experiments performed for studying the fundamentals of electromigration and electromigration-induced drift in metal conductors used very thin wires of metals, upon which transverse scribes were placed as markers. As schematically shown in Fig. 5.5, the movements of these scribed lines with time were measured. The advantage of such methodology over Blech structure (see Fig. 5.4) is that the current density throughout the sample is constant and the electromigration drift is not affected by the substrate or the interlayer. Therefore, some of the earlier studies proposing the quantitative models of electromigration, e.g., by Huntington and Grone [6], used this methodology. If a sample with nonuniform cross-section is fabricated, then this method can also be used to measure the effect of current density on the drift velocity. However, since most of interconnects in the microelectronic devices and MEMS are placed on a substrate with an interlayer and have bends (and hence nonuniform distribution of electric current density as well as temperature), this methodology is not widely used for studying electromigration in thin film interconnects.

As mentioned in Section 5.1.2, another approach for studying electromigration is targeted towards predicting the “service” life of the current carrying structures. Such an approach is based on the fact that the electrical resistance of a conductor increases due to the electromigration. This occurs as voids, even when they are not terminal in the sense that they have not yet grown through the entire cross-section of the film causing complete open circuiting, will decrease the overall cross-sectional area through which the current can flow. Hence, growth of voids will lead to an increase in the overall resistance of the conductor. Therefore, this methodology for predicting the lifetime of

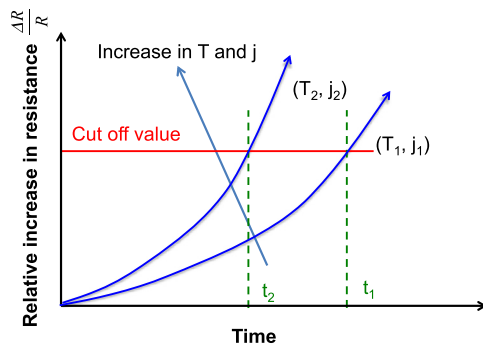


Figure 5.6 Schematic representation of evolution of electrical resistance with progress of electromigration damage, as measured under resistance based life prediction experiments. The time taken to reach a cut-off relative change in the resistance, e.g., t_1 and t_2 in above schematic for test conditions of (T_1, j_1) and (T_2, j_2) , respectively, is termed as the lifetime of the device.

a device containing a conductor susceptible to electromigration damages relies on the continuous measurement of resistance of the conductor with time (see Fig. 5.6) and ascertains the total time taken before the resistance increases by a certain fraction, e.g., 2%, 5%, etc., as the “service life” of the device. Therefore, the setup for such tests – either using samples in Blech configuration or just plain thin wire structure – comprise a current source, furnace (or heater) and a voltmeter.

Often tests in the lab are conducted under accelerated conditions, wherein the test temperature and current density are several degrees and orders of magnitude, respectively, larger than those in the actual service conditions. Once the relationship between the temperature, current density, and failure time, e.g., Eqs. (5.8) and (5.9), is established, predictions for any other combination of temperature and current density can be made (see Fig. 5.3). Such an approach, thus, saves time; however, care must be taken in measuring the effect of Joule heating on the actual temperature of the test sample. In addition, predicting behavior using Eq. (5.9) under conditions other than the lab test conditions is an extrapolation approach and extreme care should be taken. For example, it must be ensured that the values of activation energy for electromigration (or, diffusion), n , etc. under the test conditions and the service conditions remain the same.

5.1.3 Stress Generation due to Electromigration

As shown in Fig. 5.7, one interesting observation from Blech’s classic experiment is as follows [7,25,26]: The amount of electromigration-induced drift at the cathode is inversely proportional to the length of the metallic strip. This result is attributed to the fact that drift of metal atoms from the cathode to the anode generates a *back-stress* in the film with a negative stress gradient from the cathode to the anode. The origin of this back-stress lies in the fact that equilibrium concentrations of vacancies near the anode

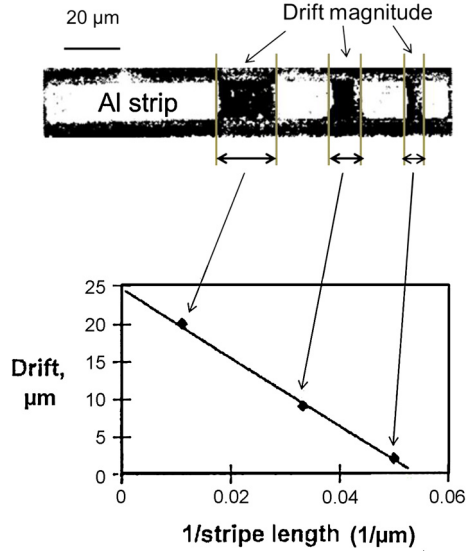


Figure 5.7 Variation of the net drift of Al strip from the cathode as function of the total strip length [26]: The top image shows the actual sample, whereas the bottom image shows the quantitative data.

and the cathode change due to the continued electromigration [25,26]. For example, when the net material is being transported from the cathode to the anode, then the anode becomes deprived of vacancies, thereby, generating significant compressive stress and establishing a stress gradient from the anode to the cathode. Therefore, the generated back stress induces a linearly superimposed back flow of the atoms, leading to a slower drift velocity and possibly a fractional recovery of the electromigration-induced drift upon stopping the electric current. The following expression accounts for the effect of back-stress on the net electromigration induced drift velocity (which is otherwise given by Eq. (5.8)) [26]:

$$v = \frac{D_0}{kT} e^{-\frac{Q}{RT}} \left(Z^* e \rho j - \Omega \frac{d\sigma}{dx} \right) \quad (5.10)$$

where σ is the stress and x is distance along the conductor in the direction of the electron flow. It should be noted that the back-stress always opposes the electromigration induced drift velocity and hence the value of Z^* in the above equation should be taken as positive and direction of material transport should be decided before applying “scalar” Eq. (5.10).

From the graph shown in Fig. 5.7, we can infer that below a certain strip length, i.e., above a certain back stress gradient, electromigration induced drift or damage may not occur. This minimum or critical length below which a material becomes electromigration-immune is called *Blech length* (L_B). In addition, the value of L_B de-

creases with increase in the current density. It has been reported that the product of Blech length and the critical current density (j_c) required for electromigration drift to occur is constant for a particular temperature [26]. This discovery of staying below the critical product is adopted by the circuit designers for increasing the reliability of interconnects. Nevertheless, generation of stress and stress gradient in the film due to electromigration have implications on growth of whiskers and hillocks, as it will be discussed in Section 5.3.

5.1.4 Electromigration in Liquid Metals

Electromigration is not only limited to solid metallic conductors, as it has also been reported in pure liquid metals [8–10,27]. Nevertheless, discovery of electromigration in pure liquid metals is relatively recent compared to that in solid metals. Electromigration in liquid metals is also captured by the same expression that has been derived for solid metals (i.e., Eq. (5.8)). However, since it involves flow of liquids, viscous forces may arise opposing the electromigration-driven flow. This is especially important when the thickness of liquid film is a few nanometers [28]. There are several implications of electromigration in liquid metals. One such implication is that, as shown in Fig. 5.8, application of electric field through liquid metal bead paced on top of a conductor leads to long-range continuous directional flow of liquid metals. In this process, the substrate is conformally coated with the liquid metal.

In case of a solid material, an atom is strongly bonded to its adjoining atoms by strong interatomic forces and the frequency of jump to neighboring sites is limited. On the other hand, in the case of liquid metals, this interatomic binding force is much smaller. Thus, diffusion is significantly faster in the liquids due to the weak bonding amongst the atoms. As discussed earlier, the mass flux density linearly increases with diffusivity of the material. Since, as explained above, diffusivity in a material is several orders of magnitude higher in its liquid state as compared to its solid state, the electromigration driven material flow velocity is dramatically faster in the liquid state relative to the solid material.

Unlike solid state electromigration, material does not always move from the cathode to the anode side in the case of liquid state electromigration. In liquid state, material movement direction depends on the metal flowing [10]. For some materials, such as liquid Pb and an CrNO_3 compound, the material flow occurs from the cathode to the anode; however, for some other metals, such as Al, Ga, In, Bi, Sn, etc., the direct force is greater than the wind force, resulting in metal atoms moving from the anode to the cathode [10,29].

In addition to the continuous flow of liquid metal, liquid metals have also been shown to flow as discrete beads if placed on a poorly wetting substrate [10]. In a classic work by Ichinokawa et al. [30], molten metallic islands were formed by heating an ultra-thin film of metal (Au, Ag, etc.) deposited on Si at high temperature ($\sim 800^\circ\text{C}$).

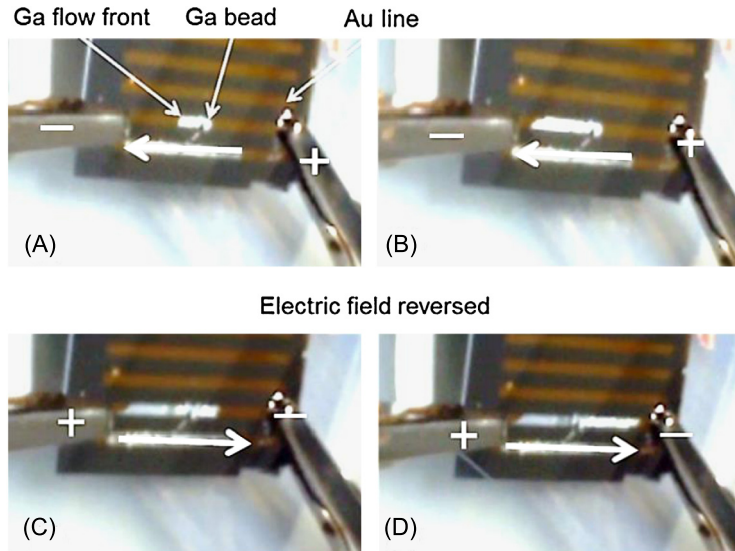


Figure 5.8 Time-lapse snapshots showing the flow of liquid Ga on Au substrate: In (A) and (B) the right electrode is positive and the left one is negative. In (C) and (D) the electric field is reversed, resulting in the reversal of direction of Ga flow. Horizontal thick arrows in each image show the flow direction. The images are adapted from [19].

Subsequently, current was passed through the semiconducting substrate (Si), which made the islands migrate over Si. Fig. 5.9(A) shows electromigration-induced movement of Au islands on the Si substrate. It was observed that the velocity of flow increased exponentially with temperature and linearly with the island radius [30]. The direction and speed of the migration was found to be different for various metals; for example, Au islands often moved faster compared to Ag islands. Similarly, as shown in Fig. 5.9(B), thin layer of liquid CrNO_3 film has been shown to flow in radially symmetric fashion away from the pointy cathode towards the pointy anode.

Since diffusivity in liquid state is orders of magnitude larger than the solid metals, the electromigration in liquid metals is significantly more aggressive. Nevertheless, this also provides several opportunities to harness the processing prowess of electromigration in liquid metals, such as maskless coating of conductors [8], fabrication of structures with very high surface-to-volume ratios [19], electrolithography [29], creation of structures with periodic surface patterns [31], etc.

5.1.5 Electromigration in Alloys or Multielement Material Systems

Electromigration in multielement material systems or alloys, both in liquid and solid states, have been studied for several decades [32–34]. Since Z^* and the diffusivity of different elements in an alloy can be widely different and in certain cases, especially in

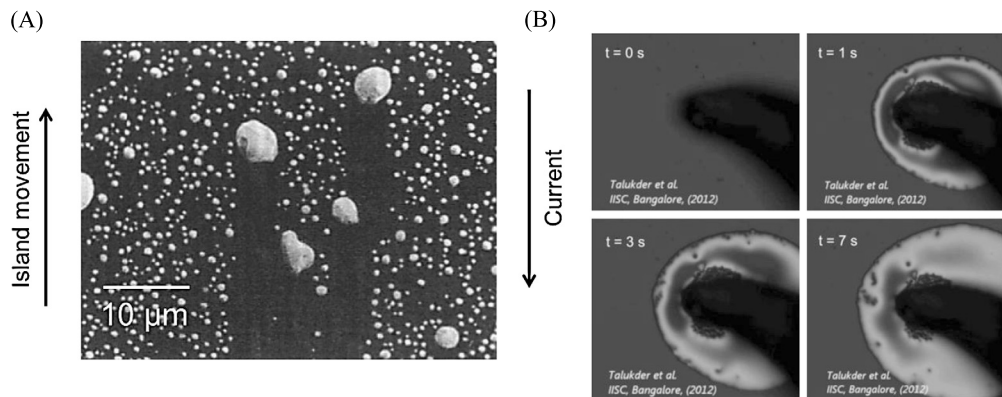


Figure 5.9 (A) SEM micrograph showing electromigration induced movement of Au islands over Si surface. The test temperature was 800°C [30]. (B) Time-lapse images showing radial flow of liquefied CrNO₃ upon application of direct current using two point electrodes placed far away from each other. The electrode shown in (B) is cathode.

alloys with well-separated phases, the current density passing through different phases can also be different, owing to substantial differences in their electrical resistivities, various elements in an alloy or multielement system may move with different drift velocities. Therefore, as shown in Fig. 5.10, electromigration in an alloy will result in separation of elements, wherein one end of the conductor becomes richer in one element as the second end becomes richer in another element. Therefore, electromigration, in principle, can be used to purify a metal by removing all impurities to one of the ends of a bar. Nevertheless, besides creation of voids and hillocks, such elemental separation may pose as another electromigration related reliability issue in conductors where composition uniformity is very critical for proper functioning of the device.

5.1.6 Effect of Electromigration on Reaction Kinetics

Electric current, especially when flowing with very high densities, provides sufficiently many electrons to participate in chemical reaction. Thus, this may change the activation energy for the reaction and hence alter the total growth rate of the reaction product. One of the implications of such an electric current effect is rapid growth of intermetallic compounds (IMCs) in various metallic diffusion couples, such as Cu–Sn where the activation energy of Cu₃Sn IMC formation was reported to decrease from 0.54 eV under isothermal aging condition to 0.40 eV under aging-under-current stressing (at a current density of 1.5×10^5 A/cm²) condition [36]. Moreover, it has been reported that the Cu–Sn IMC growth kinetics transforms from diffusion controlled (i.e., parabolic) under isothermal aging condition to chemical reaction controlled (i.e., linear) under aging-under-current stressing condition [37].

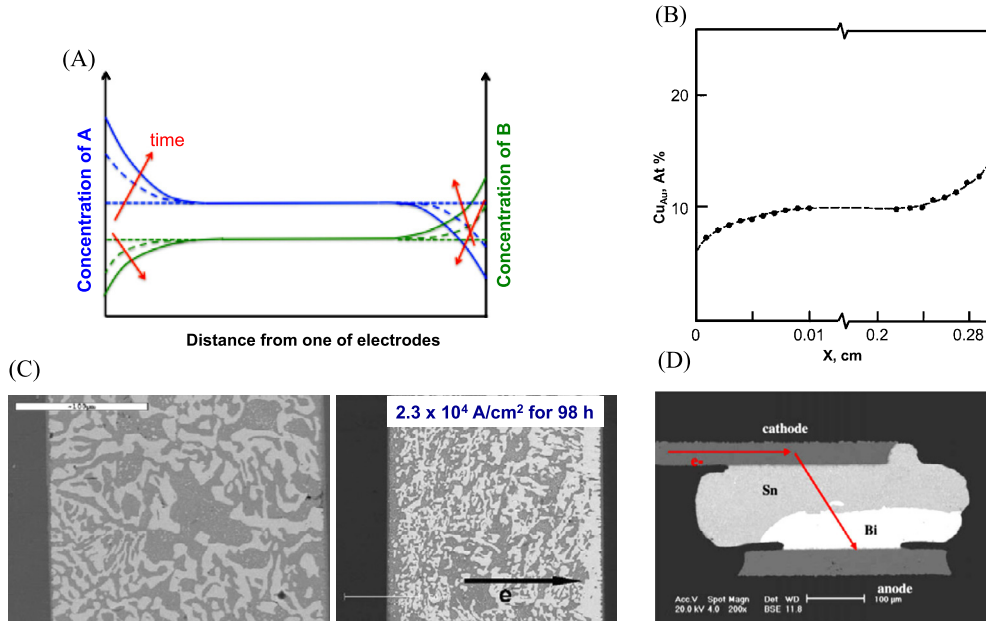


Figure 5.10 (A) Schematic illustration of concentration profile along the length of a 2-element conductor. Arrows show concentration profile evolution with time. (B) Concentration profile of Au as function of distance from anode in Ag–10%Au alloy after electromigration [33]. (C) Segregation of Bi in an Sn–Bi solder along the electron flow direction: (left) as-reflowed microstructure and (right) microstructure after electromigration [34]. (D) SEM micrograph showing accumulation of Bi in an Sn–58Bi solder near anode after electromigration at 5×10^3 A/cm² at 75°C [35].

Interestingly, as shown in Fig. 5.11, the total thickness of IMC layer formed at the two ends of a Cu–Sn rich solder–Cu joint often varies widely due to the flow of electric current: The IMC at the Sn–Cu interface from where the electrons leave the Sn-rich solder (i.e., anode) is much thicker than the other end [38]. A good curve fit between the square of the IMC thickness and time suggests a diffusion-controlled growth of IMC layer [38], which, as mentioned previously, is different than the chemical reaction controlled growth in Cu–Sn diffusion couple [37]. Although the exact reasons for this observation and the dichotomy in the rate controlling mechanism are not clear, presence of excess electrons, back-stress, and excess vacancy concentration at the cathode (and their lack at the anode) have been considered as the contributing factors [35–38].

5.1.7 Coupling Between Electromigration and Thermomigration

As mentioned earlier while describing Blech structure for conducting an electromigration experiment (see Section 5.1.2), real interconnects have sharp bends and short discontinuity, which are often filled by low conducting interlayers. Such bends and dis-

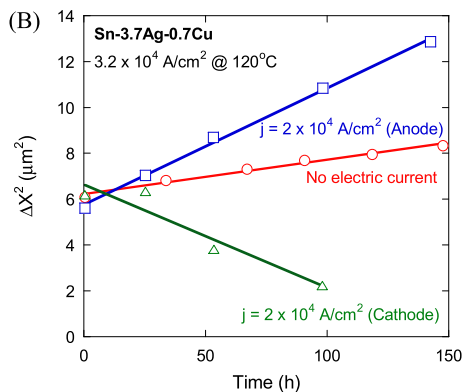
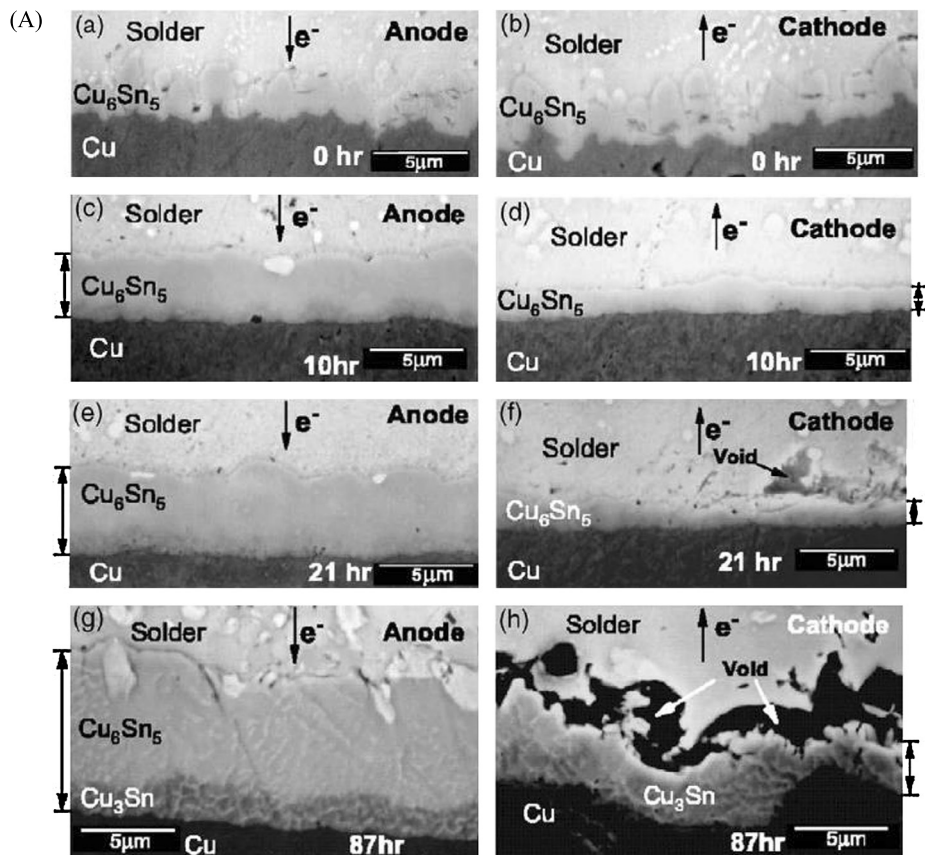


Figure 5.11 (A) Time-lapse SEM micrographs showing dramatic difference in the growth behavior of IMC layer at the anode and the cathode ends of an Sn-rich solder joint with Cu [38], and (B) effect of electric current and its direction on the thickness of interfacial IMC layer in the solder joint shown in (A) [38].

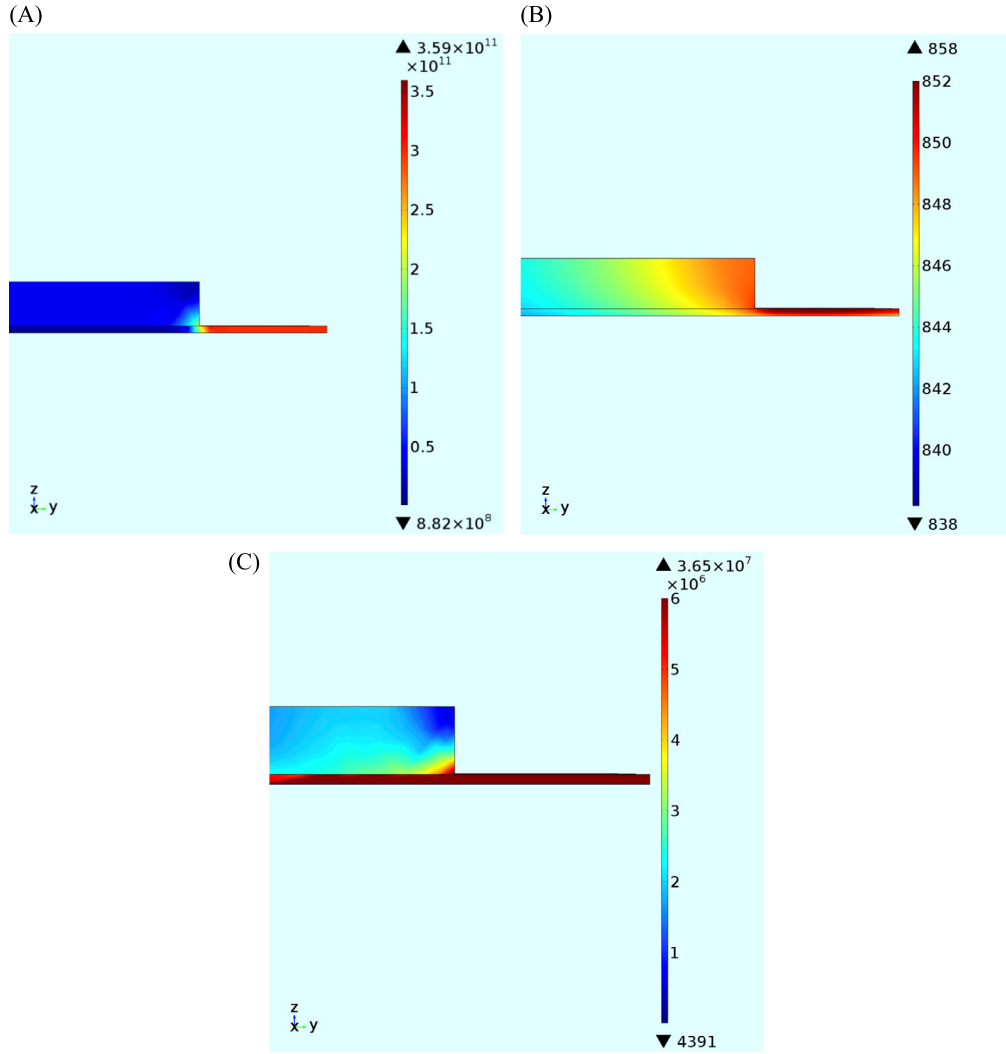


Figure 5.12 Finite element simulation results showing distribution of (A) current, (B) temperature, and (C) temperature gradient at one of the ends of the sample in Blech structure [23].

continuity in interconnects lead to current crowding at the corners and near the entry and exit points (see Fig. 5.12(A)). Since Joule heating is associated with the electric current, current crowding will generate an inhomogeneous distribution of temperature field inside a conductor. In this condition, as shown in Fig. 5.12(B), the temperature at the ends of the conductor can be significantly higher than that in the central region of the conductor. Such temperature profile will generate very high temperature gradient, especially near the ends of the conductor, as shown in Fig. 5.12(C). Interestingly, large

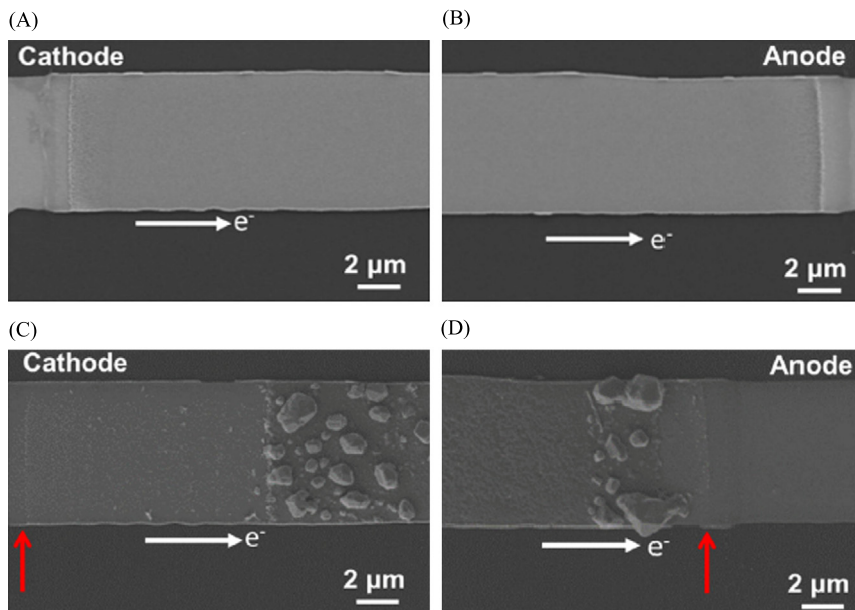


Figure 5.13 SEM micrographs showing (A) cathode and (B) anode ends of Cu film on W interlayer in as-deposited conditions, and (C) cathode and (D) anode ends of the same sample after passage of electric current [23].

temperature gradients may lead to mass transport due to thermomigration, or Sorret effect, wherein atoms move from the hotter terminal to the cooler one (and in some cases from the cooler to hotter terminal) [39]. In metals, especially Cu, thermomigration occurs from the hot to the cold terminal [39].

As a result of large temperature gradient, and hence associated thermomigration, the metal film may start to drift from the hotter end regions towards the cooler central region. Since electromigration is also associated with the electric current, which leads to directional transport of the material from one end to another, the coupling between or superposition of these two types of mass transport mechanisms – i.e., electromigration and thermomigration – may lead to some interesting type of mass transport, such as that shown in Fig. 5.13, where the mass transports due to electromigration and thermomigration at the cathode are augmented, leading to void formation over very long distances, while the effects of these two mass transport mechanisms are opposite at the anode, leading to, in this case, a small backflow or void formation at the anode, too. Interestingly, Fig. 5.13 also shows formation of hillocks at both the cathode and anode ends of the Cu film. Thus, the conventional wisdom of open-circuiting at the cathode and short-circuiting at the anode due to the passage of electric current breaks down if large temperature gradients can be produced due to the passage of electric

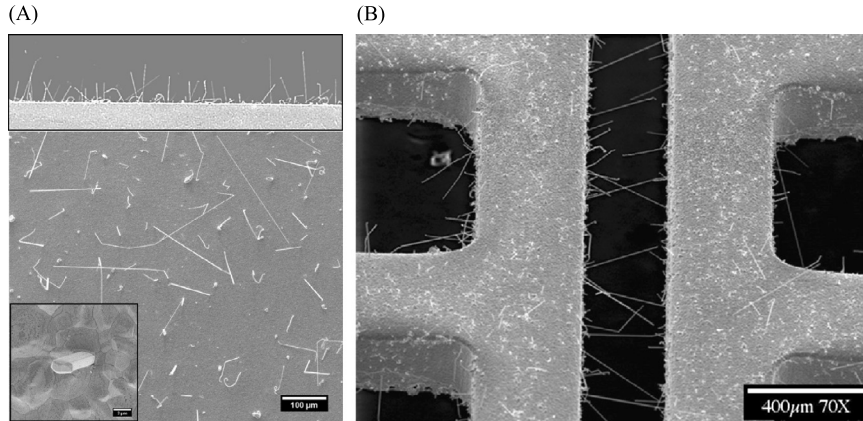


Figure 5.14 (A) Growth of variety of whiskers in Sn coating at room temperature after 30 days. Inset shows a high magnification micrograph of a whisker and the top image shows the side view of a Sn coating with whiskers. (B) Short-circuiting due to whisker growth in Sn-plated Cu lead-frame after 3 years of storage in ambient conditions [41].

currents. Under such thermomigration–electromigration coupling conditions, both the short-circuiting and open-circuiting can occur at both the cathode and anode ends, resulting in an even more severe reliability issue in real interconnects with bends and discontinuity.

5.2 INTRODUCTION TO WHISKERING IN TIN COATINGS

Whiskers are very high aspect ratio (e.g., aspect ratio of as high as $\sim 10,000$) filamentary structures, which often grow spontaneously in a coating, e.g., a few micrometer-thick Sn coatings on Cu, Cd coatings, Al films on Si, etc. As an example, Fig. 5.14(A) shows growth of multiple whiskers from a 4 μm -thick Sn coating on brass substrate. As shown in Fig. 5.14(A), whiskers grow in different shapes, sizes, and orientations, and they can grow very long. They are often more than 300 μm long with a diameter of a few micrometers. Interestingly, a few centimeter long whiskers have also been observed in Sn coatings. It has often been reported that these whiskers are high purity defect-free single crystals [40]. Also, it is generally thought that whiskers grow in response to buildup of high compressive stresses in coatings, and hence the residual stresses in the coating decrease once whiskers start to grow [40]. From reliability perspective, whiskering is generally not a welcome phenomenon. This is so because if whiskers grow long enough to bridge the gap between two adjacent interconnects or electrical leads (see Fig. 5.14(B)), they can cause short-circuiting, which may lead to partial or complete failure of the electronic device.

The problem of whisker growth is expected to become more aggressive in next generation microelectronic devices because the spacing between interconnects or lead frames in these devices will be significantly smaller than the current ones (e.g., they may be $<100\text{ }\mu\text{m}$). The problem may further be exuberated in the presence of electric current of high density (see Section 5.3 for more details). It is therefore important to understand the whisker growth as it is critical from both the scientific and technological points of views.

Interestingly, the problem of whiskering, as well as the development of technologies to contain it, is fairly old. Whisker growth was first reported in the 1940s in Cd-plated condenser plates, where they were reported to be responsible for failure of some military equipment during World War II [42]. Similarly, failure in the transmission lines due to Sn whisker-induced short-circuiting was reported by Bell Labs in the 1950s [43–45]. Thereafter, several failures in electronic devices were reported; a comprehensive list of such instances is available on the website of NASA Goddard Space Flight Center [41].

5.2.1 Fundamentals of Whiskering Phenomenon

Since the discovery of whiskering, several research groups have investigated the fundamentals of this interesting, but often dreaded phenomenon. Although the complete picture of whiskering is still elusive, there are a few aspects that are now universally accepted, which we describe briefly next. It is now well accepted that whiskers grow only after an incubation period, during which compressive stress builds up in the coating, while it remains whisker-free [46]. In addition, the whisker growth rates have been reported to be linear [46], as well as nonlinear [47], while it may saturate after finite period of time [46]. It is also widely accepted that during whisker growth the surrounding area does not get depleted of Sn atoms and hence long range atomic transport mechanism must be operative during whisker growth [48]. In this context, it has also been reported that mass transport normal to the substrate is more important than lateral mass transfer [49]. Overall, it is well established that for growth of whiskers we need to have fast atomic diffusion at room temperature, a minimum driving force for mass transport from the bulk to the whisker root and a surface oxide layer that impedes the uniform stress relaxation over the entire coating. Some of the salient features of whisker growth phenomena are described below.

5.2.1.1 Regeneration of Compressive Stress

It is widely accepted that stress is the driving force for whisker growth: Whiskering acts as a stress relaxation phenomenon [50], which causes reduction in the compressive stress in the Sn coatings by continuously extruding the material out from the relatively compressed region of the coating to the stress-free surface [51]. For continuous growth of Sn whiskers, a continuous stress regenerative mechanism is required. The diffusion of Cu, Zn, and other atoms from the substrate [52,53], formation of Cu_6Sn_5

intermetallic compound (IMC) at the coating–substrate interface as well as at Sn grain boundaries [54–56], Sn–oxide formation at the Sn surface [50,55,57], thermal stresses due to mismatch between coefficients of thermal expansion (CTE) of the Sn coating and the substrate [58], and segregation of impurities at Sn grain boundaries [59] have been proposed as the possible stress regenerative mechanisms. Nevertheless, it appears that growth of Cu_6Sn_5 IMC, which involves increase in the molar volume of the product phase relative to the reactant phases [60], at the interface of Sn coating and the reacting substrate (e.g., Cu, brass, etc.) is the major stress regenerative mechanism for spontaneous growth of whiskers. For Sn coating on a substrate with which Sn does not chemically react, CTE mismatch between the Sn coating and the substrate might be the driving force; however, this becomes important only when the CTE mismatch between coating and the substrate is very high [58].

5.2.1.2 Mass Transport From Bulk to Whisker Root

Another important thing to understand is how the mass is transported from the bulk of Sn coating, which is under higher compressive stress, to the root of whisker, which is relatively less compressed. In other words, what is the diffusion mechanism responsible for the transport of Sn atoms along the negative stress gradient? Early experiments on whisker growth have shown that a whisker grows by continuous addition of atomic flux into the root of the whisker [61]. Since Sn has a very low melting point of 232°C , room temperature corresponds to $0.6T_m$, where T_m is the melting temperature of the material, for Sn. Therefore, very fast grain boundary diffusion is expected and has also been often proposed as a responsible mechanism for mass transport [55,57,61]. However, contributions of diffusion through interfacial region between Sn coating and the substrate and of the lattice diffusion in the overall mass transport remain unclear. Lattice diffusion may become important at relatively high temperatures; however, direct evidence of diffusion mechanism, such as using tracer elements, in Sn coating responsible for the whiskering is still elusive.

5.2.1.3 Identification of Location of Whisker Grain

Several mechanisms predicting the most favorable site for whisker growth have been proposed. The dislocation theories [62–64] failed to explain the growth of whiskers in commonly observed $\{100\}$ -growth direction, which is a non-preferred slip direction in Sn. Later, recrystallization based mechanism was also proposed [52,65]. However, direct evidence of recrystallization as mechanism responsible for whiskering and, more importantly, absence of whisker growth in the absence of recrystallization has not been shown unambiguously. Due to the lack of general consensus on mechanism of whisker growth, locating whiskering grain in coating before whisker growth has been elusive. However, some circumstantial evidence is available which can be used to locate whisker grains. For example, it has been proposed that grains which have low elastic modulus

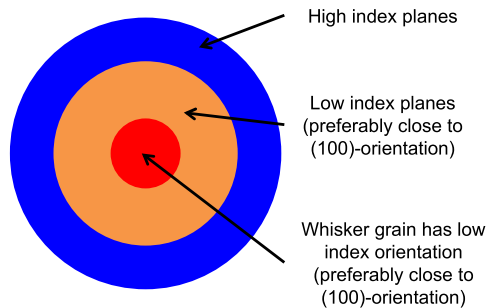


Figure 5.15 A schematic illustration of 2-ring configuration that has been recently proposed for identifying whisker locations in Sn coatings on brass or Cu substrate [69].

and can be plastically deformed easily compared to the neighboring grains can grow as whiskers [66]. It was proposed that due to elastic anisotropy, grains may develop different out-of-plane strains, which then rupture the Sn-oxide layer on the surface [50]. Thus, the weakest spot on Sn-oxide layer becomes the site for whisker growth. Simulation studies indicate the presence of high strain energy density near a whisker grain as a prerequisite for whisker growth [67]. A recent study has shown growth of whiskers from those low index planes which are surrounded by another set of similarly low index planes, which are then completely or partially surrounded by high index planes as the second nearest neighbors (see Fig. 5.15 for a schematic illustration) [68,69]. A majority of reports show that whiskers in Sn coatings preferred to grow in low index directions, such as $\langle 100 \rangle$, $\langle 101 \rangle$, and $\langle 001 \rangle$ [50,70]. However, other studies reporting high index directions $\langle 123 \rangle$, $\langle 211 \rangle$, and $\langle 103 \rangle$ are also available [71].

5.2.1.4 Effect of Service Conditions on Whisker Growth

During service, a device may be exposed to various temperatures, humidity level, as well as thermal cycling due to the periodic switching on and off of the device. These externally applied stimuli can also have a significant impact on the whisker growth [58, 72]. For example, it is shown that whisker growth increases significantly by isothermally aging at moderately high temperatures of 50–70°C and then drastically decreases at higher temperatures due to the stress relaxation because of creep and recrystallization [43,44,52,50,55]. Similarly, temperature cycling can also produce thermal stresses inside the Sn coats due to CTE mismatch between Sn and the substrate, especially when there is a significant difference in their CTE values (e.g., Sn coatings on Fe–Ni alloys). These thermal stresses can interact with the intrinsic stress-state of the Sn coats and may enhance (or diminish) the whisker growth [58,72]. Overall, isothermal aging at 50–70°C is the most aggressive condition for spontaneous growth of whiskers over the longest period of times [68].

5.2.1.5 Role of Stress and Stress Gradient

In recent years, many researchers have studied the stress state in the Sn coatings and correlated it with the whisker growth kinetics. Common methods for stress analysis in Sn coatings include X-ray diffraction (XRD) [73], cantilever beam bending [58], and measurement of curvature of the substrate using laser based multibeam optical sensor [74]. XRD is a popular method for stress measurement for its simplicity; however, the penetration depth of X-rays is often only up to a few hundreds of nanometers and the stress in Sn coatings may change with the distance from the surface towards the Sn–substrate interface. Therefore, recently it was proposed to use glancing angle XRD for measuring stress state in the top layer of the Sn coating and curvature measurement based stress measurement technique for measuring the bulk stress. With this approach, both the evolution in the average bulk stress and the out of plane stress gradient can be measured.

It has been suggested that high compressive stresses are required for whiskers to grow [46]. It was shown that whiskering started in Sn coatings as soon as certain critical compressive stress was achieved [66,74]. However, reports suggesting rapid growth of whiskers in coatings under tensile stress are also available [75]. Recently, carefully planned experiments revealed that the magnitude of the out-of-plane stress gradient, wherein more compressive stress prevails at the bottom of the coating compared to the top, is more critical compared to the mere sign and magnitude of the stress [75].

5.2.2 Suppression of Whiskering Phenomenon

Besides studying the fundamentals of whiskering phenomenon in Sn coatings, several suggestions for suppressing it over extended period or eliminating it altogether have also been made. The most popular one was proposed by Arnold of Bell Labs, who observed that minor alloying of Sn with Pb (typically 3–10 wt.%) stopped whisker growth in Sn plating altogether [51]. As shown in Fig. 5.16, it was later observed that minor alloying with Pb decreased the maximum compressive stress in Sn coatings – both under the as-deposited and aged conditions – and hence the driving force necessary for whiskering could not buildup [66,74]. As shown in Fig. 5.16(B), it was also suggested that the growth of interfacial Cu_6Sn_5 IMC was retarded due to the presence of Pb in Sn coating [54].

However, the problem of Sn whisker-induced failures has reemerged due to the recent legislation by European Union on Restriction of Hazardous Substance Act (RoHS), which imposes a ban on usage of Pb in all electronic components [76], and it has necessitated search for alternatives of Pb. In this context, a recent study [77] investigating the effect of alloying Sn with In on the whisker growth is an important one. It was reported that addition of In into Sn reduced whisker density compared to pure Sn films under identical thermal excursions [77]. It was shown through molecular dynamics simulation that In, similar to Pb, segregated along the Sn grain boundaries and hence

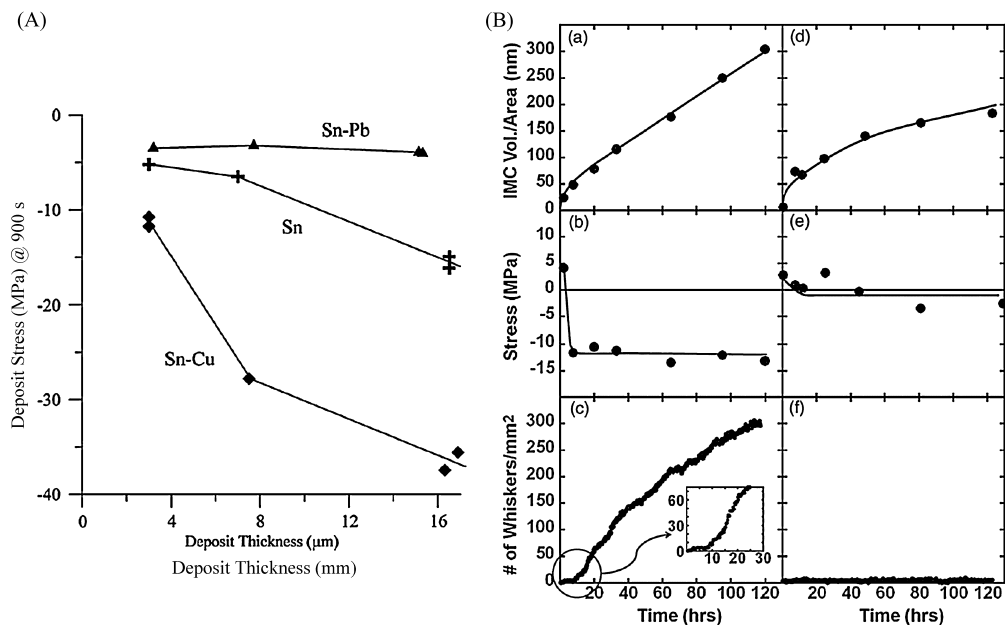


Figure 5.16 (A) Stress in the various as-deposited coatings (i.e., after 15 min of electro-deposition) as a function of thickness [60], and (B) measurements of IMC volume, average stress, and whisker density in layers of (a)–(c) pure Sn and (d)–(f) Pb–Sn alloys on Cu substrate, respectively [80].

reduced the grain boundary diffusion, thereby, reducing whisker growth [78]. Also, it was suggested that incorporated In reduced tenacity of Sn oxide on the free surface [77]. Similarly, adding a small amount of Bi into Sn has also been shown as an effective way for suppressing whisker growth [79]. Nevertheless, as it will be shown later, addition of Bi, similar to addition of Pb, also reduces the buildup of compressive residual stress in the Sn coating.

A major set of suggestions for suppressing spontaneous whiskers originate from the fact that whiskering is a diffusion-controlled phenomenon, wherein diffusion is required for growth of IMC (Cu_6Sn_5) layer at the interface of Sn and the substrate, which then induces the compressive stress in the Sn coating, as well as for migration of Sn atoms from the bulk of the coating to the roots of whiskers. If any of these two diffusion processes or routes is inhibited, whisker growth will be suppressed. Now, the growth of IMC layer can be slowed down by placing a diffusion barrier in between Sn and the substrate. For example, placing a thin layer of Ni in-between Cu and Sn or brass effectively stops whisker growth by slowing down the growth of interfacial IMC as well as by changing its morphology [81]. It should be noted that Ni interlayer results in growth of disc/platelet-shaped IMC layer instead of round scallopy IMC [81]; this further aids in reducing the total compressive stress near the IMC layer. Overall, as

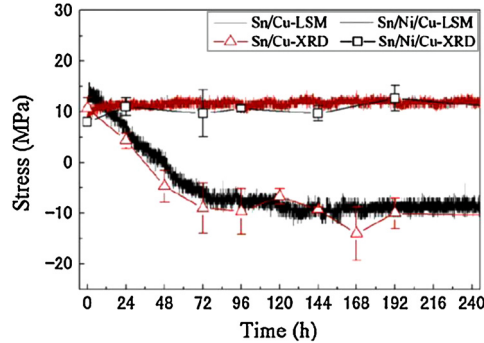


Figure 5.17 Evolution of stress in Sn coatings placed on Cu substrate with and without Ni underlayer. Stress measured using XRD and cantilever deflection using laser sensor method (LSM) superimposed each other [83].

shown in Fig. 5.17, the stress in Sn coating with Ni underlayer is less compressive as compared to that without such an interlayer. Similarly, as mentioned above, the grain boundary diffusivity, which has been reported as the main conduit for mass transport from the bulk of the coating to the whisker root, can be decreased by placing impurities, such as In, Bi, etc., at the grain boundaries and hence the whisker growth could be slowed down [82]. However, it is worth mentioning here that contradictory reports, suggesting that minor alloying of Sn with Cu as well as placing a thin layer of Ni underlayer in between Sn and substrate, leads to a higher rate of whisker growth, are also available in the open literature [59].

In this context, it is also worth mentioning that the net diffusive flux through grain boundary can also be reduced by grain boundary engineering, i.e., without placing any additional alloying element or interlayer. For example, if the number fraction of grain boundary perpendicular to the substrate, i.e., along the direction of negative stress gradient, is reduced, then the net diffusivity will also reduce, resulting in a net decrease in whisker growth. Furthermore, existence of interior grain faces with grain boundaries parallel to surface of the deposit promotes uniform stress relaxation by Coble creep mechanism. There are a few methods of attaining non-columnar grain boundaries: one such method is prestraining the coating and then recrystallizing the coating by annealing (e.g., 5% straining followed by annealing at 150°C for 1 h) (Fig. 5.18) [84], while other methods can be minor alloying with certain elements, e.g., Pb, Bi, etc. (see Fig. 5.19) [80], and a change in the plating current (e.g., plating with direct and pulsed current may lead to the growth of columnar and equiaxed grains in Sn coating, respectively [79]). As shown in Fig. 5.20, the buildup stress in the Sn coating with equiaxed grains is less compressive compared to the Sn coating with columnar grains. The mechanistic relationship between the diffusion route, diffusivity, and the stress state is not yet well established.

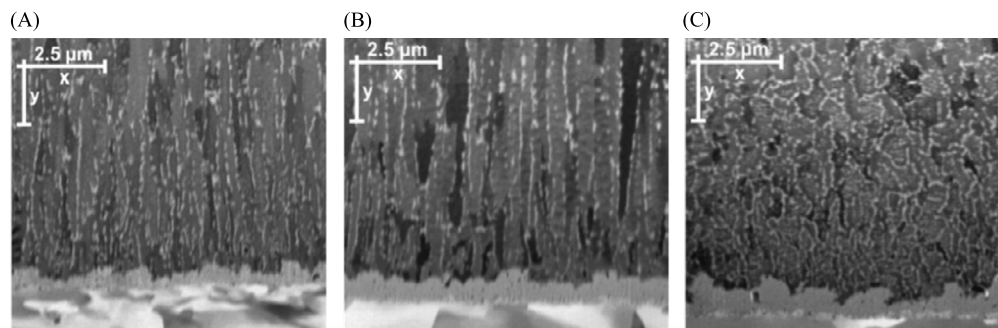


Figure 5.18 Grain structure in Sn coatings: (A) reference, (B) annealed, and (C) recrystallized samples [84]. The grains in (A) and (B) were columnar, whereas they were close to equiaxed in (C) (i.e., after recrystallization).

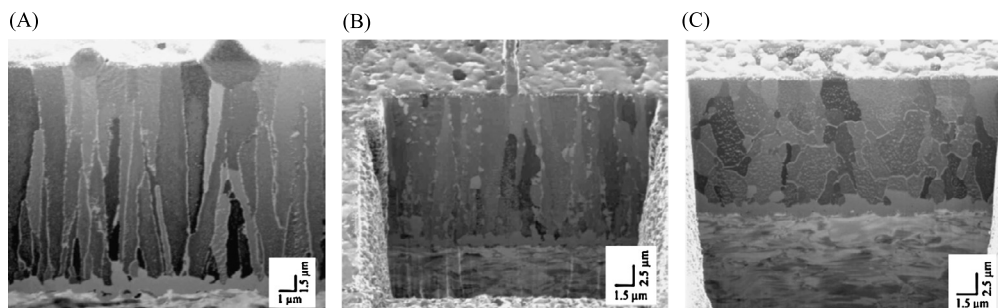


Figure 5.19 SEM micrographs showing a cross-section of (A) pure Sn, (B) Sn-Cu, and (C) Sn-Pb coatings, revealing the grain structure along thickness. The trenches were prepared using FIB [60].

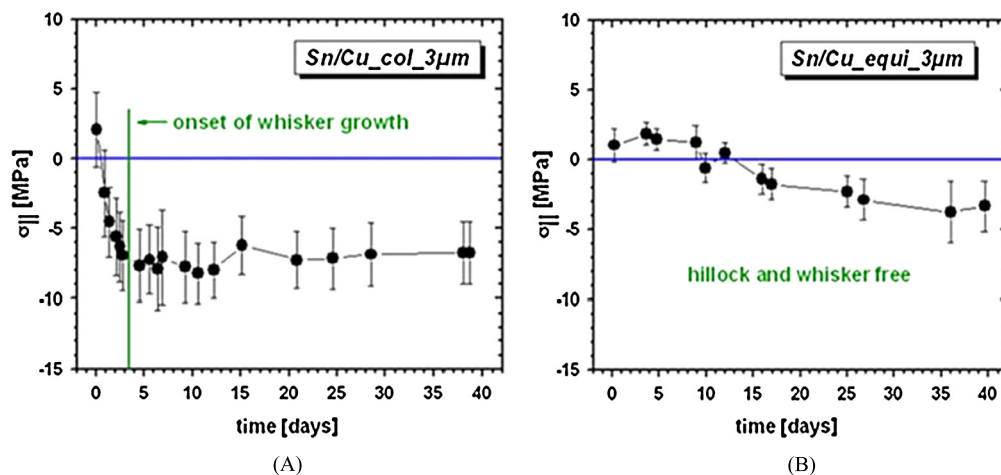


Figure 5.20 Stress evolution in various Sn on Cu coatings with (A) columnar and (B) equiaxed grains [85].

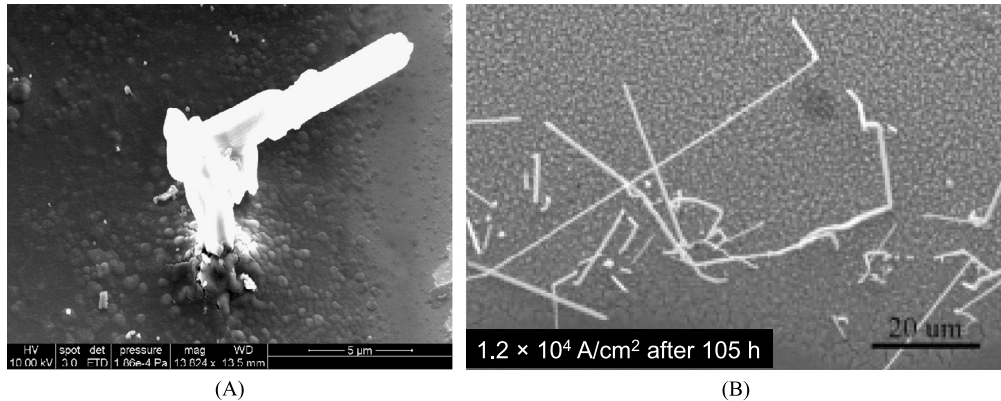


Figure 5.21 Example of whisker growth due to electromigration at the cathode side of (A) Al thin film on Si on TaN interlayer, and (B) Sn film on glass with Ti interlayer [86].

5.3 ROLE OF ELECTROMIGRATION IN WHISKERING

As discussed in Sections 5.1 and 5.2, both the electromigration and whiskering are diffusion-controlled phenomena; however, electromigration may generate a compressive stress as well as a negative stress gradient, whereas whisker growth occurs in response to a compressive stress (or, more precisely, negative stress gradient), and the overall compressive stress decreases as an outcome of the whisker growth. In addition, electromigration is a directional phenomenon, which deprives the anode of vacancies and hence generates compressive stress build up in the anode region. Therefore, it is imperative to argue that by producing excessive compressive stress near the anode electromigration provides a spot for whiskers to grow and then it “nurtures” the growth of whiskers by continuously transporting the material from the cathode to the whisker root near the anode. In this process, the back-stress reduces and electromigration continues. Indeed, as shown in Fig. 5.21, whisker growth occurs due to the electromigration at the anode end of a thin film metallic conductor. It should be noted that hillocks (see Figs. 4(B) and 13 for a few examples), which are often formed at the anode end of a conductor due to the electromigration, are structurally different from the whiskers: the aspect ratio of whiskers are much higher than those of hillocks.

It should be noted that electromigration by itself can regenerate the compressive stress required for continuous growth of whiskers. Thus, the growth of a layer of IMC having relatively higher specific volume at the film and the substrate interface, large CTE mismatch between the substrate and the coating, etc., are not required for the growth of whiskers in the conductors susceptible to electromigration damages. Moreover, as shown in Fig. 5.22, electromigration-induced whiskering has also been reported in systems that often do not show spontaneous whisker growth (i.e., whisker growth under isothermal storage conditions), such as Pb–Sn solders. These observations make whisker

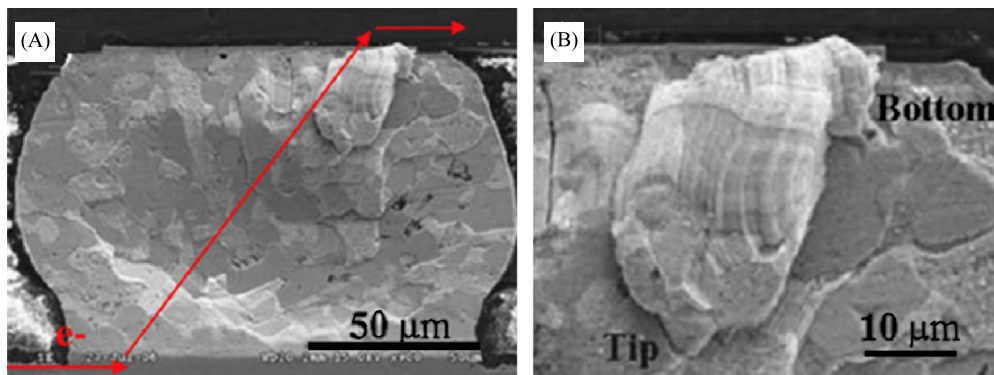


Figure 5.22 Whisker growth in eutectic Sn–Pb solder at the anode side upon passage of current of 10^4 A/cm² for 48 h: (A) low and (B) high magnifications SEM micrographs [87]. The arrows in (A) show the electron path.

growth in current carrying interconnects even more serious; however, it also provides an avenue for performing accelerated tests for studying whiskering in metallic films.

5.3.1 Critical Length for Electromigration-Induced Whisker Growth

As shown in Fig. 5.23, the whisker length (as well as overall whisker number density) decreases with a decrease in the length of the conducting film, which is electromigration-tested in form of Blech structure. In addition, a decrease in the current density also results in a net decrease in the length and the whisker number density. These observations are interesting as they suggest that similar to the Blech length, below which electromigration induced damages do not occur in a thin film conductor (see Fig. 5.7) [25,26], electromigration-induced whiskering in thin film conductors will not occur if the length of the conductor and the current density are kept below some critical limits. The inhibition of mass transport from the cathode towards the anode because of the opposing stress gradient generated due to the back stress at the anode (see Eq. (5.10)) may stop the supply of required number of atoms to the root of the whisker, which is about to grow at the anode end. Hence, the existence of a critical product of length of the conductor and the current density for inhibition of the whiskering is also reasonable.

5.3.2 Minimizing Electromigration-Induced Whiskering Through Grain Boundary Engineering

The general methodologies for minimizing spontaneous whisker growth, as outlined in Section 5.2.2, may not be very useful for minimizing electromigration-induced whiskering in metallic films. However, as discussed in Section 5.3.1, minimizing electromigration can minimize whiskering in the conductors susceptible to electromigration-

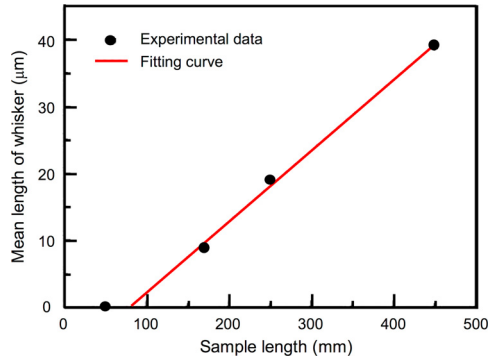


Figure 5.23 Variation of the mean length of whisker as a function of the length of the Sn film on glass substrate with Ti interlayer [86].

induced whiskering. It is generally considered that grain boundary diffusion can be the rate controlling process for electromigration as well as whiskering. Therefore, removal of grain boundaries along the direction of electron flow can reduce net electromigration flux and hence also electromigration-induced voiding at the cathode and whiskering at the anode end. In this regard, a film having bamboo-grained structure is preferred (i.e., grain boundaries perpendicular to the “main” flux direction). As mentioned previously, this strategy is quite effective in reducing the spontaneous whisker growth in Sn coatings (see Figs. 5.18–5.20). Interestingly, in thin metallic films susceptible to electromigration and electromigration-induced whiskering, this type of grain structure can be achieved by either reducing the width of the conducting film to be equal to or less than the average grain size or by annealing the film using some special technique (such as through abnormal grain growth [88], site specific laser treatment [89], etc.). This strategy also reduces the number of triple points, which often act as the location for flux divergence, and hence the spots for void formation as well as whisker growth are overall reduced in films with bamboo-grained structure. This, as shown in Fig. 5.24, then leads to longer time to failure. In addition, minor alloying with appropriate elements, such as adding a few at.% of Cu into Al, can also reduce the overall diffusivity through grain boundaries, resulting in decrease of electromigration flux and hence whisker growth.

It should be noted here that, unlike the case of spontaneous growth of whiskers in Sn coatings, the role of crystallographic texture on electromigration induced whisker growth is not very well understood. It is expected that tailoring the crystallographic texture, especially in low symmetry crystals (e.g., Sn), may also lead to a technology for reducing electromigration and hence whiskering.

However, diffusion through surface or the interface between the film and the substrate may become important when the width of the film becomes very small, especially in the films which do not form a defect-free oxide layer. This is particularly the case

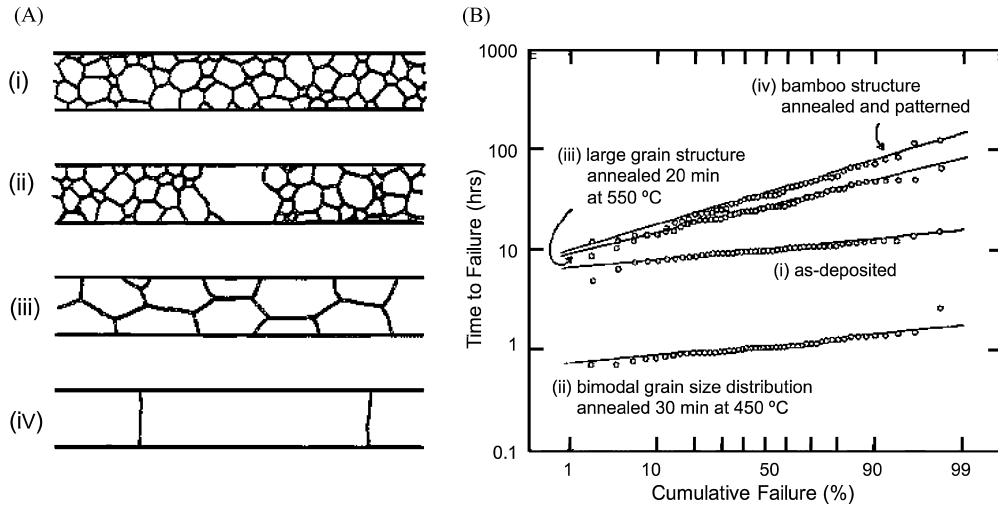


Figure 5.24 (A) Schematic illustration of evolution of grain structure of an Al-Cu-Cr film due to annealing. The schematics are based on the micrographs obtained using transmission electron microscope (TEM) [90]. (B) Variation of mean time to failure under identical electromigration condition for various samples having microstructures shown in (A). It is clear from (B) that the sample having bamboo grain structure has the highest mean time to failure [90].

in Cu films that do not form a surface oxide layer, which is as tenacious as Al_2O_3 on Al [90,91]. Thus, as shown in Fig. 5.25, a decrease in the width of film, and thereby an increase in the surface-to-volume ratio, increases the overall drift velocity due to electromigration and hence, possibly, whiskering also. For such film structures, it may be useful to place an interlayer or an overlayer of appropriate material (e.g., Ti for Cu instead of W, etc. [92]) for reducing diffusion through surface and hence reducing the overall effect of electromigration.

5.4 SUMMARY

- Electromigration is a diffusion-controlled phenomenon that leads to transport of material in a set direction. This transport is often from the cathode to the anode in solid metals, leading to voiding at the cathode and hillocking or whiskering at the anode. On the other hand, the material transport direction is not so well defined in liquid metals. With some exception, such as liquid Pb, most of the liquid metals move from the anode to the cathode. Since electromigration is a diffusion-controlled phenomenon, it is often very slow at service/low temperatures. Hence, accelerated tests are performed in a lab for quickly obtaining relevant electromigration parameters.

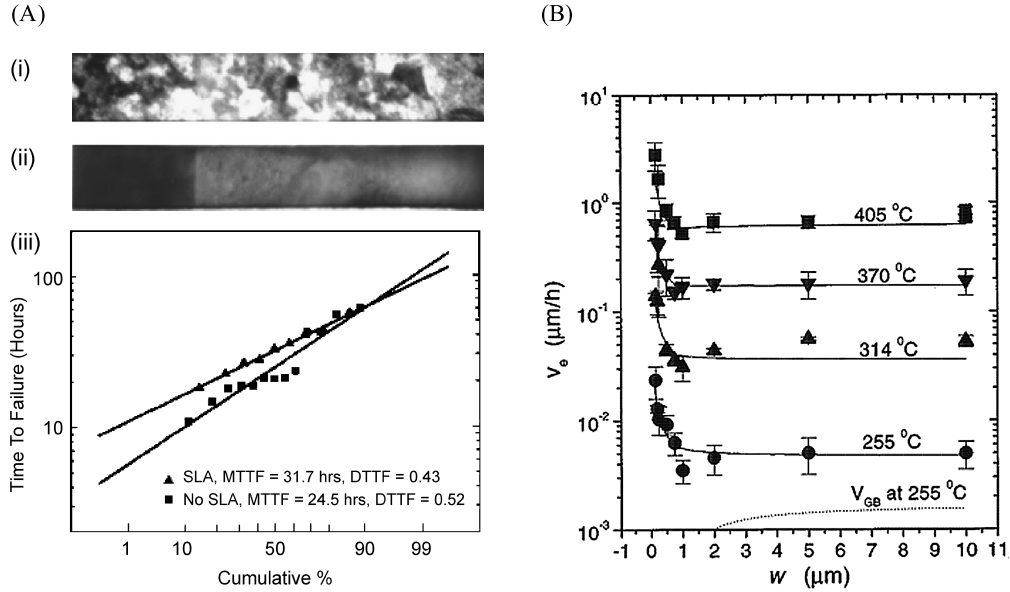


Figure 5.25 (A) Microstructure of Cu films in (i) as-deposited and (ii) after laser treatment during which grains having lengths several factors larger than the film width were produced, and (iii) the time to failure due to electromigration for Cu films with non-bamboo (i.e., no SLA) and bamboo (i.e., SLA) grain structures [89]. (B) The variation of the electromigration driven drift velocity of Cu film with width of the film at various temperatures [91].

- The drift velocity due to electromigration depends linearly on both the electric field (or current density) and diffusivity. Since the effective charge number, diffusivity, and electrical resistivity (and hence electric field) of various metals are different, electromigration may lead to separation of elements (or dealloying) in multi-element systems.
- Due to the drift of atoms from the cathode to the anode, there is accumulation of excessive vacancies at the cathode and depreciation of vacancies at the anode. This imbalance leads to generation of tensile and compressive stresses at the cathode and anode, respectively, thus creating a back-stress gradient from the cathode to the anode. If the back-stress gradient induced chemical potential is larger than electromigration induced forward chemical potential, there will be no electromigration damage. This often happens when the length of the conducting film is small and the current densities are low.
- Whisker growth is a stress relaxation phenomenon where atoms from highly compressed region diffuse to the stress-free region near the whisker root. Spontaneous whiskering occurs in several materials systems, such as Sn, Cd, Zn, etc. For continuous growth of whiskers, a self-regenerating source for stress and stress gradient, and

- a fast, unhindered diffusion path are required. In general, methods that can reduce the net diffusive flux in coatings can effectively reduce whisker growth.
- Since electromigration in solid metals generates a stress gradient and directionally transfer atoms from the cathode to the anode, it often leads to growth of whiskers near the anode. The whisker growth under electromigration condition is accelerated and usually the methodologies for suppressing spontaneous whisker growth are less effective in inhibiting electromigration-induced whisker growth. Electromigration and hence electromigration-induced whiskering can be minimized by reducing the length of the metallic film, minimizing temperature and current density, and by either reducing the width of the film or placing tenacious defect-free underlayer or overlayers around the film.
 - A general strategy for minimizing electromigration and whiskering is to reduce the overall diffusivity. One way to achieve it is via grain boundary engineering.

ACKNOWLEDGEMENTS

Help received from Dr. Santanu Talukder and Mr. Piyush Jagtap regarding the literature review on electromigration and whisker growth, respectively, is gratefully acknowledged. Some of the results reported in this chapter were obtained by Dr. Santanu Talukder, Mr. Piyush Jagtap, and Mr. Nalla Somaiah. The financial support from Indian Institute of Science – Indian Space Research Organization (IISc-ISRO) Space Technology Cell (STC) (Grant # ISTC 0367) and Department of Science and Technology, Government of India (Grant # DSTO 1526) is also acknowledged.

REFERENCES

- [1] K.-N. Tu, *Electronic Thin-Film Reliability*, Cambridge University Press, Cambridge, UK, 2010.
- [2] D.G. Pierce, P.G. Brusius, *Electromigration: a review*, *Microelectronics Reliability* 37 (1997) 1053.
- [3] J.R. Black, *Electromigration: a brief survey and some recent results*, *IEEE Trans. Electron. Devices* 16 (1969) 338.
- [4] A. Scorzoni, B. Neri, C. Caprile, F. Fantini, *Electromigration in thin-film interconnection lines: models, methods and results*, *Materials Science Reports* 7 (1991) 143.
- [5] J.R. Lloyd, *Electromigration in thin film conductors*, *Semiconductor Sci. Technol.* 12 (1997) 1177.
- [6] H.B. Huntington, A.R. Grone, *Current-induced marker motion in gold wires*, *J. Phys. Chem. Solids* 20 (1961) 76.
- [7] I.A. Blech, *Electromigration in thin aluminum films on titanium nitride*, *J. Appl. Phys.* 47 (1976) 1203.
- [8] I. Dutta, P. Kumar, *Electric current induced liquid metal flow: application to coating of micropatterned structures*, *Appl. Phys. Lett.* 94 (2009) 184104.
- [9] S. Talukder, N. Somaiah, P. Kumar, *Effect of substrate surface roughness on electric current induced flow of liquid metals*, *Appl. Phys. Lett.* 102 (2013) 054101.
- [10] P. Kumar, J. Howarth, I. Dutta, *Electric current induced flow of liquid metals: mechanism and substrate-surface effects*, *J. Appl. Phys.* 115 (2014) 044915.
- [11] P.S. Ho, T. Kwok, *Electromigration in metals*, *Rep. Prog. Phys.* 52 (1989) 301.
- [12] K.N. Tu, *Electromigration in stressed thin films*, *Phys. Rev. B* 45 (1992) 1409.
- [13] I. Ames, F.M. d'Heurle, R.E. Horstmann, *Reduction of electromigration in aluminum films by copper doping*, *IBM Journal of Research and Development* 14 (1970) 461.

- [14] Y. Chai, P.C.H. Chan, Y. Fu, Y.C. Chuang, C.Y. Liu, Electromigration studies of Cu/carbon nanotube composite interconnects using Blech structure, *IEEE Trans. Electron. Device Letters* 29 (2008) 1001.
- [15] F.M. d'Heurle, The effect of copper additions on electromigration in aluminum thin films, *Metallurgical Transactions* 2 (1971) 683.
- [16] F.M. d'Heurle, N.G. Ainslie, A. Gangulee, M.C. Shine, Activation energy for electromigration failure in aluminum films containing copper, *Journal of Vacuum Science & Technology* 9 (1972) 289.
- [17] J.T. Cook, Y.K. Joshi, R. Doraiswami, Interconnect thermal management of high power packaged electronic architectures, in: *Proc. 20th Annual IEEE Semiconductor Thermal Measurement and Management Symposium*, San Jose, 2004.
- [18] T. Nemoto, T. Nogami, Segregation of Cu to grain boundaries by aging treatment and its effect on EM resistance for AlCu/TiN lines, in: *Proc. of 1994 International Reliability Physics Symposium*, San Jose, 1994.
- [19] S. Talukder, P. Kumar, R. Pratap, Controlled material transport and multidimensional patterning at small length scales using electromigration, *Current Science* 108 (2015) 2167.
- [20] V.K. Andleigh, Modeling of and Experiments Characterizing Electromigration-Induced Failures in Interconnects, PhD Thesis, MIT, 2001.
- [21] S. Kondo, O. Deguchi, K. Hinode, Fast electromigration-lifetime prediction of Al-based layered metallization using the similarity of resistance increase curve, *Japanese J. Appl. Phys.* 36 (1997) 2077.
- [22] R. Frankovic, G.H. Bernstein, Electromigration drift and threshold in Cu thin-film interconnects, *IEEE Trans. Electron. Devices* 4 (1996) 2233.
- [23] N. Somaiah, D. Sharma, P. Kumar, Electric current induced forward and anomalous backward mass transport, *J. Phys. D* 49 (2016) 20LT01.
- [24] S. Strehle, S. Menzel, A. Jahn, U. Merkel, J.W. Bartha, K. Wetzig, Electromigration in electroplated Cu(Ag) alloy thin films investigated by means of single damascene Blech structures, *Microelectronic Engineering* 86 (2009) 2396.
- [25] I.A. Blech, C. Herring, Stress generation by electromigration, *Appl. Phys. Lett.* 29 (1976) 131.
- [26] I.A. Blech, Diffusional back flows during electromigration, *Acta Mater.* 46 (1998) 3717.
- [27] S. Talukder, P. Kumar, R. Pratap, Electric current induced mass flow in very thin infinite metallic films, *IEEE Trans. Electron. Devices* 60 (2013) 2877.
- [28] S. Talukder, P. Kumar, R. Pratap, Film thickness mediated transition in the kinetics of electric current induced flow of thin liquid metal films, *Appl. Phys. Lett.* 104 (2014) 214102.
- [29] S. Talukder, P. Kumar, R. Pratap, Electrolithography – a new and versatile process for nano patterning, *Scientific Reports* 5 (2015) 17753.
- [30] T. Ichinokawa, H. Iizumi, C. Haginoya, H. Itoh, Electromigration of metallic islands on the Si (001) surface, *Nanotechnology* 3 (1992) 147.
- [31] S. Talukder, P. Kumar, R. Pratap, Periodic pattern formation using electric field driven material transport, submitted.
- [32] R.S. Sorbello, Electromigration in liquid metal alloys, *Phys. Stat. Sol. B* 86 (1978) 671.
- [33] G.L. Hofman, A.G. Guy, Electromigration in gold–silver alloys, *J. Phys. Chem. Solids* 33 (1972) 2167.
- [34] Q.L. Yang, J.K. Shang, Interfacial segregation of Bi during current stressing of Sn–Bi/Cu solder interconnect, *J. Electronic Mater.* 34 (2005) 1363.
- [35] Y.C. Chan, D. Yang, Failure mechanisms of solder interconnects under current stressing in advanced electronic packages, *Prog. Mater. Sci.* 55 (2010) 428.
- [36] S.-H. Kim, G.-T. Park, J.-J. Park, Y.-B. Park, Effects of annealing, thermomigration and electromigration on the intermetallic compounds growth kinetics of Cu/Sn–2.5Ag microbump, *J. Nanoscience Nanotechnology* 15 (2015) 8593.
- [37] B. Chao, S.-H. Chae, X. Zhang, K.-H. Lu, M. Ding, J. Im, P. Ho, Electromigration enhanced intermetallic growth and void formation in Pb-free solder, *J. Appl. Phys.* 100 (2006) 084909.

- [38] H. Gan, K.N. Tu, Polarity effect of electromigration on kinetics of intermetallic compound formation in Pb-free solder V-groove samples, *J. Appl. Phys.* 97 (2005) 063514.
- [39] C.J. Meechan, G.W. Lehman, Diffusion of Au and Cu in a temperature gradient, *J. Appl. Phys.* 33 (1962) 634.
- [40] G.T. Galyon, Annotated tin whisker bibliography and anthology, *IEEE Trans. Electronics Packaging Manufacturing* 28 (2005) 94.
- [41] NASA Tin Whisker Homepage, <http://nepp.nasa.gov/whisker/index.html>.
- [42] H.L. Cobb, Cadmium whiskers, *Monthly Rev. Am. Electroplaters Soc.* 33 (1946) 28.
- [43] K.G. Compton, A. Mendizza, S.M. Arnold, Filamentary growths on metal surfaces whiskers, *Corrosion* 7 (1951) 327.
- [44] S.E. Koonce, S.M. Arnold, Growth of metal whiskers, *J. Appl. Phys.* 24 (1953) 65.
- [45] S.M. Arnold, The growth of metal whiskers on electrical components, in: *Proc. IEEE Electronic Components Technology Conf.*, 1959, pp. 75–82.
- [46] M. Fisher, L.S. Darken, K.G. Carroll, Accelerated growth of tin whiskers, *Acta Metall.* 2 (1954) 368.
- [47] C.H. Pitt, R.G. Henning, Pressure-induced growth of metal whiskers, *J. Appl. Phys.* 35 (1964) 459.
- [48] P.L. Key, Surface morphology of whisker crystals of tin, zinc, and cadmium, in: *Proc. IEEE Electronic Components and Technology Conf.*, May 1970, pp. 155–160.
- [49] H.P. Kehr, H.G. Kadereit, Tracer experiments on the growth of tin whiskers, *Appl. Phys. Lett.* 16 (1970) 411.
- [50] B.Z. Lee, D.N. Lee, Spontaneous growth mechanism of tin whiskers, *Acta Mater.* 46 (1998) 3701.
- [51] S.M. Arnold, Repressing the growth of tin whiskers, *Plating* 53 (1966) 96.
- [52] V.K. Glazunova, N.T. Kudryavtsev, An investigation of the conditions of spontaneous growth of filiform crystals on electrolytic coatings, *Zhurnal Prikladnoi Khimii* 36 (1963) 543, translated from Russian.
- [53] S.C. Britton, M. Clarke, Effects of diffusion from brass substrates into electrodeposited tin coatings on corrosion resistance and whisker growth, in: *Proc. 6th Int. Metal Finishing Conf.*, May 1964, pp. 205–211.
- [54] K.N. Tu, Inter-diffusion and reaction in bimetallic Cu–Sn thin films, *Acta Metall.* 21 (1973) 347.
- [55] K.N. Tu, Irreversible processes of spontaneous whisker growth in bimetallic Cu–Sn thin-film reactions, *Phys. Rev. B* 49 (1994) 2030.
- [56] E. Chason, N. Jadhav, W.L. Chan, L. Reinbold, K.S. Kumar, Whisker formation in Sn and Pb–Sn coatings: role of intermetallic growth, stress evolution, and plastic deformation processes, *Appl. Phys. Lett.* 92 (2008) 171901.
- [57] W.J. Choi, T.Y. Lee, K.N. Tu, N. Tamura, R.S. Celestre, A.A. MacDowell, Y.Y. Bong, L. Nguyen, Tin whiskers studied by synchrotron radiation scanning X-ray micro-diffraction, *Acta Materialia* 51 (2003) 6253.
- [58] M. Dittes, P. Oberndorff, P. Crema, V. Schroeder, The effect of temperature cycling on tin whisker formation, in: *Proc. IPC-JEDEC Conf.*, Frankfurt, Germany, Oct. 2003, pp. 105–111.
- [59] K.W. Moon, M.E. Williams, C.E. Johnson, G.R. Stafford, C.A. Handwerker, W.J. Boettinger, The formation of whiskers on electroplated tin containing copper, in: *Proc. 4th Pacific Rim Inter. Conf. Advanced Materials and Processing*, 2001, pp. 1115–1118.
- [60] W.J. Boettinger, C.E. Johnson, L.A. Bendersky, K.W. Moon, M.E. Williams, G.R. Stafford, Whisker and hillock formation on Sn, Sn–Cu and Sn–Pb electrodeposits, *Acta Mater.* 53 (2005) 5033.
- [61] U. Lindborg, A model for the spontaneous growth of Zn, cadmium, and tin whiskers, *Acta Metallurgica* 24 (1976) 181.
- [62] F.C. Frank, On tin whiskers, *Phil. Mag.* 44 (1953) 854.
- [63] J.D. Eshelby, A tentative theory of metallic whisker growth, *Phys. Rev.* 91 (1953) 755.
- [64] S. Amelinckx, W. Bontinck, W. Dekeyser, F. Seitz, On the formation and properties of helical dislocations, *Phil. Mag.* 2 (1957) 355.

- [65] W.C. Ellis, D.F. Gibbons, R.C. Treuting, Growth of metal whiskers from the solid, in: R.H. Doremus, B.W. Roberts, D. Turnbull (Eds.), *Growth and Perfection of Crystals*, Wiley, New York, NY, 1958, pp. 102–120.
- [66] N. Jadhav, E. Buchovecky, E. Chason, A. Bower, Real-time SEM/FIB studies of whisker growth and surface modification, *JOM* 62 (7) (2010) 30.
- [67] W. Chen, P. Sarobol, J.R. Holaday, C.A. Handwerker, J.E. Blendell, Effect of crystallographic texture, anisotropic elasticity, and thermal expansion on whisker formation in Sn thin films, *J. Mater. Res.* 29 (2014) 197.
- [68] P. Jagtap, P. Kumar, Manipulating crystallographic texture of Sn coatings by optimization of electrodeposition process conditions to suppress growth of whiskers, *J. Electronic Mater.* 44 (2015) 1206.
- [69] P. Jagtap, P. Kumar, Identification of whisker grain in Sn coatings using micro-texture analysis using electron back-scatter diffraction, submitted.
- [70] J. Stein, U. Welzel, A. Leineweber, W. Huegel, E.J. Mittemeijer, The crystallographic growth directions of Sn whiskers, *Acta Mater.* 86 (2015) 102.
- [71] J.B. LeBret, M.G. Norton, Electron microscopy study of tin whisker growth, *J. Mater. Res.* 18 (2003) 585.
- [72] F. Pei, A.F. Bower, E. Chason, Quantifying the rates of Sn whisker growth and plastic strain relaxation using thermally-induced stress, *J. Electronic Materials* 45 (2016) 21.
- [73] U. Welzel, E.J. Mittemeijer, Stress evolution in thin films; diffusion and reactions, *Defect Diffusion Forum* 264 (2007) 71.
- [74] E. Chason, F. Pei, Measuring the stress dependence of nucleation and growth processes in Sn whisker formation, *J. Electronic Materials* 67 (2015) 2416.
- [75] P. Jagtap, P. Kumar, Critical evaluation of relative importance of stress and stress gradient in whisker growth in Sn coatings, submitted.
- [76] Directive 2002/95/Ec of the European Parliament and of the council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment, <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:037:0019:0023:en:PDF>.
- [77] L. Meinshausen, S. Bhassivasantha, B.S. Majumdar, I. Dutta, Influence of indium addition on whisker mitigation in electroplated tin coatings on copper substrates, *J. Electronic Materials* 45 (2016) 791.
- [78] S. Banerjee, I. Dutta, B.S. Majumdar, A molecular dynamics evaluation of the effect of dopant addition on grain boundary diffusion in tin: implication for whisker growth, *Mater. Sci. Eng. A* 666 (2016) 191.
- [79] N. Jadhav, M. Williams, F. Pei, G. Stafford, E. Chason, Altering the mechanical properties of Sn films by alloying with Bi: mimicking the effect of Pb to suppress whiskers, *J. Electronic Materials* 42 (2013) 312.
- [80] E. Chason, N. Jadhav, W.L. Chan, L. Reinbold, K.S. Kumar, Whisker formation in Sn and Pb–Sn coatings: role of intermetallic growth, stress evolution, and plastic deformation processes, *Appl. Phys. Lett.* 92 (2008) 171901.
- [81] P. Jagtap, P. Kumar, Role of substrate composition in whisker growth and evaluation of Ni underlayer as a whisker mitigation technique, submitted.
- [82] R. Schetty, Whisker growth studies, in: *Proc. IPC Annu. Meeting and Technical Conf.*, Oct. 2001, pp. S03-7-1–S03-7-4.
- [83] A. Baated, K.S. Kim, K. Suganuma, Effect of intermetallic growth rate on spontaneous whisker growth from a tin coating on copper, *J. Mater. Sci.: Mater. Electronics* 22 (2011) 1685.
- [84] B. Horvath, B. Illes, T. Shinohara, G. Harsanyi, Whisker growth on annealed and recrystallized tin platings, *Thin Solid Films* 520 (2012) 5733.
- [85] M. Sobiech, U. Welzel, E.J. Mittemeijer, W. Hügel, A. Seekamp, Stress relaxation mechanisms of Sn and SnPb coatings electrodeposited on Cu: avoidance of whiskering, *J. Electronic Materials* 40 (2011) 2300.

- [86] W. Zhou, H. Zhang, P. Wu, Whisker growth in Sn and SnPb thin films under electromigration, *Vacuum* 107 (2014) 103.
- [87] F.Y. Ouyang, K. Chen, K.N. Tu, Y.S. Lai, Effect of current crowding on whisker growth at the anode in flip chip solder joints, *Appl. Phys. Lett.* 91 (2007) 231919.
- [88] H.P. Longworth, C.V. Thompson, Abnormal grain growth in aluminum alloy thin films, *J. Appl. Phys.* 69 (1991) 3929.
- [89] C.S. Hau-Reige, C.V. Thompson, Electromigration in Cu interconnects with very different grain structures, *Appl. Phys. Lett.* 78 (2001) 3451.
- [90] J. Cho, C.V. Thompson, Grain size dependence of electromigration-induced failures in narrow interconnects, *Appl. Phys. Lett.* 54 (1989) 2577.
- [91] C-K. Hu, R. Rosenberg, K.Y. Lee, Electromigration path in Cu thin-film lines, *Appl. Phys. Lett.* 74 (1999) 2945.
- [92] N. Somaiah, P. Kumar, Effect of interlayer on extent of electromigration damage in Cu thin films, submitted.

CHAPTER 6

Diffusion Couple Technique: A Research Tool in Materials Science

Alexander Kodentsov^{*}, Alope Paul[†]

^{*}Mat-Tech BV, Son, The Netherlands

[†]Indian Institute of Science, Bangalore, India

6.1 INTRODUCTION

The diffusion couple technique is a widely used experimental method in solid-state and materials science. This can be appreciated just by glancing through the current journals related to materials science and technology. The basic simplicity and versatility have undoubtedly contributed to the success of this technique as a “research tool.” For the same reasons, variations of the method are developing rapidly, and the field of their application is constantly widening. In view of the strong interest in this experimental approach, it was considered worthwhile to revisit this topic.

When contemplating writing a chapter for the handbook like the present one, it is necessary to ask: what does this account offer that is not already available? Since a number of good publications on this subject have appeared during the past decade [1–4], a new text has to be especially justified. Here, its main justification lies in its focus specifically on practical aspects of the diffusion couple method including experimental procedures used and error sources encountered, rather than on mere explanation of the techniques and their applications.

No attempt will be made to introduce any new experimental technique. However, the use of diffusion couples in phase diagram research, determination of diffusion characteristics of binary and ternary solid solution alloys and intermetallic compounds, as well as the application of the method in studying composition–structure–property relationships in inorganic materials, will be discussed in detail.

This chapter is based mainly on the authors’ own experience in the research on multi-phase diffusion, phase diagrams, and electron-probe microanalysis. It is not an intention here to present a complete annotated bibliography of the recent literature on the subject. It is proposed, instead, to single out for detailed description those investigations, which have made the most notable contributions to knowledge in this field. Throughout this chapter, references will be made to our original publications upon which much of the text is based. By reading these original articles, one gains a broader understanding and clear insights into the finer nuances of the diffusion couple method.

The approach adopted in the chapter is to demonstrate most of the ideas by selected examples of diffusion couple investigations in well-defined systems, each chosen for its clarity of illustration and related to the particular point of discussion. The inclusion of actual cases in the text should help reduce the difficulties often experienced in the interpretation of experimental observations.

The material is presented with a dual purpose. The systematic arrangement within each section, beginning with the introduction of the principle of the particular diffusion couple technique intended to use as a “research tool” and ending with the description of different error sources that may be encountered in this type of experiments, should make it possible for the newcomer to decide whether this method is suitable for his/her research problem. In the case of a positive answer, he/she should be able to design diffusion couple experiments best satisfying his/her needs. For the experienced investigator, in turn, there should be enough details available on specific experimental arrangements to add in solving a particular problem and comparing this approach to that of others.

It is also believed that the present chapter will be valuable to students in materials science and stimulating for their teachers.

Before considering applications of diffusion couple methods, it is important to make some general comments concerning sample preparation and analytical techniques employed. This will set the stage for better understanding of various aspects of the diffusion couple experiments, essential to the proper use of the technique as a “research tool”.

6.2 BASIC EXPERIMENTAL PROCEDURES USED IN DIFFUSION COUPLE METHOD

6.2.1 Preparation of Diffusion Couples

Several techniques are available to make diffusion couples, i.e., to bring two (or more) materials in such intimate contact that each diffuses into the other. In the most commonly used procedure, the bonding faces of the couple components are ground and polished flat, clamped together, and annealed at the temperature of interest. Depending on the initial materials, various ambient atmospheres can be used (e.g., vacuum, inert gas, etc.). After the heat treatment, quenching of the sample is desirable in order to freeze the high-temperature equilibrium.

For some metallic systems, different electrolytic and electroless plating techniques can also be utilized to fabricate diffusion couples. In this case, one half of the couple is typically a piece of a bulk alloy. The second half of the couple is formed by plating the second alloy onto the bulk alloy substrate.

Other plating (coating) techniques have also been employed, including plasma spraying and chemical vapor deposition (CVD). These techniques are suitable for both metals and nonmetals. Thermal evaporation, electron beam evaporation, or laser evaporation can be used as well to deposit the second component layer onto a bulk substrate.

It is also possible to create a multiphase diffusion couple by annealing a substrate material in a reactive gas atmosphere. Such experiments can be carried out in a conventional way (under isothermal conditions) or by imposing a temperature gradient perpendicular to the diffusion direction in the couple. The latter method enables one to observe competing phase reactions “simultaneously” as a function of temperature [5].

In order to study Kirkendall effect manifestations accompanying interdiffusion process, inert particles are often introduced as fiducial markers at the contact surface between the initial end-members. It should be stressed that selection of fiducial markers suitable for the visualization of Kirkendall effect is one of the challenging issues in diffusion couple experiments, and claims of the determination of the dominant diffusing species without the use of really inert markers may lead to confusing results.

Firstly, the markers must be “chemically” inert with respect to the reactants (end-members of the diffusion couple) as well as the reaction products. Secondly, the markers should be identifiable (unambiguously!) inside the reaction zone.

In the case of metallic systems, thorium dioxide (ThO_2) turned out to be an ideal material to use as a “fiducial” marker. This thermodynamically very stable oxide is not only chemically inert with respect to the initial materials and the reaction products but, more importantly, the ThO_2 -particles are easily identifiable in the diffusion zone by means of Scanning Electron Microscopy. Owing to the high atomic number of thorium, these particles exhibit a distinct contrast on backscattered electron images. In addition, their presence can be substantiated with Electron Probe Microanalysis simply by monitoring, for example, the characteristic ThM_α line when an electron probe is positioned in such a way that the anticipated volume of X-ray generation includes the oxide particle. The ThO_2 -markers are also recognizable (without any etching) by optical microscopy using bright-field and, in some cases, dark-field illumination.

Another important issue related to this subject is the size of particles used as fiducial markers. Obviously, too large particles may hinder interdiffusion. On the other hand, too small particles can be dragged inside the interaction zone by the moving grain boundaries [6]. The particles can be swept out of a volume of grain and accumulate on the grain boundary, which leaves a particle-denuded zone behind it.

In the majority of the examples described in this chapter, particles of thorium dioxide were introduced prior to annealing as fiducial (inert) markers at the contact interface between the initial end-members. The oxide powder with particle size of $\sim 0.5\text{--}1\text{ }\mu\text{m}$ was dispersed in acetone and then applied to the bonding faces. By means of this technique, agglomerates (up to $5\text{ }\mu\text{m}$) of ThO_2 plate-like crystals can more or less evenly be spread at the contact surfaces in the couple. No experimental evidence was found to indicate that the behavior of the ThO_2 -inclusions of this size has been affected by the presence of the grain boundaries within the interdiffusion zones. In other words, the ThO_2 -particles are too big to be dragged by the moving grain boundaries.

6.2.2 Analytical Techniques and Specimen Preparation

Sometimes phases present in the reaction zone of the diffusion couples can be detected with polarized light microscopy just by their polarization effect. Grains of crystalline phases exhibiting optical anisotropy show distinctly different colors in white polarized light due to reflection pleochroism. Further, Scanning Electron Microscopy (SEM), especially in combination with Electron Backscatter Diffraction (EBSD), can also be used to obtain information about microstructural features (grain morphology and orientation, the presence of texture, etc.) of the reaction zone.

However, in order to deduce any quantitative information from diffusion couple experiments, concentration profiles across the interaction zones have to be measured. In the case, when Kirkendall effect manifestations are the issue, the behavior of the inert markers during interdiffusion has to be monitored as well.

Different measurement techniques can be used to determine the chemical composition in the diffusion zone. These are Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectrometry (SIMS), Rutherford Backscattering Spectrometry (RBS), Electron Probe Microanalysis (EPMA), and Analytical Electron Microscopy (AEM). In the present discussion we shall be concerned only with the latter two methods, which are the most suitable for the investigation of “bulk” diffusion couples. The others are used for determining composition depth profiles in studies of interdiffusion and reactions in thin-film couples.

The EPMA has been used since the early 1960s to measure concentration profiles in interaction zones and has proven itself as an indispensable tool in diffusion couple experiments. By contrast, the AEM has become available for diffusion couple investigations somewhat later. Currently, the EPMA is a widely accepted technique for the quantitative analysis of the diffusion zone compositions. On the other hand, the complexities in specimen preparation and quantification of the results have prevented AEM from becoming a common method for diffusion couple studies. Nevertheless, these two techniques could form a powerful combination for the study of phase stability and reactive diffusion in solids.

In the EPMA high energy electrons are focused to a fine probe and directed at the point of interest in the diffusion couple. The incident electrons interact with the atoms in the sample and generate, among other signals, characteristic X-rays. These X-rays are detected and identified for qualitative analysis and with the use of suitable standards they can be corrected for matrix effects in order to perform quantitative analysis. In the EPMA bulk solid samples are investigated while the AEM is dealing with electron transparent thin films. Also the procedures used for X-ray quantification are quite different in both techniques.

The principal advantage of the EPMA is the ability to measure compositions of very small volumes of a specimen. The spatial resolution for bulk specimens is limited to approximately 1 μm . For thin foils, resolutions better than 50 nm are attainable routinely.

Obviously, in order to obtain the most reliable results, the operating conditions must be optimized. Accelerating voltage, beam current, and counting time are, perhaps, the most critical parameters. The optimization of these parameters has been discussed in detail [7] and will only be summarized briefly here.

- A ratio of operating accelerating voltage to excitation potential for the measured characteristic X-ray radiation of approximately 2 to 3 is desirable in order to maximize peak to background ratio and minimize the X-ray excitation volume.
- The value of beam current has to be chosen such that the X-ray counts are maximized for a statistically meaningful analysis without greatly increasing the electron beam size.
- Counting times must be long enough to allow the accumulation of sufficient X-ray counts for statistically meaningful results (without producing too much carbon contamination).

Presently, two different techniques, Wavelength Dispersive Spectrometry (WDS) and Energy Dispersive Spectrometry (EDS), can be used to collect X-ray spectra from the samples being analyzed. Both systems have specific advantages and disadvantages, and the choice will depend on the materials studied. In many modern instruments both types of spectrometers can be used simultaneously.

Some of the characteristics of these analytical systems, which are important with respect to quantitative analysis of diffusion zones, include the following.

For WDS: (i) elemental detection for atomic numbers $Z \geq 4$; (ii) X-ray energy resolution as good as 5 eV; and (iii) a high counting rate and low background which gives detectability limits on the order of 100 ppm. The disadvantages of the WDS include: (i) sequential detection of the elements; (ii) significantly higher equipment cost; and (iii) a relatively high beam current required.

For EDS: (i) elemental detection for atomic numbers $Z \geq 4$ with windowless and ultra-thin window detectors; (ii) maximum X-ray energy resolution approximately 130 eV at MnK_{α} ; (iii) a low count rate and a low peak to background ratio compared with the WDS system; and (iv) detectability limits of the order of 1000 ppm which is much higher compared to that of WDS. On the other hand, simultaneous detection for all elements is possible!

In this context, perhaps, one more issue deserves special attention. In the cases, when elements like boron, carbon, nitrogen, oxygen, or fluorine, which have an atomic number $Z \leq 9$, are present in the diffusion zone, a quantitative X-ray microanalysis is a real challenge. The practical problems which have to be faced during the analysis of these so-called “light elements” (with low-energy (<0.7 keV) K_{α} -lines) have been discussed in detail in [7,8]. We will only recall here a number of the most important points:

- **Low yield of X-rays** coupled with a relatively inefficient detection system (even when using spectrometers with advanced synthetic multilayer “crystals”, like, for example, W/Si or Mo/B₄C).
- **Dead-time-problems** for the characteristic X-ray lines of metals if these are to be measured simultaneously with the light element, which will usually be the case.
- **Interference** of higher-order characteristic X-ray lines of metal with the light-element line can be quite a nuisance, mainly in the analysis of carbon, nitrogen, and oxygen.
- **Contamination** problems, which play a very important role in the analysis of carbon, nitrogen, and oxygen. Because NK_α and OK_α X-rays are excessively absorbed in carbon, it is vital to prevent carbon build-up on the specimen during electron bombardment.
- The choice of **suitable standards** can often be quite a problem.
- The knowledge of the **mass absorption coefficients** (mac’s) is an extremely important issue. It has been pointed out by Bastin and Heijligers [8] that, as rule of thumb, an uncertainty of 1% in these values will in general produce an uncertainty of 1% in the calculated concentrations. Now, it seems highly unlikely that the published sets of mac’s for light elements are anywhere near within 1%. As a matter of fact, published values of mass absorption coefficients for light element X-rays may differ by as much as 100%!
- **The choice of a matrix correction program** still appears to be quite a problem, because it is still difficult to assess the performance of correction programs on light-element work as long as there are so many doubts about the correctness and consistency of the published values of mass absorption coefficients. Besides, there is a severe lack of reliable and consistent data on which correction programs could be tested.
- The intensity measurements for light-element radiation can be seriously influenced by **peak shift** and **peak shape alteration** which can occur simultaneously in the light-element-K_α emission spectrum when moving from standard to specimen. While the first problem can easily be dealt with by returning the spectrometer, the second problem is much more difficult to tackle. The direct consequence of peak shape alterations is that the net peak intensity, which is usually measured in day-to-day practice, is no longer a correct measure for the emitted intensity. In fact, this routine practice is based on the tacit assumption that the peak intensity is proportional to the integral intensity emitted by the specimen. Due to the sometimes extreme variations in peak shapes in light-element K_α-lines, however, this assumption no longer holds. As a result it is imperative to perform integral measurements, which is not a very attractive option, certainly not, of course, for a Wavelength Dispersive Spectrometer (WDS).

The conclusion of this part must be that accurate quantitative analysis of light elements (B, C, N, O, F) is definitely possible, provided that the measurements are performed carefully and on conductive specimens relative to a conductive standard, a good correction program is used and, last but not least, a consistent set of mass absorption coefficients is used.

Before terminating this discussion, some comments about preparation of diffusion couple specimens for EPMA should be made. As is the case in any microanalytical technique, specimen preparation is crucial. One must take care not to introduce into the experimental results any artifacts connected with the preparation of diffusion couple samples, which are to be analyzed with the EPMA.

Standard metallographic procedures can be used to prepare bulk diffusion couples for analysis by EPMA. The critical requirement is to prevent “smearing” across the interphase interfaces. Good metallographic practice, and, perhaps, on some occasions a final electropolish may prevent contamination of a given phase from an adjacent area of the sample. In addition, special care has to be taken so that there are no apparent height differences between the components of the couple.

In some cases, in order to improve electrical conductivity of the samples and make them suitable for electron microscopic investigations, a thin layer of carbon can be deposited in vacuum on the metallographically prepared surfaces.

Clearly, the proper choice of the analytical technique (and equipment) as well as specimen preparation procedures could mean the difference between getting correct answers about the sample and being totally wrong!

6.3 DERIVATION OF KINETIC DATA FROM DIFFUSION COUPLE EXPERIMENTS

6.3.1 General Considerations: Acquisition of Diffusion Data for Binary Solid Solution Systems

At the elemental level, a classical diffusion couple is nothing more than the juxtaposition of two “infinite” samples, one of which has uniform concentration C_1 and the other has concentration C_2 of the diffusing species. In this section, different parameters determined by the diffusion couple technique will be introduced. We will start this introduction by giving the necessary and useful equations in a rather general form. It is to be noted at the outset that reproduction of the mathematical expressions is presented here only to the extent necessary to facilitate discussion. More details concerning calculations of diffusion coefficients can be found in standard texts on diffusion [4,9,10].

The first difficulty is the definition of the dimensions for concentration and distance in the compositional profiles across the reaction zone. In fact, the frame of reference which is chosen for the description of the interdiffusion process determines the definition of the evaluated diffusion coefficients, and indeed quite a variety of definitions

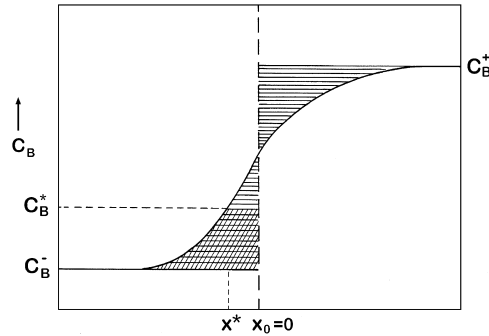


Figure 6.1 Concentration–penetration curve for component B in a diffusion couple between two alloys with starting compositions C_B^- and C_B^+ , respectively.

exist. As long as one is working in a consistent system, every evaluation is equally good, and the various diffusion coefficients can be transformed one into another.

For a binary interdiffusion process in which volume diffusion is a rate-limiting step, the evaluation of diffusion data from concentration profile is the same for single-phase and multiphase systems. It should be mentioned that the interdiffusion coefficient in a solid-state system is a single-valued function of composition only as long as local thermodynamic equilibrium for the formation of point defects within the reaction zone, viz. vacancies (and interstitials), is virtually established. It is also presumed that there are no voids or changes in the local cross-section of the diffusion couple (e.g., no formation of bulges and grooves in the vicinity of the moving phase boundary). In this case the *interdiffusion coefficient*, $\tilde{D}$, for a bulk diffusion-controlled process with constant partial molar volumes of the components can be derived in a simple and straightforward manner by a direct application of Matano–Boltzmann solution to Fick’s second law [11, 12]. The relationship so obtained takes into account the concentration dependence of the diffusion coefficient and the parabolic time dependence of the interdiffusion zone thickness. Utilization of the method is illustrated by Fig. 6.1.

The interdiffusion coefficient [m^2/s] is defined by Fick’s first law in the form $\tilde{J} = -\tilde{D} \times \frac{\partial C_i}{\partial x}$, where $\tilde{J}_i$ is the interdiffusion flux with respect to Matano plane of reference (see below) and C_i is the concentration of component i in mole/ m^3 . The interdiffusion coefficient can be determined at each composition C_B^* from the concentration profile of a diffusion couple as

$$\tilde{D}(C_B^*) = -\frac{1}{2t} \left(\frac{\partial x}{\partial C_B} \right)^* \int_{C-\infty}^{C_B^*} x dC \quad (6.1)$$

where x is the position parameter with respect to Matano plane, which is defined in such a way that

$$\int_{C_B^-}^{C_B^+} x dC = 0 \quad (6.2)$$

with C_B^- and C_B^+ being equal to the starting compositions of the end-members of the reaction couple (in mole/m³). This is the so-called Matano frame of reference.

The position of Matano interface, $x_0 = 0$, can be found by making the vertically enclosed areas in Fig. 6.1 equal. (The number of moles of material (component B) that entered the left-hand side of the couple equals the number of moles that disappeared from the right-hand side.)

In most cases it is impossible to solve Eq. (6.1) analytically. However, from the concentration profile of a diffusion couple (Fig. 6.1) the interdiffusion coefficient can be determined graphically. The integral in Eq. (6.1) is equal to the double-hatched area in Fig. 6.1, and the term $(\frac{\partial x}{\partial C_B})^*$ is the reciprocal of the concentration gradient at C_B^* . Using this procedure, the interdiffusion coefficient can be calculated as a function of the composition.

So far we have ignored the volume change during interdiffusion, i.e., we assumed that the partial molar volumes are independent of concentration. However, in practice this frequently will not be allowed, and the consequences of a variable molar volume for the determination of diffusion coefficients in binary systems have been thoroughly discussed by various authors [13–16].

For the sake of explanation, we consider here the use of Sauer and Freise method for acquiring diffusion characteristics of Ni–Pd solid solution alloys from the results obtained in diffusion couple experiments [17]. In Fig. 6.2 the variation, with composition, of the molar volume of a binary Ni–Pd solid solution at 900°C calculated based on the crystallographic information reported in [18] is given. One can see that the molar volume variation with composition of the Ni–Pd solid solution exhibits a positive deviation from Vegard's law. This means that interdiffusion in the Ni/Pd couple will result in an increase of the total volume of the reaction couple.

By definition, the partial molar volumes of Ni and Pd (V_{Ni} and V_{Pd}) in the solid solution are related to the molar volume V_m by [19]

$$V_m = N_{Ni} \times V_{Ni} + N_{Pd} \times V_{Pd} \quad (6.3)$$

and can be obtained graphically at any composition of the solid solution alloy as explained in Fig. 6.2.

No pore formation after heat-treatment of the Ni/Pd diffusion couples at 900–1200°C was observed. Concentration profiles in the annealed couples were measured with EPMA. As an example, the experimentally found distribution of nickel across

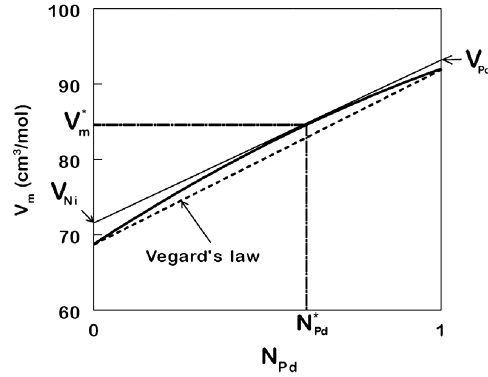


Figure 6.2 Concentration dependence of molar volume, V_m and partial molar volumes of nickel (V_{Ni}) and palladium (V_{Pd}) in a binary Ni-Pd solid solution at 900°C computed with the lattice parameter data reported in [18]. The partial molar volumes V_{Ni} and V_{Pd} for the composition of interest are given by the intercepts of the tangent to the curve at $N_{Ni} = 1$ and $N_{Pd} = 1$, respectively. (V_m^* is the molar volume of the solid solution alloy with composition N_{Pd}^* .)

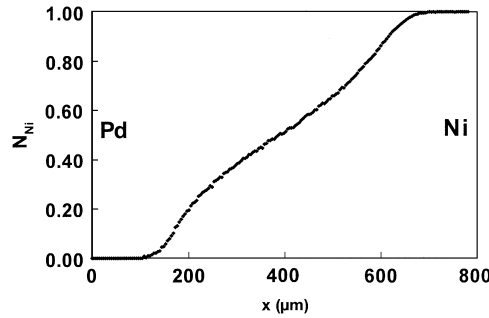


Figure 6.3 Concentration profile developed in a Ni/Pd diffusion couple after annealing at 1100°C for 196 hours.

interdiffusion zone (i.e., mole fraction N_{Ni} vs distance x) developed after interaction at 1100°C for 196 hours is shown in Fig. 6.3.

The experimentally measured concentration profile can be evaluated using Sauer and Freise method [13]. This analysis takes into account the total volume change during interaction and enables us to calculate the diffusion coefficients as

$$\tilde{D}(Y^*) = \frac{V_m}{2t} \left(\frac{dx}{dY} \right)^* [(1 - Y^*)] \int_{-\infty}^{x^*} \frac{Y}{V_m} dx + Y^* \int_{x^*}^{+\infty} \frac{1 - Y}{V_m} dx \quad (6.4)$$

where Y is defined as $\frac{(N_i - N_i^-)}{(N_i^+ - N_i^-)}$; N_i is the mole fraction of the component i , with N_i^- and N_i^+ being the mole fraction of component i at the unreacted left-hand ($x = -\infty$) and right-hand ($x = +\infty$) ends of the couple, respectively, and V_m is the molar volume.

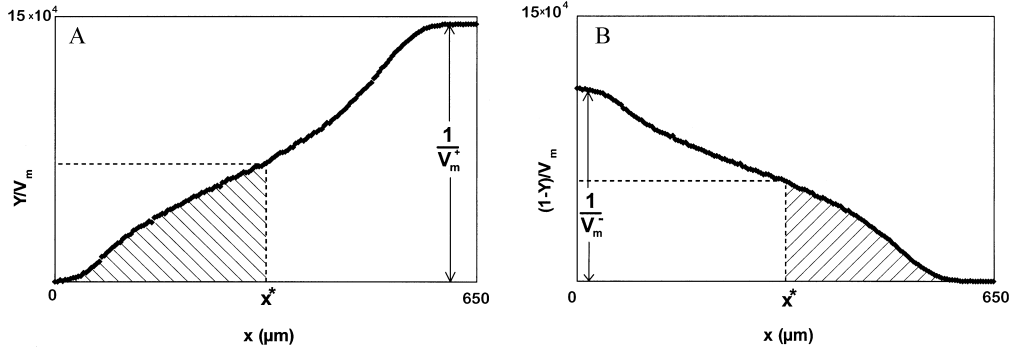


Figure 6.4 Penetration curves for an annealed Ni/Pd diffusion couple (1100°C; 196 hrs) constructed according to the Sauer and Freiser method. $Y = \frac{N_{Ni} - N_{Ni}^-}{N_{Ni}^+ - N_{Ni}^-}$; V_m^+ and V_m^- are the molar volumes of the right-hand and left-hand end-member of the couple, respectively, which are in this case equal to the molar volumes of pure Ni and Pd at 1100°C.

If values of the molar volume are known as a function of concentration, Eq. (6.4) can be solved graphically. To this end, we need to construct two graphs, namely $\frac{Y}{V_m}$ versus x , and $\frac{1-Y}{V_m}$ versus x . Such plots (penetration curves) for the annealed Ni/Pd couple (1100°C; 196 hours) derived based on the experimentally measured concentration profile and the available molar volume information are given in Fig. 6.4.

It follows from these graphs that the integrals $\int_{-\infty}^{x^*} \frac{Y}{V_m} dx$ and $\int_{x^*}^{+\infty} \frac{1-Y}{V_m} dx$ in Eq. (6.4) correspond to the enclosed areas.

Sauer and Freise approach was also used to determine interdiffusion coefficients in Ni–Pd solid solution from data obtained in the experiments with four *incremental* couples. In this particular case, homogeneous alloys with the compositions Ni 70 at.% Pd and Ni 30 at.% Pd were used as end-members in diffusion couples with pure Ni or Pd. The concentration dependence of the interdiffusion at 1100°C is shown in Fig. 6.5.

One can see that values derived from analysis of the incremental couples are consistent with those obtained by investigating the diffusion couple with pure Ni and Pd as end-members. This result is not unexpected since the interdiffusion coefficient is a material constant, which depends only on temperature and concentration. This also indicates that under the experimental conditions used, local thermodynamic equilibrium for the formation of point defects within the diffusion zone developed during annealing is virtually established.

It is to be recalled that the interdiffusion coefficients is only an “overall” measure for the redistribution of the elements, and give no information on the relative mobilities of the species involved in the interaction. A more fundamental quantity related to the latter issue is the *intrinsic diffusion coefficient*, D_i , of a component i pertinent to the particular alloy composition. This coefficient is directly related to the atom flux with respect to

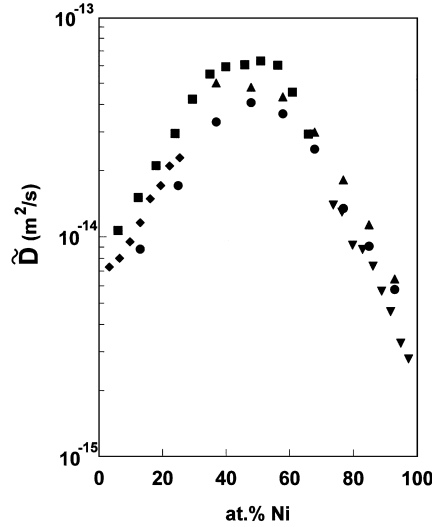


Figure 6.5 Interdiffusion coefficients in the Ni–Pd system at 1100°C, obtained with different diffusion couples: (●) Ni/Pd; (▲) Ni/Ni 70 at.% Pd; (▼) Ni/Ni 30 at.% Pd; (◆) Pd/Ni 70 at.% Pd; (■) Pd/Ni 30 at.% Pd.

the position of inert (fiducial) markers placed in the diffusion zone. In practice, the original interface, also called *Kirkendall plane*, is a convenient plane of reference. The position of that plane can be revealed by, for example, inert particles introduced at the original contact surface between end-members prior to annealing.

In general, the intrinsic diffusion fluxes, J_i [mole/m²s], of the components, which reflect the mobilities of species involved in the interaction, are then defined with respect to this array of inert markers, the so-called Kirkendall frame of reference:

$$J_i = -D_i \frac{\partial C_i}{\partial x} \quad (6.5)$$

where D_i [m²/s] is the intrinsic diffusion coefficient, C_i [mole/m³] is the concentration of component i , and x is the position parameter [m].

The sum of the oppositely directed intrinsic (volume) diffusion fluxes is equal to the velocity, v [m/s], of the inert markers with respect to the laboratory fixed-frame of reference,

$$v = - \sum_i V_i J_i, \quad (6.6)$$

with V_i [m³/mole] being the partial molar volume of component i .

Although the present analysis is valid for the general case of multicomponent diffusion, we will, in the present discussion, consider only interactions in binary systems.

In the case of a diffusion couple in a binary A–B system, the equations for the intrinsic fluxes can be written as

$$J_A = -D_A \frac{V_B}{V_m^2} \times \frac{\partial N_A}{\partial x} \quad \text{and} \quad J_B = -D_B \frac{V_A}{V_m^2} \times \frac{\partial N_B}{\partial x} \quad (6.7)$$

where N_i is the mole fraction of component i , V_m [m³/mole] is the molar volume, and V_i is the partial molar volume [m³/mole]; this is found through the tangent construction in the V_m vs. N_i plot [19].

The marker velocity is dependent on the difference in intrinsic diffusivities of the species and the concentration gradients developing in the zone of interdiffusion at the marker plane composition [20]

$$v = -(V_B J_B + V_A J_A) = V_B (D_B - D_A) \frac{\partial C_B}{\partial x}. \quad (6.8)$$

Of fundamental significance here is the fact that in a volume diffusion-controlled interaction, the inert markers positioned at the location of the original interface between the reactants (“Kirkendall plane”) are the only markers that (from the beginning) stay at a constant composition and move (during the whole interdiffusion process) parabolically in time with a velocity

$$v_K = \frac{dx}{dt} = \frac{x_K - x_0}{2t} = \frac{x_K}{2t}. \quad (6.9)$$

Here, x_K and $x_0 (= 0)$ are the positions of Kirkendall plane at times t and *zero*, respectively.

This concept of Kirkendall plane assumed a prominent place in the diffusion studies, as it provides a framework for evaluating relative mobilities of the species from diffusion couple experiments.

The location of Kirkendall plane in the diffusion zone can be found graphically as the intersection between the marker velocity plot $2v$ vs. x and the straight line $2v_K = x_K$ given by Eq. (6.9). Obviously, in order to draw the line $2v_K = x_K$, one needs to know the position of the plane in the diffusion zone where “Kirkendall markers” were located at time $t = 0$ (i.e., $x_0 = 0$).

It was found that in a diffusion-controlled interaction, Kirkendall plane, identified by inert particles placed at the initial interface between the reactants, need not be unique. Kirkendall plane can microstructurally (spatially) be stable as well as unstable, and can, under predictable circumstances, bifurcate and even trifurcate. However, in the present chapter, we will not go in details of this phenomenon, and the reader seeking more information on this fascinating, but rather complex subject is invited to access our original publications [3,4].

It is also possible to analyze Kirkendall effect accompanying interdiffusion in a series of *incremental* diffusion couples. In this case, the intrinsic diffusion coefficient

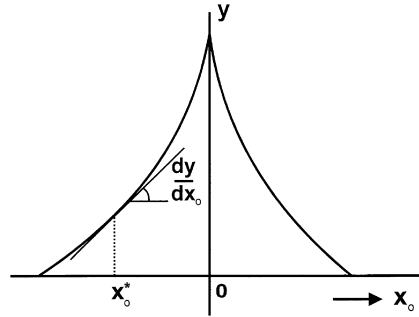


Figure 6.6 Schematic representation of marker displacement, y , vs. its original position x_0 in a multifoil diffusion couple.

can be obtained at the concentration, C_i^K , corresponding to the position of the stable Kirkendall plane using Sauer and Freise treatment with the following equation [21]:

$$D_i(C_i^K) = \frac{1}{2t} \left(\frac{\partial x}{\partial C_i} \right)_{x_K} \left[N_i^+ \int_{-\infty}^{x_K} \frac{Y}{V_m} dx - N_i^- \int_{x_K}^{+\infty} \frac{1-Y}{V_m} dx \right]. \quad (6.10)$$

Here again, Y is defined as $\frac{N_i - N_i^-}{N_i^+ - N_i^-}$, with N_i being the mole fraction of component i . The superscripts $+$ and $-$ refer to the mole fraction at the unreacted left-hand ($x = -\infty$) and right-hand ($x = +\infty$) ends of the couple, respectively. x_K is the position of the stable Kirkendall plane and V_m is the molar volume.

The usual method of placing inert markers only at the initial contact surface of the couple allows the determination of the intrinsic diffusion coefficients at only one composition (that of the stable Kirkendall marker plane). To extend these measurements over the entire range of concentrations, a “multi-foil” diffusion couple technique has been introduced [22].

The characteristic feature of a “multi-foil” sample is that each end-member of the diffusion couple is composed of several foils with fiducial markers in between. The total number of foils within the end-members and their thickness may vary depending on the interaction rate in the material system at the temperature of interest. Interdiffusion in such a multi-layered system will cause the markers to move relative to a laboratory-fixed frame of reference with Kirkendall velocity given by Eq. (6.8).

By measuring the shift of the markers, “Kirkendall displacement” can be determined over the entire diffusion zone and, subsequently, a displacement curve can be constructed (Fig. 6.6).

Levasseur and Philibert proposed a method to obtain Kirkendall velocity and the intrinsic diffusion coefficients from the displacement curve [23]. Later, this analysis was developed further due mainly to the work of Cornet and colleagues [24,25] and of van Loo and coworkers [26].

Kirkendall velocity can be found as

$$v = \frac{1}{2t} \left(\gamma - x_0 \frac{d\gamma}{dx_0} \right) \quad (6.11)$$

with x_0 being the original location of the markers and γ the displacement of the markers relative to x_0 . As can be seen from Eq. (6.9), the position of Kirkendall plane within the interdiffusion zone, as marked by inert markers placed at the initial interface ($x_0 = 0$), is given by $v_K = \gamma/2t$ (v_K is the velocity of the markers placed at the initial contact interface). The intrinsic diffusion coefficients can be calculated with the following equation [26]:

$$\frac{D_A}{D_B} = \frac{1 + Q \times C_A}{1 - Q \times C_B (V_B/V_A)} \quad \text{with} \quad Q = \frac{v}{\tilde{D} \times (dC_A/dx)} \quad (6.12)$$

where

$$\tilde{D} = D_A \times V_B \times C_B + D_B \times V_A \times C_A. \quad (6.13)$$

$\tilde{D}$ is the interdiffusion coefficient, which can be found from the measured concentration profile in the diffusion couple [12,13].

The present analysis provides the means to determine intrinsic diffusion coefficients in a binary metallic system over the whole concentration range from, in principle, one single experiment.

Let us return to our “case study” about diffusion in the Ni–Pd solid solution. A multi-foil diffusion couple was made in the following way. Twenty foils (20 μm thick) of Pd and 19 foils (21 μm thick) of Ni were pressed together between the plan-parallel slices (~ 1 mm thick) of pure metals (end-members). Thorium dioxide (ThO_2) particles (0.5–1 μm) were used as fiducial markers between the foils. The couple was annealed at 1100°C first for 9 hours, cross-sectioned and analyzed in order to determine the distances between the original foil interfaces. Then, the sample was annealed further at this temperature for up to 121 hours. Fig. 6.7 shows a cross-section of the couple after the heat-treatment.

No pore formation was observed in the diffusion zone. The ThO_2 -markers are clearly visible as straight rows of inclusions exhibiting a “white” contrast on the backscattered electron micrograph. From the concentration profile measured across the interaction zone, the interdiffusion coefficients for various compositions of the Ni–Pd solid solution at 1100°C were computed using Sauer and Freise method. As expected, the results are compatible with the values found by analyzing the incremental couples and the couples with the pure metals as end-members. This indicates that the initial foil interfaces and the ThO_2 -particles present across the diffusion zone do not interfere with the overall diffusion process.

The displacement of markers within the diffusion zone was calculated taking the first “marked” plane at the pure Ni-side of the couple as a reference (Fig. 6.8). The original

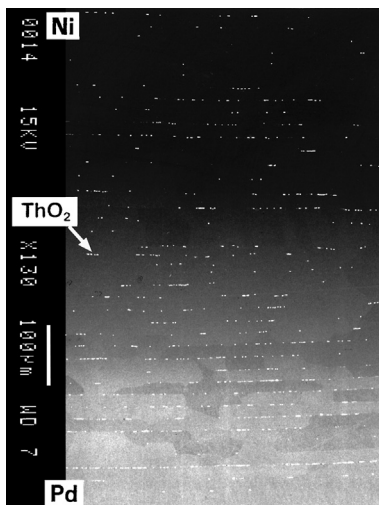


Figure 6.7 Backscattered electron image (BEI) of an Ni/Pd multifoil diffusion couple annealed at 1100°C for 121 hours in vacuum. The rows of ThO₂-particles used as fiducial markers correspond to the interfaces between the initial foils. Note that no pore formation occurred after the heat treatment.

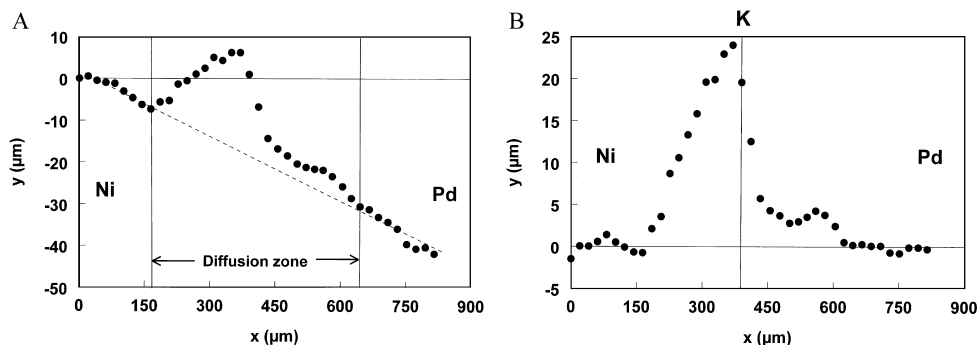


Figure 6.8 Displacement curves $[y(x)]$ (A) determined experimentally and (B) corrected for plastic deformation of a Ni/Pd multifoil diffusion couple annealed at 1100°C for 121 hours. (Letter K indicates the position of Kirkendall plane.)

marker positions were determined using the average values of the foil thicknesses (nickel or palladium) in the parts of the couple where after annealing at this temperature for 9 hours interdiffusion has not taken place, yet after annealing at this temperature for 9 hours.

It turned out that the markers located outside the interdiffusion zone are also shifted. Obviously, this is a direct outcome of the sample deformation (creep) caused by the pressure applied during the joining and annealing. To take into account the possible effect of plastic deformation and determine the genuine Kirkendall displacement, the following

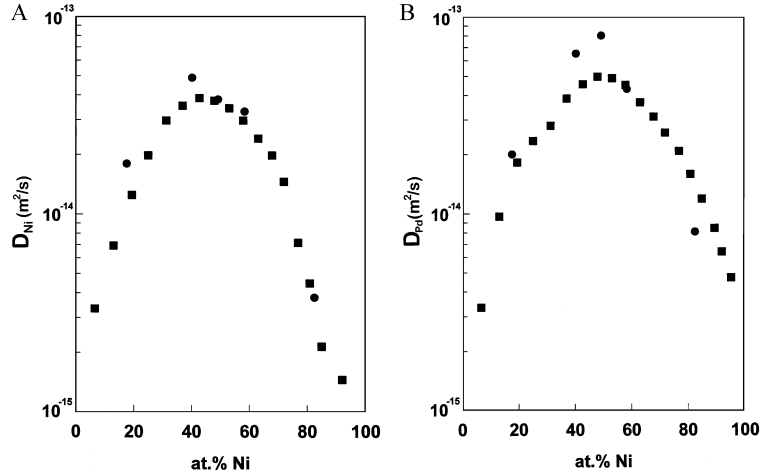


Figure 6.9 Intrinsic diffusion coefficients of (A) of nickel, D_{Ni} , and (B) palladium, D_{Pd} , in the Ni–Pd solid solution at 1100°C obtained with Ni/Pd (pure end-members) and incremental couples (●) and derived from the multifoil experiment (■).

procedure can be adopted. As a first approximation, the deformation rate at the end-members of the couple is assumed to be equal and constant. In such a case the line in Fig. 6.8(A) connecting the marker position inside the “unreacted” parts of the couple, i.e., outside the interdiffusion zone, represents the displacement of the markers resulting from the plastic deformation. The difference between the apparent marker displacement and the value corresponding to the “base-line” gives the actual Kirkendall shift. In this manner the displacement curve shown in Fig. 6.8(B) is constructed. Further, the intrinsic diffusion coefficients can readily be calculated for various concentrations of the binary Ni–Pd solid solution using the procedure explained above (Eqs. (6.11), (6.12) and (6.13)). The results are presented in Fig. 6.9.

The results are, in general, consistent with those obtained in the experiments on the Ni/Pd and incremental diffusion couples. It is relevant to notice that the intrinsic diffusion coefficient of Ni and Pd in the binary solid solution as a function of concentration goes through a maximum. That is somewhat similar to the behavior found for the interdiffusion in the system (Fig. 6.5). The maximum of the intrinsic diffusivities is also situated near the equatomic composition, which corresponds to the minimum of the melting point in the system [18].

As a variation of the “multifoil” method, another technique is to be mentioned [9]. An “oblique” interface can be created across a couple A/B with inert particles (markers) which are often simpler to prepare than the sample composed of many foils. Unfortunately, the interpretation of the results obtained in this type of experiments is by no means a straightforward procedure. Perhaps, for this reason it has been but little used.

Further, the intrinsic diffusion coefficients are related to the *tracer diffusion coefficients* D_i^* in the homogeneous phase of the same composition. For a binary A–B system this relation is given by [20]

$$D_B = D_B^* \times \frac{V_m}{V_A} \times \left[\frac{d \ln a_B}{d \ln N_B} \right] \quad (6.14)$$

with $\frac{d \ln a_B}{d \ln N_B} = \frac{d \ln a_A}{d \ln N_A}$ being the thermodynamic factor (a_A and a_B are the chemical activity of components A and B, respectively, with the pure elements under the experimental conditions as the reference state). V_m and V_A are the molar volume and partial molar volume of A, respectively. To put differently, diffusion couple experiments enable us to acquire also tracer diffusivities (mobilities) of species in solid solution alloys, provided that pertinent thermodynamic information is available.

6.3.2 Relations Between Thermodynamic Stabilities and Growth Kinetics of a Binary Stoichiometric Compound

It may be recalled that a diffusion-controlled reaction in a multiphase binary system will invariably result in single-layered diffusion zone morphology with a product layer sequence governed by the corresponding phase diagram. The reason for the development of only straight interfaces with fixed composition gaps follows directly from the phase rule. Three degrees of freedom are required to fix temperature and pressure and to vary the composition. Reaction morphologies consisting of two-phase structures (i.e., precipitates or wavy interfaces) are, therefore, thermodynamically forbidden since then only two degrees of freedom are allowed, assuming that only volume diffusion takes place.

In the ensuing discussion we will examine bulk semiinfinite diffusion couples in which one single-phased layer of intermetallic compound is diffusion-grown from its saturated adjacent phases. The parabolic growth constant determined in this way measures a unique property of a given phase, which is independent of the adjacent phases [14]. This provides a framework to determine all important diffusion parameters of the intermetallic phase in question if also the thermodynamic data are known.

Let us consider the diffusion-controlled growth of an intermetallic compound γ between the adjacent α and β phases in the A–B binary system (Fig. 6.10(A)). Suppose that all these phases have a narrow homogeneity range (“line-compounds”), i.e., have virtually constant composition with mole fractions as $N_A(\alpha) > N_A(\gamma) > N_A(\beta)$. Despite the very small concentration gradient within the growing γ phase layer, there may be, however, a rather high activity gradient providing the necessary driving force for diffusion.

As explained in the previous section, a fundamental quantity reflecting the mobilities of the species involved in the interaction is the intrinsic diffusion coefficient, D_i , of a component i in the product intermetallic layer. This coefficient is directly related

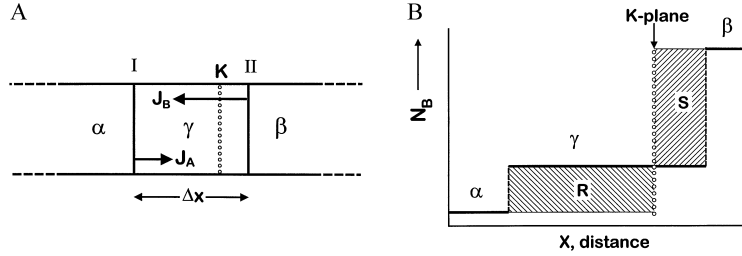


Figure 6.10 (A) A hypothetical reaction couple of the binary A–B system with a product layer of the γ -phase (line-compound) growing between the line compounds α and β and (B) corresponding distribution of component B across the diffusion zone. (Letter K indicates the position of Kirkendall plane.)

to the atom flux with respect to the position of fiducial markers placed in the diffusion zone. The markers introduced at the original interface at $t = 0$ define Kirkendall plane, as a reference plane. In the diffusion couple considered here, the ratio of intrinsic diffusivities, D_A/D_B , in the γ intermetallic can be found as [21]:

$$\frac{D_A}{D_B} = \frac{V_A}{V_B} \times \left[\frac{N_A^+ \times R - N_A^- \times S}{-N_B^- \times R + N_B^- \times S} \right] \quad (6.15)$$

where R and S equal the hatched areas in Fig. 6.10(B), N_i is the mole fraction, and V_i is the partial molar volume of the component i . The superscripts $+$ and $-$ refer to the mole fraction of component i in the end-member of the diffusion couple. In this case, $N_i^+ = N_i(\beta)$ and $N_i^- = N_i(\alpha)$.

It should be remarked that for line-compounds, the values of partial molar volumes are generally not available. One could circumvent this problem by taking $D_A \times V_B$ and $D_B \times V_A$ as material constants, which can be determined.

As already mentioned, the intrinsic diffusion coefficients are related to the tracer diffusion coefficients D_i^* as given by Eq. (6.14).

Substituting Eq. (6.14) in Fick's first law, we obtain the flux equations:

$$J_B = -D_B^* \times \frac{V_m}{V_A} \frac{d \ln a_B}{d \ln N_B} \times \frac{\partial C_B}{\partial x} \quad (6.16)$$

and

$$J_A = -D_A^* \times \frac{V_m}{V_B} \frac{d \ln a_A}{d \ln N_A} \times \frac{\partial C_A}{\partial x} = D_A^* \times \frac{V_m}{V_B} \frac{d \ln a_B}{d \ln N_B} \times \frac{\partial C_B}{\partial x}. \quad (6.17)$$

Here, we assume that A and B move independently across the reaction product layer, which is, in general, true in the case of non-ionic solids. Assuming further that the molar volume of the “line-compound” is constant over its (negligible) homogeneity range, the

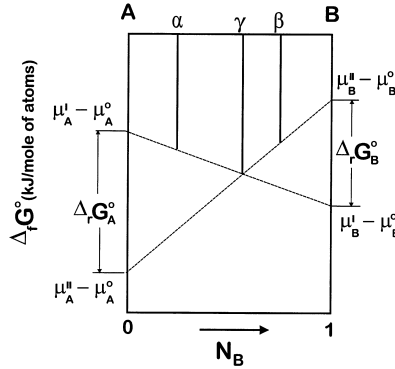


Figure 6.11 Stability diagram of the A–B system with three line-compounds, α , γ , and β . $\Delta_r G_A^o$ and $\Delta_r G_B^o$ indicate the change of the Gibbs free energy during the isothermal formation of the γ -phase in the α/β couple per mole of moving A- and B-atoms, respectively.

flux Eqs. (6.16) and (6.17) can be integrated using $dC_A = (\frac{V_B}{V_m})dN_A$ and $dC_B = (\frac{V_A}{V_m})dN_B$:

$$J_A \times \Delta x = -D_A^* \times \frac{N_A}{V_m} (\ln a_A^{\text{II}} - \ln a_A^{\text{I}}), \quad (6.18)$$

$$J_B \times \Delta x = -D_B^* \times \frac{N_B}{V_m} (\ln a_B^{\text{I}} - \ln a_B^{\text{II}}) \quad (6.19)$$

where superscripts I and II refer to the phase boundaries (Fig. 6.10(A)).

Eqs. (6.18) and (6.19) can be written in terms of change in Gibbs free energy, i.e., $\Delta_r G_A^o = RT \ln a_A^{\text{II}} - RT \ln a_A^{\text{I}}$ and $\Delta_r G_B^o = RT \ln a_B^{\text{I}} - RT \ln a_B^{\text{II}}$ [27]:

$$J_A \times \Delta x = -D_A^* \times \frac{N_A(\gamma)}{V_m(\gamma)} \times \frac{\Delta_r G_A^o}{RT}, \quad (6.20)$$

$$J_B \times \Delta x = D_B^* \times \frac{N_B(\gamma)}{V_m(\gamma)} \times \frac{\Delta_r G_B^o}{RT}, \quad (6.21)$$

with $V_m(\gamma)$ being the molar volume of the growing phase γ . $N_A(\gamma)$ and $N_B(\gamma)$ are mole fractions of A and B in the product line-compound.

The values of $\Delta_r G_A^o$ and $\Delta_r G_B^o$ can be visualized with the help of the thermodynamic stability diagram of the A–B system using the common tangent construction. This procedure is shown in Fig. 6.11.

It can be seen that, for example, $\Delta_r G_A^o$, the Gibbs energy of reaction per mole of moving A-atoms is equal (by definition) to $\Delta\mu_A$, which is the difference of the intersections of the common tangents to the $\Delta_f G^o$ “curves” of the coexisting phases on the ordinate at $N_B = 0$.

Following Wagner [14], the diffusion-controlled growth of the line-compound γ in between phases α and β coexisting with γ in the binary A–B system can be described by the parabolic rate constant:

$$k_p = \frac{(\Delta x)^2}{2t} \quad (6.22)$$

where Δx is the reaction layer thickness and t is the annealing time.

On the other hand, when phases with a very narrow region of homogeneity are formed during solid-state reaction, the concept of the *integrated diffusion coefficient*, $\tilde{D}_{\text{int}}$, can be used to describe the redistribution of the elements across the interaction zone [14]. This material constant is defined for a line-compound as the interdiffusion coefficient, $\tilde{D}$, in this phase integrated over its (unknown) homogeneity limits N' and N'' (N is the mole fraction):

$$\tilde{D}_{\text{int}} = \int_{N'}^{N''} \tilde{D} dN. \quad (6.23)$$

If in the binary reaction couple only one phase j grows between its saturated end-members, then $\tilde{D}_{\text{int}}$ of phase j can be found using the following equation:

$$\tilde{D}_{\text{int}}^j = (N - N^-) \times \frac{(N^+ - N^j)}{N^+ - N^-} \times \frac{(\Delta x^j)^2}{2t}. \quad (6.24)$$

N^j is the mole fraction of the components in phase j . Again, the superscripts + and – pertain to the mole fraction of that component in the end-members of the diffusion couple.

In the general case when phase γ is growing next to other compounds, Eq. (6.23) takes the form:

$$\tilde{D}_{\text{int}}(\gamma) = \left[\frac{a \times b}{a + b} \right] \times \frac{(\Delta x_\gamma)^2}{2t} + \frac{\Delta x_\gamma}{2t} \times \left[\frac{b \times P + a \times Q}{a + b} \right] \quad (6.25)$$

with P and Q equal the hatched areas in Fig. 6.12 and $a = N_B^\gamma - N_B^-$ and $b = N_B^+ - N_B^\gamma$, respectively. In the same way the integrated diffusion coefficients for the phases α and β can be found.

Since the integrated diffusion coefficient is a material constant, its value does not depend on the starting materials of the reaction couple. This means that the values of $\tilde{D}_{\text{int}}(\gamma)$ in the γ -phase (Fig. 6.12) will be the same in an A/B and an α/β incremental diffusion couple.

It was shown [27] that combining Eqs. (6.20), (6.21), and (6.23) leads to a general expression for the integrated diffusion coefficient in the γ compound:

$$\tilde{D}_{\text{int}}(\gamma) = -(N_B \times D_A^* + N_A \times D_B^*) \times \frac{N_A \times \Delta_r G_A^0}{RT}. \quad (6.26)$$

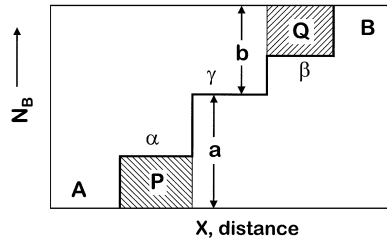


Figure 6.12 Schematic concentration profile of a diffusion couple A/B showing the formation of three line-compounds (α , γ , and β) and no terminal solid solutions.

It should be noticed that the term $N_A \times \Delta_r G_A^\circ$ equals $N_B \times \Delta_r G_B^\circ$, with $\Delta_r G_B^\circ$ being the Gibbs energy of the net reaction in the case one mole of B-atoms moves from the interface II to I (see Fig. 6.10(A)). Note that if phase γ grows directly in-between pure A and B, then there is a direct relation between the measured $\tilde{D}_{\text{int}}$ and the Gibbs energy of formation of the compound, $\Delta_f G^\circ(\gamma)$, as can be appreciated from the stability diagram (Fig. 6.11):

$$\tilde{D}_{\text{int}}(\gamma) = -(N_B \times D_A^* + N_A \times D_B^*) \times \frac{\Delta_f G^\circ(\gamma)}{RT}. \quad (6.27)$$

For the sake of illustration let us now consider a relatively simple example of interaction in the incremental diffusion couple $\text{Ni}_3\text{Si}/\text{Ni}_2\text{Si}$ at 900°C . In view of the Ni–Si phase diagram, the line-compound $\gamma\text{-Ni}_5\text{Si}_2$ forms between $\beta_1\text{-Ni}_3\text{Si}$ and $\delta\text{-Ni}_2\text{Si}$ phases, and practically no changes in molar volume occur during the reaction [18]. It should be noted that the chemical composition of the hexagonal Ni_5Si_2 -phase is, in fact, $\text{Ni}_{31}\text{Si}_{12}$, and Ni_3Si proved to be a phase which could be more accurately described as $\text{Ni}_{29}\text{Si}_9$. We will ignore these details for the moment and compare later on the results when they are taken into account.

In Fig. 6.13 a backscattered electron image of the diffusion zone of a $\text{Ni}_3\text{Si}/\delta\text{-Ni}_2\text{Si}$ couple after reaction at 900°C for 25 hours is given.

The position of Kirkendall plane is revealed by a row of markers inside the product Ni_5Si_2 layer. A pronounced columnar structure of grains on both sides of Kirkendall plane (“duplex” microstructure) is clearly visible. The grains within the reaction layer are oriented along the direction of the diffusion fluxes and are differently nucleated at the interfaces I and II. Therefore, they meet at Kirkendall plane, which can easily be seen even without the presence of any fiducial markers.

Since hardly any changes in total volume of the couple occur during diffusion interaction, relative mobilities of the Si- and Ni-atoms within the Ni_5Si_2 intermetallic layer can be estimated just from the resulting microstructure using the following reaction scheme.

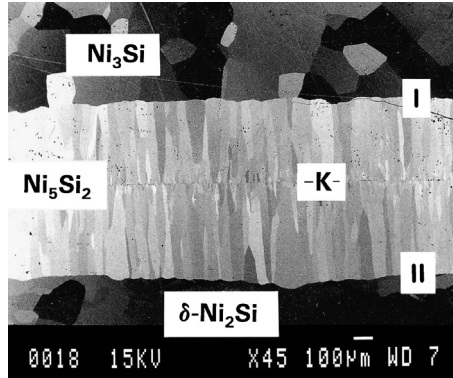
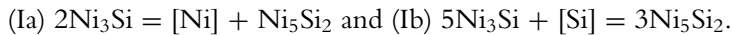


Figure 6.13 Backscattered electron image (BEI) of the reaction zone in the $\text{Ni}_3\text{Si}/\delta\text{-Ni}_2\text{Si}$ diffusion couple after annealing at 900°C for 25 hours in vacuum. (Letter K indicates the position of Kirkendall plane.) Note that the exact compositions of the Ni_3Si and Ni_5Si_2 phases are $\text{Ni}_{29}\text{Si}_9$ and $\text{Ni}_{31}\text{Si}_{12}$, respectively.

If the species have equal mobilities within the product layer, then the following reactions take place at the interface I (see Fig. 6.13):



At the interface II, on the other hand, the formation of the product phase results from the reactions: (IIa) $2\text{Ni}_2\text{Si} + [\text{Ni}] = \text{Ni}_5\text{Si}_2$ and (IIb) $5\text{Ni}_2\text{Si} = [\text{Si}] + 2\text{Ni}_5\text{Si}_2$.

In this situation the ratio of volumes of Ni_5Si_2 formed on either side of Kirkendall plane is 4:3. This is certainly not the case as it can immediately be seen from the micrograph shown in Fig. 6.13.

Suppose now that only silicon diffuses through the growing product layer and Ni-atoms are virtually immobile. Then growth of the Ni_5Si_2 -phase is mediated by the reactions (Ib) and (IIb), from which it follows that the Kirkendall plane in this case would divide the product phase layer into two parts in the ratio 3:2.

Consider the converse, i.e., that nickel is the only diffusing species. Then the interfacial reactions are given by the equations (Ia) and (IIa), which leads to the ratio 1:1. The last value is very close to that observed experimentally in the diffusion couple. If the exact stoichiometries had been used, the ratio would have been calculated as 0.9. This brings us to conclusion that the intrinsic diffusion of nickel in the Ni_5Si_2 -phase is much faster than that of silicon.

Let us now analyze the results one step further and ask about a quantitative measure for the material transport during the interaction. Since silicon atoms are virtually immobile in the reaction between Ni_3Si and Ni_2Si , a simplified form of Eq. (6.26) can be used to describe the relation between integrated diffusion coefficient in the Ni_5Si_2 -phase, $\tilde{D}_{\text{int}}(\text{Ni}_5\text{Si}_2)$, and tracer diffusivity (mobility) of nickel, D_{Ni}^* , in this in-

intermetallic compound:

$$\tilde{D}_{\text{int}}(\text{Ni}_5\text{Si}_2) = -\frac{5}{7} \times \frac{2}{7} \times D_{\text{Ni}}^* \times \frac{\Delta_r G_{\text{Ni}}^0}{RT}. \quad (6.28)$$

On the other hand, from Eq. (6.24) it follows that $\tilde{D}_{\text{int}}(\text{Ni}_5\text{Si}_2) = \frac{1}{49} \times k_p$. From this one finds a relation between measurable quantities, which can be verified:

$$k_p = -10 \times D_{\text{Ni}}^* \times \frac{\Delta_r G_{\text{Ni}}^0}{RT}. \quad (6.29)$$

As it was already discussed, $\Delta_r G_{\text{Ni}}^0$ refers to the Gibbs energy of the reaction $2\text{Ni}_3\text{Si} + 2\text{Ni}_2\text{Si} = 2\text{Ni}_5\text{Si}_2$, which is the net reaction when one mole of Ni-atoms is transported through the product layer from $\text{Ni}_3\text{Si}/\text{Ni}_5\text{Si}_2$ -interface (I) to the $\text{Ni}_5\text{Si}_2/\delta\text{-Ni}_2\text{Si}$ -interface (II). Also the factor 10 in Eq. (6.29) now becomes transparent: 1 mole of diffusing Ni atoms results in 10 moles of Ni in the growing Ni_5Si_2 -layer (2 moles Ni_5Si_2).

As to the information required to obtain value of $\Delta_r G_{\text{Ni}}^0$, it should be mentioned that a number of attempts have been made to carry out a thermodynamic evaluation of this system. Chart [28] published a critical assessment of thermochemical data for Ni-silicides, but the information was not complete. An analytical description of the system was performed by Kaufman [29] and an Mey [30]. In Fig. 6.14 the stability diagram of the Ni–Si system at 900°C constructed based on these two sets of data is given. In the both studies all nickel silicides were considered as line-compounds. However, it is unclear whether the authors treat Ni_3Si_2 and high-temperature phase $\theta\text{-Ni}_2\text{Si}$ as one phase or omit $\theta\text{-Ni}_2\text{Si}$ completely. (Note that, according the Ni–Si phase diagram [18], the $\varepsilon\text{-Ni}_3\text{Si}_2$ phase is not stable above 845°C.)

Although the results of the evaluations differ appreciably, both sets of data still allow the experimentally observed phase equilibria to be reasonably reproduced (in a sense that the phases stable according to the experimentally determined phase diagram are also stable according to the analytical description). This is no surprise because it is the difference in values of standard Gibbs energy of formation that determines the relative stability of phases. In such a situation it is not easy to make a “best” choice of thermodynamic parameters for further calculations because it is impossible to judge the quality of the assessments made since the pertinent experimental information is incomplete. Therefore, the following practical approach is recommended to work out the problem.

In Fig. 6.15 the isothermal cross-section through the ternary Ni–Si–C phase diagram at 900°C is given [32]. The phase relations were established by examining equilibrated powder compacts using X-ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis (EPMA).

The topology of the diagram implies that the chemical potential of silicon, μ_{Si} , in $\delta\text{-Ni}_2\text{Si}$ pertaining to the three-phase equilibrium $\delta\text{-Ni}_2\text{Si} + \text{SiC} + \text{C}$ has a value be-

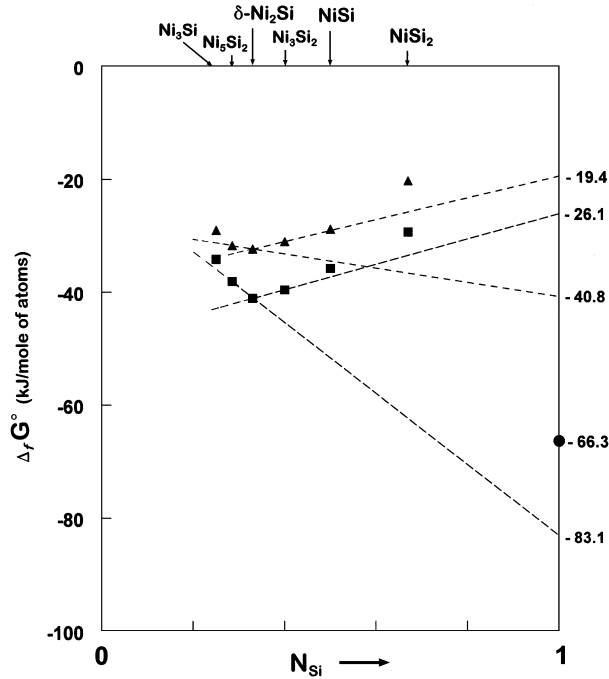


Figure 6.14 Stability diagram of Ni-silicides at 900°C based on data of Kaufman [29] (■) and an Mey [30] (▲). The value for the chemical potential of silicon in α -SiC, μ_{Si} , fixed by the monovariant equilibrium $SiC + C + \delta-Ni_2Si$ in the ternary Ni-Si-C system at 900°C was calculated with data from [31] and depicted as (●).

tween the values in the two-phase fields $Ni_5Si_2 + \delta-Ni_2Si$ and $\delta-Ni_2Si + "Ni_3Si_2"$ of the Ni-Si binary system. On the other hand, the chemical potential of silicon in silicon carbide fixed by the monovariant equilibrium involving SiC, $\delta-Ni_2Si$, and carbon can be found from the Gibbs energy of formation of SiC. Kleykamp [31] conducted a comprehensive study of the thermodynamic stability of the different polytypes (α -hexagonal and β -cubic) of SiC using the EMF-method. For the temperature interval 900–1050°C it was reported that $\Delta_f G^\circ (\alpha-SiC) = -94770 + 24.24T$ (T in K). With these data the chemical potential of silicon in α -SiC phase in equilibrium with $\delta-Ni_2Si$ and carbon was calculated to be -66.3 kJ/mole. This value is depicted in Fig. 6.14 on the ordinate at $N_{Si} = 1$.

Using the common tangent construction on the stability diagram, it can be determined which phase is in equilibrium with SiC in the ternary Ni-Si-C system. The procedure displayed in Fig. 6.14 is self-explanatory. It can be seen that the set of values for Gibbs energy of formation for Ni-silicides proposed by Kaufman in combination with the thermodynamic data of Kleykamp for silicon carbide are consistent with the experimental observations. Contrary, the data reported by an Mey, in combination with

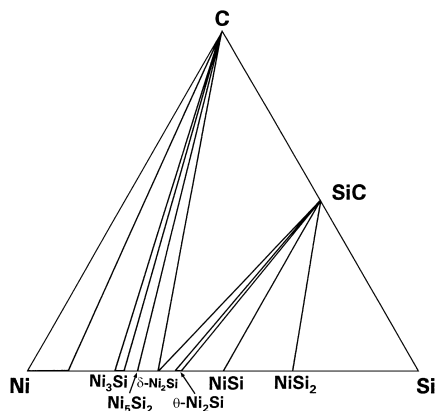


Figure 6.15 Experimentally determined isothermal cross-section through the Ni-Si-C phase diagram at 900°C [32].

the same value for Gibbs energy of formation of silicon carbide, will not lead to the right three-phase equilibrium as it can be appreciated from the stability diagram. They predict Ni_3Si to be stable next to SiC at this temperature. (Note that thermodynamic data on silicon carbide available in the literature are quite numerous and also show large scatter. We found that the assessment of an Mey, in combination with any of these data, will not predict the monovariant equilibrium $\delta\text{-Ni}_2\text{Si} + \text{SiC} + \text{C}$ in the Ni-Si-C system. Throughout this work Kleykamp's results were used because these measurements are performed over the temperature range pertinent to the present discussion.)

The integrated diffusion coefficient for the $\gamma\text{-Ni}_5\text{Si}_2$ intermetallic phase, $\tilde{D}_{\text{int}}$ (Ni_5Si_2) was determined at 900°C as $9.8 \cdot 10^{-14} \text{ m}^2/\text{s}$. This value, together with the Gibbs free energy of formation of Ni-silicides taken from the work of Kaufman (-34.2 , -38.1 , and $-41.1 \text{ kJ/mole of atoms}$ for $\beta_1\text{-Ni}_3\text{Si}$, $\gamma\text{-Ni}_5\text{Si}_2$, and $\delta\text{-Ni}_2\text{Si}$, respectively), leads to the tracer diffusion coefficient of Ni in the γ -phase, D_{Ni}^* (Ni_5Si_2), of approximately $4.8 \cdot 10^{-13} \text{ m}^2/\text{s}$.

Independent measurements of the diffusion rates of radioactive ^{63}Ni tracer in the lattice of equilibrated “bulk” Ni_5Si_2 samples [33] gave a value for the volume tracer diffusion coefficient of about $3.2 \cdot 10^{-13} \text{ m}^2/\text{s}$ at 900°C. This is quite compatible with the value derived from diffusion couple experiments.

Before leaving this topic, it is necessary to mention that in addition to the classical “diffusion-based” approach to evaluation of data obtained in diffusion couple experiments, another method of attack has proven very valuable. This involves the use (as a starting point) of chemical reaction equations occurring at the interphase interfaces formed in the interdiffusion zone. The proposed model is purely phenomenological, and its use is convenient, since no explicit assumption of the underlying mechanism is required. The analysis is valid irrespective of the diffusion mechanism (substitutional,

interstitial, or otherwise), supposing that the right thermodynamic definition of the partial molar volume is used. More details about application of the “physico-chemical” treatment to diffusion growth of intermetallic compounds can be found in [3,4].

6.3.3 Deficiencies of the Proposed Method

From a theoretical as well as practical point of view, it is interesting to have means that enable us to obtain tracer diffusivities (atomic mobilities) of species in solid solution alloys and ordered phases (intermetallic compounds) using just data that are relatively easily attainable in experiments (like intrinsic mobilities, growth constants or integrated diffusion coefficients and thermodynamic information). Such a technique has an obvious advantage. It is not necessary to produce phases of interest in their pure form and apply radioactive tracers, which can be not only very tedious and time-consuming, but also frequently (especially in the case of intermetallics) it is not possible at all. The latter can be due to the lack of a relevant radioactive tracer or to technical difficulties in preparing of single-phase intermetallic alloys.

However, judicious cautions should be exercised in applying the proposed general deductions in evaluating diffusion transport during intermetallic formation. In this respect, several points are to be noted.

As demonstrated in the previous section, the first problem that may arise is the reliability of the thermodynamic information that can be found in the literature or in various databanks. It is important to emphasize that the accuracy in calculating Gibbs energy change, $\Delta_r G_i^\circ$ (per one mole of moving i -atoms) cannot be expected to be very high. Apparently, this is because of the change in Gibbs energy in the net reactions per one mole of moving atoms is much smaller than the Gibbs energies of formation of the product intermetallic.

Secondly, the term V_m/V_i in the flux equations (6.16) and (6.17) can be determined only if the variation of the molar volume of the phase within the homogeneity region is known. Especially for phases with a very narrow region of homogeneity, this relation is commonly unknown and there is no simple experiment to obtain it. If this term is assumed to be equal to unity then it implies that the molar volume is constant over the very small homogeneity range. At first sight, this seems to be a reasonable assumption. However, one has to realize that even a small deviation from a constant volume may affect the V_m/V_i -ratio considerably because the change in atomic fraction from one compositional limit of the stability region to another is very small, too.

Thirdly, in the analysis employed in the present paper the vacancy wind factor is not taken into account (see Eq. (6.14)). It should be remembered that this term was introduced by Manning [34] on the basis of his random-alloy model. It is not clear for now whether and how the Manning’s approach can be applied to ordered alloys. Apart from theoretical studies (see, for example, [35,36]), it should be remarked here that to

the best of authors' knowledge no consistent experimental data on the vacancy wind factor have been published.

Another question that might cause uneasiness in determining diffusion coefficients in the ordered phases regards the stable Kirkendall plane location within a product phase layer.

Very great accuracy in measuring the position of the (stable) Kirkendall plane is required to get reliable values for the ratio of the intrinsic diffusivities. Bastin and Rieck [37] pointed out that the accuracy of the measured position of Kirkendall plane is not enough to differentiate between values of 10 and infinity for the ratio of the intrinsic diffusion coefficients.

It was also observed that under certain conditions, fiducial markers originally situated at the contact surface of the multiphase diffusion couple may accumulate upon interdiffusion at one specific interphase interface because they cannot end up in any of the product phases [3]. This finding appears to be particularly significant. The position of the marker plane at such interface does not necessarily result in conclusions about the diffusion properties of both phases. Only a position of the (stable) Kirkendall plane within a phase layer leads to reliable information about the relative mobilities of the components.

Perhaps, in this context one more complication that may arise in describing reactive phase formation in diffusion couples is to be mentioned. The presence of pores (voids) in the diffusion-growing layer may render the interpretation of growth kinetics quite problematic.

A very illustrative example of such a situation is provided by the study of the formation of CoSi-phase in the reaction zone of a Co₂Si/CoSi₂ diffusion couple [38]. Fig. 6.16 shows the reaction zone between Co₂Si and CoSi₂ intermetallics after annealing at 1000°C for 49 hours. Prior to joining, small particles (~0.5 μm) of thorium dioxide (ThO₂) as fiducial markers were introduced between the initial end-members.

It can be seen that the morphology of the growing phase layer is quite different on either side of Kirkendall plane. On the Co-rich side of the reaction zone, grains of CoSi are relatively large and have a columnar shape, whereas the Si-rich side favors a smaller size but still of more or less columnar morphology. The location of Kirkendall plane is such that the ratio of thicknesses of CoSi on either side of the plane is approximately 1:1.5. If all Co-silicides are considered as purely stoichiometric line-compounds (which is a good approximation [39]), then the analysis, explained in details earlier for the case of the Ni₃Si/δ-Ni₂Si couple, yields the ratio of intrinsic(tracer) diffusivities in the CoSi intermetallic as $\frac{D_{Si}}{D_{Co}} = \frac{D_{Si}^*}{D_{Co}^*} \approx 4$.

Regarding this estimate, a few words of caution are desirable. By contrast with the previous example of Ni₃Si/δ-Ni₂Si interaction, where hardly any change in total volume occurs, the formation of the CoSi-phase during solid state reaction between Co₂Si and CoSi₂ is accompanied by a significant shrinking of the reaction couple. (The molar

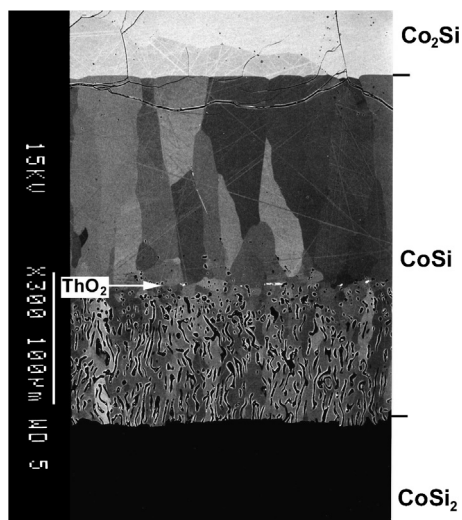


Figure 6.16 Backscattered electron image (BEI) of the $\text{Co}_2\text{Si}/\text{CoSi}_2$ diffusion couple after reaction at 1000°C in vacuum for 49 hours. (Letter K indicates the position of Kirkendall plane.)

volumes of the Co_2Si , CoSi and CoSi_2 are 6.65, 6.62, and $7.75 \text{ cm}^3/\text{mole}$ of atoms, respectively [40].) Given the rather poor mechanical characteristics of the Co-silicides, it is conceivable that the volume difference is not healed through plastic deformation, but persists as pores. It is also interesting that the pore formation occurs only in the part of the CoSi -reaction layer, which is contiguous with the CoSi_2 end-member.

In the case at hand, the kinetic data derived directly from diffusion couple experiments has to be corrected by taking into account the porosity of the CoSi -product layer. To this end, a sufficiently large number of randomly selected cross-sections of the CoSi -layer were subjected to an areal analysis using image processing software. In this manner, an average porosity value of this part of the product layer (i.e., the part of the CoSi layer between Kirkendall plane and the $\text{CoSi}/\text{CoSi}_2$ phase boundary) was estimated as about $(23 \pm 2)\%$ relative for all $\text{CoSi}/\text{CoSi}_2$ diffusion couples annealed in the temperature interval $914\text{--}1217^\circ\text{C}$. In all further calculations, the thickness measurements have been corrected for this volume effect. As an example, three sets of corrected data at different temperatures are shown in Fig. 6.17.

The square of the CoSi -layer thickness in the $\text{CoSi}_2/\text{Co}_2\text{Si}$ reaction couple increases linearly with time, which is indicative for a diffusion-limited kinetics. The corrected results of the layer thickness measurements were also used to determine the integrated diffusion coefficient for the CoSi , $\tilde{D}_{\text{int}}(\text{CoSi})$, at different temperatures. The values computed with Eq. (6.24) are given in Table 6.1.

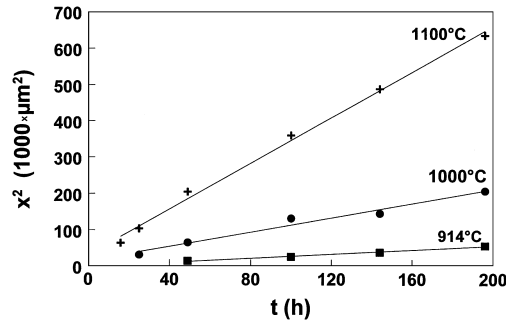


Figure 6.17 Parabolic growth of the CoSi-intermetallic layer in Co₂Si/CoSi₂ diffusion couples.

Table 6.1 Ratio of intrinsic diffusivities of Si and Co, $\frac{D_{Si}}{D_{Co}}$, the integrated diffusion coefficient, $\tilde{D}_{int}$, and the tracer diffusion coefficient of Si, D_{Si}^* , in the CoSi compound at various temperatures between 914–1217°C as determined using approach described in the text

t (°C)	$\frac{D_{Si}}{D_{Co}}$	$\tilde{D}_{int}$ (10^{-15} m ² /s)	D_{Si}^* (10^{-15} m ² /s)
914	20–∞	3.24	1.49
955	69	8.19	6.57
1000	48–∞	13.9	11.7
1048	87	21.7	19.1
1100	20–∞	43.6	40.5
1156	∞	91.7	89.8
1217	∞	208	216

If these data are plotted in Arrhenius coordinates, an essentially straight line is obtained (Fig. 6.18). From this graph, the apparent activation energy of about 192 kJ/mole (~ 2.0 eV) and the preexponential factor of $\sim 9.7 \cdot 10^{-7}$ m²/s were found.

For each analyzed CoSi₂/Co₂Si-couple, the ratio of intrinsic diffusivities of the components in the CoSi-phase, $\frac{D_{Si}}{D_{Co}} = \frac{D_{Si}^*}{D_{Co}^*}$, was deduced from the observed location of Kirkendall plane by applying Eq. (6.15) (see also construction in Fig. 6.10(B)). The pore formation within the reaction product layer was taken into account. The results are summarized in Table 6.1.

As seen from the table, the values of the $\frac{D_{Si}}{D_{Co}} = \frac{D_{Si}^*}{D_{Co}^*}$ ratio found in these experiments are ranging from 20 to, in principle, infinite. As already stated, the accuracy of the measured position of Kirkendall plane is not enough to differentiate between values of 10 and infinity for the ratio of the intrinsic diffusion coefficients.

The described investigation proves that at 914–1217°C silicon is by far the most (or even virtually the only) mobile species in the CoSi intermetallic, i.e., $D_{Si}^* \gg D_{Co}^*$. This may also explain why the porosity appeared only in the part of the diffusion-grown CoSi-layer, which is contiguous with CoSi₂ end-member. Since Si is virtually the only

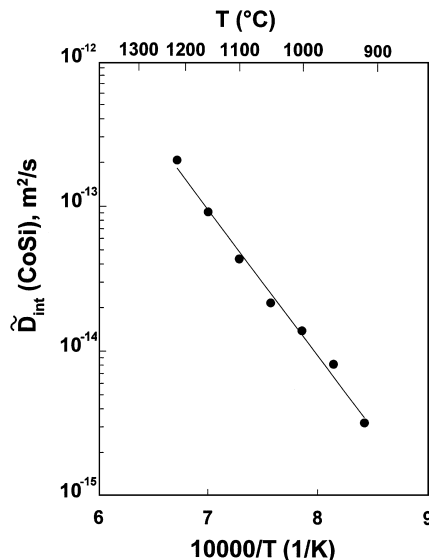


Figure 6.18 Arrhenius plot of the integrated diffusion coefficient for the CoSi-phase.

mobile species in the CoSi-intermetallic, the Kirkendall effect-induced pore formation takes place exclusively at the “CoSi₂-side” of the reaction product, which loses half its Si-content.

Now, using data on the integrated diffusion coefficient, $\tilde{D}_{\text{int}}(\text{CoSi})$, and the thermodynamic parameters given in Table 6.1, the corresponding values of tracer diffusion coefficients of silicon, D_{Si}^* , in the CoSi ordered phase can be obtained with Eq. (6.26). The results so estimated for the temperature interval 914–1217°C are listed in Table 6.1. The same set of computed values is also presented graphically in Fig. 6.19 as a function of the reciprocal temperature.

In this case, least-squares fit of an Arrhenius equation yields for tracer diffusion of silicon in the CoSi intermetallic:

$$D_{\text{Si}}^* = 3.2 \times 10^{-6} \exp\left(\frac{-206000}{RT}\right) [\text{m}^2/\text{s}]. \quad (6.30)$$

Finally, it should be stressed that in the foregoing discussion we tacitly assumed that the initial end-members of the couple (reactants) and products are monocrystalline materials. Obviously, this is not the case here. Diffusion along grain boundaries, being commonly orders of magnitude faster than through the bulk of the crystal, may play a definite role (especially at low homologous temperatures) in the overall mass transport within the reaction zone. It is possible that the tracer diffusion coefficients obtained with Eq. (6.26) are effective ones, which comprise lattice and grain boundary diffusivi-

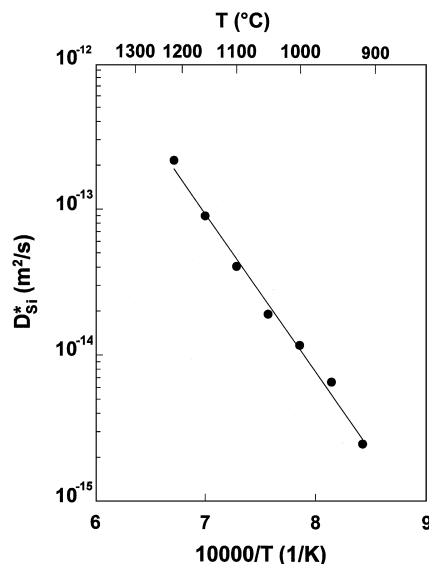


Figure 6.19 Arrhenius plot of the tracer diffusivity of Si in the CoSi-phase.

ties. At relatively high temperatures, however, the contribution of diffusion along grain boundaries to reactive growth is not expected to be significant, providing the grains within the product layers are sufficiently large.

In our particular example confirmation that short-circuit diffusion might contribute to the growth of Ni_5Si_2 came from the binary diffusion couple experiments performed in the temperature interval 600–1100°C. The study demonstrated that under these experimental conditions the growth of Ni_5Si_2 is a diffusion-controlled process and nickel is virtually the only mobile species in the product layer. The data are presented in Fig. 6.20, where one sees that the temperature dependence of the integrated diffusion coefficient for the Ni_5Si_2 product phase cannot be described by a simple Arrhenius relation in the entire temperature range.

In general, the temperature dependence of the integrated diffusion coefficient does not necessarily follow the Arrhenius law because the homogeneity region of a phase, although very narrow, may also change with the temperature. The latter can make the relation between $\bar{D}_{int}$ and T somewhat more complicated. However, in the case considered here, the Arrhenius plot for the integrated diffusion coefficient exhibits a distinct transition point where the apparent activation energy changes notably. The values of activation energies were estimated as ~ 2.1 eV (~ 210 kJ/mole) and ~ 1.0 eV (95 kJ/mole) for high (900–1100°C) and low (600–850°C) temperature domains, respectively. This observation suggests that besides volume (lattice) diffusion (high temperature part of the graph) also some form of short-circuit diffusion with a much smaller activation

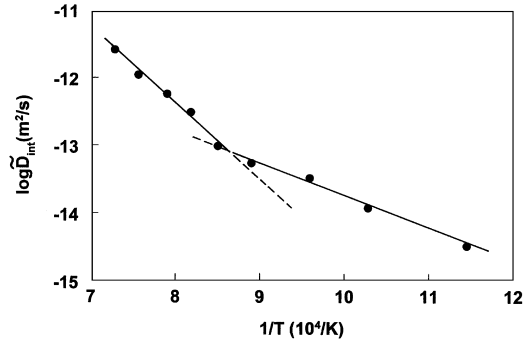


Figure 6.20 Arrhenius plot of the integrated diffusion coefficient for the Ni_5Si_2 ($\text{Ni}_{31}\text{Si}_{12}$) phase, showing two linear regimes.

energy contributes significantly to the mass transport at low temperatures. It follows that even in the case of a parabolic growth rate the tracer diffusion coefficient of nickel obtained with Eq. (6.29) is a combination of lattice and grain boundary diffusivities.

As already mentioned, the newly formed layer of Ni_5Si_2 in the reaction zone of the $\text{Ni}_3\text{Si}/\delta\text{-Ni}_2\text{Si}$ couple exhibits a columnar morphology (Fig. 6.13). Columnar type morphology of the crystals within a product layer is usually associated with anisotropic diffusion behavior. If this were the case, crystals of the new phase in the reaction layer would grow with their “fast growth direction” parallel to the direction of diffusion fluxes. The latter would result in developing of a texture in the diffusion-grown layer. Indeed, the presence of a weak texture was detected [33] in the Ni_5Si_2 -phase, grown in the diffusion couple $\text{Ni}_3\text{Si}/\delta\text{-Ni}_2\text{Si}$ at 900°C . However, such a texture in a layer with columnar morphology is not always present [41,42].

It was found on basis of the autoradiographic analysis performed on a number of cross-sections of $^{63}\text{Ni}/\text{Ni}_5\text{Si}_2$ coarse-grained samples that volume diffusion of the radioactive isotope exhibits an anisotropic behavior [33]. The rate of diffusion is depending on the orientation of the hexagonal Ni_5Si_2 ($\text{Ni}_{31}\text{Si}_{12}$) crystals within the bulk material. It is clear that from the measured penetration profile of ^{63}Ni -tracer in an annealed Ni_5Si_2 alloy only an average volume diffusion coefficient can be obtained. As said before, a weak form of texture was observed in the growing Ni_5Si_2 -phase layer. As a result, one finds a higher tracer diffusion coefficient calculated from the results of the diffusion couple experiments (Eq. (6.29)) than from the experiments with ^{63}Ni radioactive tracer, where the crystallographic orientation of grains in the Ni_5Si_2 is random.

6.4 THE DIFFUSION COUPLE TECHNIQUE IN PHASE DIAGRAM DETERMINATION – REVISITED

Phase diagrams play an important role in the understanding of many scientific and technological disciplines. Therefore, it is not surprising that substantial efforts have been given to developing experimental and theoretical methods of establishing phase relations in multicomponent systems. Phase equilibria in rather complex systems may now be calculated with a certain degree of confidence. However, in the nearest future, the theoretical assessments will likely remain a complementary tool only and not a replacement for experiment.

Application of diffusion couple technique in phase diagram determination came into use more than 50 years ago, when a number of good papers emerged on diffusion behavior in ternary multiphase systems. Although we are indebted to Frederick Rhines and his associates for the first enunciation of a diffusion couple experiment as “a research tool” for establishing phase relations in ternary systems [43], it was not till 1963 when Kirkaldy and Brown [44] provided a theoretical background and formulated a number of rules, which relate the composition of the reaction zone to the phase diagram. Later, these rules were conventionalized by Clark [45]. Rapid advances in electron microscopy and electron probe microanalysis in the early 1960s as well as the introduction of new sample preparation techniques created a sound base for and contributed to the further development of the diffusion couple method. There are now literally hundreds of studies which employed this experimental approach in phase diagram investigations.

Before we consider applying the diffusion couple method for phase diagram research in any details, we shall remind the reader the underlying principles of this experimental technique. This information will form a natural introduction to our subject.

6.4.1 General Principles

The use of diffusion couples in phase diagram studies is based on the assumption of local equilibria in the diffusion zone. The latter implies that each infinitesimally thick layer of such a diffusion zone is effectively in thermodynamic equilibrium with its neighboring layers. In a translated sense, this means that chemical potential (activity) of species varies continuously through the product layers of the reaction zone and has the same value at both sides of an interphase interface. An experimental consequence of local equilibrium is the proportionality of the product layer thickness to the square root of the reaction time.

This concept of local equilibrium being attained at interfaces plays a prominent role in the diffusion theory. It is to be remarked, however, that since diffusion takes place only by virtue of a thermodynamic potential gradient, the total system in which diffusion occurs cannot be at equilibrium. Throughout this discussion, we assume that local equilibrium is established and maintained in the diffusion zone, which means that

diffusion is very slow compared with the rate of reaction to form a new phase, i.e., overall kinetics of the process is *diffusion-controlled*.

To explain the main features of the diffusion couple method, we will confine the ensuing discussion to phase diagram determination in ternary systems. Let us first restrict our attention to *isothermal, isobaric ternary* system of well-defined state.

In contrast to a diffusion-controlled interaction in a multiphase binary system, invariably resulting in a reaction zone with single-phase product layers separated by parallel interfaces, an additional component in a ternary system provides one extra degree of freedom, which allows for the appearance of two-phase areas in the diffusion zone. The diffusion zone morphology, which develops during solid-state interaction in a ternary couple, is defined by type, structure, number, shape, and topological arrangement of the newly formed phases. In general, unlike the case of a binary system, the phases which are formed and morphology of the reaction product layers in a ternary diffusion couple cannot be unambiguously deduced from the corresponding phase diagram. However, the resulting microstructure of the reaction zone can be visualized with the aid of the so-called *diffusion path*. This is a line on the ternary isotherm, representing the locus of the average composition in planes parallel to the original interface throughout the diffusion zone. Naturally, the diffusion path in a ternary system must fulfill the law of conservation of mass. If no material is lost or created during the interaction, then the diffusion path is impelled to cross the straight line between the end-members of the reaction couple (so-called *mass balance line*) at least once.

If phases are separated by planar interfaces, the diffusion path crosses the two-phase region on the isotherm parallel to a tie-line, and it can be assumed that local equilibrium exists along the whole interface. However, this is not necessarily the case: regions of supersaturation can be formed near the interfaces. A thermodynamically unstable structure will then be created which will give rise to wavy interfaces or isolated precipitates.

For a given couple under conditions of chemical equilibrium, the reaction path involves a *time-independent sequence* of intermediate layers. This plot gives information about the order of the product layers, their morphology, and compositions.

Referring for details especially to the paper by Clark [45], we will summarize here the main rules relating the diffusion zone morphology to the phase diagram using (for the visual appreciation) a hypothetical reaction couple of an A–B–C ternary system shown in Fig. 6.21.

For example, in the hypothetical system shown in Fig. 6.21, a solid line crossing a single phase field on the isothermal section (e.g., a–b) denotes an existing layer of that phase in the reaction zone of the couple A/Z. A dashed line parallel to a tie-line in a two-phase field (g–h) represents a straight interface between two single phases. A solid line crossing tie-line on the isotherm (b–c) represents a locally equilibrated two-phase zone (in fact, a wavy interface) in the couple. A solid line entering a two-phase field and returning to the same phase field (d–e–f) represents a region of isolated precipitates.

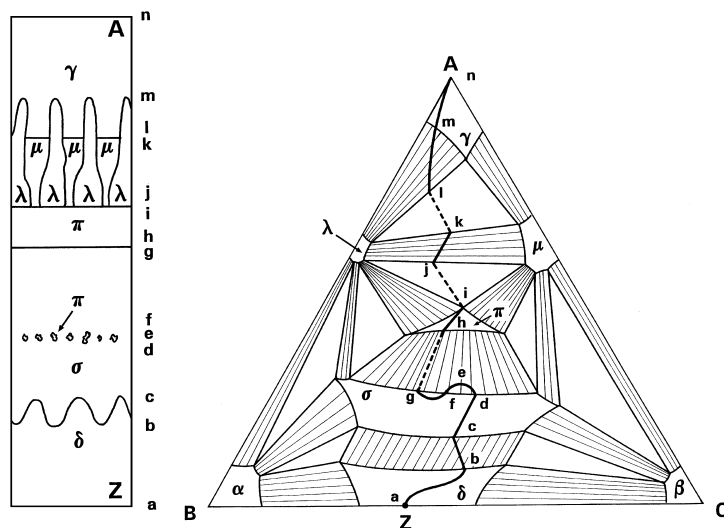


Figure 6.21 Reaction zone structure in a hypothetical couple A/Z of the A–B–C system (on the left) and the corresponding diffusion path plotted on the isotherm of the ternary diagram (on the right). The lower-case letters relate the structure to the appropriate composition on the isotherm. (Note that all paths in three-phase fields must be denoted by dashed lines, as a three-phase layer cannot form in a ternary diffusion couple.)

A dashed line crossing a three-phase field (e.g., i–j or k–l) implies an interface in the diffusion structure with equilibrium between three phases, either a two-phase layer adjacent to a layer consisting of a different phase (e.g., i/j interface) or adjacent two-phase layers with one common phase (e.g., k/l interface).

Before terminating this part of demonstration, two points should be mentioned. First, a diffusion path depicted onto a ternary isotherm gives only very limited kinetic information: sometimes the relative thicknesses of the reaction product layers can be estimated from mass balance considerations. Second, it is important to emphasize once again that in the most general case, the actual morphology of the two-phase zone developed in the reaction couple cannot be exactly deduced from the diffusion path.

6.4.2 Variations of the Diffusion Couple Method

There are several variations of the diffusion couple method. In the first variant, the sample to be studied is a classical *semiinfinite* diffusion couple, which means that after the diffusion annealing the couple ends still have their original compositions. If volume diffusion in a semiinfinite couple is the rate-limiting step, local equilibrium is supposed to exist, in which case the rules described above can be used to relate the reaction zone morphology, developed during isothermal diffusion, to the phase diagram. The main feature of this variation of the diffusion couple method is that the phase composition

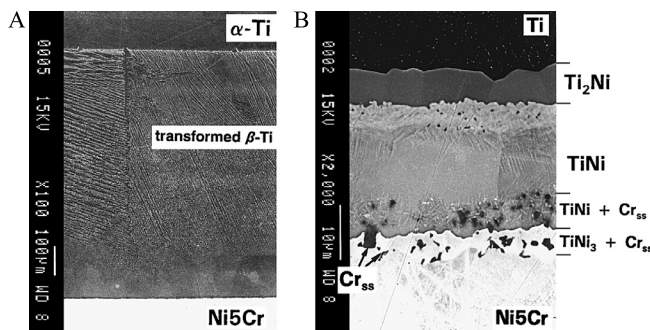


Figure 6.22 Microstructure of the reaction zone in the diffusion couple Ti/Ni 5 at.% Cr after annealing at 850°C in vacuum for 100 hours: (A) general view and (B) magnified area of the interfacial region. (Backscattered electron images (BEIs); Cr_{ss} denotes Cr(Ni, Ti)-based solid solution.)

of the reaction zone is independent of time and that the diffusion path is fixed. This allows for meaningful information to be obtained from studying growth kinetics of the product phases, which is required to determine whether under experimental conditions used, local equilibria prevails across the diffusion zone.

The utility of this approach in constructing isothermal cross-sections of ternary systems has been demonstrated repeatedly (see, e.g., [46–48]). Perhaps, one of the most illustrative examples of phase diagram determination using classical diffusion couples is provided by “a case study” of phase relations in the Ni–Cr–Ti system at 850°C [46]. It is interesting to mention that a great deal of the results that will be outlined below were actually obtained by undergraduate students at Eindhoven University of Technology (The Netherlands) in the framework of their practical traineeship in Materials Chemistry. This emphasizes, once again, the simplicity and accessibility of the method.

In Fig. 6.22 a typical microstructure of the reaction zone in the couple Ti/Ni 5 at.% Cr after annealing at 850°C in vacuum for 100 hours is given. Essentially, the microstructure consists of three layers of the binary intermetallic compounds TiNi₃, TiNi, and Ti₂Ni, and a very thick layer of β-Ti. (Note that hereafter in the discussion the various phases are denoted in their binary formulae.) Concentration of Cr was measured to be about 1.2 and 2.3 at.% in the TiNi₃ and TiNi-phase, respectively, whereas practically no chromium was found with EPMA in the Ti₂Ni-reaction product.

Nickel can also be detected in the β-Ti solid solution beyond the intermetallic layers within a “Widmanstätten”-type structure that is clearly visible in Fig. 6.22(A). The maximum concentration of Ni in the vicinity of Ti₂Ni/β-Ti-interface was estimated as about 2.5 at.%.

At this point it is worth mentioning that a small amount of Ni or Cr increases the stability of the body-centered cubic (BCC) β-Ti structure. It can be seen from the binary Ti–Ni and Ti–Cr phase diagrams [49]. The layer of the β-Ti(Ni)-solid solution

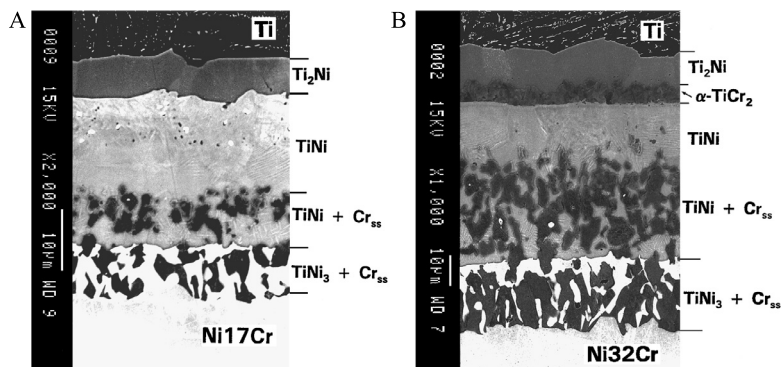


Figure 6.23 Backscattered electron images (BEIs) of the reaction zones developed after heat-treatment at 850°C in vacuum: (A) in the diffusion couple Ti/Ni 17 at.% Cr after annealing for 100 hours and (B) in the Ti/Ni 32 at.% Cr couple after interaction for 400 hours.

was formed in the couple at 850°C and, then, transformed into the α -Ti structure upon the cooling.

Close inspection of the transition zone revealed isolated precipitates of the Cr-based (BCC) solid solution (Cr_{ss}) dispersed inside the TiNi₃-layer and also within the TiNi-phase in the vicinity of the TiNi₃/TiNi interface (Fig. 6.22(B)). In some areas of the interfacial region the precipitates are rooted to the Ni–Cr end-member. This reaction morphology indicates the existence of the three-phase equilibria $\text{TiNi}_3 + \text{Cr}_{ss} + \text{Ni}_{ss}$ and $\text{TiNi}_3 + \text{Cr}_{ss} + \text{TiNi}$ in the Ni–Cr–Ti system at this temperature. (Note that hereafter Ni_{ss} denotes face-centered cubic (FCC) Ni(Cr,Ti)-based solid solution.)

Similar reaction products were also found in the diffusion zone of the couple Ti/Ni 17 at.% Cr after heat treatment at 850°C in vacuum for 100 hours (Fig. 6.23(A)). However, the volume fraction of the Cr-based solid solution within the product layer is considerably higher and the Cr-based precipitates are generally coarser.

The concentration of chromium in the TiNi₃- and TiNi-matrix layers is also increased (up to approximately 2.7 and 3.5 at.%, respectively), while the Cr-content in the Ti₂Ni remains very low (about 0.5 at.%).

When a Ni-solid solution containing 32 at.% of Cr was used as an end-member of the diffusion couple, the reaction with titanium at 850°C led to the formation of a α -TiCr₂ layer between the TiNi and Ti₂Ni intermetallics (Fig. 6.23(B)). The concentration of nickel in this phase was found of about 2 at.%.

At the Ni–Cr-side of the couple, an interpenetrating type structure was observed. Domains of the TiNi₃-phase (with approximately 6 at.% of Cr) are rooted in the adjoining Ni–Cr substrate, and the elongated precipitates of Cr-based solid solution are also constituents of the next two-phase product layer TiNi + Cr_{ss}. The microstructure changes gradually into the TiNi-layer, free of the precipitates.

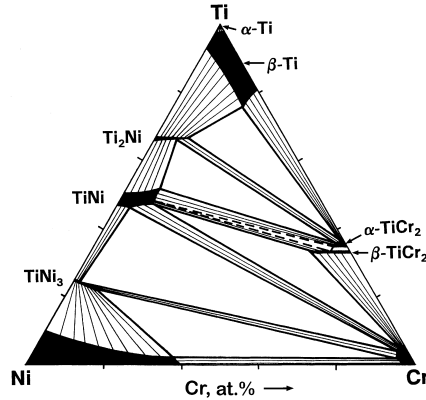


Figure 6.24 Isothermal cross-section through the ternary phase diagram Ni–Cr–Ti at 850°C [46].

Analysis of the reaction zone morphology evolved in these diffusion couples shows the three-phase equilibria $\text{TiNi}_3 + \text{Cr}_{\text{ss}} + \text{Ni}_{\text{ss}}$, $\text{TiNi}_3 + \text{Cr}_{\text{ss}} + \text{TiNi}$, and $\text{TiNi} + \text{Ti}_2\text{Ni} + \alpha\text{-TiCr}_2$ in the Ni–Cr–Ti system at 850°C (Fig. 6.24).

An interesting feature of the diffusion zones developed in these samples is a significant enrichment of chromium the Ni-based solution in the vicinity of the alloy/reaction product-interface. This implies that in the phase field of the Ni-based solid solution on the ternary isotherm the diffusion paths proceed in the direction of increasing chromium concentration before entering the three-phase region $\text{TiNi}_3 + \text{Cr}_{\text{ss}} + \text{Ni}_{\text{ss}}$. This is connected with the higher affinity of Ni towards titanium as compared with that for chromium and mass balance requirements.

Since for a semiinfinite diffusion couple a unique diffusion path is followed, in principle, a large number of couples must be studied experimentally to construct a ternary isotherm. However, the number of samples can be decreased appreciably by using polyphase terminal materials in diffusion couples. In the studying a ternary system, the chance “to hit” interfaces at which three phases are in equilibrium, is much larger when two-phase alloys are used as end-members. Schematically this procedure is shown Fig. 6.25.

If a diffusion couple between P and Q is assembled, the reaction zone after annealing at a specified temperature might exhibit the morphology indicated in Fig. 6.25(B). In area 1 microprobe measurements will reveal the three-phase equilibrium $\alpha + \mu + \text{T}$, whereas from area 2 the equilibrium triangle $\beta + \gamma + \text{T}$ existing on the isotherm can be found.

Application of this technique can be best demonstrated by a frequently cited example of studying phase relations in the ternary Ag–Fe–Ti system at 850°C [50]. The microstructure of the reaction zones in the diffusion couples based on silver and various two-phase binary Fe–Ti alloys are given in Fig. 6.26.

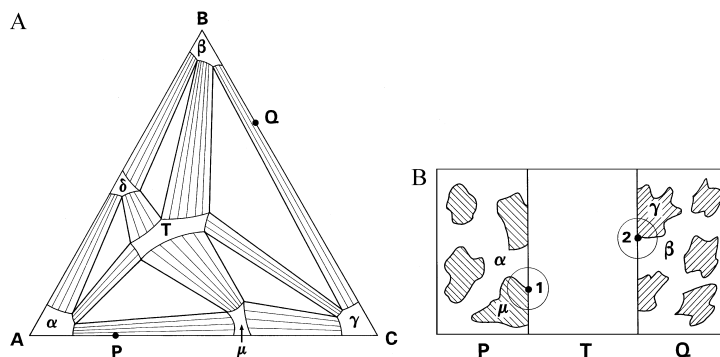


Figure 6.25 Determination of the phase equilibria on the isotherm of the ternary A–B–C system using two-phase alloys as end-members (A) and schematic view of a possible reaction zone in a hypothetical diffusion couple P/Q (B).

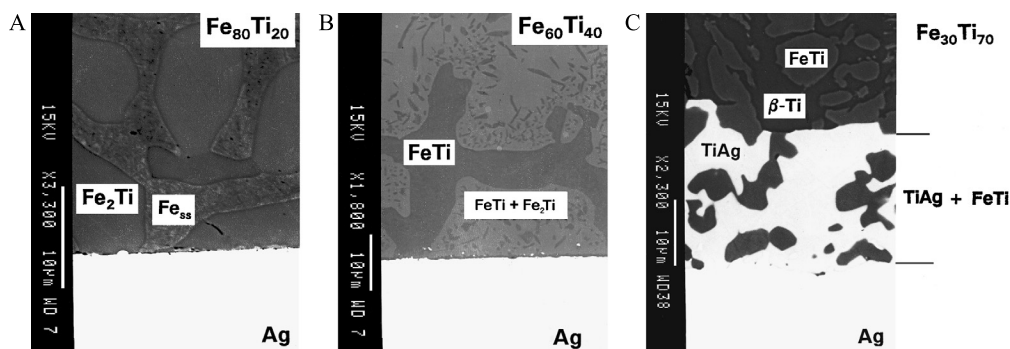


Figure 6.26 Reaction zone morphologies developed in the diffusion couples based on binary two-phase Fe–Ti alloys and Ag after annealing at 850°C in vacuum for 100 hours: (A) $\text{Fe}_{80}\text{Ti}_{20}/\text{Ag}$ (BEI); (B) $\text{Fe}_{60}\text{Ti}_{40}/\text{Ag}$ (BEI), and (C) $\text{Fe}_{30}\text{Ti}_{70}/\text{Ag}$ (Secondary Electron Image (SEI)).

At the interface in the transition zone between an equilibrated two-phase alloy with the nominal composition $\text{Fe}_{80}\text{Ti}_{20}$ and silver after annealing at 850°C for 100 hours in vacuum, three phases were found in equilibrium: α -Fe-based solid solution (Fe_{ss}), Fe_2Ti , and Ag-based solid solution (Fig. 6.26(A)). Obviously, such a morphology indicates a three-phase equilibrium $\text{Fe}_{\text{ss}} + \text{Fe}_2\text{Ti} + \text{Ag}$ in the Ag–Fe–Ti system at this temperature. No silver was detected in the Fe-based solid solution or in the Fe_2Ti inside the diffusion zone. Approximately 0.5 at.% of titanium was found in the Ag-based solid solution in equilibrium with Fe_{ss} and Fe_2Ti at the contact surface. The solubility of iron in silver is very low and could not be determined by EPMA.

A similar type of morphology was developed in the diffusion zone between silver and equilibrated alloy $\text{Fe}_{60}\text{Ti}_{40}$ ($\text{Fe}_2\text{Ti} + \text{FeTi}$) after heat treatment under these conditions (Fig. 6.26(B)). The intermetallic compounds Fe_2Ti and FeTi are in equilibrium with

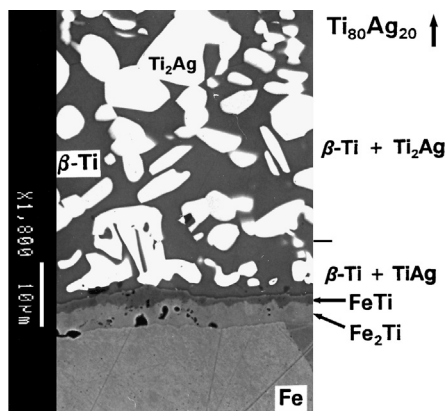


Figure 6.27 BEI of the reaction zone in the diffusion couple $\text{Ti}_{80}\text{Ag}_{20}/\text{Fe}$ after heat treatment in vacuum at 850°C for 100 hours. Note that the original (α -Ti + Ti_2Ag) alloy is much further away from the interface (about $500\ \mu\text{m}$).

silver within the reaction zone. This implies the three-phase equilibrium $\text{Fe}_2\text{Ti} + \text{FeTi} + \text{Ag}$ at the Ag–Fe–Ti isotherm at 850°C . No iron is dissolved in the silver solid solution, whereas titanium concentration in the solid solution near the interface was estimated as $\sim 1.0\ \text{at.}\%$.

Interaction between an equilibrated two-phase alloy with the nominal composition $\text{Fe}_{30}\text{Ti}_{70}$, consisting of FeTi intermetallic and β -Ti (with nearly $18\ \text{at.}\%$ of Fe) and Ag at 850°C leads to the formation of the two-phase layer $\text{TiAg} + \text{FeTi}$ in the diffusion zone (Fig. 6.26(C)). Two interfaces where three phases exist in equilibrium are found. The TiAg -matrix is in equilibrium with both β -Ti (with $\sim 14.5\ \text{at.}\%$ of Fe and $\sim 2.0\ \text{at.}\%$ of Ag) and FeTi , which is a constituent of the starting two-phase alloy. The solubility of iron in the TiAg -matrix is negligible and the solubility of silver in the FeTi is estimated as $\sim 0.5\ \text{at.}\%$. This two-phase reaction layer also adjoins the Ag-based solid solution. The observed morphology indicates the existence of the three phase equilibria $\text{FeTi} + \text{TiAg} + \text{Ag}$ and $\text{FeTi} + \text{TiAg} + \beta$ -Ti on the isotherm.

When a two-phase $\text{Ti}_{80}\text{Ag}_{20}$ alloy, containing after equilibration the Ti_2Ag -intermetallic and α -Ti, is used as an end-member of the diffusion couple, the reaction with Fe at this temperature results in the formation of continuous layers of the binary compounds Fe_2Ti and FeTi (Fig. 6.27).

The micrograph in Fig. 6.27 shows only a part of the diffusion zone close to the reaction product/Fe-interface. The original end-member, composed of α -Ti and Ti_2Ag , is much further away from the interface (about $500\ \mu\text{m}$). Deeper in the alloy, a two-phase layer β -Ti and TiAg was formed. The β -Ti matrix is also a constituent of the next two-phase layer β -Ti + Ti_2Ag adjacent to the initial two-phase Ti–Ag alloy. (Note that silver stabilizes the hexagonal α -Ti structure while the presence of Fe increases the

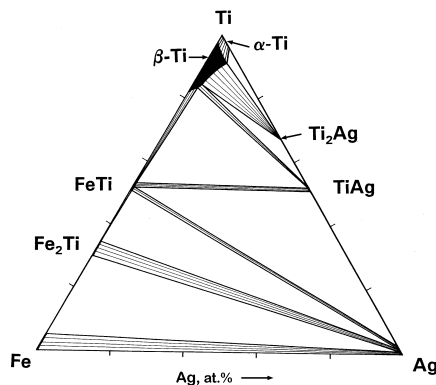


Figure 6.28 Isothermal cross-section through the ternary phase diagram Ag-Fe-Ti at 850°C [50].

stability of the BCC β -Ti based solid solution [51].) The composition of the β -Ti based solid solution in equilibrium with the intermetallic compounds Ti_2Ag and TiAg inside the diffusion zone was determined as $\text{Ti}_{84.0}\text{Fe}_{13.5}\text{Ag}_{2.5}$. Analysis of the morphology developed in this diffusion couple reveals the three-phase equilibria $\text{FeTi} + \text{TiAg} + \beta\text{-Ti}$, $\beta\text{-Ti} + \text{TiAg} + \text{Ti}_2\text{Ag}$, and $\beta\text{-Ti} + \text{Ti}_2\text{Ag} + \alpha\text{-Ti}$ in the Ag-Fe-Ti system at 850°C. All equilibria found in the polyphase diffusion couples are consistent with the ternary Ag-Fe-Ti diagram given in Fig. 6.28.

The experimentally established phase relations were also confirmed by examining a number of ternary equilibrated alloys and, in addition, they were verified by a thermodynamic evaluation of this system [50].

In the quest for the increasing efficiency of the diffusion couple method in studying phase diagrams, attempts have been made to change the “macrostructure” of the classical diffusion couple. In the simplest case, a sample is prepared by joining two plane-parallel slices of metal (alloy) through a thin layer of the third metal (alloy). In such a layered system, in which the central part is eventually consumed, the *diffusion path is not fixed* as in the semiinfinite couple. The phase composition of the complex diffusion zone is changing continuously with time as a result of the overlapping of two quasi-equilibrated diffusion zones. To relate the morphology and composition of the reaction zone to the phase diagram, rules similar to those explained before still can be used.

In order to elucidate this variant, let us consider a relatively simple example of constructing an isothermal section of the ternary Ni-Cr-V system at 1150°C [52]. In this case, the basic idea of the technique was realized in the following way: the “sandwich” samples were prepared by joining and subsequent annealing at 1150°C in vacuum of vanadium and chromium discs (about 2 mm thickness) with an intermediate Ni-foil. It is imperative that before the process of interference starts, local equilibria have been established inside the reaction zone in each of the “semiinfinite” couples of

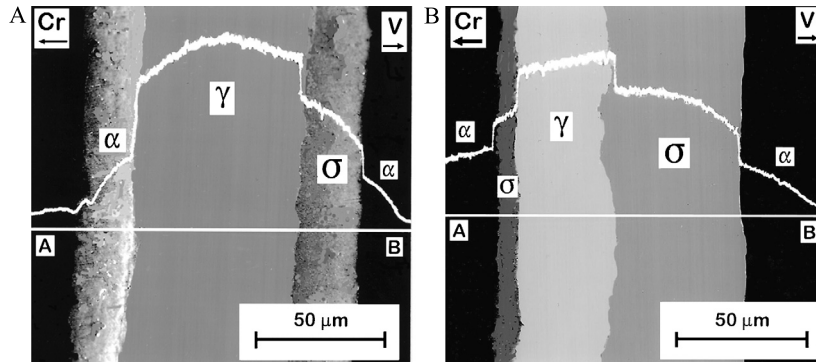


Figure 6.29 Microstructure of the diffusion zone in the finite “sandwich” sample V/Ni, foil (100 μm)/Cr after annealing at 1150°C in vacuum for: (A) 16 hours and (B) 49 hours. (Backscattered electron images together with the variation the $\text{NiK}\alpha$ signal across the zone of interaction (along the line AB). The FCC Ni-based and BCC solid solutions based on Cr or V are denoted as γ and α , respectively.)

which the “sandwich” sample was originally composed. Based on the information about diffusion kinetics in the constituent Ni/V and Cr/Ni binary couples, the thickness of the Ni-interlayer was chosen as 100 μm .

Examination of the “sandwich” samples after heat treatment at 1150°C for 4, 16, and 25 hours revealed the formation at the vanadium-side of a continuous layer of the σ -“VNi” phase containing some chromium. A typical microstructure of the reaction zone after the annealing is shown in Fig. 6.29(A). The chromium content in the product layer was found to increase with increasing reaction time.

Subsequent annealing of the sample up to 49 hours led to the reaction zone morphology shown in Fig. 6.29(B). A characteristic feature of the diffusion zone developed under these conditions is the formation of two layers of the σ -phase, separated by a layer of the Ni(V,Cr)-based solid solution. The latter observation indicates that the diffusion path crosses the σ -phase field on the ternary Ni–Cr–V isotherm twice.

This isotherm was also investigated using “semiinfinite” couples of the NiCr/V type and by means of traditional methods of equilibrated alloys. Fig. 6.30 represents the experimentally determined isotherm and the diffusion paths found in the “sandwich” samples after various annealing times. One can see that the results obtained by the different techniques are in good agreement.

During past few decades, this variation of the diffusion couple technique has proven itself as a valuable tool in phase diagram studies (see, for example, [53–56]). The efficiency of this method is very high: by making only one finite “sandwich” sample, re-annealing and investigating after various annealing times, a lot of information can be gained about the whole isotherm.

Further development of this approach is connected with the preparation and investigation of so-called diffusion multiples. A diffusion multiple is an assembly of three or

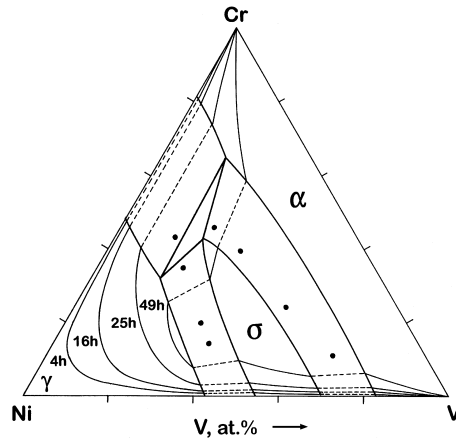


Figure 6.30 Experimentally determined isothermal cross-section through the Ni–Cr–V phase diagram at 1150°C [52]. The compositions of the equilibrated alloys examined are depicted as points.

more different metal (or ceramic) blocks, in intimate interfacial contact, arranged as a triple, quadruple, etc., and subjected to heat treatment to allow interdiffusion to occur. (The reader seeking more details on this subject should assess relevant publications of Zhao [2,57,58].)

In this context it should be stated that however elegant these experiments might be, judicious cautions should be exercised in correlating composition of the reaction products formed during interaction in such complicated diffusion zones with the corresponding equilibrium phase diagram. Especially when two-phase regions are developed within the diffusion structures, one must be careful not to attribute too much precision to the locations of the phase field boundaries deduced from electron microprobe measurements on such multiples.

At this point, it has to be stressed that a rigorous analysis of the information obtained in diffusion couple experiments (as any solid-state reaction) is possible only under the assumption that local thermodynamic equilibrium prevails in the reaction zone. If, on the other hand, local thermodynamic equilibrium in solid nonequilibrium system is not attained, the interpretation of the results is very difficult. In such a case, instead of applying phenomenological theories, one has to explain **an infinite number of situations**, all individually.

The inherent problem of diffusion multiple method in phase diagram studies is that the sample configuration itself makes it practically impossible to derive any meaningful information about growth kinetics of the reaction product phases formed in the often very complex interdiffusion zone. In such a situation, it is not unequivocally clear whether local thermodynamic equilibria are prevailed in the reaction zone, which pos-

sesses serious questions about validity of the approach in relating results of microprobe measurements to the actual topology of the equilibrium phase diagram.

In order to give to this ambiguity the appearance of unambiguity, even a particular expression “mapping of phase diagrams” (and “properties”) has been introduced [57]. However, it must be conceded that simple ideas may be esthetically satisfying, but nature is complex. One should be modest and not claim too much. If one wants to establish precisely phase equilibria in a multicomponent system based on the results of diffusion couple experiments, one has to study relevant diffusion couples under the conditions of local equilibrium prevailing in the reaction zones, point!

From the preceding discussion, we have learned that in the phase diagram research, the diffusion couple technique is nothing more than a tool for establishing a correlation between the morphology developed in the diffusion zone of the couple and a certain type of phase relations in the system. However, it must be added immediately that like in the case of other seemingly simple methods used in materials science, the proper use of diffusion couples for determination of multicomponent phase diagrams is by no means a trivial procedure as it might look at first sight. A number of error sources may appear when multiphase diffusion experiments are used for establishing phase equilibria.

6.4.3 Error Sources Encountered in the Diffusion Couple Experiments

The experimental results may contain errors directly attributable to the nature of the sample. One of the possible dangers of technical importance is a system in which the terminal compositions (end-members) are solids, but a liquid phase exists at the annealing temperature. It is then possible for the diffusion path to wander into this field, with disastrous results indeed! Poor adherence at the interfaces in the diffusion zone and accelerated reaction rates due to defects such as cracks, grain boundaries, etc., may also render the interpretation of diffusion couple experiments cumbersome.

Micro- and macrocracks developed in the diffusion zone may have a pronounced influence on the course of a chemical reaction and determine the topological arrangement of the product phases within the resulting microstructure.

The latter statement can be exemplified by the situation observed in the course of the study reaction phenomena in the GaSb/Co diffusion couples [59,60]. In Fig. 6.31 the isothermal cross-section through the Co–Ga–Sb phase diagram at 500°C is given. The phase relations were established by analyzing powder compacts equilibrated in glass ampoules under 150 mbar of argon. X-ray diffraction analysis, Scanning Electron Microscopy, and Electron Probe Microanalysis were employed.

No ternary phases are formed in the Co–Ga–Sb system at 500°C. An interesting point here is that CoGa-intermetallic is in thermodynamic equilibrium with all intermediate phases stable in the corresponding binary systems.

A representative microstructure of the central part of the GaSb/Co diffusion couple after reaction at 500°C for 600 hours is shown in Fig. 6.32. The couple was annealed in

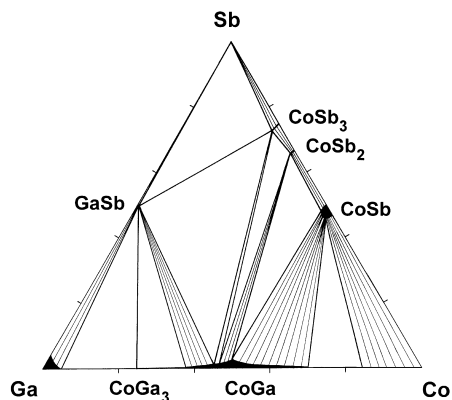


Figure 6.31 Isothermal cross-section through the ternary phase diagram Ga-Sb-Co at 500°C [59].

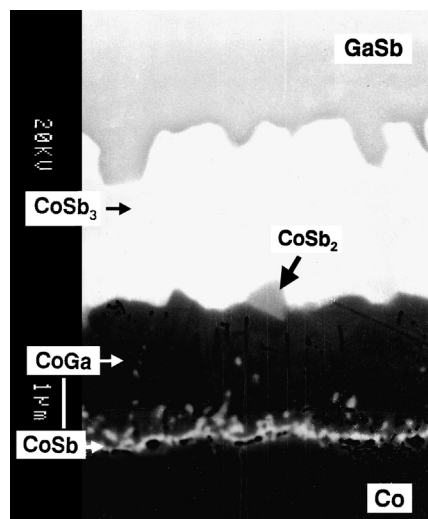


Figure 6.32 Backscattered electron image of the central part of the reaction zone in a GaSb/Co diffusion couple after reaction at 500°C for 600 hours in vacuum.

a dynamic vacuum ($\sim 10^{-6}$ mbar) under a uniaxial external load of ~ 2 MPa, insuring a good contact between the end-members.

From the micrograph it can be seen that the dominant phases formed in the reaction zone are CoGa and CoSb₃. A fragmented thin layer of the CoSb compound was found next to Co. The formation of CoSb₂ intermetallic was detected only in some areas of the CoSb₃/CoGa interfacial region. The diffusion path in the reaction couple proceeds in the phase sequence: GaSb | CoSb₃ | CoSb₂ | CoGa | CoSb | Co, which is in accord with

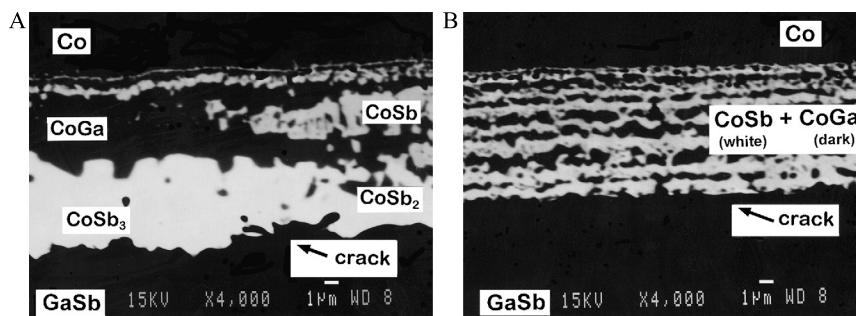


Figure 6.33 Backscattered electron micrographs showing the formation of an interwoven-aggregate arrangement of phases within the transition zone of the GaSb/Co couple (500°C; 600 hrs; vacuum): (A) A domain of the reaction layer in the vicinity of the tip of the crack developed along the reaction product/GaSb interface; (B) a typical reaction zone morphology evolved at the edges of the couple.

the experimentally determined phase equilibria. The reaction layer grows parabolically with time, underlining a diffusion-controlled process.

However, close to the edges of the GaSb/Co couple the reaction product layer exhibits a different morphology. An interwoven-aggregate arrangement of phases was formed within the microstructure (Fig. 6.33).

Inspection of this area of the transition zone revealed the presence of a crack developed along the reaction product /GaSb contact surface. This portion of the reaction product layer appears to be physically separated from the unreacted GaSb. However, the couple did not fall apart after the annealing.

The crack begins at the triple point of the couple where starting materials as well as reaction products are in contact with the ambient atmosphere and propagates in the interior of the sample. This is a direct outcome from the mechanism of the generation and relaxation of the stresses induced during the interaction.

Apparently, the crack developed between the product layer and the initial end-member affects the evolution of the microstructure in the GaSb/Co couple in two ways:

1. By limiting supply of the reaction species: Appearance of the crack between the product layer and GaSb-end-member hinders the supply of gallium and antimony to the reaction interface, i.e., the diffusion couple in this region is not semiinfinite. In this case the product morphology reflects a result of the interaction in the multilayered system $\text{CoSb}_3 \mid \text{CoSb}_2 \mid \text{CoGa} \mid \text{CoSb} \mid \text{Co}$.
2. By promoting evaporation of the part of the reaction product (CoSb_3) formed at the early stage of interaction: It is important to realize that the isotherm shown in Fig. 6.31 implicitly assumes that the partial pressure of antimony in ambient environment is higher than the dissociation pressure of CoSb_3 . This situation was

attained in the experiments with powder compacts used for establishing the isothermal cross-section, which were carried out in small, argon-filled silica ampoules.

However, under certain circumstances, for example, in a dynamic vacuum, the CoSb_3 -phase can be on the “border” of its thermodynamic stability. From the reaction equation $\text{CoSb}_2 + 1/4 \text{Sb}_{4(g)} = \text{CoSb}_3$, the value of the equilibrium partial pressure of the gaseous species Sb_4 was estimated at 500°C as about 7.4×10^{-6} mbar. The necessary thermodynamic data were taken from [61]. Accordingly, the equilibrium vapor pressure of $\text{Sb}_{4\text{-gas}}$ above CoSb_3 is higher than that usually maintained during vacuum anneals ($\sim 10^{-6}$ mbar). It is evident that under these conditions, the topology of the Ga–Sb–Co diagram will differ from that shown in Fig. 6.31. This was also confirmed experimentally: no CoSb_3 -compound was detected by means of X-ray diffraction in a sample with nominal composition $(\text{GaSb})_{0.35}\text{Co}_{0.30}$ annealed at 500°C in dynamic vacuum. Instead, a three-phase equilibrium involving GaSb, CoSb_2 , and CoGa was found to be present on the isothermal section. This situation profoundly affects the phase composition and morphology of the diffusion zone in the vicinity of the “triple point” in the GaSb/Co couple, where reaction layers meet at ambient atmosphere.

Another source of error is in the experimental measurements themselves. The difficulties connected with the accurate determination of the boundary concentrations in the reaction zone are a problem for both semiinfinite and finite diffusion couple techniques. Several items concerning the electron-beam microanalytical techniques used are to be noted here.

Firstly, the determination of a chemical composition with EPMA has an inherent experimental error associated with data counting statistics and data correction procedures.

Secondly, the volume of X-ray generation in the “bulk” samples is determined by the electron scattering in the target, and not by the incident electron beam size. Because of the scattering effects, it is impossible to generate characteristic X-rays from (and hence, to determine the chemical composition of) a volume much smaller than $1\text{--}2\text{ }\mu\text{m}$ in diameter. In other words, explicit measurements of interfacial compositions are not possible with any electron-beam technique. It is, however, possible to measure concentration gradients in the vicinity of the interfaces in the multiphase diffusion zone. When the phases in question have a reasonable layer width, the composition at the interface can be determined by extrapolation the measured concentration profile to extract the actual concentration profile, and therefore the interface composition. This approach, however, is not always very accurate. In most cases, the necessity for extrapolation is the most serious limitation of the EPMA. Especially when steep concentration gradients occur near the phase boundaries in the diffusion-grown layers, the extrapolation may lead to large errors. The same problem arises, by the way, when the equilibrium compositions at precipitate/matrix interfaces in a two-phase reaction product are determined.

Thirdly, the X-ray absorption effect may cause problems. This occurs when X-rays produced at one point within the specimen travel through materials of different compositions, and, perhaps, of different mass absorption coefficients on their way to the spectrometer. To avoid such absorption effects, it is necessary to orient the phase boundary in the diffusion couple perpendicular to the sample surface and the interphase interface parallel to the X-ray path to the spectrometer.

Finally, accurate microprobe analysis near the interfaces is sometimes very difficult owing to fluorescence effects. When dealing with the problem of spatial resolution in quantitative electron probe microanalysis, it is very often the range of electron propagation that people are primarily concerned about. The latter can be defined as the distance the electrons diffuse away from the point of impact of the incident electron beam on the specimen until they have lost so much energy as to be no longer capable of exciting primary characteristic X-ray radiation. As already mentioned, this range is typically of the order of 1–2 μm , yielding a volume of primary excitation of approximately 2–4 μm in diameter. In many cases, however, the primary characteristic X-ray radiation can be powerful enough to excite one or more other elements present in the sample, thus giving rise to enhanced X-ray production, i.e., fluorescence. In other words, if the sample contains a species of atoms with a critical excitation energy less than the energy of the primary characteristic X-rays being absorbed, fluorescence will occur. The main trouble here is that this “characteristic” fluorescence usually takes place in a much larger volume. The latter can be an order of magnitude greater than the volume of primary excitation due to the fact that X-rays can travel much more easily through matter than electrons can. As a consequence, the spatial resolution can be drastically lowered. In fact, in analyzing multiphase couples the additional X-ray excitation may occur on one side of the phase interface even though the electron beam and the analysis point is on the other side of the interphase interface. This may lead to the peculiar observation that X-rays of a certain element may be detected in locations where the element is not present. In this context, it is relevant to mention that for the case of K – K fluorescence (K_α -radiation of one element exciting K_α -radiation of another), the excitation of secondary radiation is especially bad in targets containing elements with atomic numbers differing by two (for atomic number $Z > 21$), like combinations of the elements Fe/Ni, Cu/Co, etc.

In general, in order to avoid the problem of fluorescence (and absorption) “uncertainty”, a number of correction schemes have been introduced [7]. One should, however, keep in mind that in all these correction procedures it is implicitly assumed that the primary and secondary production of X-ray radiation, as well as subsequent absorption, all take place in the same homogeneous (single phase) matrix. Apparently, these conditions are violated to increasing extent as the incident electron beam approaches an interface or when the size of particles decreases below a certain limit. Corrections for this effect are possible but difficult [62]. It is best to determine how large the effect is

by using “undiffused” couples and to correct the data accordingly. In a binary diffusion couple, usually one of the elements does not suffer from the fluorescence effect and one could measure the concentration of that element by microprobe analysis to describe the distribution of elements across the reaction zone. If, for instance, pure copper and cobalt are clamped together, without any diffusion taking place, CoK_α characteristic X-ray radiation can apparently be measured at a distance of up to 40 μm from the interface in the pure Cu [62]. About 4.8 at.% of Co appears to be in Cu at the interface. Measuring CuK_α radiation diminishes the error, but still an apparent Cu concentration of 2 at.% is found in cobalt near the interface, whereas Cu X-ray radiation can be detected at about 15 μm from the interface in cobalt.

Obviously, in the case of a ternary system, the situation can be even more intricate. The reader interested in greater details concerning the correction procedures is invited to turn his/her attention to the references cited.

Yet another group of problems that might cause uneasiness in interpreting results of diffusion couple experiments arise from the formation of a quasi-equilibrated diffusion zone. As already explained, when the diffusion couple techniques are used for phase diagram determination, it is of fundamental importance to be sure that equilibrium values are “really” attained at the interphase interfaces and that all equilibrium phases, pertaining to the system under the conditions of the diffusion couple experiment, are formed in the reaction zone.

Sometimes certain phases seem to be missing in a diffusion couple when investigated by microscopic or microprobe analysis. One of the reasons for the absence of an equilibrium phase might be the presence of a barrier layer at the interface, such as, for example, oxide films at the contact surface or the presence of impurities in the starting materials. In the latter case, the segregation of impurities, which may be present only in the ppm-range in one of the end-members can cause enrichment in the diffusion zone, making nucleation of a certain phase difficult.

Even though the absence of certain phases might be due primarily to difficulties in nucleation, it is important to point out that the apparent absence of a particular intermediate phase in a diffusion zone cannot automatically be interpreted as the result of nucleation problems. It is possible that the phase is present in such a minute quantity that it cannot be determined easily by the experimental techniques available. It should be noted that a kinetic consideration of product phase growth in itself is not so essential for the present discussion. However, when taken in the overall context of a diffusion couple experiment, the question of the apparent absence of a certain equilibrium phase in a reaction zone or, conversely, the formation of metastable phases during interaction, becomes an important issue. For instance, in a “notorious” example of a Ti/Al diffusion couple only TiAl_3 was found [63]. Yet, several other intermetallic phases should have been formed according to the phase diagram [51]. On the other hand, when incremental Ti/TiAl₃ diffusion couples were annealed at 800°C, all the possible intermetallic phases

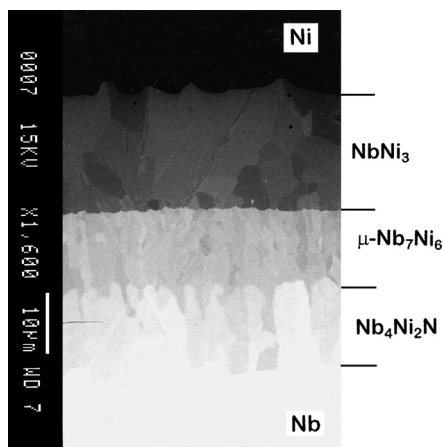


Figure 6.34 Backscattered electron image of an annealed (1100°C; 196 hrs; vacuum) binary Nb/Ni couple showing the formation of the “impurity stabilized” phase $\text{Nb}_4\text{Ni}_2\text{N}$ within the reaction zone.

according to the equilibrium phase diagram were indeed found in the reaction zone: $\text{Ti}/\text{Ti}_3\text{Al}/\text{TiAl}/\text{TiAl}_2/\text{TiAl}_3$. However, when a layer of Al was joined on the outside of the TiAl_3 layer of the above couple and annealed at 625°C for 15 hours, the compounds TiAl_3 , TiAl , and TiAl_2 disappeared, resulting in the basic original configuration of $\text{Ti}/\text{TiAl}_3/\text{Al}$. Clearly, in this case nucleation of Ti_3Al , TiAl , and TiAl_2 cannot be the problem. Rather, the apparent absence of the other phases is due to the relatively slow diffusion in these compounds, i.e., due to slow growth kinetics.

An additional reason for caution here is that occasionally a nonequilibrium phase, often stabilized by impurities present in terminal materials, can grow in a diffusion zone. Very illustrative examples of such a situation are carbides like $\text{Mo}_5\text{Si}_3\text{C}$ [64] or $\text{Mo}_6\text{Ni}_6\text{C}$ [65], which might be confused with the purely binary phases Mo_5Si_3 and MoNi . The same is true for oxides, e.g., $\text{Ti}_4\text{Ni}_2\text{O}$, and nitrides like $\text{Nb}_4\text{Ni}_2\text{N}$, which might be confused with the binary compound Ti_2Ni or with an in fact non-existing binary “compound” Nb_2Ni . Further complications may result from the fact that the “impurity stabilized” phases often grow in series with genuine binary compound layers, like it is shown in Fig. 6.34 for the Nb/Ni couple annealed at 1100°C.

Three distinct product layers are clearly visible on the micrograph. According to the binary Ni–Nb phase diagram, however, only two products are expected to form in the reaction zone of the Nb/Ni couple at this temperature, NbNi_3 and the μ -phase Nb_7Ni_6 (Fig. 6.35).

Electron probe microanalysis revealed that the reaction layer formed at the Nb-side of the diffusion zone is a ternary compound with a composition close to the η - $\text{Nb}_4\text{Ni}_2\text{N}$, which indeed exists in the ternary Ni–Nb–N system at 1100°C Fig. 6.36 [66]. Nitrogen was present as an impurity in the starting material Nb.

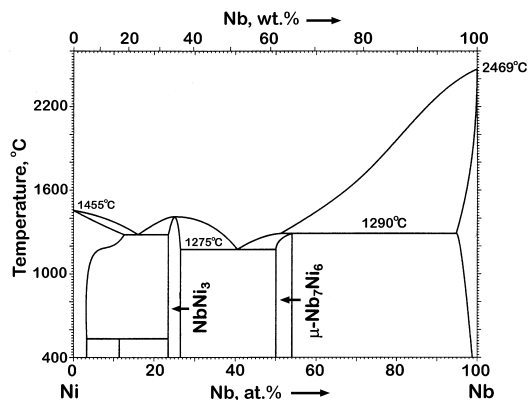


Figure 6.35 The binary Ni–Nb phase diagram [49].

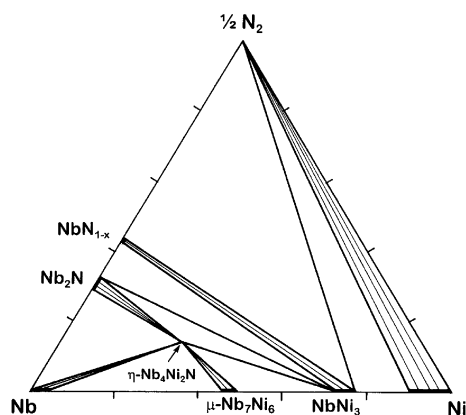


Figure 6.36 The ternary Nb–Ni–N phase diagram at 1100°C and 10^{-8} bar of nitrogen partial pressure [66].

An easy way to verify the purely binary character of an equilibrium phase layer is the use of incremental couples. The terminal compositions are then chosen quite close to the apparent phase in question, in such a way that only this phase might be formed. The end-members may be single-phase or two-phase alloys. A true equilibrium phase then grows parabolically with time as a relatively thick layer, whereas an impurity-stabilized phase ceases to grow after some time since the impurity from the end-member is totally consumed [21].

Before closing this part of demonstration, we would like to show one important example which will help the reader to comprehend the use of diffusion couple techniques as “a research tool” in the systems in which gaseous species such as oxygen, nitrogen,

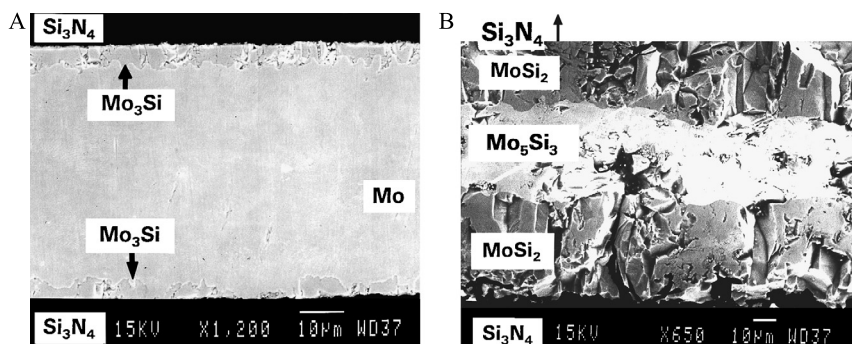


Figure 6.37 (A) Secondary Electron Image (SEI) of the transition zone between Mo and dense Si_3N_4 after annealing during 32 hours at 1300°C in vacuum and (B) SEI of the reaction zone between Mo and 50% porous Si_3N_4 after annealing at 1300°C for 50 hours under flowing argon containing of about 500 vpm of nitrogen.

and under some circumstances also sulfur, phosphorous, arsenic, or antimony, take part in the interaction. The gas atmosphere may influence which diffusion path occurs.

In this respect, the case study of the Mo–Si–N system is an instructive illustration of how the formation of a volatile reaction product affects the diffusion path. The interesting point in this system is the dependence of the reaction path upon the total pressure and, especially, the partial pressure of nitrogen. This can be appreciated looking at Fig. 6.37, which represents reaction zone morphologies developed between Si_3N_4 and Mo after annealing at 1300°C in vacuum.

Two different types of Si_3N_4 were used in these experiments, fully dense hot isostatically pressed ceramics (Fig. 6.37(A)) and 50% porous silicon nitride (Fig. 6.37(B)). It can be seen that despite the apparent “chemical” identity of the reactants in these couples, the corresponding diffusion paths were found to be remarkably different. In the reaction couple based on dense Si_3N_4 -ceramics, only Mo_3Si was detected in the diffusion zone, whereas layers of MoSi_2 and Mo_5Si_3 are formed in the diffusion couple consisting of porous silicon nitride. From the last micrograph it can also be noticed that the whole initial Mo end-member of the couple has been consumed, as well as the Mo_3Si layer that must have been present after shorter annealing times.

The differences in the behavior of these couples is attributed to the fact that the type of reaction product which can be formed at an elevated temperature in the diffusion zone between Si_3N_4 and any metal (or alloy) depends on the chemical potential (activity) of silicon and, hence, on the activity (fugacity) of nitrogen at the contact surface. When using diffusion couples consisting of dense Si_3N_4 -ceramics and non-nitride forming metals the interior of the couple is not in direct contact with the surrounding atmosphere. Nitrogen, which formed by the interfacial reaction, cannot escape easily. Nitrogen pressure (fugacity) will be built up at the contact surface. This pressure

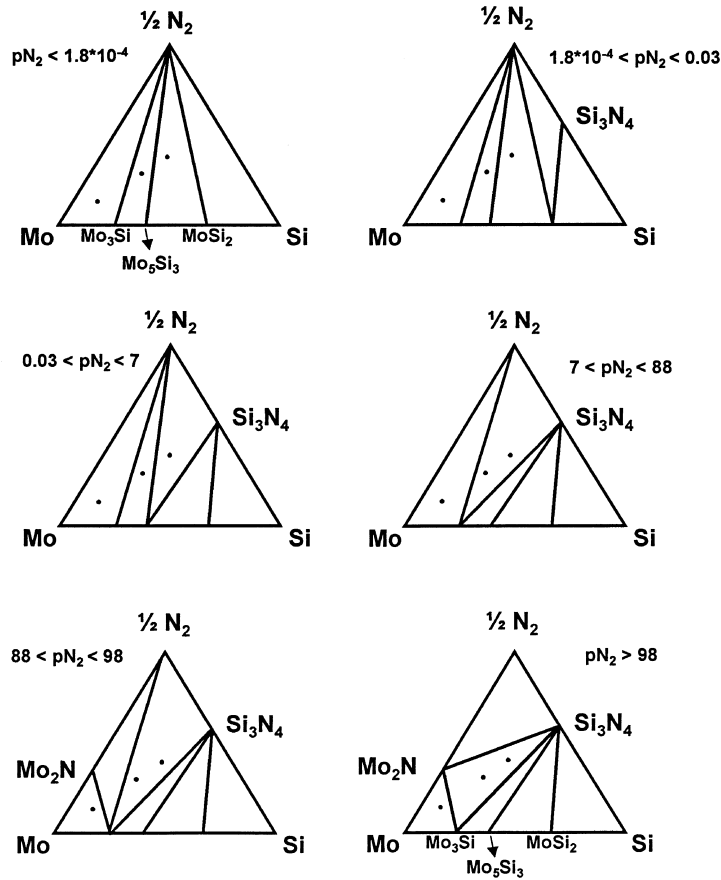


Figure 6.38 The isothermal cross-sections through the Mo–Si–N phase diagram at 1300°C at various partial pressures (bar) of nitrogen. The compositions of the experimentally investigated powder mixtures are depicted as points.

determines the activity of Si at the metal/ceramic interface. In turn, the isothermal cross-section through the phase diagram Me–Si–N and, more specifically, the position of the monovariant equilibrium $\text{N}_2\text{-gas} + \text{Si}_3\text{N}_4 + \text{Me}_x\text{Si}_y$ is dependent on this partial pressure.

For a generalization, let us turn our attention to Fig. 6.38 which is a representation of the phase equilibria in the Mo–Si–N system at 1300°C and various partial pressures (fugacities) of nitrogen.

These isothermal cross-sections were created using thermodynamic data on pertinent binary systems [67] and the results of X-ray diffraction analysis of the Mo + Si_3N_4 powder compacts equilibrated at 1300°C under various nitrogen pressures [68].

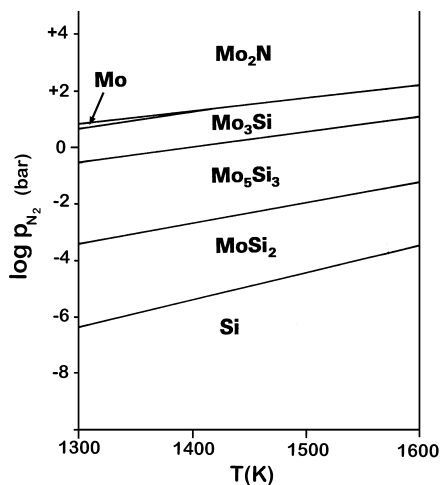


Figure 6.39 Stability diagram showing solid phases in equilibrium with solid Si_3N_4 in the Mo-Si-N system as a function of temperature and nitrogen partial pressure (fugacity).

There are, of course, other ways of presenting the same information as shown in Fig. 6.39. This type of constructions (stability diagram) displays condensed phases in equilibrium with solid Si_3N_4 as a function of temperature and nitrogen partial pressure (fugacity). The thermodynamic activity of silicon at the metal/ceramic interface is related to the N_2 -partial pressure through the equilibrium constant of Si_3N_4 .

If now we look at Figs. 6.38 and 6.39 and try to predict the type and sequence of the reaction products in a Si_3N_4 /Mo diffusion couple at one bar partial pressure of N_2 , we would suggest the following layer sequence: Mo | Mo_3Si | Mo_5Si_3 | (N_2) | Si_3N_4 . Experimentally, however, only Mo_3Si was found in the reaction zone after interaction of dense Si_3N_4 with Mo at 1300°C under 1 bar of nitrogen or argon (containing N_2), or in vacuum ($\sim 10^{-6}$ mbar), and no Mo_2N had been formed (Fig. 6.37(A)).

These observations indeed suggest that nitrogen pressure in the gas atmosphere surrounding the couple does not influence the interfacial reaction in the central part of the joint. This becomes quite clear from considering that N_2 -gas has to escape somehow from the interior of the transition zone and this is difficult in a fully dense diffusion couple. Therefore, nitrogen pressure (fugacity) will build up at the contact surface. According to calculations for the Mo-Si-N system at 1300°C, this pressure is in between 7 and 88 bar because Mo_3Si has been found in equilibrium with Si_3N_4 , but Mo_2N has not been formed.

On the other hand, no N_2 -pressure can build up at the reaction interface when 50% porous ceramics is used as a material of the end-member because nitrogen can escape through the open pores in the Si_3N_4 , and the reaction products in this couple will

entirely depend on N_2 -partial pressure in the ambient atmosphere, because this pressure determines the activity of silicon at Si_3N_4 /metal interface.

In fact, the message here is very simple: the formation of volatile products during interfacial reactions can profoundly affect direction of the diffusion path, which must be taken into consideration when interpreting results of diffusion couple experiments.

6.5 A DIFFUSION COUPLE APPROACH IN STUDYING COMPOSITION–STRUCTURE–PROPERTY RELATIONSHIPS IN SOLID SOLUTION ALLOY SYSTEMS

In recent years, the use of diffusion couple experiments took on a new lease of life due primarily to the introduction of combinatorial methodologies and tools for accelerated materials research and discovery [58]. Transition zones in annealed diffusion couples, which have smoothly varying compositional profiles, can be probed using sophisticated analytical techniques for local composition-specific property measurements. By performing localized micro- (or nano-)scale property measurements on single-phase compositions, many composition–structure–property relationships can be established. This approach significantly extends applications of diffusion couple method and certainly will be useful in design of new materials.

In this section, the utilization of the proposed methodology will be illustrated by two relatively simple examples, namely ternary Ni–Co–Pt and pseudo-binary TiNi–TiPd solid solution alloy systems. Obviously, the same approach can be used for higher order systems as well. For a comprehensive analysis of interdiffusion in multicomponent systems and more complete bibliography, the reader is referred to the excellent book of Kirkaldy and Young [69] and review paper of Dayananda [70].

Here, we will show how to combine interdiffusion study with indentation (hardness) testing, which enables us to (i) to examine the strengthening effects in the Ni–Co–Pt solid solution alloys [71] and (ii) introduce a methodology for screening useful compositions for high-temperature shape memory alloys in the Ni–Ti–Pd system [72].

6.5.1 Interdiffusion Coefficients and Hardness Profiles in the Ni–Co–Pt System at 1200°C

An extended form of Fick's law is employed for the general treatment of diffusion in multicomponent systems. According to this formalism [4], the interdiffusion flux, $\tilde{J}_i$ of an i th component in a multicomponent system is written as

$$\tilde{J}_i = - \sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{\partial C_j}{\partial x}. \quad (6.31)$$

The interdiffusion fluxes obtained from the composition profiles of different components are related by

$$\sum_{i=1}^n \bar{V}_i \tilde{J}_i = \bar{V}_1 \tilde{J}_1 + \bar{V}_2 \tilde{J}_2 + \dots + \bar{V}_n \tilde{J}_n = 0. \quad (6.32)$$

Eq. (6.32) indicates that in the case of system with n component, we need to find interdiffusion fluxes for $(n - 1)$ components, and the flux for the n th component can be estimated from the values found for other components. Compositions of different components are related by $N_1 + N_2 + \dots + N_n = 1$. This implies that $(n - 1)^2$ interdiffusion coefficients are required to express the interdiffusion fluxes of all the $(n - 1)$ independent components where the n th component is a dependent variable.

The interdiffusion flux of the i th component can be found from the measured concentration profiles using Sauer–Frieze analysis [4,13] as

$$\tilde{J}_i(Y_i) = -\frac{(N_i^+ - N_i^-)}{2tv_m} \times \left[(1 - Y_i) \int_{x^*}^{x^*} Y_i dx + Y_i \int_{x^*}^{x^*} (1 - Y_i) dx \right] \quad (6.33)$$

where $Y_i = \frac{N_i - N_i^-}{N_i^+ - N_i^-}$.

From Eq. (6.31), it follows that for a ternary system ($n = 3$), the interdiffusion fluxes $\tilde{J}_1$ and $\tilde{J}_2$ can be expressed as

$$\tilde{J}_1 = -\tilde{D}_{11}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{12}^3 \frac{\partial C_2}{\partial x} = -\tilde{D}_{11}^3 \frac{1}{V_m} \frac{\partial N_1}{\partial x} - \tilde{D}_{12}^3 \frac{1}{V_m} \frac{\partial N_2}{\partial x}, \quad (6.34a)$$

$$\tilde{J}_2 = -\tilde{D}_{21}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{22}^3 \frac{\partial C_2}{\partial x} = -\tilde{D}_{21}^3 \frac{1}{V_m} \frac{\partial N_1}{\partial x} - \tilde{D}_{22}^3 \frac{1}{V_m} \frac{\partial N_2}{\partial x}. \quad (6.34b)$$

Since the concentration dependence of lattice parameters is not known for most of the ternary alloy systems, a constant molar volume over the entire composition range is considered. The latter can be found following that the average (constant) molar volume is $V_m(av) = \frac{1}{n} \sum_{i=1}^n V_m^i$, with V_m^i being the molar volume of the pure component i .

From Eqs. (6.34a) and (6.34b), it can be understood that the expression for interdiffusion flux of components consists of two parts. One part involves the main (or direct) interdiffusion coefficient, such as $\tilde{D}_{11}^3$ for component 1 or $\tilde{D}_{22}^3$ for component 2, which are influenced by concentration gradient of the same component. Whereas the other part of the flux equation involves the cross (or indirect) interdiffusion coefficients, viz. $\tilde{D}_{12}^3$ for component 1 and $\tilde{D}_{21}^3$ for component 2, which are influenced by the concentration gradient of the other component. The third component is considered as dependent concentration variable, and therefore, the values of four coefficients, $\tilde{D}_{11}^3$, $\tilde{D}_{12}^3$, $\tilde{D}_{21}^3$, and $\tilde{D}_{22}^3$, are required to estimate interdiffusion fluxes in a ternary system.

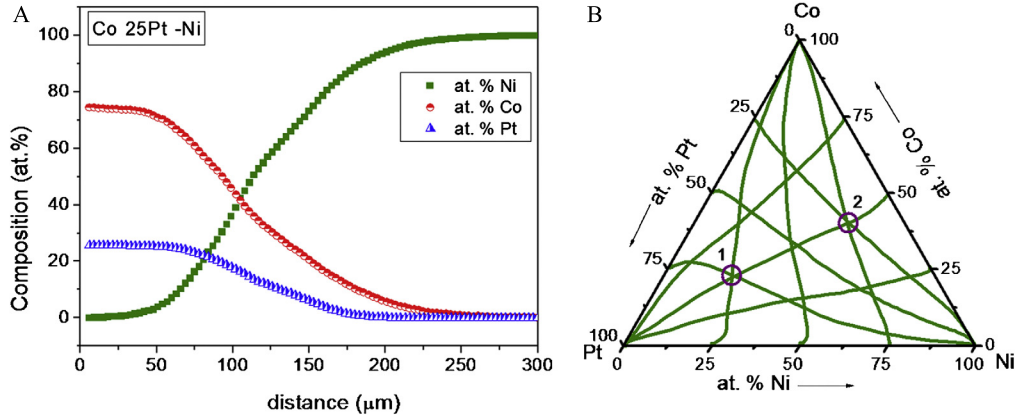


Figure 6.40 (A) Composition profiles across interdiffusion zone of a Co25Pt/Ni couple annealed at 1200°C for 25 hours and (B) concentration profiles (diffusion paths) developed in different diffusion couples during heat-treatment under the same experimental conditions superimposed on the Ni–Co–Pt Gibbs compositional triangle. Note that concentrations at which three diffusion paths are found to intersect each other (Points 1 and 2) are circled.

By now the increase in complexity that can arise going from diffusion in binary to ternary alloy systems should be established in the reader mind. Let us consider an example of a single diffusion couple (DC1) in the Ni–Co–Pt system as shown in Fig. 6.40(A).

The interdiffusion fluxes, for example, of Co and Pt, keeping the third component, Ni, as dependent variable, can be related to the diffusion coefficients corresponding to the composition of interest by

$$\tilde{J}_{Co}(DC1) = -\tilde{D}_{CoCo}^{Ni} \frac{1}{V_m} \left(\frac{\partial N_{Co}}{\partial x} \right)_{DC1} - \tilde{D}_{CoPt}^{Ni} \frac{1}{V_m} \left(\frac{\partial N_{Pt}}{\partial x} \right)_{DC1}, \quad (6.35a)$$

$$\tilde{J}_{Pt}(DC1) = -\tilde{D}_{PtCo}^{Ni} \frac{1}{V_m} \left(\frac{\partial N_{Co}}{\partial x} \right)_{DC1} - \tilde{D}_{PtPt}^{Ni} \frac{1}{V_m} \left(\frac{\partial N_{Pt}}{\partial x} \right)_{DC1}. \quad (6.35b)$$

As already explained, there are four interdiffusion coefficients to be determined, but only two flux equations can be defined based on the results of a single diffusion couple experiment. The experimental determination of interdiffusion coefficients in a ternary system requires two independent diffusion couples with a common composition. Interdiffusion flux equations defined for a second diffusion couple (DC2) can be similarly written as

$$\tilde{J}_{Co}(DC2) = -\tilde{D}_{CoCo}^{Ni} \frac{1}{v_m} \left(\frac{\partial N_{Co}}{\partial x} \right)_{DC2} - \tilde{D}_{CoPt}^{Ni} \frac{1}{v_m} \left(\frac{\partial N_{Pt}}{\partial x} \right)_{DC2}, \quad (6.35c)$$

$$\tilde{J}_{Pt}(DC2) = -\tilde{D}_{PtCo}^{Ni} \frac{1}{v_m} \left(\frac{\partial N_{Co}}{\partial x} \right)_{DC2} - \tilde{D}_{PtPt}^{Ni} \frac{1}{v_m} \left(\frac{\partial N_{Pt}}{\partial x} \right)_{DC2}. \quad (6.35d)$$

Table 6.2 Interdiffusion coefficients determined for one particular composition from three different pairs of intersecting diffusion paths in the Ni–Co–Pt system at 1200°C

Composition, at.%	$\tilde{D}_{CoCo}^{Ni}$ (10^{-14} m ² /s)	$\tilde{D}_{CoPt}^{Ni}$ (10^{-15} m ² /s)	$\tilde{D}_{PtCo}^{Ni}$ (10^{-15} m ² /s)	$\tilde{D}_{PtPt}^{Ni}$ (10^{-14} m ² /s)
19.8 Ni;	0.8	−5	−6.2	1.1
22.7 Co;	0.3	−1.7	−6.9	1.2
57.5 Pt	1.2	−1.9	−7.1	1.2

From these four flux equations one can find the four interdiffusion coefficients after estimating interdiffusion fluxes (Eq. (6.33)) directly from the concentration profiles obtained in diffusion couple experiments.

It is to be remarked that the interdiffusion coefficients are material constants and their values should be the same at a particular composition, no matter which pair of diffusion couples having that common composition is used in the experiment. The correctness of the above formalism can, in principle, be verified: it is necessary to design an experiment in which **three** diffusion paths cross each other at the same concentration on the Gibbs compositional triangle. It is then possible to calculate complete set of interdiffusion coefficients at the intersection point choosing any two of the three diffusion paths. This type of diffusion couple study was performed on the Ni–Co–Pt solid solution system. Two points on the Ni–Co–Pt compositional triangle at which three diffusion paths intersect each other at the same (within the experimental accuracy) concentrations were found (Fig. 6.40(B)). Interdiffusion fluxes for each component were determined for the composition of intersection points from the concentration profiles measured in pertinent diffusion couples using Eq. (6.33), and then interdiffusion coefficients were computed. Three data sets of interdiffusion coefficients for 19.8 Ni; 22.7 Co; 57.5 Pt solid solution (in at.%) at 1200°C, obtained from the analysis of the concentration profiles in the three different pairs of annealed diffusion couples, are given in Table 6.2 as an example.

Experimental studies have revealed that relatively large errors arise when the interdiffusion coefficients are calculated from crossing diffusion paths. However, it is to be noticed that despite the apparent difference in values, there is no difference in the “sign” of the diffusion coefficient. Errors in the calculations should not change sign of the obtained interdiffusion coefficients, which otherwise will be misleading with regard to the operational diffusion mechanism.

Another important question here is which component in a ternary system should be considered as a dependent component. As explained by Kirkaldy and Young [69], dependent variable should be chosen such that the relations expressed in Eq. (6.36) are fulfilled for thermodynamic requirements and stability of the solutions:

$$\tilde{D}_{11}^3 + \tilde{D}_{22}^3 > 0, \quad (6.36a)$$

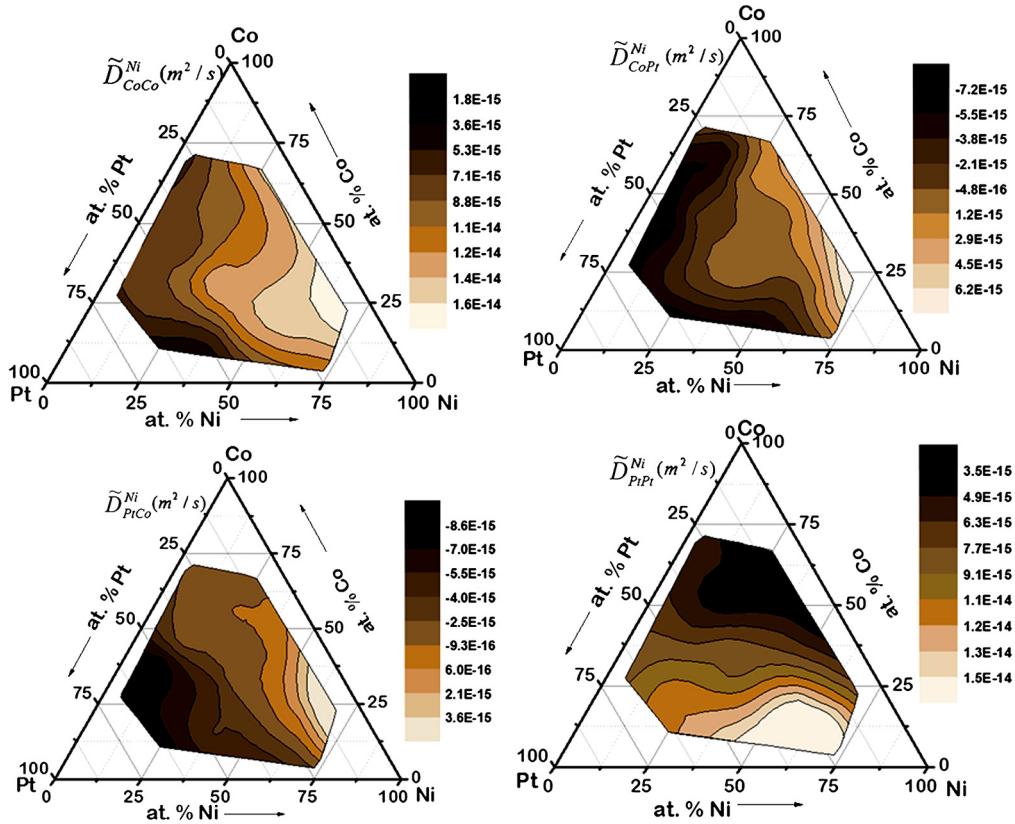


Figure 6.41 Variation of interdiffusion coefficients in the ternary Ni–Co–Pt solid solution system at 1200°C.

$$(\tilde{D}_{11}^3 + \tilde{D}_{22}^3)^2 \geq 4(\tilde{D}_{11}^3 \tilde{D}_{22}^3 - \tilde{D}_{12}^3 \tilde{D}_{21}^3), \quad (6.36b)$$

$$(\tilde{D}_{11}^3 \tilde{D}_{22}^3 - \tilde{D}_{12}^3 \tilde{D}_{21}^3) \geq 0. \quad (6.36c)$$

When diffusion couple experiments are conducted in a small concentration range, the solvent (major) component is, in general, considered as a dependent variable. In the present example, the diffusion coefficients are estimated in a very wide compositional range and, based on the above equations, we concluded that any of the three components can be considered as a dependent variable. The experimentally found variations of the interdiffusion coefficients in the Ni–Co–Pt solid solution at 1200°C are shown in Fig. 6.41.

It is also possible to look at diffusion couple experiments in ternary systems from a somewhat different angle. Interdiffusion zone can be considered as a sequence of single-phase compositions created upon annealing, which provides a framework for evaluation

of, for example, mechanical properties of solid solution alloys. For the solid solutions, there is a strong correlation between hardness and yield strength (more precisely flow stress), and therefore, composition–hardness data are very useful for alloy design, since they contain critical solution–hardening and solution–strengthening information.

The same samples that have been used for interdiffusion study were subjected to nanoindentation testing for measurements of alloy hardness in the Ni–Co–Pt system. Hardness measurements, using instrumented nanoindentation, are rather straightforward. Since both the load and displacement are monitored simultaneously, there is no need to measure the indent size as one would do for conventional microhardness [73].

Representative Secondary Electron Image of the annealed Co50Ni/Pt diffusion couple (1200°C; 25 hours) subjected to nanoindentation testing is shown in Fig. 6.42(A). In all cases, the distance between each indent was maintained to be four to five times the size of the indents, so that the strain fields induced upon indentation did not interact.

In order to determine concentrations of the Ni–Co–Pt solid solution corresponding to the indent positions in the interdiffusion zone, compositions along parallel lines just below the locations of the indents were measured using EPMA. Results of the hardness survey across the entire Ni–Co–Pt system are summarized in Fig. 6.42(B). There are three compositional regions where hardness of the ternary alloys is found to have higher values. To illustrate this point further, the results of hardness measurements are plotted in Fig. 6.42(C) as a function of Ni-content for a fixed Pt-content of 25, 50, and 75 at.%. One can notice that the hardness curve has a single hump for first two examples and two humps in the latter case.

It is apparent that the rapid hardness testing on wide alloy compositions generated in diffusion couples during annealing has obvious advantages compared to the conventional “one-alloy-at-a-time” approach. Both diffusion and mechanical properties can be measured in ternary systems by utilizing the same set of diffusion couples.

It is important to realize that further increase in the number of component renders estimation of interdiffusion coefficients (at best) extremely difficult or (at worst) close to impossible. Already in a quaternary system, according to Eq. (6.31), nine interdiffusion coefficients are required to relate with the interdiffusion fluxes. Therefore, it is necessary to design an isothermal interdiffusion experiment in which diffusion paths deduced from **three** different couples cross each other at the same point on the corresponding isotherm, which is almost impossible to achieve! Because of a “serpentine” shape of the diffusion path in a quaternary isotherm, one cannot predict the right combination of the initial end-member compositions of three diffusion couples which will satisfy the above explained conditions.

A number of alternative techniques are being developed to study diffusion in multicomponent systems [4]. However, this topic is going beyond the scope of the present chapter. Interested readers can read Chapters 3 and 4 in Volume 1 for further details.

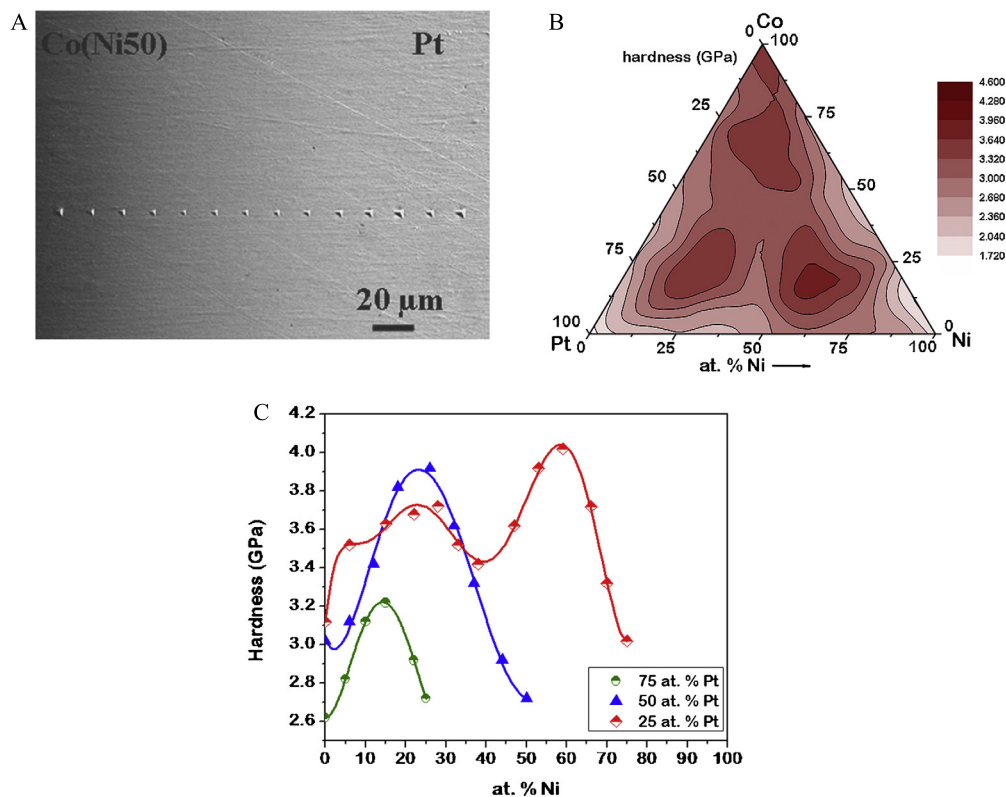


Figure 6.42 (A) Secondary Electron Image showing a linear array of Berkovich indentation impressions across the transition zone developed in the Co50Ni/Pt diffusion couple after annealing in vacuum at 1200°C for 25 hours; (B) hardness variation in the Ni–Co–Pt solid solution, and (C) hardness of several Ni–Co–Pt ternary alloys as a function of Ni-content.

Very often diffusion couple experiments in multicomponent systems are used to generate new alloy compositions by interdiffusion, specifically aimed at determination of other properties only, instead of estimation of diffusion parameters. This is explained by an example of accelerated identification of potential compositions for high-temperature shape memory alloys in the TiNi–TiPd pseudo-binary system.

6.5.2 Screening of Composition Dependent Shape Memory Effect in the TiNi–TiPd System

Fig. 6.43 shows a back-scattered electron image of the interdiffusion zone in the diffusion couple between equiatomic TiNi and TiPd intermetallics and concentration profiles developed after annealing in vacuum at 1150°C for 100 hours.

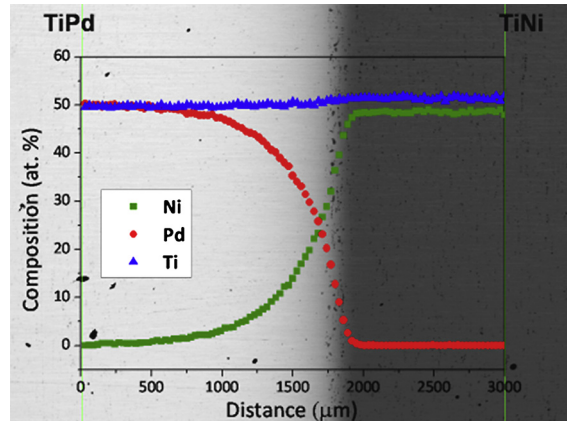


Figure 6.43 Backscattered electron image of the TiPd/TiNi couple together with composition profiles developed in interdiffusion zone during annealing in vacuum at 1150°C for 100 hours. Note that small $\text{Ti}_2\text{Pd}(\text{Ni})$ -precipitates are present in the β -Ti(Ni,Pd)-based matrix of the interdiffusion zone close to the TiNi end-member.

As expected, diffusion interaction under these conditions resulted in a smooth composition profiles across the transition zone; both the phases, β -TiNi and β -TiPd have the same B2 crystal structure ($cP2$) and they are completely miscible above 525°C. Small isolated $\text{Ti}_2\text{Pd}(\text{Ni})$ -precipitates were found in the β -Ti(Ni,Pd)-based matrix of the interdiffusion zone close to the TiNi end-member. This observation indicates that diffusion path on the Ti–Ni–Pd ternary isotherm goes out of the β -phase region into the $\beta + \text{Ti}_2\text{Pd}$ two-phase field and then again comes back to the β -phase [45].

To explore the shape memory effect, interaction zone in the annealed diffusion couple was subjected to indentation testing. Subsequently, heat-treatments at various temperatures for 15 minutes were conducted in order to study healing of the indentation impressions, which is indicative to the shape memory effect. It is to be noted that in such investigations, spherical indenter should be used, since sharp-tipped Berkovich or Vickers indenters induce some strain beneath the indenter, which is not completely recoverable by the shape memory affect. Fig. 6.44 shows an array of indentations over the interdiffusion zone of the annealed TiNi/TiPd diffusion couple (1150°C; vacuum; 100 hours).

One can notice from Fig. 6.44(B) that after subsequent heat-treatment at 200°C for 15 minutes, complete recovery of the indentation impressions on the NiTi-side of the interdiffusion zone has occurred. This suggests that the annealing temperature is higher than the *austenite finish*, A_f , temperatures for these location-specific compositions. Correspondingly, no recovery of the indentation depth means that the annealing temperature is below the *austenite start*, A_s .

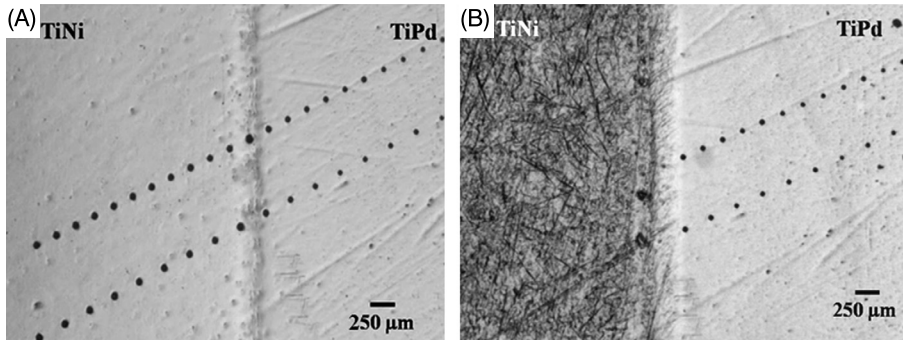


Figure 6.44 Bright-field optical images of the transition zone of the annealed TiNi/TiPd diffusion couple (1150°C; vacuum; 100 hours) showing an array of indentations made with a spherical (50 μm) diamond tip: (A) after interdiffusion annealing and (B) after subsequent annealing at 200°C for 15 minutes all indentation impressions on the TiNi-side of the interdiffusion zone are vanished.

Appearance of the shape memory effect can be examined using depth recovery analysis explained in details in [72]. A depth recovery ratio, $\eta_{d,h}$, is defined as

$$\eta_{d,h}(\%) = \frac{h_b - h_a}{h_b} \times 100 \quad (6.37)$$

where h_b and h_a are the depth of the indentation before and after annealing at a particular temperature which can be monitored by means of, for example, profilometry. It was demonstrated that value of the $\eta_{d,h}$ is a good criterion for the appearance of shape memory effect in a particular alloy.

Variation of depth recovery ratio determined over the whole composition range of the interdiffusion zone in the annealed TiNi/TiPd couple after subsequent heat-treatment for 15 minutes at different temperatures is shown in Fig. 6.45.

Comparing with the data available in the literature, it was concluded that 80% recovery can be considered as an efficient criterion for the appearance of shape memory effect in a particular alloy. Therefore, using construction given in Fig. 6.45 one can get an indication of required annealing temperature for the effective appearance of the shape memory effect for various alloy compositions.

From the application point of view, in the present case of TiNi–TiPd pseudo-binary system there was no necessity of estimating diffusion parameters. However, a single diffusion couple experiment, combined with the indentation testing and annealing at various temperatures, showed rather strong compositional dependency of the shape memory effect occurrence. This otherwise requires an astronomical effort to screen the materials over a wide composition range following the conventional route.

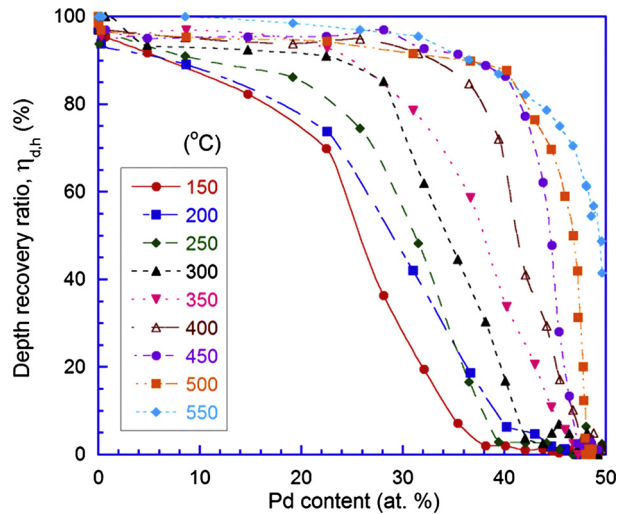


Figure 6.45 Variation of depth recovery ratio, $\eta_{d,h}$, underneath spherical indenter used in the testing of interdiffusion zone in the annealed (1150°C; vacuum; 100 hours) TiNi/TiPd couple during subsequent heat-treatment for 15 minutes at different temperatures as a function of Pd-content.

6.5.3 Concluding Remarks

The diffusion couple technique is a unique research tool in materials science. This method provides a framework to determine interdiffusion parameters of solid solution phases and integrated diffusion coefficients for intermetallic compounds with a narrow homogeneity range. Although the integrated diffusion coefficient is a material constant, one should be careful when extrapolating its values to low temperatures. Firstly, the integrated diffusion coefficient depends on the homogeneity range of the phases, which might change with the temperature. Secondly, processes other than lattice (volume) diffusion (e.g., diffusion along grain boundaries) may contribute to the growth of the product layer, thus leading to faster kinetics than expected for high-temperature experiments.

An additional complication can arise here: the presence of pores (voids) in the diffusion zone will make the interpretation of the experimental results rather difficult.

From simple marker experiments with incremental diffusion couples, information about relative mobilities of diffusing species in solid solution and intermetallic phases can be obtained, provided that at least one stable Kirkendall plane exists in the reaction zone.

It was also demonstrated that tracer diffusion coefficients can be deduced from diffusion couple experiments if pertinent thermodynamic data are at hand. This means that it is practically possible to acquire the self-diffusion coefficient of an element even if no tracers of that element are available.

The diffusion couple technique is also a viable approach in establishing phase relations in ternary and higher-order systems. The efficiency of this method is very high. Yet, it is not without shortcomings. One area which has room for improvement is the spatial resolution of the microanalytical techniques used. Errors attributable to extrapolated interface compositions can then be minimized, and steeper concentration gradients can be measured. In this respect, Analytical Electron Microscopy (AEM) has a promising future. However, problems of specimen contamination, X-ray absorption and quantification procedures, as well as preparation of reproducible thin-film samples in the AEM, have yet to be solved.

It cannot be overemphasized that although the diffusion couple technique is a very powerful tool, it is especially useful in conjunction with other methods. For instance, in order to increase the reliability of the information obtained about an isothermal cross-section of an equilibrium phase diagram, a combination of the diffusion methods with an investigation of selected equilibrated alloys (or powder compacts) is desirable. Multiphase diffusion couples can be used to map out a constitutional diagram and select the compositions of the alloys to be examined. The precise location of the phase field boundaries, as well as direction of tie-lines on the isotherm, can be obtained from equilibrated samples. It is to be said that hindsight is always easy, and the principles upon which the use of diffusion couples in phase diagram research is based appear quite simple to us now when viewed from vantage of more than 50 year development of the subject, but they were not all obvious in the 1950s, and these ideas and their experimental verification must stand as a great intellectual achievement.

Reaction zones in diffusion couples can also be probed using analytical techniques for local composition-specific property measurements. By performing localized property measurements on single-phase compositions generated in interdiffusion zone, many composition–structure–property relationships can be established. This approach significantly extends applications of the diffusion couple method and provides methodologies and tools for accelerated materials research and discovery.

The present chapter was written to provide the reader with the salient features of the diffusion couple technique, and our goal was to offer a guide to anyone interested in using this experimental approach in the solid-state and materials science studies.

REFERENCES

- [1] A.A. Kodentsov, G.F. Bastin, F.J.J. van Loo, Application of diffusion couples in phase diagram determination, in: J.-C. Zhao (Ed.), *Methods for Phase Diagram Determination*, Elsevier, Oxford, 2007, pp. 222–245.
- [2] J.-C. Zhao, Phase diagram determination using diffusion multiples, in: J.-C. Zhao (Ed.), *Methods for Phase Diagram Determination*, Elsevier, Oxford, 2007, pp. 246–272.
- [3] A.A. Kodentsov, A. Paul, M.J.H. van Dal, Cs. Cserhádi, A.M. Gusak, F.J.J. van Loo, On the spatial stability and bifurcation of the Kirkendall plane during solid-state interdiffusion, *Critical Reviews in Solid State and Materials Sciences* 33 (2008) 210–232.

- [4] A. Paul, T. Laurila, V. Vuorinen, S.V. Divinski, *Thermodynamics, Diffusion and the Kirkendall Effect in Solids*, Springer International Publishing, Switzerland, 2014.
- [5] W. Lengauer, The titanium–nitrogen system: a study of phase reactions in the subnitride region by means of diffusion couples, *Acta Metall. Mater.* 39 (1991) 2985–2996.
- [6] M.F. Ashby, I.G. Palmer, The dragging of solid particles through metals by grain boundaries, *Acta Metall.* 15 (1967) 420–423.
- [7] J.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, A.D. Romig Jr., C.E. Lyman, C. Fiori, E. Lifshin, *Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press, New York, 1992.
- [8] G.F. Bastin, H.J.M. Heijligers, Quantitative electron probe microanalysis of carbon in binary carbides, *X-ray Spec.* 15 (1986) 135–150.
- [9] J. Philibert, *Atom Movements. Diffusion and Mass Transport in Solids*, Les Éditions de Physique, Les Ulis, 1991.
- [10] H. Mehrer, *Diffusion in Solids*, Springer-Verlag, Berlin, Heidelberg, 2007.
- [11] L. Boltzmann, Zur Integration der Diffusionsgleichung bei Variablen Diffusions-Coefficienten, *Ann. Physik.* 53 (1894) 959–964 (in German).
- [12] C. Matano, On the relation between the diffusion-coefficients and concentrations of solid metals (the nickel–copper system), *Jap. J. Phys.* 8 (1933) 109–113.
- [13] F. Sauer, V. Freise, Diffusion in Binären Gemischen mit Volumenänderung, *Z. Electrochem.* 66 (1962) 353–363 (in German).
- [14] C. Wagner, The evaluation of data obtained with diffusion couples of binary single-phase and multi-phase systems, *Acta Metall.* 17 (1969) 99–107.
- [15] F.J.A. den Broeder, A general simplification and improvement of the Matano–Boltzmann method in the determination of the interdiffusion coefficient in binary systems, *Scripta Metall.* 3 (1969) 321–326.
- [16] F.J.J. van Loo, On the determination of diffusion coefficients in a binary metal system, *Acta Metall.* 18 (1970) 1107–1111.
- [17] M.J.H. van Dal, M.C.L.P. Pleumeekers, A.A. Kodentsov, F.J.J. van Loo, Intrinsic diffusion and Kirkendall effect in Ni–Pd and Fe–Pd solid solutions, *Acta Mater.* 48 (2000) 385–396.
- [18] P. Nash, *Phase Diagrams of Binary Nickel Alloys*, ASM International, Materials Park, Ohio, 1991.
- [19] D.R. Gaskell, *Introduction to the Thermodynamics of Materials*, Taylor & Francis, London, 1995.
- [20] L.S. Darken, Diffusion, mobility and their interrelation through free energy in binary metallic systems, *Trans. AIME* 175 (1948) 184–201.
- [21] F.J.J. van Loo, Multiphase diffusion in binary and ternary solid-state systems, *Prog. Solid St. Chem.* 20 (1990) 47–99.
- [22] Th. Heumann, G. Walther, Der Kirkendall-Effekt in Silber–Gold-Legierungen im gesamten Konzentrationsbereich, *Z. Metallkd.* 48 (1957) 151–157 (in German).
- [23] J. Levasseur, J. Philibert, Détermination des coefficients de diffusion intrinsèques par mesure de l’effect Kirkendall, *Phys. Stat. Solidi* 21 (1967) K1–K3 (in French).
- [24] J.-F. Cornet, D. Calais, Etude de l’effect Kirkendall d’après les equations de Darken, *J. Phys. Chem. Solids* 33 (1972) 1675–1684 (in French).
- [25] J.-F. Cornet, Compléments à l’étude de l’effect Kirkendall selon les equations de Darken, *J. Phys. Chem. Solids* 35 (1974) 1247–1252 (in French).
- [26] F.J.J. van Loo, G.F. Bastin, G.D. Rieck, Marker displacements as a result of diffusion in binary metal systems, *Sci. Sintering* 11 (1979) 9–26.
- [27] J.H. Gülpen, A.A. Kodentsov, F.J.J. van Loo, Thermodynamics and kinetics of solid-state reactions in the Ni–Si and Ni–SiC systems, in: P. Nash, B. Sundman (Eds.), *Application of Thermodynamics in the Synthesis and Processing of Materials*, The Minerals, Metals & Materials Society, Pennsylvania, 1995, pp. 127–139.
- [28] T.G. Chart, Thermochemical data for transition metal–silicon systems, *High Temp. – High Press.* 5 (1973) 241–252.

- [29] L. Kaufman, Coupled phase diagrams and thermochemical data for transition metal binary systems-VI, CALPHAD 1 (1979) 45–76.
- [30] S. an Mey, A thermodynamic evaluation of the Ni–Si system, Z. Metallkd. 77 (1986) 805–810.
- [31] H. Kleykamp, Gibbs free energy of formation of SiC: a contribution to the thermodynamic stability of the modifications, Ber. Bunsenges. Phys. Chem. 102 (1998) 1231–1234.
- [32] J.H. Gülpen, A.A. Kodentsov, F.J.J. van Loo, Growth of silicides in the Ni–Si and Ni–SiC bulk diffusion couples, Z. Metallkd. 86 (1995) 530–539.
- [33] J.H. Gülpen, Reactive Phase Formation in the Ni–Si and Ni–SiC System, PhD thesis, Eindhoven University of Technology, The Netherlands, 1995.
- [34] J.R. Manning, Diffusion and the Kirkendall shift in binary alloys, Acta Metall. 15 (1967) 817–826.
- [35] I.V. Belova, G.E. Murch, The manning relations for atomic diffusion in a binary ordered alloy, Phil. Mag. A 75 (1997) 1715–1723.
- [36] I.V. Belova, G.E. Murch, Test of the validity of the Darken/Manning relation for diffusion in ordered alloy taken the $L1_2$ structure, Phil. Mag. A 78 (1998) 1085–1092.
- [37] G.F. Bastin, G.D. Rieck, Diffusion in the titanium–nickel system: II. Calculations of chemical and intrinsic diffusion coefficients, Metall. Trans. 5 (1974) 1827–1831.
- [38] M.J.H. van Dal, D.G.G.M. Huibers, A.A. Kodentsov, F.J.J. van Loo, Formation of Co–Si intermetallics in bulk diffusion couples, Part I. Growth kinetics and mobilities of species in the silicide phases, Intermetallics 9 (2001) 409–421.
- [39] K. Ishida, T. Nishizawa, M.E. Schlesinger, The Co–Si (cobalt–silicon) system, J. Phase Equilibria 12 (1991) 578–586.
- [40] P. Villars, L. Calvert, Pearson's Handbook for Crystallographic Data for Intermetallic Phases, American Society for Metals, Metals Park, Ohio, 1985.
- [41] J. Maas, G. Bastin, F.J.J. van Loo, R. Metselaar, The texture in diffusion-grown layers of trialiminides MeAl_3 (Me = Ti, V, Ta, Nb, Zr, Hf) and VN_3 , Z. Metallkd. 74 (1983) 294–299.
- [42] J. Maas, G. Bastin, F.J.J. van Loo, R. Metselaar, On the texture in diffusion-grown layers of silicides and germanides with the FeB structure, MeX (Me = Ti, Zr; X = Si, Ge) or the ZrSi_2 structure (ZrSi_2 , HfSi_2 , ZrGe_2), J. Appl. Cryst. 17 (1984) 103–110.
- [43] J.B. Clark, F.N. Rhines, Diffusion layer formation in the ternary system aluminum–magnesium–zinc, Trans. ASM 51 (1959) 199–221.
- [44] J.S. Kirkaldy, L.C. Brown, Diffusion behaviour in ternary, multiphase systems, Can. Metall. Quat. 2 (1963) 89–117.
- [45] J.B. Clark, Conventions for plotting the diffusion paths in multiphase ternary diffusion couple on the isothermal section of a ternary phase diagram, Trans. Met. Soc. AIME 227 (1963) 1250–1251.
- [46] J.A. van Beek, A.A. Kodentsov, F.J.J. van Loo, Phase equilibria in the Ni–Cr–Ti system at 850°C, J. Alloys Comp. 270 (1998) 218–223.
- [47] J.A. van Beek, P.J.T.L. Oberndorff, A.A. Kodentsov, F.J.J. van Loo, Interactions in the Co–Ni–Si system at 800°C, J. Alloys Comp. 297 (2000) 137–143.
- [48] A.A. Kodentsov, F.J.J. van Loo, Phase relations in the Nb–Ni–Cr system at 1100°C, Monatsh. Chem. 143 (2012) 1309–1314.
- [49] T.B. Massalski, Binary Alloy Phase Diagrams, American Society for Metals, Metals Park, Ohio, 1986.
- [50] J.A. van Beek, A.A. Kodentsov, F.J.J. van Loo, Phase relations in the Ag–Fe–Ti system at 1123 K, J. Alloys Comp. 221 (1995) 103–108.
- [51] J.L. Murray, Phase Diagrams of Binary Titanium Alloys, American Society for Metals, Metals Park, Ohio, 1990.
- [52] A.A. Kodentsov, S.F. Dunaev, E.M. Slusarenko, Determination of the phase diagram of the V–Ni–Cr system using diffusion couples and equilibrated alloys, J. Less-Common Metals 135 (1987) 15–24.
- [53] A.A. Kodentsov, S.F. Dunaev, E.M. Slusarenko, Diffusion paths and phase equilibria in the Mo–Ni–Cr system at 1425 K, J. Less-Common Metals 141 (1988) 225–234.

- [54] A.A. Kodentsov, E.M. Slusarenko, Solid-phase interaction in the Mo–Ni–V system at 1425 K, *J. Less-Common Metals* 153 (1989) 351–362.
- [55] J.A. van Beek, A.A. Kodentsov, F.J.J. van Loo, Phase equilibria in the Cu–Fe–Ti system at 1123 K, *J. Alloys Comp.* 217 (1995) 97–103.
- [56] M.R. Rijnders, J.A. van Beek, A.A. Kodentsov, F.J.J. van Loo, Solid-state reactions in the Ag–Ti–Si system – periodic layer formation, *Z. Metallkd.* 87 (1996) 732–739.
- [57] J.-C. Zhao, A combinatorial approach for efficient mapping of phase diagrams and properties, *J. Mater. Res.* 16 (2001) 1565–1578.
- [58] J.-C. Zhao, Combinatorial approaches as effective tools in the study of phase diagrams and composition–structure–property relationships, *Progress in Materials Science* 51 (2006) 557–631.
- [59] S.L. Markovski, M.J.H. van Dal, M.J.L. Verbeek, A.A. Kodentsov, F.J.J. van Loo, Microstructology of solid-state reactions, *J. Phase Equilibria* 20 (1999) 373–388.
- [60] A.A. Kodentsov, S.L. Markovski, C. Cserhádi, F.J.J. van Loo, Interfacial reactions in GaSb/Co metal-lization contacts during thermal processing, *Chem. Mater.* 15 (2003) 218–224.
- [61] I. Barin, O. Knacke, O. Kubaschewski, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Berlin, 1977.
- [62] G.F. Bastin, F.J.J. van Loo, P.J.C. Vosters, J.W.G.A. Vrolijk, A correction procedure for characteristic fluorescence encountered in microprobe analysis near phase boundaries, *Scanning* 5 (1983) 172–183.
- [63] F.J.J. van Loo, G.D. Rieck, Diffusion in the titanium–aluminium system – I. Interdiffusion between solid Al and Ti or Ti–Al alloys, *Acta Metall.* 21 (1973) 61–71.
- [64] F.J.J. van Loo, F.M. Smet, G.D. Rieck, G. Verspui, Phase relations and diffusion paths in the Mo–Si–C system at 1200°C, *High Temp. – High Press.* 14 (1982) 25–31.
- [65] C.P. Heijwegen, G.D. Rieck, The influence of carbon on the interdiffusion of Mo and Ni, *Metall. Trans.* 4 (1973) 2159–2167.
- [66] H. Holleck, *Binäre und ternäre Carbide- und Nitridsysteme der Übergangsmetalle*, Gebrüder Borntraeger, Berlin–Stuttgart, 1984 (in German).
- [67] P. Rogl, J.C. Schuster, *Phase Diagrams of Ternary Boron Nitride and Silicon Nitride Systems*, American Society for Metals, Materials Park, Ohio, 1992.
- [68] E. Heikinheimo, A. Kodentsov, J.A. van Beek, J.T. Klomp, F.J.J. van Loo, Reactions in the systems Mo–Si₃N₄ and Ni–Si₃N₄, *Acta Metall. Mater.* 40 (1992) S111–S119.
- [69] J.S. Kirkaldy, D.J. Young, *Diffusion in Condensed State*, The Institute of Metals, London, 1987.
- [70] M.A. Dayananda, Zero-flux planes, flux reversals and diffusion paths in ternary and quaternary diffusion, in: M. Dayananda, G. Murch (Eds.), *Diffusion in Solids: Recent Developments*, The Metallurgical Society, Inc., Pennsylvania, 1985, pp. 195–230.
- [71] V.D. Divya, U. Ramamurty, A. Paul, Interdiffusion and solid solution strengthening in Ni–Co–Pt and Ni–Co–Fe ternary systems, *Phil. Mag.* 93 (2013) 2190–2206.
- [72] V.V. Shastri, V.D. Divya, M.A. Azeem, A. Paul, D. Dye, U. Ramamurty, Combining indentation with diffusion couples for combinatorial materials discovery of high temperature shape memory alloys, *Acta Mater.* 61 (2013) 5735–5742.
- [73] W.C. Oliver, G.M.J. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *Mater. Res.* 7 (1992) 1564–1583.

CHAPTER 7

Diffusion-Controlled Internal Precipitation Reactions

Alexander Kodentsov

Mat-Tech BV, Son, The Netherlands

7.1 INTRODUCTION

Amongst large variety of diffusion-controlled processes in solids, internal precipitation in metallic systems is, perhaps, one of the most intriguing reaction phenomena. Internal solid-state reactions can be defined as “chemical processes occurring in isothermal heterogeneous systems when the reaction product forms in the interior of a solid, after reactant has been brought into contact with its surface” [1].

Several types of internal solid-state reaction may be distinguished. However, in the present chapter, we shall be concerned with reactions of internal precipitation in metallic (*nonionic*) materials only and will not trespass on the complementary field of the ionic solids as well as internal reduction reactions in nonmetallic systems. The reader seeking more information on this fascinating, but rather complex subject should access excellent book of Schmalzried [2].

Every person dealing with high-temperature corrosion of metals is familiar with the phenomenon of internal oxidation (sometimes referred to as a subscale formation), and this topic has been a subject of considerable research activity. Although internal precipitation involving oxygen atoms is the most familiar, analogous internal solid-state reactions have also been studied for other oxidants: carbon, nitrogen, sulfur, fluorine, and chlorine. Seen in a wider context, internal solid-state reactions in metals involving oxygen should not be ranked as a higher basic importance than, for example, internal carburization, sulfidation, or nitridation. As rightly remarked by Goldschmidt [3], the special role of oxygen is mainly incidental to our living in the particular atmosphere of this planet in which molecular oxygen happens to be ubiquitous and inescapable, and, in contrast to nitrogen, to be of greater reactivity with most metals.

When a homogeneous binary alloy A–B is exposed to an environment containing a reactive element F (e.g., C, N, O, S, etc.), selective chemical reaction may take place if the thermodynamic activity of F (“*foreign element*”) at the alloy surface is sufficient to combine with B (solute) but not with A. The species F can react with solute to form a surface product layer. However, if the permeation of F into the base metal A is appreciable or if the concentration of B is low, the reaction between solute B and

the penetrating element may also occur inside the alloy. As the interaction proceeds, an internal zone of discrete precipitates may develop beneath the alloy surface.

From a practical standpoint, internal precipitation has long been recognized as something that may have various detrimental effects, since it is a means by which inclusions can be introduced in an otherwise clean material. There are, however, also instances where controlled internal precipitation reactions are desired. This applies to a variety of engineering processes including the ancient technology of the blanching of silver–copper alloys as well as modern practices such as nitriding/nitrocarburizing of steels and dispersion hardening of alloys by internal precipitation.

For the first time, the formation of discontinuous oxide particles within the continuous alloy phase (internal oxidation) was observed in Fe–Ni alloys by Pfeil in 1929 [4]. However, the first systematic study of the internal oxidation was made by C.S. Smith [5], who identified and described this phenomenon in alloys of copper with small addition of cobalt, silicon, nickel, and chromium, and who measured the growth rate of the subscale as a function of temperature. He is responsible too for introducing the term “subscale” in the sense in which it is being used since. Subsequent studies of the internal oxidation of copper- and silver-based alloys by Rhines et al. [6–8], Meijering and Druyvesteyn [9,10], and theoretical treatment by Darken [11] have provided further information towards a detailed understanding of the microstructure and kinetics of internal precipitation in alloy oxidation. However, it was not until 1959 when Carl Wagner published a paper [12] in which a thorough analysis of internal precipitation reactions was presented. Since then, a great number of articles dealing with the reactions of internal precipitation have appeared. It has been the subject of reviews by Rapp [13], Swisher [14], Meijering [15], Schmalzried and Backhaus-Ricoult [1], and Douglass [16]. Information on internal precipitation can also be found in any textbook on high-temperature oxidation and corrosion of metals [17–20].

It is normal for the Introduction to explain the motivation behind the writing of the chapter. For more than 20 years, there has been no scientific review on diffusion-controlled internal precipitation reactions of a length suitable for a continuous reading. Certainly, considerable interest in this phenomenon has persisted over the years and has led to numerous new publications. However, meaningful comparisons using the published results are often difficult in view of enormous variation in alloy compositions studied and reactive environments used. The drive to solve “real industrial problems” is clearly traceable in many published papers, but the vital information necessary to elucidate the underlying mechanisms is very often lost.

The present chapter, therefore, was written to try to correct this shortcoming by providing a text that would summarize, in logical and systematic order, the ideas and concepts that have led to and resulted from the great advance in the understanding of the internal solid-state reactions. The main objective here is to make precipitation reactions in metals understandable, that is, to describe reactions of internal precipitation

in terms of interactions and diffusion motion of reacting species of the system under consideration.

There are many ways to write about internal precipitation reactions in solids because this subject is essentially classical in nature. The present text is written with the intention of providing the reader with the framework for understanding and applying the fundamental principles which govern reactions of internal precipitation in metals, and is not meant to be a complete literature survey or a total overview. Emphasis is laid on the concepts, but data for specific systems are also presented in order to illustrate the application of general relations, although limitation of space precluded every topic being described exhaustively.

Most of the basic ideas will be explained by the relatively simple examples of internal precipitation reactions in well-defined systems, each chosen for its clarity of illustration and pertinence to the particular point of discussion. The examples are mainly taken from the research in which the present author has participated over the years. Undoubtedly, numerous other examples by other investigators could also have served as equally good illustrations, and the author apologizes for such omissions.

Before we start to discuss diffusion-controlled precipitation reactions in detail, it is important to make some general comments about oxidant species that may be involved in the interaction at the alloy surface and analytical techniques used in studying internal precipitation in metals. This will form a natural introduction to our subject.

7.2 BASIC EXPERIMENTAL PROCEDURES USED IN RESEARCH ON SOLID-STATE INTERNAL REACTIONS

Two important things should be mentioned here:

1. In the present chapter we shall be only concerned with diffusion-controlled internal precipitation reactions in semiinfinite samples. The latter implies that after the interaction completed, there exists an unreacted domain (side) of the sample which still retains the initial alloy composition.
2. No reactions involving multiple oxidants will be considered. Only internal precipitation resulted from the attack by single oxidant will be analyzed.

In order to obtain a comprehensive understanding of diffusion-controlled precipitation in metals, it is necessary to study various aspects of internal solid-state reactions, such as reaction kinetics, composition, crystal structure and morphology of the precipitates, as well as microstructural evolution of the reaction zone.

Another question that often causes uneasiness in describing reactions of internal precipitation concerns the oxidant identity and specification of its thermodynamic activity (potential) at the alloy surface during the interaction. We will start this part of the discussion with the last issue.

7.2.1 Thermodynamic Activity of an Oxidant Species Imposed by Ambient Environment on the Metal Surface During High-Temperature Interaction

Let us begin with the situation when only oxygen atoms are acting as an oxidizing species. As already mentioned, this type of internal solid-state reactions, better known as *internal oxidation* has been carefully studied experimentally and theoretically in the past. If the only reacting component present in the gas phase is oxygen, then the only means of controlling the oxygen potential (partial pressure) required for selective (internal) oxidation of a particular alloy is through changes (usually a reduction) in the total pressure of the system.

It is important to realize that the best level of vacuum routinely attainable in laboratory experiments on internal oxidation is about 10^{-6} – 10^{-7} mbar, which is well above dissociation pressures of most metal oxides. The latter can be appreciated just by looking at the pertinent Ellingham diagram [21]. For this reason, these low partial pressures of oxygen in the ambient environment are seldom realized in practice by means of vacuum systems.

The most convenient means of controlling the oxygen potential of an atmosphere, and thus oxidation reactions occurring in its presence, is through control of the chemical composition of the gas phase. The simplest and, perhaps, most common atmospheres that provide this control incorporate mixtures of carbon monoxide (CO) and carbon dioxide (CO₂) or water vapor (H₂O) and hydrogen (H₂). The essential equilibria for these gas mixtures are:



At any temperature, the change of Gibbs free energy during these reactions can be found as

$$\Delta_r G^\circ = -RT \ln K \quad (7.3)$$

with K being equilibrium constant of the reaction, T the absolute temperature, and R the gas constant.

The equilibrium constants for reactions (7.1) and (7.2), assuming the gas mixtures to be ideal, are $K_1 = \frac{p_{\text{CO}}^2 \times p_{\text{O}_2}}{p_{\text{CO}_2}^2}$ and $K_2 = \frac{p_{\text{H}_2}^2 \times p_{\text{O}_2}}{p_{\text{H}_2\text{O}}^2}$, respectively. It is to be remarked that equilibrium constants are always dimensionless. The standard pressure p° has been taken as unity (1 bar) and has therefore not been included explicitly in the expression for the equilibrium constants; in fact, each p_i in K is really a ratio $\frac{p_i}{p^\circ}$.

The corresponding partial pressures of oxygen (oxygen potential imposed by the gas mixtures) can be expressed as $p_{\text{O}_2} = K_1 \times \left(\frac{p_{\text{CO}_2}}{p_{\text{CO}}}\right)^2$ and $p_{\text{O}_2} = K_2 \times \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}\right)^2$. Notice that

for constant ratios of $\frac{p_{\text{CO}_2}}{p_{\text{CO}}}$ or $\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$, the partial pressures (potentials) of oxygen will be independent of the total pressure of the system. The values of oxygen partial pressures corresponding to various ratios of CO_2 to CO and H_2O to H_2 may also be read from the pertinent Ellingham diagram.

Another common method to avoid scale (external reaction product layer) formation in studying internal oxidation is to control oxygen potential at the level set by dissociation oxygen pressure of the lowest oxide of the base metal, so that only the oxide of the less noble solute element can be formed. This is accomplished most readily using a “Rhines pack” [6]: oxidation of an alloy is conducted in a sealed, evacuated capsule containing a large amount of the base metal intimately mixed with its lowest oxide.

Similar procedure was also used in studying *internal fluoridation* and *chloridation* of dilute Ni–Cr alloys [22,23]. In these experiments, the alloy samples are surrounded by a “Rhines pack” consisting of a mixture of Ni + NiF_2 (or Ni + NiCl_2) powder inside a sealed capsule. During annealing, fluorine (or chlorine) partial pressure (potential) is maintained at the dissociation pressure of NiF_2 (or NiCl_2), so that only chromium fluoride (or chromium chloride) can be formed inside the alloy while the nickel is maintained noble.

Internal sulfidation reactions can be carried out at low sulfur potentials (partial pressures) of the ambient environment in order to avoid external sulfide scale formation. Gas mixtures of hydrogen and hydrogen sulfide (H_2S) have often been used in laboratory reactors to control p_{S_2} values. At elevated temperatures, low sulfur potential results from the gas phase equilibrium



The corresponding partial pressure of sulfur in gas atmosphere can be expressed as

$$p_{\text{S}_2} = K_3 \times \left(\frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}} \right)^2 \quad (7.5)$$

where K_3 is the equilibrium constant of the dissociation reaction (Eq. (7.4)).

One can see that for any temperature there is a unique value of the ratio $\frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}}$ for any value of the partial pressure of sulfur, and for constant ratio of $\frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}}$, the partial pressure (potential) of sulfur is independent of the total pressure of the system. Again, the values of sulfur partial pressures corresponding to various ratios of H_2S to H_2 may be read from the pertinent Ellingham diagram.

Most reports on *internal nitridation* concern reactions with ammonia-containing atmospheres. They are, of course, relevant to a number of chemical processing industries and to the heat-treatment of steels. However, internal nitridation in alloys can also be produced by nitrogen itself.

Nitriding of alloys at 1 bar (or lower) of nitrogen can be performed in an ordinary vacuum furnace equipped with a gas inlet system which enable heat-treatment in isostatic or under flowing gas conditions. For the total nitrogen-pressures up to several hundred bars, standard sintering furnaces can be employed, and for the nitriding experiments at higher N_2 -pressures (fugacities) Hot-Isostatic-Pressure (HIP) furnaces or specialized ultrahigh pressure equipment can be used, too. To avoid any possibility of oxide formation, all nitriding experiments have to be carried out in high purity nitrogen or in nitrogen/hydrogen mixtures.

Another possible (and widely used) way to create a high nitrogen fugacity (activity) at the alloy surface is to employ a flowing ammonia/hydrogen mixture as a nitriding agent. The nitrogen activity at the gas/metal interface generated in such a manner can vary in a wide range of values depending on the $NH_3:H_2$ -ratio, temperature, and gas flow rate, and can be equivalent with an effective nitrogen pressure (fugacity) of thousands of bars [24,25].

By flowing gaseous ammonia through a hot zone of the furnace at sufficiently high speed, the thermal dissociation reaction



can be effectively suppressed. The nitrogen uptake by the metal during nitriding in an $NH_3 + H_2$ -gas mixture can be expressed by the following reaction equation:



where $[N]$ represents nitrogen dissolved in the metal. The latter equation implies that the chemical potential of nitrogen in the alloy at the surface is equal to the chemical potential of nitrogen in the flowing ammonia/hydrogen mixture.

The reaction (7.7) can formally be considered as a sum of the two processes: (i) thermal decomposition of ammonia (Eq. (7.6)) and (ii) dissolution of nitrogen in the metal, i.e., $N_2 = 2[N]$.

It can be seen that the fugacity of the N_2 -gas, f_{N_2} , under conditions of local equilibrium at the metal surface can be found as

$$f_{N_2} = K_4 \times \frac{f_{NH_3}^2}{f_{H_2}^3} \times (p^\circ)^2. \quad (7.8)$$

Here, f_{NH_3} and f_{H_2} denote the fugacities of NH_3 and H_2 in the initial gas mixture which are also supposed to be present at the metal surface. K_4 is the dissociation constant for ammonia (Eq. (7.6)) that can be calculated with the pertinent thermodynamic data, and p° is the standard pressure. The assumption of attaining local equilibrium at the gas/metal interface is discussed thoroughly in [26,27].

From Eq. (7.8) it follows that when nitriding in flowing $\text{NH}_3 + \text{H}_2$ -gas mixtures under conditions where no thermal decomposition of ammonia occurs, the effective nitrogen fugacity generated at the gas/metal interface is determined by the $\text{NH}_3:\text{H}_2$ -ratio. In this situation controlling the gas composition entering the furnace provides a means to estimate the virtual N_2 -fugacity of the nitriding agent.

As previously explained, at elevated temperatures, mixtures of CO and CO_2 generate oxygen activity as determined by the reaction (7.1). It is recognized that the same gas mixtures also establish a carbon potential (activity) according to the following equilibrium (“Boudouard reaction”):



When an alloy is exposed to such carbonaceous atmosphere, *internal carburization*, i.e., formation of carbide precipitates inside the metal matrix may occur.

At any temperature, the gaseous carbon activity in the gas-mixture can be found as

$$a_{\text{C}} = K_5 \times \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \quad (7.10)$$

with K_5 being the equilibrium constant for the reaction (7.9), that can be calculated with the pertinent thermodynamic data.

Many carburization reactions have been studied in hydrocarbon–hydrogen mixture. The decomposition (“cracking”) of methane, for example, can be written as



The gas phase carbon activity for the $\text{CH}_4 + \text{H}_2$ mixtures at specified temperature is given by

$$a_{\text{C}} = K_6 \times \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} \quad (7.12)$$

where K_6 is the appropriate equilibrium constant. Again, the standard pressure p° has been taken as unity (1 bar), and therefore, each p_i in Eqs. (7.10) and (7.12) is really a ratio $\frac{p_i}{p^\circ}$.

It is to be noticed that since the CO- and H_2 -partial pressures enter the corresponding equations (7.10) and (7.12) as p_{CO}^2 and $p_{\text{H}_2}^2$ while p_{CO_2} and p_{CH_4} are not squared, the carbon activity is dependent on the total pressure of the system (even with constant $\text{CO}_2 : \text{CO}$ or $\text{CH}_4 : \text{H}_2$ ratios in the gas mixtures). This is clearly in contrast to the behavior found for the oxygen activity generated by the $\text{CO}_2 + \text{CO}$ and $\text{H}_2\text{O} + \text{H}_2$ gas mixtures. Thus, the carbon activity in the gas can be fixed by the composition (CO_2 to CO or CH_4 to H_2 ratio) and total pressure of gas mixture.

In this context, it is also important to emphasize that carbon is unique among the common “oxidants” (penetrating elements) in that it is thermodynamically stable as a solid over a wide temperature range, provided that environment is sufficiently reducing. For this reason, in the above derivations, the thermodynamic reference state is chosen as pure (solid) graphite, for which $a_C = 1$. Obviously, internal carburization experiment requires carbon activity values less than one, but large enough to precipitate solute carbide inside the alloy.

When the gas atmosphere is supersaturated with respect to carbon (i.e., $a_C > 1$), then basically two phenomena may occur:

1. If gas can be brought to equilibrium, carbon deposits from the gas phase on alloy surfaces. This process is described as coking.
2. If the gas phase remains supersaturated, carbon deposition catalyzed by the metal surface can lead to disintegration of alloy in an extremely rapid corrosion process known as metal dusting.

Space being limited, the reader interested in more details about these interesting corrosion phenomena is invited to turn his/her attention to the work of Grabke [28] and to the book of Young [20]. Here, we must be satisfied with some rather brief remarks relevant to the topic of the present chapter.

7.2.2 Investigation of Reaction Kinetics

Experimental studies of reaction kinetics provide information about reaction mechanisms of internal precipitation and serve as a basis for quantitative description of oxidation behavior of alloys, which is invaluable for comparison with theoretical models.

When interaction of an alloy with an oxidizing environment results in internal precipitation of oxidizable solute, a metal sample continuously increases in weight during the reaction. It is, therefore, convenient to follow and study internal reaction rates by measuring the weight change of a metal specimen. Generally, there are two possibilities:

- The first is to take a number of alloy specimens of the same type, expose them in a closed furnace to respective atmosphere with a specific activity of the penetrating element, and take the specimens out after different reaction times. Before and after the test, the specimens are weighed and values of the weight change per unit area of the sample surface have to be determined accurately.
- A more elegant way, of course, is to use continuous thermogravimetry. For this purpose different types of balances may be employed [19,20]. The specimens should be in a chamber made of highly corrosion resistant material so that defined gas atmosphere can be used in the tests. The interior of the microbalance has to be shielded against the aggressive gas atmosphere, which is usually accomplished by a counter flux of a non-reactive gas, like argon.

It is absolutely necessary in both methods to perform metallographic investigations as well. In particular, for continuous thermogravimetric investigations, at the end of each test a metallographic cross-section should be prepared in order to check whether the measured mass-change effects are really due to the precipitation of internally oxidized solute or reaction product layer (scale) is also formed at the alloy surface. More details about relations between rate constants for internal reactions in binary alloys in terms of weight gain or thickness of the internal precipitation zone can be found in [29].

7.2.3 Examination of Reaction Products and Precipitation Zone Microstructure

As already noted, information about composition, crystal structure, reaction product morphology as well as microstructural evolution of the precipitation zone is required in order to obtain a comprehensive understanding of internal solid-state reactions.

Different analytical techniques can be used for these purposes. The reacted sample surfaces can be examined by X-ray Diffraction (XRD). In this case, a special attention should be given to the selection of the suitable XRD techniques. It is advisable to utilize only those XRD methods that are eminently suited for the characterization of thin-films on solid substrates and the determination of texture, rather than to employ (as it is often reported in the literature!) the conventional (often the only available) powder diffractometer.

Many features of the reaction morphology are reveled in metallographic cross-sections. Samples of this type can be prepared by using standard metallographic procedures (sectioning, embedding in epoxy-based resin, grinding, polishing, etching, etc. [30]). Sometimes, for “edge retention” during sample preparation, it can be advantageous to deposit a layer of nickel on the reacted alloy surface prior to sectioning.

The polished cross-sections (in some cases after an appropriate etching) should first be examined by optical microscopy, and then by Scanning Electron Microscopy (SEM) in combination with Electron Probe Microanalysis (EPMA). In addition, Electron Backscatter Diffraction (EBSD) attachment to SEM is also used to obtain information on microstructural features (grain morphology and orientation, distribution of stresses, etc.) of the precipitation zone.

To improve electrical conductivity of the samples (as for example, in the case of specimens taken from internally oxidized alloys) and make them suitable for electron microscopic investigations, a thin layer of carbon can be deposited in vacuum on the metallographically prepared surfaces.

In studies of internal precipitation in alloys, and particularly for characterizing the distribution of elements in the reaction zone and identification of the reaction products, the Electron Probe Microanalysis (EPMA) is valuable, and perhaps, most widely used technique.

In the EPMA high energy electrons are focused to a fine probe and directed at the point of interest in the specimen. The incident electrons interact with the atoms in the sample and generate, among other signals, characteristic X-rays. These X-rays are detected and identified for qualitative analysis, and with the use of suitable standards the measured X-ray intensities can be corrected for matrix effects in order to perform quantitative analysis.

The principal advantage of the EPMA is the ability to measure compositions of very small volumes of a specimen. The spatial resolution for bulk specimens is limited to approximately 1 μm . Obviously, in order to obtain the most reliable results the operating conditions must be optimized. Accelerating voltage, beam current, and counting time are, perhaps, the most critical parameters. Optimization of these parameters has been discussed in detail in [31].

Other techniques to be mentioned here are Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM). Because it is essential for electron diffraction with convergent beam and for microanalysis using Energy Dispersive Spectrometry (EDS) and/or Electron Energy-Loss Spectroscopy (EELS) to illuminate the specimen with a focused electron beam of small diameter, STEM imaging is obviously more compatible with these analytical techniques. On the other hand, the ability to obtain crystallographic information locally gives TEM in combination with Selected-Area Electron Diffraction (SAED) a great advantage in studying precipitate/matrix orientation relationships within the zone of internal oxidation.

It is to be stressed at this point that a series of detailed rules for investigation of the precipitation zones developed during internal reactions cannot be formulated because of the diverse nature of the problems likely to be encountered. Each problem must be treated on its merits. For a very detailed account of the practical electron microscopy in materials science the excellent book by Williams and Carter [32] should be consulted.

Before terminating this part of the discussion, some comments about specimen preparation for electron microscopic investigations should be made. It cannot be overemphasized that good specimen preparation is the key to producing reliable results using electron microscopy. Unfortunately, the preparation of thin-foil TEM specimens is still more an art than a science.

There are many conditions which the ideal specimen should fulfill and most preparation methods involve a compromise with respect to some of them. The most obvious requirement that the specimen be transparent for electrons is clearly of great importance, but it should not be thought that this is the only prerequisite for TEM investigation. Because of the drastic measures (chemical etching, electropolishing, ion-beam thinning) used to generate electron-transparent specimen, much debate has occurred as to whether or not the thin-foil microstructure is characteristic of the bulk material. In other words, the microstructure should be unaltered by the preparation procedure. It is also very important to realize what artifacts each preparation method could possibly

introduce. This can be very annoying since in most cases it is difficult (even impossible) to check electron microscopic observations by any other technique.

Specimens from the internally oxidized alloys can be prepared by mechanical thinning, dimple grinding, and subsequent low-angle argon-ion milling. TEM specimens can also be made using Dual Beam Technology, which is a combination of Scanning Electron Microscopy (SEM) and Focused-Ion Beam (FIB) system. In this case, a so-called “lift-out” technique is used.

It is important to keep in mind that both methods can introduce a number of artifacts as a result of specimen heating and ion damage. On the other hand, (electro)chemical etching tends to remove material quite slowly and therefore (electro)chemical dissolution techniques are preferred for the specimen preparation suitable for TEM studies of, for example, defect structure developed in the reaction zone as well as precipitate/matrix interphase interfaces. One caveat, however, is in order here. Because of different properties of the precipitate compound and matrix material, differential “etching” by ions or differential chemical attack by electrolyte may occur during thinning of the samples taken from the zone of internally oxidized alloy. This can result in an uneven surface of the specimen. It is therefore, essential to find and perfect a suitable preparation technique before embarking upon a detailed microstructural investigation. Further details concerning specimen preparation for Transmission Electron Microscopy can be found in [33,34].

7.3 DIVERSITY OF FORMS AND VARIATIONS OF MICROSTRUCTURES GENERATED BY INTERNAL PRECIPITATION REACTIONS – SELECTED EXPERIMENTAL RESULTS

For the sake of illustration, let us now consider some typical reaction morphologies of internally oxidized Ni–Cr alloys after high-temperature exposure to gaseous atmospheres of various nitrogen activities. In the case of nitriding of Ni–Cr alloys, the nitridation behavior of the material at specified temperature was found to be dependent on the concentration of oxidizable solute in the initial solid solution and pressure (fugacity) of the nitrogen applied upon the system [35–37]. The influence of chromium content in the binary alloy is clearly seen in the reaction zone microstructures shown in Fig. 7.1.

When nitrogen pressure of 6000 bar was applied upon the system at 1125°C, the exclusively internal nitridation in the absence of the surface nitride layer was observed in the alloys with the chromium content up to 15 at.%. Internal precipitates near the metal–gas interface are small and generally rounded, becoming coarser and acicular with increasing depth. With increasing chromium content in the initial solid solution up to 22 at.%, formation of the surface layer of CrN and internal nitride precipitates were found. Relatively small, rounded precipitates of CrN were formed close to the surface

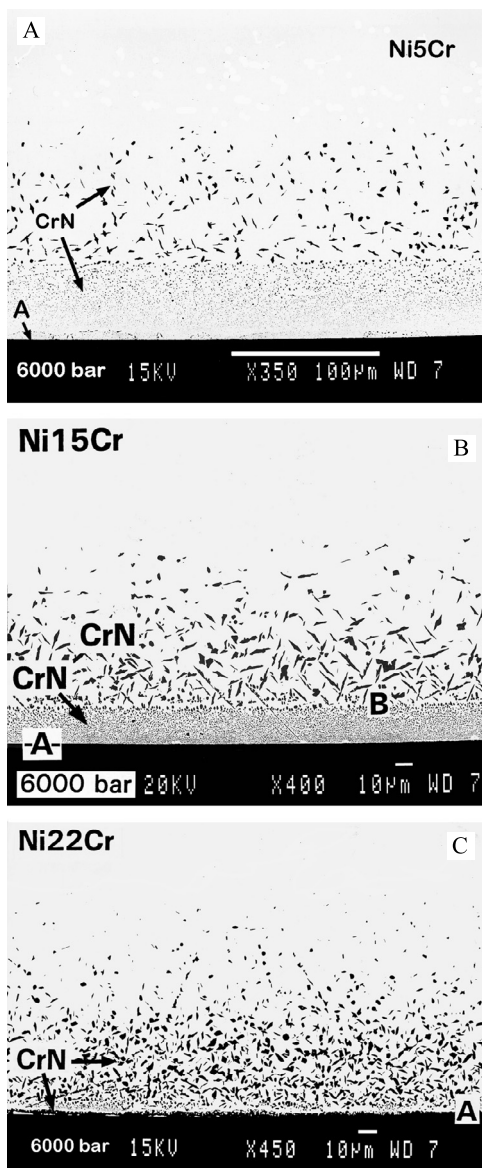


Figure 7.1 Backscattered electron images (BEIs) of the nitrided zone in different Ni-Cr alloys after annealing at 1125°C and 6000 bar of N₂ for 4 hrs: (A) Ni 5 at.% Cr; (B) Ni 15 at.% Cr, and (C) Ni 22 at.% Cr. (Letter A indicates gas-metal interface, and B in (B) is position of the plane in the reaction zone where rounded precipitates are transformed into a plate-like structure.)

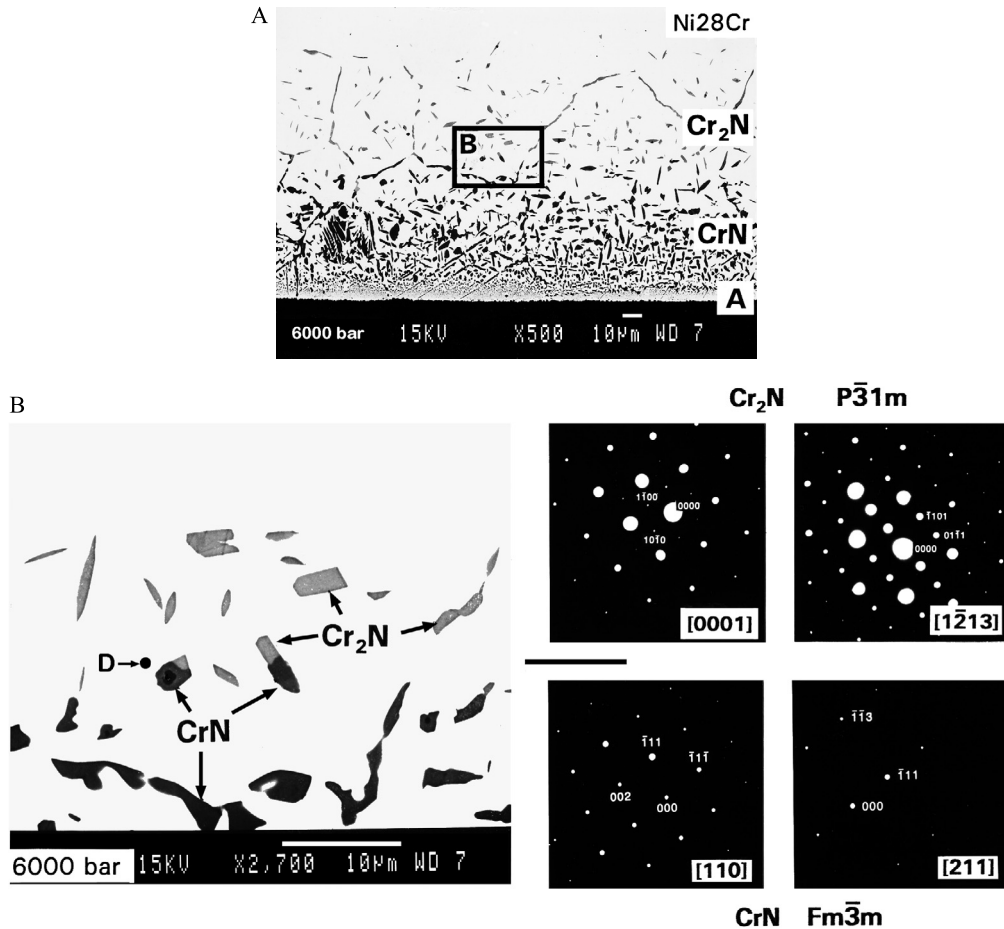


Figure 7.2 Reaction zone microstructure developed in Ni 28 at.% Cr alloy during nitriding at 1125°C and 6000 bar of N_2 for 4 hrs: (A) general view (BEI; Letter A indicates gas–metal interface); (B) magnified area B in (A) together with selected area electron diffraction (SAED) patterns taken from the nitride particles showing the transition from cubic CrN to hexagonal Cr_2N precipitation.

nitride layer. Deeper in the alloy precipitates become coarser, somewhat angular and average precipitate spacing increases.

When chromium content in the alloy was increased to 28 at.%, nitriding under these conditions resulted in the formation within the precipitation zone of both cubic CrN ($cF8$; $Fm\bar{3}m$) and hexagonal Cr_2N ($hP9$; $P\bar{3}1m$) (Fig. 7.2). In some areas of the reaction zone, precipitates have a blocky morphology, and deeper into the alloy, intergranular nitride formation with plate-like particles inside of grains was observed.

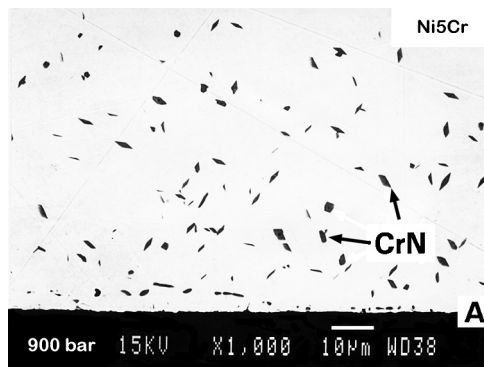


Figure 7.3 Secondary electron image (SEI) of the nitrided zone in Ni 5 at.% Cr alloy after annealing at 1125°C and 900 bar of N_2 for 4 hrs. (Letter A indicates gas–metal interface.)

The effect of the oxidant activity imposed on the alloy surface by nitrogen gas can be appreciated just by looking at Fig. 7.3. After nitriding at 1125°C and 900 bar of nitrogen pressure, exclusive internal nitridation in the absence of surface nitride layer formation occurs in the alloy with 5 at.% of chromium. The reaction zone consists of numerous isolated angular precipitates of CrN with an orientation relationship to the matrix phase. One sees that in this case, the number of CrN-particles per unit volume of the precipitation zone is much lower compared to that found in the Ni 5 at.% Cr alloys nitrided at the same temperature under 6000 bar of N_2 .

It is especially interesting to compare reaction behavior of Ni–Cr solid solutions with chromium content of 28 at.% and higher during nitridation at different nitrogen pressures. Upon nitriding at 1125°C and 6000 bar (as well as 900 bar [35]), the reactant metal forms two different precipitates corresponding to different oxidation states of chromium, and, as shown above, the transition from CrN to Cr_2N precipitation takes place along the whole internally nitrided zone. At lower nitrogen pressures, however, the reaction pattern is found to be completely different (Fig. 7.4).

For instance, after nitridation of Ni 32 at.% Cr alloy at 100 bar of nitrogen, the reaction zone consists of a surface layer of CrN and Cr_2N -precipitates inside the alloy. The characteristic feature of the nitrided zone is the presence of a precipitate-free layer of Ni–Cr solid solution between the surface nitride layer and the zone of internal precipitates.

In contrast, only the hexagonal nitride Cr_2N was detected at the surface and inside the Ni–Cr alloy with a chromium content higher than 28 at.% after annealing at 1125°C under 1 bar of N_2 when samples were cooled down quite fast (about 600 deg/hr). Under these circumstances, internal precipitation also occurs along the grain boundaries even beyond the nitrided front.

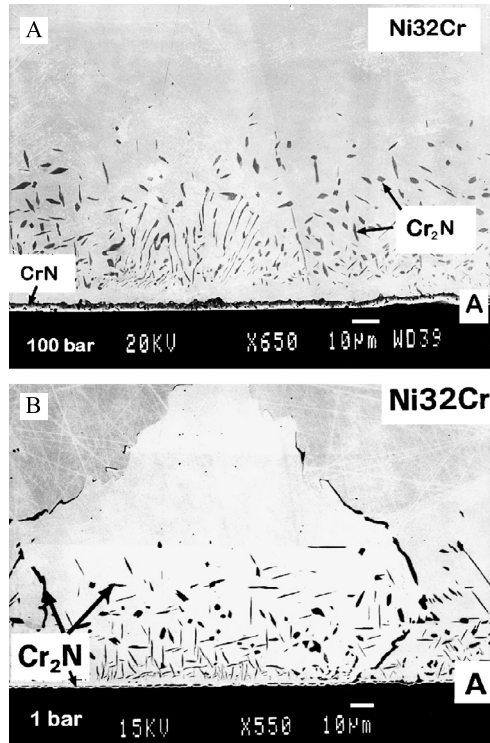


Figure 7.4 Secondary electron images of the nitrided zones developed in Ni 32 at.% Cr alloy after reaction at 1125°C and different nitrogen pressure: (A) at 100 bar of N₂ for 4 hrs and (B) at 1 bar of N₂ for 16 hrs and fast cooling (600 deg/hr) in the furnace at 1 bar of N₂. (Letter A indicates gas–metal interface.)

The curious nature of internal nitridation is also illustrated by the interaction of dilute Ni–Cr alloys with a flowing ammonia/hydrogen gas mixture [38,39]. As explained above in Section 7.2, nitrogen activity at the gas/metal interface generated by a flowing ammonia/hydrogen gas mixture can be very high and vary in a wide range of values depending on the NH₃:H₂ ratio, temperature, and flow rate.

In Fig. 7.5 a typical morphology of an Ni 5 at.% Cr alloy after nitriding in an NH₃ + H₂ mixture (15 vol.% NH₃ and 85 vol.% H₂) at 700°C is presented as an example.

The nitrogen penetration was observed as a very uniform, sharp, featureless grayish band along the exposed surface (Fig. 7.5(A)). The formation of the nitrided zone was also detected by X-ray mapping of the reacted alloy with EPMA using NK_α characteristic X-ray radiation (Fig. 7.5(B)). The nitrogen-containing rim around the sample coincides with the grayish band along the surface exposed to the NH₃ + H₂-gas mixture that was observed in the light microscope.

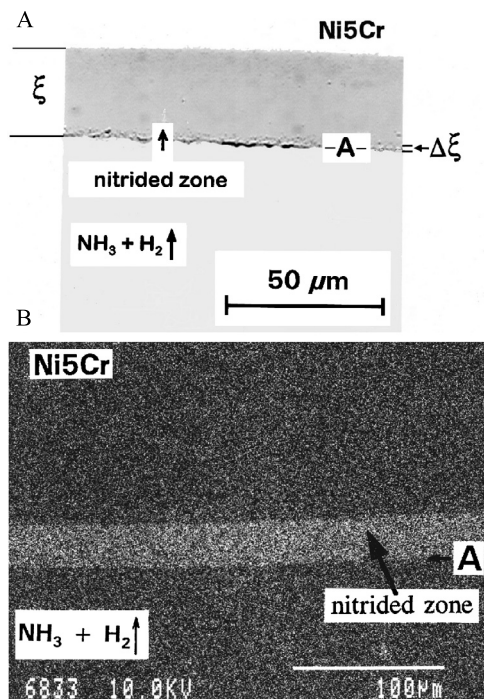


Figure 7.5 (A) Bright-field optical image of the nitrided zone in Ni 5 at.% Cr alloy after annealing at 700°C for 49 hrs under a flowing $\text{NH}_3 + \text{H}_2$ -gas mixture; (B) distribution of characteristic X-rays NK_α across the reaction zone. (Letter A indicates gas-metal interface and ξ is the internal nitridation depth.) Note that a layer of virtually pure Ni of thickness $\Delta\xi$ is present at the surface of the nitride alloy.

Individual precipitates within the internally nitrided layer were not resolvable by optical microscopy or SEM. The microstructure of the precipitation zone was studied with TEM.

A bright-field image of the precipitation zone in an Ni 5 at.% Cr alloy after annealing at 700°C for 49 hrs in flowing $\text{NH}_3 + \text{H}_2$ -gas mixture is shown in Fig. 7.6(A). The TEM specimen was taken from part of the nitrided zone close to the precipitation front. Under the given imaging conditions, the moiré fringes are clearly visible on the TEM micrograph (Fig. 7.6(A)). These are formed due to the double diffraction of the transmitting electron beam on the overlapping plate-like crystals of CrN-precipitates and the Ni-based matrix. In Figs. 7.6(B)–(C) selected area electron diffraction (SAED) patterns taken from a two-phase domain of the nitrided zone are given. The location of the spots arising from double diffraction indicates that $\langle 100 \rangle$ and $\langle 110 \rangle$ directions in the lattices of the matrix phase (Ni) and CrN-precipitates are parallel. In a translated sense, the CrN-precipitates are topotactically (“cube-on-cube”) oriented with respect

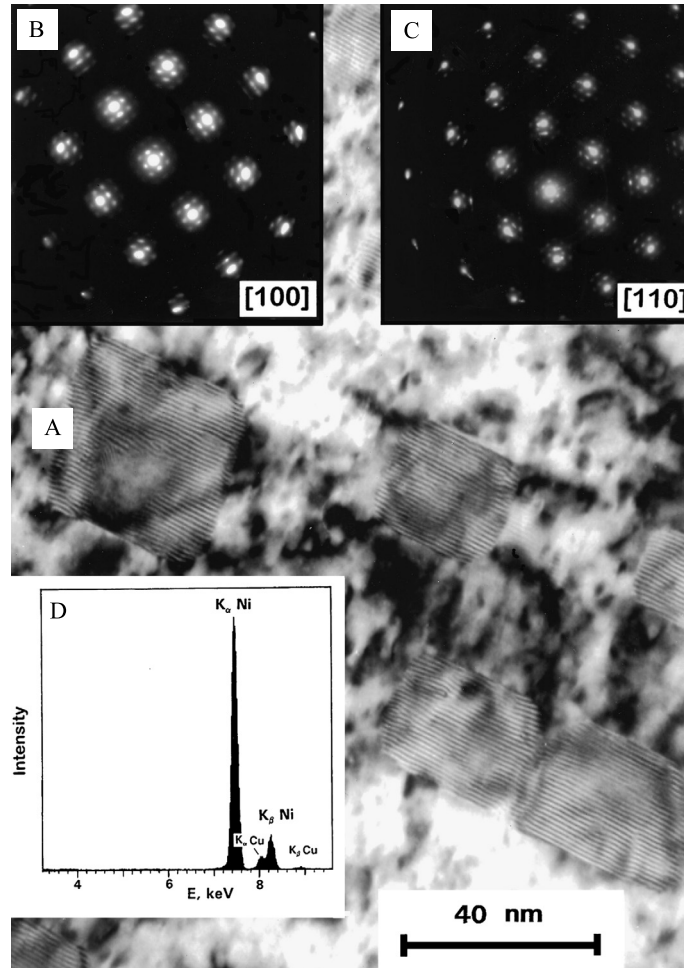


Figure 7.6 (A) Bright-field TEM image of the nitrided zone in an Ni 5 at.% Cr alloy after annealing at 700°C for 49 hrs under a flowing $\text{NH}_3 + \text{H}_2$ -gas mixture (specimen was taken from domain of the reaction zone in the vicinity of the precipitation front); (B)–(C) SAED patterns ([100] and [110]) taken from a two-phase domain of the nitrided zone indicating topotactic relations between the parent phase and CrN -particles; (D) characteristic X-ray spectrum taken from the matrix phase in (A). (Note that the Cu-signal in the spectrum stems from the sample holder.)

to the matrix, so that every crystallographic plane of the precipitate is parallel to the corresponding plane of the nickel, i.e., $(001)_{\text{Ni}} \parallel (001)_{\text{CrN}}$ and $[100]_{\text{Ni}} \parallel [100]_{\text{CrN}}$.

One further point is of interest here: no chromium inside the matrix phase was detected by an energy dispersive spectrometer (EDS) (Figs. 7.6(D)). Obviously, the solute (Cr) is precipitated out completely in the form of cubic CrN within the nitrided zone.

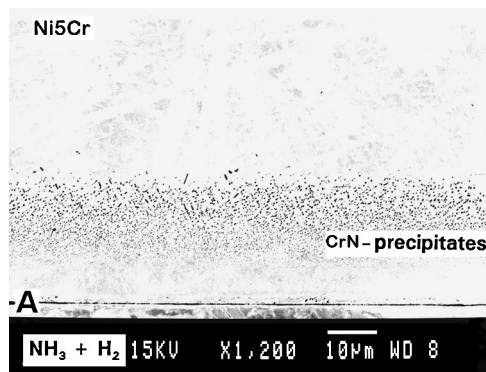


Figure 7.7 Backscattered electron image of the nitrided zone in Ni 5 at.% Cr alloy after annealing at 800°C for 49 hrs under a flowing $\text{NH}_3 + \text{H}_2$ -gas mixture. (Letter A indicates gas-metal interface.)

With increasing nitriding temperature, the internal precipitation reaction results in the development much coarser microstructure. As an example, morphology of an Ni 5at.% Cr alloy after nitriding in a flowing $\text{NH}_3 + \text{H}_2$ -gas mixture at 800°C is shown in Fig. 7.7.

Immediately beneath of the alloy surface, the precipitates are very small and cannot be resolved by optical and scanning electron microscopy. Deeper in the alloy, the CrN-particles become coarser and spacing between the precipitates is much larger compared to that found in the nitridation experiments at 700°C (Fig. 7.5(A)). Nevertheless, the internal nitride particles are generally rounded and the precipitation front is still well defined. No preferable nitride formation along grain boundaries of the Ni-based solid solution was observed.

In the next two sections, a number of practical approaches which can be used for analysis of the observed reaction phenomena will be introduced. Throughout the discussion, use is made of equilibrium thermodynamics and diffusion kinetics in predicting the variation of chemical composition of the reaction zone.

7.4 THERMODYNAMIC-DIFFUSION KINETICS APPROACH IN EVALUATING INTERNAL SOLID-STATE REACTIONS

It was demonstrated on numerous occasions that phase diagrams provide vital information in any attempt to rationalize internal precipitation reactions. In the case of nitriding of Ni-Cr alloys, for example, the nitridation behavior of the material at specified temperature was found to be dependent on the concentration of chromium in the initial solid solution and the nitrogen pressure (fugacity) applied upon the system (see Section 7.3). In Fig. 7.8 the calculated stability (potential) diagram of chromium nitrides at 1125°C in various Ni-Cr alloys is given as a function of nitrogen fugacity [35]. The

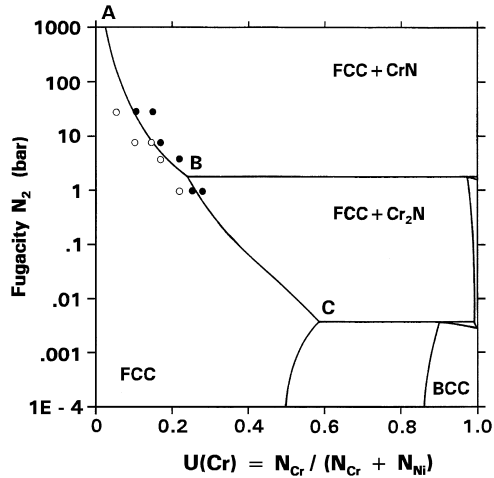


Figure 7.8 Calculated stability diagram of chromium nitrides at 1125°C in various Ni–Cr alloys as a function of nitrogen fugacity together with experimental data: (●) chromium nitride was detected at the surface of alloy with XRD, and (○) no nitride formation. (The FCC and BCC denote Ni-based and Cr-based solid solution with face-centered cubic and body-centered cubic structure, respectively.)

values of the nitrogen fugacity as a function of the metal ratio $U(\text{Cr}) = N_{\text{Cr}} / (N_{\text{Ni}} + N_{\text{Cr}})$ were calculated using the Thermo-Calc databank assuming that the molar volumes of the condensed phases are independent of the external gas pressure (fugacity).

The stability diagram shown in Fig. 7.8 contains all the information needed to predict which nitride phase will be formed at the gas/metal interface under a certain external pressure (fugacity) of nitrogen. For example, the curve AB on this graph represents three-phase equilibria when CrN is in equilibrium with the FCC Ni–Cr solid solution with a specified concentration of chromium and N_2 -gas with a specified pressure (fugacity). Similarly, the curve BC displays three-phase equilibria $\text{Cr}_2\text{N} + \text{FCC} + \text{N}_2$ -gas. Point B in this diagram is fixed by a four-phase (invariant) equilibrium in the ternary Ni–C–N system at 1125°C.

The thermodynamic calculations were verified experimentally by the direct nitriding of various Ni–Cr alloys under 1–100 bar of nitrogen pressure assuming ideal behavior of the nitrogen gas under these circumstances. Well-polished slices of the alloys with different chromium content (5–32 at.%) were exposed at 1125°C for 4 hrs to various pressures of pure nitrogen. The nitride formation at the surface of the alloys was monitored with XRD-analysis and SEM [35]. The results of the verification are depicted in Fig. 7.8.

The correctness of the thermodynamic description used can be checked indirectly at a higher value of nitrogen fugacity as well. Exclusively internal nitrides were found inside the Ni–Cr alloy with 5 at.% of Cr after annealing at 1125°C and 900 bar of

nitrogen (Fig. 7.3) which corresponds with a fugacity of ~ 1070 bar according to the Peng–Robinson equation of state [40]. The experimental observation tending to substantiate the thermodynamic calculations is that in some places of the reaction zone (in fact, at the alloy surface) the CrN-precipitates are in equilibrium with FCC Ni–Cr solid solution and N_2 -gas (Fig. 7.3). The solid solution which is equilibrated with CrN-particles and N_2 -gas after nitridation under these conditions contains 2.8 at.% of Cr as measured by EPMA. The corresponding calculated value for the fugacity of N_2 -gas in thermodynamic equilibrium with CrN and an FCC Ni-based solid solution with a chromium content of 2.8 at.% was found to be ~ 1000 bar. The thermodynamic assessments are clearly in good agreement with the experimental results.

Using the same thermodynamic assessments, isothermal cross-sections through the Ni–Cr–N phase diagram can also be calculated. In Fig. 7.9 such isotherms at 1125°C and external pressures of 100 and 1000 bar are given. To make the ternary isotherms more readable, a rectangular coordinate system was adopted.

Unfortunately, it is not possible to verify these calculated diagrams experimentally, because the concentration of nitrogen in the FCC solid solution is below the limit of detection in the analytical techniques used. However, it is important to note here one specific feature of the nitriding behavior of Ni–Cr alloys containing 28 at.% and higher of chromium, described in the previous section. The transition from cubic CrN to hexagonal Cr_2N precipitation was observed within the nitrided zone upon annealing at 1125°C and 900 or 6000 bar of nitrogen (Fig. 7.2). The average composition of the Ni–Cr solid solution, which is in equilibrium with both CrN- and Cr_2N -precipitates, was determined with EPMA on different samples (e.g., point D in Fig. 7.2(B)). These values range from 23.8 ± 0.5 to 24.5 ± 0.5 at.% of Cr, which is in accordance with the thermodynamic predictions on the three-phase equilibrium in the Ni–Cr–N system (points D in Fig. 7.9), given that the phase boundaries of the condensed phases on the isotherm are virtually unaffected by a change in the external nitrogen pressure applied upon the system.

We will end this part of the demonstration with one practical point. One must be careful not to attribute too much precision to the calculated diagrams used in the present discussion. It is important to keep in mind that these isothermal constructions are no better (and no worse) than thermodynamic data used to construct them. Nevertheless, the chemical potential diagrams and isothermal cross-sections are useful for interpreting reaction phenomena, and by identifying the domains where data are poor, they can be systematically improved. By far the most significance of these graphs is not their superior precision, but rather their ability to extract and compare information not readily perceivable otherwise.

Let us now consider some basic thermodynamic principles that govern internal precipitation in a binary alloy A–B upon exposure to the reactive environment containing a penetrating species F. Let it be supposed that metal A (solvent) is a noble metal under

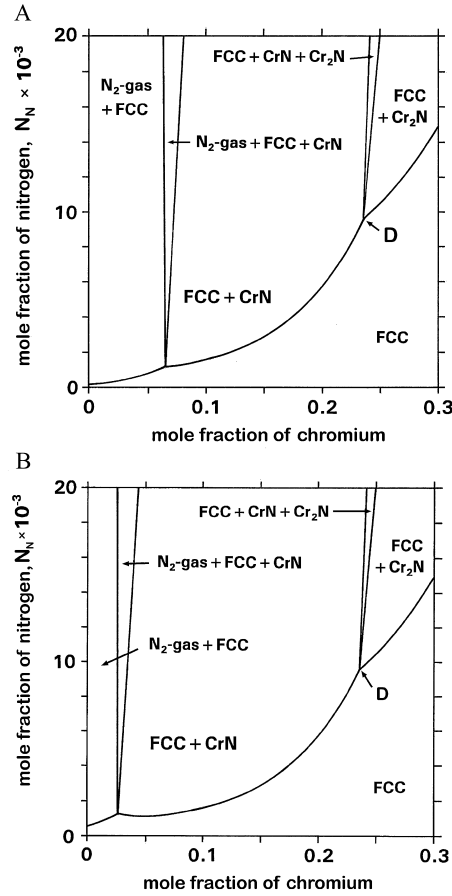
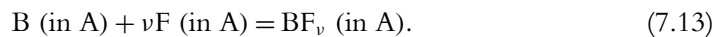


Figure 7.9 Calculated isothermal cross-sections through the Ni–Cr–N system at 1125°C under external nitrogen pressure of: (A) 100 bar and (B) 1000 bar. Note that phase boundaries of the condensed phases on the isotherms are virtually unaffected by a change in the external pressure applied upon the system.

the oxidation conditions, i.e., A cannot combine with F to form a chemical compound, whereas the reactant solute B may form a compound B_nF_m (or BF_ν with $\nu = \frac{m}{n}$).

From a phenomenological stand-point, the overall oxidation reaction can be viewed as the dissolution of element F into the alloy and subsequent reaction of the dissolved species with the oxidizable solute B. The corresponding reaction for a dilute alloy is written as



At any temperature, the change of Gibbs free energy during this reactions can be found as

$$\Delta_r G_7^\circ = -RT \ln K_7 = -RT \frac{a_{BF_v}}{a_B \times a_F^v}, \quad (7.14)$$

where a_B and a_F are the thermodynamic activities of solute B and penetrating element, relative to “Raoultian” and “Henrian” standard states, respectively. K_7 is the equilibrium constant of the reaction, T is the absolute temperature and R is the gas constant. Note that if BF_v is precipitated out as pure (stoichiometric) BF_v , then (by definition) $a_{BF_v} = 1$.

Obviously, for the reaction (7.13) to proceed the free-energy change $\Delta_r G_7^\circ$ must be *negative*. The $\Delta_r G_7^\circ$ can be evaluated from data for Gibbs energy of formation of precipitating compound BF_v ($\Delta_f G_{BF_v}^\circ$) and data for the solubility of penetrating element in the solvent metal, N_F , for any activity of oxidant species F [41]:

$$\Delta_r G_7^\circ = \Delta_f G_{BF_v}^\circ - RT \ln \gamma_F^\circ = \Delta_f G_{BF_v}^\circ - RT \left(\frac{a_F}{N_F} \right)_{eq}. \quad (7.15)$$

Here, γ_F° is the activity coefficient of F in A (“at infinite dilution”).

Using Eqs. (7.14) and (7.15), it is possible to specify the range of the oxidant activities over which internal precipitation occurs. Obviously, computing meaningful activities values of the penetrating element is possible only if Gibbs free energy of formation for precipitating compound and activity data for oxidizable solute in the binary alloy along with the information about solid-state solubility of penetrating species in the solvent A are available.

The necessary condition for precipitation of BF_v in the alloy may also be formulated in terms of the equilibrium *solubility product* K_{sp} for formation of BF_v :

$$[a_B] \times [a_F]^v = K_{sp}. \quad (7.16)$$

When the product $[a_B] \times [a_F]^v = K_{sp}$, internal precipitation of BF_v takes place. The internally oxidized zone extends to the depth at which the activity of dissolved F becomes too small for formation of the precipitating compound.

If values for the activity coefficient of solute B in a dilute binary A–B alloy and solubility of the oxidant F in A are both known, then it is often convenient to express the equilibrium solubility product in terms of mole fractions of B and F, i.e.,

$$[N_B] \times [N_F]^v = K_{sp}. \quad (7.17)$$

When the solubility product of the compound BF_v is locally exceeded, the BF_v -precipitates are nucleated and grow as solute B is depleted from the surrounding matrix upon the arrival by diffusion of atoms of dissolved oxidant F. In a translated

sense, it means that the addition of oxidant F to the binary alloy A–B moves the A–B solid solution into a two-phase field of $A + BF_v$ in the ternary A–B–F phase diagram.

From the foregoing discussion, it becomes clear that phase diagrams provide a useful framework for evaluation of reaction phenomena in ternary systems. The further step in the utilization of phase diagram information for analysis of internal precipitation reactions is connected with the use of concept of a “virtual diffusion path” (i.e., diffusion path from a single phase region that crosses into multiphase domain of phase diagram) [42–44].

It may be recalled that the resulting microstructure developed during solid-state reaction in a ternary system can be visualized by a diffusion (reaction) path. This is a line on the ternary isotherm, representing the locus of the average composition in planes parallel to the original interface throughout the reaction zone. Naturally, the diffusion path must fulfill the law of conservation of mass. If no material is lost or created during reaction, then the diffusion path is forced to cross the straight line (the so-called mass balance line) between the end-members of the reaction couple (in our case, between the alloy A–B and the oxidant F) at least once. Under conditions of local equilibria in the diffusion zone of a semiinfinite sample, the diffusion path involves a time-independent sequence of intermediate reaction product layers.

For the sake of explanation, we consider a simple situation when at specified temperature only a single compound B_nF_m (or BF_v when $v = \frac{m}{n}$) is formed in the reaction between solid solution A–B and oxidizing gas containing component F. Isothermal cross-section through the ternary A–B–F phase diagram pertinent to this case is shown schematically in Fig. 7.10. The isotherm is valid for a standard pressure p^0 of 1 bar of component F. This specified pressure defines the position of the monovariant equilibrium F-containing gas + $\gamma + B_nF_m$ and the solubility of F in the matrix metal. Since the equilibria involving only condensed phases are virtually unaffected by changes in the external gas atmosphere, the rest of the diagram is the same for all pressures.

It follows from the topology of this phase diagram that under specified temperature and pressure, interaction of A–B alloys with gas containing component F may result in *four* different morphologies. The evolution of morphology as the content of solute B in alloy is increased is (i) stable (ternary) solid solution $\gamma + F$ -containing gas, (ii) γ -solid solution with internal precipitates of B_nF_m , (iii) external (surface) layer of B_nF_m -product phase + $\gamma + B_nF_m$ -internal precipitates, and (iv) external (surface) planar layer of B_nF_m -compound + γ . The corresponding diffusion paths are depicted in Fig. 7.10.

Paths (ii) and (iii) cut tie-lines in the two-phase field $\gamma + B_nF_m$, which implies that a region of “constitutional” supersaturation is developed in the alloy in the vicinity of the gas/metal interface or in the γ -solid solution adjacent to a planar alloy/ B_nF_m phase boundary. Relief of the supersaturation can occur through morphological breakdown of the planar alloy/ B_nF_m -interface (i.e., formation of non-planar or “wavy” interface)

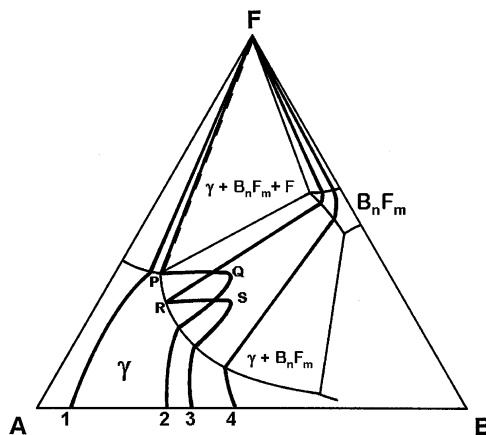


Figure 7.10 Virtual diffusion paths (schematically) between A–B solid solution alloy and gas containing reactive component F, superimposed on isothermal cross-section through the phase diagram of the A–B–F system in which solute (B) and penetrating element (F) form a B_nF_m compound. For the sake of clarity, the F-solubility (solvus) line is exaggerated.

and/or through internal precipitation of the B_nF_m in the γ -solid solution adjacent to the gas–metal interface.

In this context, it is also relevant to note that:

1. Lines PQ and RS in the “dog-leg” portions of the diffusion paths (ii) and (iii) are almost horizontal, i.e., practically parallel to the AB-side of the compositional triangle. This is because diffusion of the penetrating species F through the alloy is much faster than for the solute B.
2. Tie-lines in the two-phase $\gamma + B_nF_m$ field yield the local compositions of the solid solution matrix and precipitate phase across the reaction zone.
3. Transition from path (ii) to (iii) may be expected to occur when the volume fraction of internal precipitates deriving from path (ii) reaches a substantial fraction of the whole.

Before leaving this topic it is important to stress that because of lack of reliable thermodynamic and diffusion data on ternary A–B–F systems, it is not usually realistic to attempt to predict exact positions of virtual diffusion paths through the two-phase fields on the corresponding phase diagram. At present, the use of diffusion path concept allows for only a rather qualitative treatment of internal precipitation reactions. There is, however, every reason to believe that as better data and better theoretical models will become available, it will be possible to calculate diffusion paths corresponding to two-phase regions and deduce the actual morphology of a two-phase zone developed during internal precipitation reaction.

7.5 KINETIC ANALYSIS OF THE INTERNAL PRECIPITATION REACTIONS IN BINARY ALLOYS

7.5.1 Simplified Treatment of the Precipitation Kinetics

Kinetic description of the internal precipitation reaction is quite simple if a number of assumptions can be made:

1. The internal precipitation reaction is associated with a high thermodynamic stability of the precipitating compound. This implies that practically all solute is precipitated out in the reaction zone. The thermodynamic activity of the penetrating element drops to a near-zero value at the reaction front.
2. The solute atoms (B in the A–B alloy) are relatively immobile and the overall kinetics is controlled by the inward diffusion of the penetrating element (F).
3. The internal precipitates formed in the reaction zone do not interfere with the inward diffusion of the penetration element.
4. The solubility of the penetrating element in the base metal is negligible, diffusion coefficient is constant within the reaction layer, and the concentration of the interstitially dissolved atoms of the penetrating element decreases linearly across the matrix of the precipitation zone.
5. The uptake of the penetrating atoms from the ambient environment through the contact surface is so rapid that the concentration at the interface is virtually equal to the maximum solubility in the base metal.

A schematic drawing of the concentration profiles for reacting species under these conditions is given in Fig. 7.11.

This quasi-steady-state approximation allows us to derive a rate equation based on Fick's first law. The instantaneous flux of the penetrating element F through the precip-

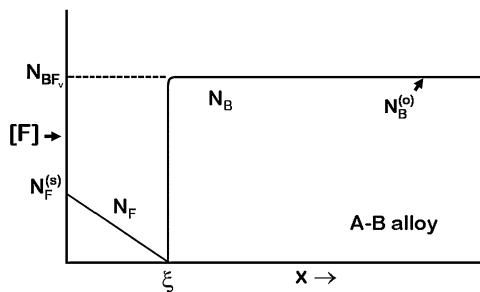


Figure 7.11 Schematic illustration of the concentration profiles for penetrating element F (N_F) and oxidizable solute B (N_B) through the reaction zone during exclusive internal precipitation of a low solubility product compound BF_v inside a binary A–B solid solution in the case when solute atoms are essentially immobile and concentration of the dissolved F-atoms decreases linearly across the matrix of the precipitation zone. Note that virtually no enrichment of solute B (as BF_v) in the precipitation zone occurs.

itation zone of a planar specimen is [45]:

$$J_F = \frac{dM}{dt} = \left| -D_F \frac{N_F^{(s)}}{\xi V_A} \right| \quad (7.18)$$

where $N_F^{(s)}$ is the mole fraction of the penetrating species F at the alloy surface, V_A is the molar volume of the solvent metal A of a binary alloy A–B, D_F is the diffusion coefficient of F in the metal matrix, and ξ is the depth of the zone of internal precipitation.

The oxidizing species F accumulated in the precipitation zone reacts to form compound B_nF_m (or BF_ν , where $\nu = m/n$), and if enrichment of solute B in the precipitation zone is assumed to be small, the amount of the penetrating element F accumulated in the zone of internal precipitation per unit area of reaction front will be given by the stoichiometric equation

$$M = N_B^{(o)} \times \frac{\nu \times \xi}{V_A}, \quad (7.19)$$

and by differentiation we arrive at

$$\frac{dM}{dt} = \frac{\nu \times N_B^{(o)}}{V_A} \times \frac{d\xi}{dt}. \quad (7.20)$$

By combining expression for $\frac{dM}{dt}$ from Eqs. (7.18) and (7.20) and integrating, we obtain

$$\xi^2 = \frac{2 \times N_F^{(s)} \times D_F}{\nu \times N_B^{(o)}} \times t. \quad (7.21)$$

One sees that the latter equation gives the penetration depth of the internal precipitation zone as a function of reaction time.

Rate equations for the internal oxidation of cylindrical and spherical specimens have also been derived using the simplified quasi-steady-state approximation [10,14].

Several points concerning Eq. (7.21) are of interest:

- The internal precipitation process follows a parabolic rate law, i.e., ξ is proportional to the square root of reaction time ($\sqrt{t}$).
- The penetration depth for a fixed time is inversely proportional to the square root of the mole fraction of oxidizable solute in the bulk alloy.
- This simple equation reflects the fact that penetration rate of the precipitation zone is proportional to the solubility-diffusivity product $N_F^{(s)} \times D_F$ (permeability) for penetrating element in the matrix metal.

It also follows from Eq. (7.21) that for a given solvent A, the rate of internal precipitation reaction is independent of the chemical identity of the oxidizable solute B, and (at specified temperature) is determined solely by the permeability of the penetrating

element (oxidant) in A, together with the stoichiometry of the precipitating compound. If these predictions are correct, this provides a method for measuring permeability of interstitial species (C, N, O, F, etc.) in metals.

It is important to keep in mind that the permeability value calculated in this way pertains to the experimental conditions used because the solubility of the penetrating element in the solvent metal, $N_F^{(s)}$, is dependent upon its thermodynamic activity (fugacity) at the metal surface. Therefore, a standard permeability (as a material constant) has to be defined in terms of specified temperature and (arbitrarily chosen) activity (fugacity) of the penetrating element.

Beginning with Rhines and Grobe [8] and Meijering and Druyvesteyn [9], many investigators measured the depth of internal precipitation and compared these measurements with kinetic expressions. Numerous values of oxygen permeability in various dilute silver and copper alloys derived from internal oxidation experiments have been collected by Meijering [15] and compared with independent permeability measurements. Agreement was found to be good.

Verfurth and Rapp [46] internally oxidized a series of dilute Ag–In alloys in air at temperatures between 500 and 800°C, and derived the solubility–diffusivity product for oxygen, $N_O^{(s)} \times D_O$, of Eq. (7.21) from the measured values of the penetration depth ξ . It was observed that the depth ξ varies inversely with the square root of the indium content in the initial alloy, $N_{In}^{(o)}$, according to Eq. (7.21). Likewise, the permeability values $N_O^{(s)} \times D_O$ in silver obtained from these measurements were found to be in excellent agreement with the product of $N_O^{(s)}$ and D_O values determined separately by another technique [47]. More information about experimental verification of this diffusion model can be found in [20].

Eq. (7.21) also allows for some estimates of the precipitate size inside the zone of internal reaction. In general, the precipitate size is determined by a competition between the rate of nucleation as the internal precipitation front passes and the subsequent growth and coarsening of the particles. It is apparent that those factors which favor high nucleation rate will decrease the particle size and those which favor high growth rate will increase the size.

Suppose that the nucleation rate is controlled by the velocity of the precipitation front, and the growth is controlled by the length of time available for growth of a precipitate. In such a case, the spherical particle size, r , should be inversely proportional to the velocity of the precipitation front, i.e., $r \propto \frac{1}{v}$. Differentiation of Eq. (7.21) with respect to time gives the precipitation front velocity for a planar specimen as

$$v = \frac{d\xi}{dt} = \frac{N_F^{(s)} \times D_F}{v \times N_B^{(o)}} \times \frac{1}{\xi}. \quad (7.22)$$

Therefore, other things being equal, one would predict the size of internal precipitates increase proportionally to penetration depth, ξ , and the oxidizable solute

concentration, $N_B^{(o)}$, in the alloy, and inversely proportional to the solubility of penetrating element in the base metal, $N_F^{(s)}$, which is dependent on its thermodynamic activity (fugacity) at the external surface.

A more rigorous and less restrictive analysis of internal precipitation kinetics in the absence of external reaction product layer has been provided by Wagner [12], allowing for the possibility that atoms of the oxidizable solute B also diffuse.

7.5.2 Wagner's Treatment of Internal Oxidation

By the time Wagner's classical paper was written, a number of experimental studies had demonstrated that internal oxidation process in metals follows a parabolic law. If diffusion control is maintained, the depth ξ of the internal precipitation zone is a parabolic function of the time, t :

$$\xi = 2\gamma\sqrt{D_F \times t}. \quad (7.23)$$

Here, D_F is the (concentration independent) diffusion coefficient of the penetrating element F in the base metal, and γ is a dimensionless parameter, which is time-independent for an isothermal reaction at constant external activity of the penetrating species.

Assuming that precipitated particles do not interfere with inward diffusion of the oxidant F in the base metal, the one-dimensional diffusion of F can be described using Fick's second law:

$$\frac{\partial N_F}{\partial t} = D_F \frac{\partial^2 N_F}{\partial x^2}, \quad (7.24)$$

where N_F and D_F are the mole fraction and diffusivity of dissolved penetrating element F in the metal matrix, and x is the distance from the outer surface.

This equation may be solved for the boundary conditions

$$N_F = N_F^{(s)} \quad \text{for } x = 0, \quad t > 0, \quad (7.25)$$

$$N_F = 0 \quad \text{for } x \geq \xi, \quad t > 0. \quad (7.26)$$

$N_F^{(s)}$ is the mole fraction of penetrating species F at the external metal surface. The solution to Eq. (7.24), subject to the above boundary conditions, is

$$N_F = N_F^{(s)} \times \left[1 - \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{D_F \times t}}\right)}{\operatorname{erf} \gamma} \right]. \quad (7.27)$$

Analogously, the solution of the diffusion equation for the oxidizable solute B, diffusing outwards from the center of the specimen to the precipitation front, namely

$$\frac{\partial N_B}{\partial t} = D_B \frac{\partial^2 N_B}{\partial x^2}, \quad (7.28)$$

is obtained with the boundary conditions

$$N_B = N_B^{(o)} \quad \text{for } x \geq 0, \quad t = 0, \quad (7.29)$$

$$N_F = 0 \quad \text{for } x \leq \xi, \quad t > 0, \quad (7.30)$$

where N_B and D_B are the mole fraction and (concentration independent) diffusivity of the solute B in the metal matrix, and $N_B^{(o)}$ is the mole fraction of B in the bulk alloy. The solution is

$$N_B = N_B^{(o)} \times \left[1 - \frac{\operatorname{erfc}\left(\frac{x}{2\sqrt{D_B \times t}}\right)}{\operatorname{erfc}(\gamma\sqrt{\Phi})} \right], \quad (7.31)$$

where the diffusion coefficient ratio is $\Phi = \frac{D_F}{D_B}$. The erf and erfc in the solutions (Eqs. (7.27) and (7.31)) are the error function and the complementary error function, respectively [48].

In his work, Wagner dealt with the mass balance at the reaction front ($x = \xi$) by supposing that all internal precipitation of the oxidizable solute B in the form of an insoluble and stoichiometric compound BF_ν takes place at this location. Therefore, the fluxes of the penetrating element F and solute B toward the precipitation front must be equivalent, i.e., at the reaction front the inward flux of F-atoms is ν times the outward flux of the B-atoms:

$$\lim_{\varepsilon \rightarrow 0} \left[-D_F \left(\frac{\partial N_F}{\partial x} \right)_{x=\xi-\varepsilon} = \nu \times D_B \left(\frac{\partial N_B}{\partial x} \right)_{x=\xi+\varepsilon} \right]. \quad (7.32)$$

In this equation, ε is a very small increment in x . It is used to indicate that the diffusion fluxes are evaluated in the close proximity to, but on opposite sides of the reaction front.

Substitution of Eqs. (7.27) and (7.31) into Eq. (7.32) leads to the following expression:

$$\frac{N_F^{(o)}}{N_B^{(o)}} = \frac{\nu \times \exp(\gamma^2) \times \operatorname{erf} \gamma}{\sqrt{\Phi} \exp(\gamma^2 \times \Phi) \times \operatorname{erfc}(\gamma\sqrt{\Phi})}, \quad (7.33)$$

from which parameter γ introduced in Eq. (7.23) may be obtained from a graphical or numerical solution.

Evaluation of γ allows the calculation of depth of internal precipitation ξ as well as velocity of the reaction front, $\frac{d\xi}{dt}$, for any time after the start of the reaction, provided that Eq. (7.32) and the boundary conditions set by Eqs. (7.25), (7.26), (7.29), and (7.30) are valid, and all the quantities (except for γ) of Eq. (7.33) are known. It is also to be noted that the calculated parameter γ cannot be expected to apply at the very start of internal reaction, since Eq. (7.23) demands an infinite initial velocity.

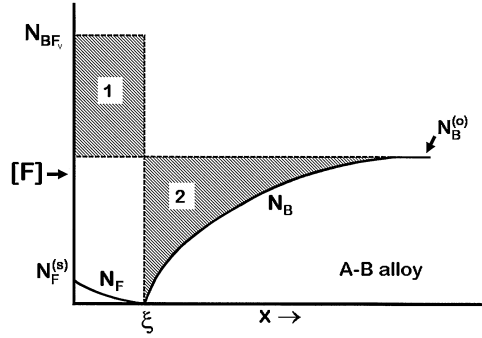


Figure 7.12 Schematic illustration of the concentration profiles for penetrating element F (N_F) and oxidizable solute B (N_B) for exclusive internal precipitation of a low solubility product compound BF_v in a binary A–B alloy. The zone of internal reaction grows by simultaneous inward diffusion of penetrating element F and outward counter-diffusion of the B-atoms, which leads to an enrichment of B as BF_v in the precipitation zone. (Note that the enclosed areas (1) and (2) are equal.)

Two limiting cases of the Eq. (7.33) may be considered:

1. For the special case when $\gamma \ll 1$ and $\gamma\sqrt{\Phi} \gg 1$, which is equivalent to $\frac{D_B}{D_F} \ll \frac{N_F^{(s)}}{N_B^{(o)}} \ll 1$ (i.e., penetrating element F is by far the most mobile species), Eq. (7.33) is simplified to

$$\gamma \cong \sqrt{\frac{N_F^{(s)}}{2\nu \times N_B^{(o)}}}, \quad (7.34)$$

hence Eq. (7.23) becomes

$$\xi \cong \sqrt{\frac{2 \times N_F^{(s)} \times D_F \times t}{\nu \times N_B^{(o)}}}, \quad (7.35)$$

which is identical to the solution previously derived under a quasi-steady-state approximation assuming predominant diffusion of the penetrating element F and virtual immobility of the solute atoms (Eq. (7.21) and Fig. 7.11).

2. In the second limiting case, if $\gamma \ll 1$, but $\gamma\sqrt{\Phi} \ll 1$, conditions are equivalent to $\frac{N_F^{(s)}}{N_B^{(o)}} \ll \frac{D_B}{D_F} \ll 1$ (i.e., counter-diffusion of the solute element is significant), and then

$$\gamma \cong \frac{N_F^{(s)} \times \sqrt{\pi \times \Phi}}{2 \times \nu \times N_B^{(o)}}, \quad (7.36)$$

Again, the depth and velocity of the precipitation front at any reaction time may be derived by substituting Eq. (7.36) into Eq. (7.23). A schematic drawing of the concentration profiles under these conditions is given in Fig. 7.12.

Under conditions of the second limiting case, an appreciable enrichment of the solute element B in the form of the compound BF_v , in the precipitation zone occurs. This enrichment may be described by an *enrichment factor* α , which is defined as the ratio of mole fraction of solute B present as BF_v in the zone of internal precipitation (φ) to the mole fraction of the oxidizable solute in the bulk alloy ($N_B^{(o)}$). Wagner [12] showed that α can be expressed quantitatively as

$$\alpha = \frac{\varphi}{N_B^{(o)}} = [\gamma \sqrt{\pi \Phi} \exp(\gamma^2 \Phi) \operatorname{erfc}(\gamma \sqrt{\Phi})]^{-1}. \quad (7.37)$$

(Here, we retain the same symbols as above.)

Under the limiting conditions yielding Eq. (7.35) and Fig. 7.11, a negligible enrichment of B (as BF_v) in the reaction zone occurs during exclusive internal oxidation of a binary alloy. In contrast, for the case when Eq. (7.36) and therefore Fig. 7.12 are valid, an enrichment of solute as BF_v in the precipitation zone and a depletion of solute from the unreacted alloy will result. It also follows from Eq. (7.37) that this phenomenon is most pronounced when values of $N_B^{(o)}$ and Φ are relatively small.

As depicted in Figs. 7.11 and 7.12 for a constant temperature oxidation at constant thermodynamic activity of the penetrating element at the alloy surface, the degree of solute enrichment is constant within the zone of internal precipitates. In Fig. 7.12, the enclosed areas (1) and (2) must be equal, that is,

$$(N_{\text{BF}_v} - N_B^{(o)}) \times \xi = \int_{x=\xi}^{x=\infty} (N_B^{(o)} - N_B) dx. \quad (7.38)$$

It is important to realize that in the proposed analysis, the boundary conditions (Eqs. (7.26) and (7.30)) used in deriving kinetic equations mean that, at a certain depth of the interaction zone, either “free” penetrating element F or “free” solute B is present. The simultaneous presence of F and B is ruled out here because they are assumed to react completely and with infinite speed. In other words, the nucleation/precipitation of BF_v -particles is assumed to be extremely rapid, so that the front of internal precipitation can be considered as a plane parallel to the original alloy surface. The latter implies that the internal precipitation front corresponds to the location in the interaction zone where the equilibrium (7.13) is just satisfied. However, new precipitate cannot form if Eq. (7.16) or (7.17) describing conditions set by local equilibrium between precipitate and matrix is precisely obeyed. To nucleate a new precipitate of BF_v , an excess of oxidant F (i.e., $N_F > (\frac{K_{sp}}{N_B})^{\frac{1}{v}}$) is required to drive the nucleation event.

The effects of supersaturation requirements on kinetics of internal reaction were examined by Kahlweit et al. [49–51], and their treatment has since been extended by Gesmundo et al. [52].

7.5.3 Analysis of the Effect of Supersaturation Requirements on Internal Precipitation Kinetics

Following the approach suggested by Wagner [12,53], Böhm and Kahlweit have introduced a model for a diffusion-controlled reaction of internal oxidation, taking into consideration the need for supersaturation as a driving force for nucleation and precipitation of internally oxidized solute. Originally, this quantitative treatment was developed for the nucleation and precipitation of an equiatomic compound in internal oxidation [49] under the assumption of a finite solubility product of the precipitating compound. Somewhat later, this analysis was used to describe internal precipitation of BO_v -oxide [51]. Obviously, the same analysis is also applicable for the general case of the internal precipitation reaction involving penetrating element F and internally oxidized solute B.

According to this theory, the internal precipitation of an internally oxidized solute B inside a binary alloy A–B requires the presence of a finite degree of supersaturation for the nucleation of new particles of the precipitating compound BF_v . As a consequence, the precipitation of oxidizable solute does not occur along a well-defined front but rather within a region of small but finite width where the distribution of F and B change with time as new precipitating particles nucleate and grow.

To illustrate the following derivations, we turn our attention to Fig. 7.13, where concentration distributions of the reactant species in the vicinity of the precipitation front are shown schematically.

At the outer boundary of the supersaturated region, i.e., at $x = X'$, the concentrations (mole fractions) of the reactants are N'_F and N'_B , and hence the corresponding equilibrium solubility product of the precipitating compound BF_v in the solvent metal A is

$$[N'_B] \times [N'_F]^v = K_{\text{sp}}. \quad (7.39)$$

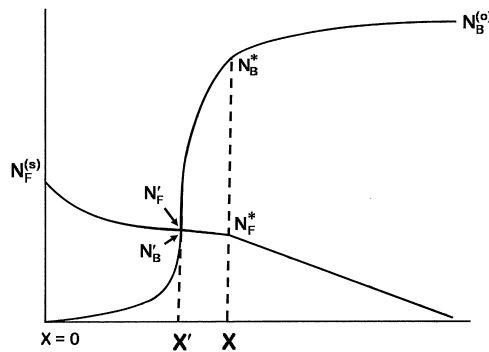


Figure 7.13 Concentration profiles (schematically) of penetrating element F and oxidizable solute B during internal oxidation of a binary alloy A–B, showing a region of supersaturation ahead of the internal precipitation zone. (Note that $x = 0$ denotes position of the original alloy surface.)

At the inner boundary (at $x = X$) of the same region, the concentrations of F and B are N_F^* and N_B^* , respectively, with $N_B^* > N_B'$ and $N_F^* < N_F'$, but with the concentration product critical to the formation of a nucleus of critical size

$$[N_B^*] \times [N_F^*]^v = S^* > K_{sp}. \quad (7.40)$$

The last equation implies the existence of a finite, critical degree of supersaturation required for the nucleation of new precipitates.

For the precipitate BF_v to develop, both reactive species must be delivered to the precipitate surface. Since in most cases, $N_B^{(o)} \times D_B \ll N_F^{(o)} \times D_F$, the precipitate growth is limited by the availability of the internally oxidized solute, which becomes depleted ahead of the precipitate. At a certain point, growth of the precipitate particle is arrested and subsequent recovery of supersaturation will occur deeper in the alloy (at the position $x = X$ in Fig. 7.13 where condition (7.40) is satisfied) by inward diffusion of the penetrating species, whereupon the precipitation cycle repeats. Nucleation/formation of the last-precipitate (at the position $x = X'$ in Fig. 7.13) relieved the local supersaturation, and at this location the condition given by Eq. (7.39) is valid, which, as a matter of fact, was observed through most of the internal precipitation zone (i.e., for $0 \leq x \leq X'$).

For parabolic (diffusion-controlled) internal precipitation kinetics, solutions of diffusion equations for reactant species were found in the form [49]:

$$N_F = N_F^{(s)} - \frac{N_F^{(s)} - N_F^*}{\text{erf } \gamma} \text{erf}\left(\frac{x}{2\sqrt{D_F \times t}}\right) \quad \text{for } x < X(t) \quad (7.41)$$

and

$$N_B = N_B^{(o)} - \frac{N_B^{(o)} - N_B^*}{\text{erfc}(\gamma\sqrt{\Phi})} \text{erfc}\left(\frac{x}{2\sqrt{D_B \times t}}\right) \quad \text{for } x > X(t), \quad (7.42)$$

with γ and $\Phi = \frac{D_F}{D_B}$ as previously defined in this section.

Parameter γ may be obtained from the experimental data following the analysis developed by Böhm and Kahlweit [49] for an equiatomic oxide BO and by Kahlweit [50] and by Bolsaitis and Kahlweit [51] for an oxide BO_v . These treatments make use of a balance between the fluxes of reacting species within the region of internal precipitation extending from X' to X , having width $\Delta X = X - X'$, using the previous expressions for the concentration profiles of penetrating element and oxidizable solute and introducing approximate expressions for their gradients at $x = X'$ and $x = X$. A general solution is given by [52]

$$\frac{N_F^{(s)} - N_F^*}{N_B^{(o)}} = v \frac{G(\gamma)}{F(\gamma\sqrt{\Phi})} + \frac{N_B^* + N_B'}{N_B^{(o)} - N_B'} G(\gamma) \quad (7.43)$$

where

$$G(u) = \sqrt{\pi} u \exp(u^2) \operatorname{erf}(u) \quad (7.44)$$

and

$$F(u) = \sqrt{\pi} u \exp(u^2) \operatorname{erfc}(u), \quad (7.45)$$

with $u = \gamma \sqrt{\Phi}$.

It was shown that under the limiting conditions $\gamma^2 \ll 1$ and $N_F^* \ll N_F^{(s)}$, when $G(\gamma) \approx 2\gamma^2$, the following expression replaces Eq. (7.35):

$$\xi \cong \sqrt{\frac{2 \times N_F^{(s)} \times D_F \times t}{v \times (N_B^{(o)} - N_B')}}. \quad (7.46)$$

One sees that the penetration depth of internal precipitation obtained using Eq. (7.46) is greater than predicted by Wagner's model, to the extent necessary to reach a higher solute concentration, N_B' , where sufficient supersaturation for precipitate nucleation can be achieved.

The theoretical treatment developed by Kahlweit et al. [49–51] is also used to evaluate the size and distribution of internal precipitates within the reaction zone.

7.5.4 Variation in Number Density and Size of Precipitates Through the Zone of Internal Reaction

As we have seen (Section 7.5.1), within the conditions set by the first limiting case of Wagner's analysis, the particle diameter should increase linearly with the distance from the alloy surface. The theoretical treatment developed by Kahlweit et al. [49–51] is more general in that it considers not only the counter-diffusion of solute, but also allows for a *finite solubility product* of the internally precipitated compound. For the case of diffusion-controlled precipitate growth, the average precipitate spacing is approximated by the distance between two successive nucleation events, that is, $\Delta X = X' - X$ (Fig. 7.13), and this distance is representative of the local precipitate number density, $Z(X)$. The number of precipitates per unit volume of the precipitation zone may be given by the expression

$$Z(X) \approx \frac{1}{(\Delta X)^3} = \left(\frac{X}{\Delta X} \right)^3 \times \frac{1}{X^3}. \quad (7.47)$$

According to Kahlweit et al. [49–51] the volume number density $Z(X)$ for BF_v -precipitates can be evaluated in terms of the unknown parameters N_F , N_B , N_F^* , and N_B^* by simultaneously solving four equations involving these four unknowns and $\frac{X}{\Delta X}$. Two of these equations are derived from the analysis of the reactant fluxes, and the third equation is based on the premise that the nucleation site at the location X

would appear at a point where the product $[N_B] \times [N_F]^v$ reaches a maximum value, which equals to $[N_B^*] \times [N_F^*]^v$. An expression for the equilibrium solubility product of the precipitating compound BF_v (Eq. (7.39)) serves as the fourth equation. A solution is obtain in terms of the unknowns N_F' , N_B' , N_F^* , and N_B^* , and the known parameters $N_F^{(s)}$, $N_B^{(o)}$, $K_{sp} = [N_B'] \times [N_F']^v$, and $\frac{D_F}{D_B} = \Phi$. Assuming that the diffusion coefficients and the concentration product critical to the formation of a nucleus of critical size, $[N_B^*] \times [N_F^*]^v$, do not depend on X or $N_F^{(s)}$, it can be shown that $\frac{X}{N_F^{(s)}} \times \Delta X$ should also be independent of X and $N_F^{(s)}$. Eq. (7.47) can therefore be rewritten as

$$Z(X) = \beta \frac{(N_F^{(s)})^3}{X^3}, \quad (7.48)$$

where the constant

$$\beta = \frac{1}{N_F^{(s)}} \times \frac{X}{\Delta X} \quad (7.49)$$

is a function of $\frac{D_F}{D_B} = \Phi$, $N_B^{(o)}$, $K_{sp} = [N_B'] \times [N_F']^v$, and $[N_B^*] \times [N_F^*]^v$, but not $N_F^{(s)}$ and X . The product $[N_B^*] \times [N_F^*]^v$ is unknown, but can be assumed to be constant.

Eq. (7.48) allows two important predictions to be made. Under fixed reaction conditions:

1. The number of precipitates per unit volume of the internally oxidized zone for a given $N_F^{(s)}$ (or thermodynamic activity of the penetrating species at the alloy surface) depends inversely on the cube of distance of the precipitation site from the external surface. In other words, during internal reaction nucleation dominates initially near the alloy surface, and numerous particles exist, whereas growth dominates subsequently, and the volume number density for precipitates decreases but their size increases (the mole fraction of the precipitating compound across the reaction zone is constant).
2. The number of precipitates per unit volume at a given location in the reaction zone, X , varies directly as the cube of the mole fraction (or activity) of the penetrating element at the external surface.

Furthermore, for systems with known K_{sp} , $[N_B^*] \times [N_F^*]^v$, D_F , D_B , and $N_F^{(s)}$, the particle number density can be quantitatively predicted.

For the conditions of very small K_{sp} and negligible solute enrichment in the internally oxidized zone ($\alpha \approx 1$), that, in fact, pertains to the first limiting case of the “Wagnerian” behavior of the system (Fig. 7.11), the radius $r(X)$ of spherical precipitates may be expressed by

$$Z \times \frac{4\pi r^3}{3} = V_p \times N_B^{(o)}, \quad (7.50)$$

or

$$r(X) = \left(\frac{3V_p \times N_B^{(o)}}{4\pi\beta} \right)^{\frac{1}{3}} \times \frac{X}{N_F^{(s)}}, \quad (7.51)$$

where V_p is the molar volume of the precipitating compound BF_v .

Böhm and Kahlweit [49] tested these predictions using internal oxidation of dilute Ag–Cd alloys at 850°C under different partial pressures of oxygen, and they confirmed experimentally that $Z(X)$ for CdO decreases with X^3 and increases with $(N_O^{(s)})^3$.

The temperature dependency of $Z(X)$ or $r(X)$ is found both in the $N_F^{(s)}$ term and implicitly in β . Although experience reveals that larger precipitates are formed at higher temperatures, a simple expression for the temperature dependency of precipitate number density and particle size cannot be achieved because generally unknown parameters like K_{sp} and $[N_B^*] \times [N_F^*]^v$ enter the calculations.

After the internal precipitation front has passed a given point in the alloy and the precipitate particles have been formed, some “overaging” or “Oswald ripening” may occur, with growth of larger particles in the expense of smaller particles. This consideration is of importance in the extended high-temperature service of dispersion hardened alloys. More information about Oswald ripening and coarsening of precipitates can be found in [54].

7.5.5 Internal Reactions Involving Low Stability Precipitating Compounds

In the preceding pages we have described diffusion-controlled internal precipitation reactions in which precipitating compound has negligible or very small solubility product. However, in reality this assumption is frequently incorrect. When the solubility product of the internally precipitated compound is not very small, the actual reaction behavior of a given system may deviate considerable from that predicted by Wagner’s analysis or by the theoretical description of Kahlweit et al.

Such a situation has been analyzed by Morral et al. [55,56]. The authors formulated a general criterion for the formation of internal oxidation zone in terms of the equilibrium solubility product of precipitated compound, initial concentration (mole fraction) of internally oxidized solute, and mole fraction (solubility) of penetrating species at the alloy surface. It was demonstrated that a zone of internal precipitates can form when the ratio $\frac{K_{sp}}{N_F^{(s)} \times N_B^{(o)}}$ falls in the range between zero and unity, i.e.,

$$0 < \frac{K_{sp}}{N_F^{(s)} \times N_B^{(o)}} < 1, \quad (7.52)$$

and accordingly two distinct types of system behavior can be realized when the ratio values fall at the extremes of this range.

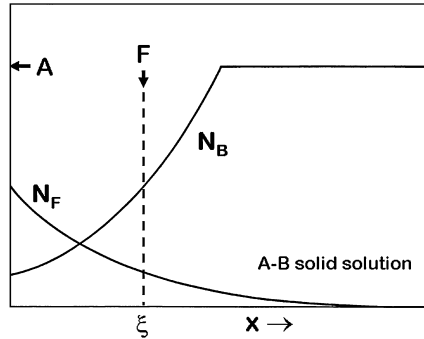


Figure 7.14 Concentration profiles (schematically) for solute (N_B) and penetrating element (N_F) across the diffusion zone developed during internal precipitation reaction in a binary A–B solid solution alloy for the case of a moderate stability of the precipitated compound. (Letters A and F denote the positions of the initial gas/metal interface and precipitation front, respectively. ξ is the thickness the internal precipitation zone.)

Obviously, Wagner's considerations fall within the low-end of the criterion because in his treatment the solubility product of internally precipitating compound is assumed to be vanishingly small. Douglass [16] proposed to classify Wagnerian behavior as Type I, and system behavior pertinent to the high-end of the criterion (i.e., involving a precipitating compound of low stability) as Type II. Hereafter, this classification will be adopted in the text.

Using analysis developed by Kirkaldy for simultaneous diffusion and precipitation in a three-component system [57], LaFlamme and Morral [55] have shown that not only diffusion-controlled internal precipitation in the systems exhibiting Wagnerian (Type I) reaction behavior but also in the systems involving lower stability precipitating compounds can be analyzed quantitatively if the alloy concentrations and external oxidant activities have suitable levels satisfying Type II behavior and the penetrating species has sufficient mobility. It was concluded that precipitation of the oxidizable solute occurs not only at (or in close proximity of) the precipitation front, but continuously throughout the entire internal oxidation zone, and the amount of precipitated compound is no longer independent of the distance from the outer alloy surface but is predicted to follow an error function solution.

Christ et al. [58] made a computer simulation of the penetration process of an element into an alloy connected with internal precipitation of a compound with moderate stability. Internal precipitation of TiC during carburization of a dilute Ni 5 at.% Ti alloy was considered as an example. Concentration profiles, computed using a finite-element method, are shown schematically in Fig. 7.14.

Two features are readily apparent that should be compared to the Wagnerian (Type I) system behavior presented in Figs. 7.11 and 7.12. First, the solute mole fraction does not

go to zero in the internal precipitation zone, but decreases from the reaction front to the alloy surface. Second, the mole fraction (and hence, activity) of the penetrating element does not approach a near-zero value at the reaction front and diffusion of this element continues beyond the zone of internal precipitates. In fact, the predicted distributions of reaction species occurring during internal precipitation are indeed somewhat similar to those suggested by Type II system behavior.

One may be reminded that a rigorous treatment of any solid-state reaction, including internal precipitation in alloys, is possible only under assumption that local thermodynamic equilibrium prevails in the reaction zone [2]. It is to be remarked, however, that since diffusion takes place only by virtue of a thermodynamic potential gradient, the total system in which diffusion occurs cannot be at equilibrium. The assumption that local equilibrium is established and maintained in the diffusion zone means that diffusion is very slow compared with the rate of reaction to form a new product, i.e., overall kinetics of the process is diffusion-controlled.

If, on the other hand, local thermodynamic equilibrium in solid nonequilibrium system is not attained, the quantitative description of the internal precipitation reactions is very difficult. In such a case, instead of applying phenomenological theories, one has to explain an infinite number of situations, all separately.

Li and Morral [59] proposed a model which assumes that local equilibrium is satisfied throughout the internal precipitation zone. This assumption eliminates the need to consider nucleation and growth of the precipitates on a local scale. The ideas used are consistent with the work of Kirkaldy [44,60] in which internal oxidation is explained in terms of virtual diffusion path (see also Section 7.4). The authors stated that for the formation of BF_v -precipitates during internal reaction in a binary A–B solid solution alloy, the conditions of local equilibrium require that:

1. Solute concentration profiles for the matrix phase across the reaction zone are continuous in value and slope. This is also true at the moving boundary of the internal oxidation region.
2. At the moving boundary of the internal oxidation zone there can be no difference in the average concentration of solute in the two-phase precipitation region and the concentration of solute in the matrix phase.
3. The internal oxidation region must lose solute to external product layer, except in special cases when the solubility product of the precipitating compound BF_v or the slope of the phase boundary between A–B based solid solution γ and two-phase region $\gamma + \text{BF}_v$ on the isothermal section of the pertinent equilibrium phase diagram (see Fig. 7.10) is zero.

Further, an error function model for internal oxidation that satisfies these conditions was derived by making use of the “zigzag” diffusion model [61] for diffusion in a multiphase region assuming a constant effective diffusivity [62] in the two-phase oxidized zone. It should be mentioned here that in addition to local equilibrium, the “zigzag”

model assumes that precipitates act as point sinks of solute and, therefore, the diffusion is independent of precipitates size or shape. Also diffusion transport along short-circuit paths is neglected.

The most important analytical feature of the proposed error function model is that it can model not only soluble concentration of the reactive solute in the two-phase internal oxidation zone with error function, but also the average concentration, which includes both the soluble and oxidized solute, with error function. The following predictions were made and supported by numerical calculations:

- The average concentration of solute in the zone of internal oxidation will always be less than the solute content in the initial alloy.
- The average solute concentration in the internal oxidation region decreases as the diffusivity of solute increases.
- The solute concentration at the moving boundary of the reaction zone approaches the initial alloy concentration as the solubility product of the precipitating compound and diffusivity of solute approach zero.

However, application of the proposed error function model is seriously limited by the assumptions made in its derivation. The assumption that local equilibria are attained across the entire precipitation zone limits it to systems with adequate nucleation and growth kinetics to avoid significant supersaturation. Assuming that the effective diffusivity is constant and that precipitates act like point sinks of solute restricts the application of the model to systems in which the volume fraction of internal precipitates is small. Even with these limitations, the work of Li and Morral must be considered as a significant contribution to our understanding of diffusion-controlled reactions of internal precipitation.

As explained in the foregoing, when a moderately stable compound is formed during an internal reaction in a binary A–B solid solution alloy, solute B is not entirely precipitated out as BF_v . Therefore, atoms of the penetrating element F diffuse in the zone of internal precipitates not through a virtually pure base metal, but through a solid solution with a certain concentration of solute. The presence of solute in the matrix of the precipitation zone may result in peculiar diffusion behavior of the penetrating element.

The possible effect of the solute present in the matrix phase of precipitation zone can be best visualized in terms of virtual diffusion path between a gas containing the reactive element F and alloy A–B (Fig. 7.15).

If ternary interactions are taken into account, two possibilities exist. The first one is shown in Fig. 7.15(A), where the mole fraction of the penetrating element F in the γ -solid solution decreases steadily with increasing amount of B. This implies that during internal precipitation the thermodynamic activity, as well as the mole fraction of F, inside the matrix of the reaction zone decreases towards the precipitation front. Diffusion of the penetrating species continues beyond the zone of internal precipitates.

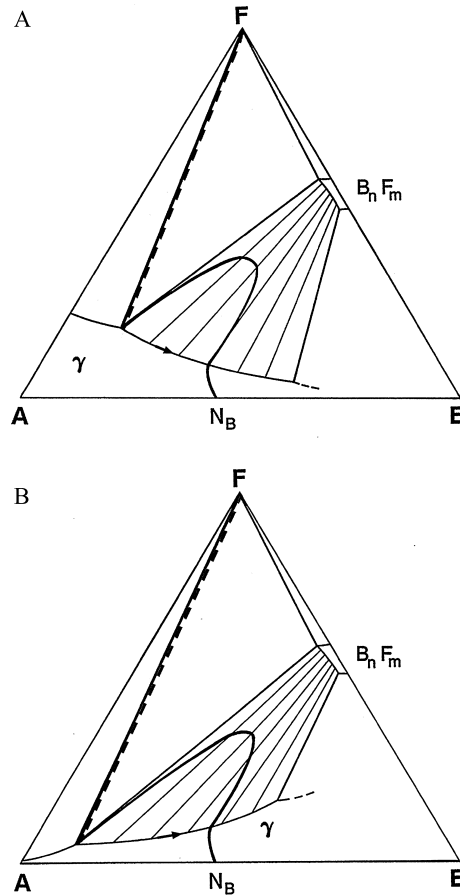


Figure 7.15 Virtual diffusion paths on the A–B–F isotherm when solute (B) and penetrating element (F) form a $B_n F_m$ compound (schematically). The penetration element solubility (solvus) curve have (A) negative or (B) positive slope, i.e., solubility of F in γ -solid solution (A) decreases and (B) increases with increasing B content. (N_B is composition of the initial binary alloy.)

On the other hand, in Fig. 7.15(B) the solubility of F increases with increasing the amount of B. In that case penetration of F into A–B solid solution results in “uphill” diffusion of this species through the A-based matrix towards the precipitation front as the arrow indicates.

A very illustrative example of such diffusion behavior is provided by the nitriding experiments with Ni–Cr alloys. In the case of internal nitridation of Ni–Cr alloys at 1125°C under N_2 -gas atmosphere, a significant concentration of chromium in the FCC matrix within the precipitation zone was found. In Fig. 7.1(B) microstructure of an Ni 15 at.% Cr alloy after nitriding for 4 hrs at 1125°C under 6000 bar of N_2 is shown,

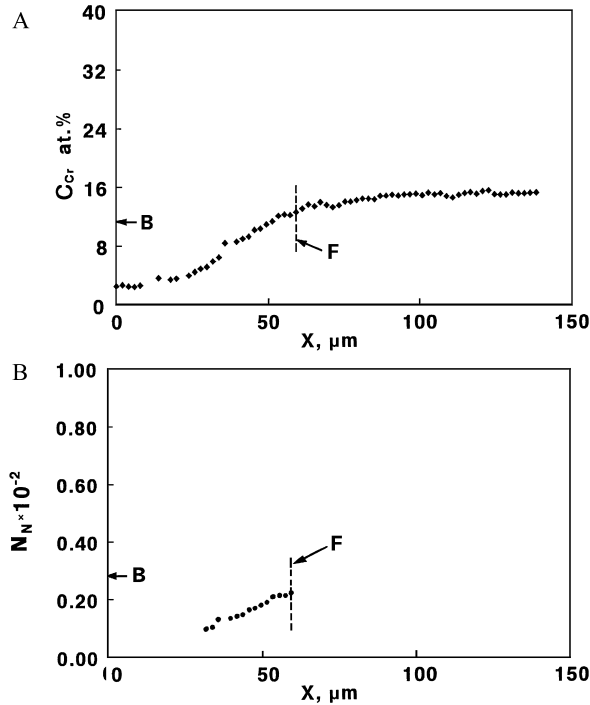


Figure 7.16 (A) Concentration profile for chromium through the matrix of the reaction zone developed after nitriding an Ni alloy with 15 at.% of Cr at 1125°C and 6000 bar of N_2 for 4 hrs, and (B) the corresponding (calculated) profile of nitrogen through the matrix within the zone of internal precipitates. (Position of the plane in the diffusion zone where rounded precipitates are transformed into a plate-like structure (Fig. 7.1(B)) is indicated by B, and F is the location of the precipitation front.)

and the corresponding concentration profile for chromium through the precipitation zone matrix is given in Fig. 7.16(A). This experimental curve represents a portion of the concentration profile across the nitrided zone where no interference with nitride particles was encountered.

As explained earlier, the phase boundaries of the condensed phases on the isotherm are virtually unaffected by a change in the external pressure applied upon the system. Therefore, the relation between the molar fraction of chromium (N_{Cr}) and nitrogen (N_N) in the FCC-matrix of the nitrided zone in equilibrium with CrN-particles can readily be found just using the isothermal sections shown in Fig. 7.9:

$$\ln N_N = 12.66N_{Cr} - 7.71 \quad (\text{for } 0.06 < N_{Cr} < 0.24). \quad (7.53)$$

Since chromium is not precipitated out entirely at the reaction front, nitrogen atoms diffuse in the nitrided zone not through a nearly pure Ni-lattice but through a solid

solution with a certain concentration of chromium. One might expect that the solubility of nitrogen in the FCC Ni–Cr solid solution increases with increasing chromium content. This can be attributed to the relatively high affinity of chromium to nitrogen.

At the isothermal cross-section of the ternary phase diagram this situation is reflected by the upward solvus curve representing the boundary of the Ni-based solid solution, which is in equilibrium with chromium nitride. This case is similar to that shown in Fig. 7.15(B). Using Eq. (7.53), the experimental penetration curve for chromium across the internally nitrified zone (Fig. 7.16(A)) can be converted into a nitrogen concentration profile through the matrix of the Ni–Cr solid solution (Fig. 7.16(B)). The last graph shows clearly the “uphill” diffusion of nitrogen towards the precipitation front, although its thermodynamic activity decreases in that direction. Behind the precipitation front, the mole fraction of nitrogen must eventually fall back to (in principle) a zero value at large (“infinite”) distance from the gas/metal interface.

A somewhat similar behavior of a penetrating element forming internal precipitates was also mentioned by Swisher [63]. He found evidence for “uphill” diffusion of sulphur near the precipitation front during the internal sulfidation of an iron alloy with 0.38 wt.% of titanium at 1300°C in a $\text{H}_2\text{S} + \text{H}_2$ mixture. This phenomenon was attributed to the relative instability of titanium sulphide and strong Ti–S interaction in the iron-based solid solution within the sulfidized zone.

7.5.6 Transition From Internal to External Oxidation

It was recognized by Darken back in 1942 [11] that the extent of diffusion-controlled internal reaction is influenced by the volume fraction of precipitates in the reaction zone, and that internal precipitation could only take place up to the maximum of the degree of solute enrichment in the precipitation zone, and hence, the mole fraction of oxidizable solute in the initial alloy.

There are several interrelated important factors in determining whether the oxidizable solute will precipitate internally or form as a continuous layer on the alloy surface. Wagner [12] has proposed that the transition from internal precipitation to exclusive external oxidation should occur when the solute content is sufficient to form a critical volume fraction of internal precipitates at the reaction front. His model is based on the fact that the cross-section available for penetrating element diffusion into the metal phase is reduced, owing to the presence of particles of the precipitated compound. As internal precipitates are formed, these virtually impermeable inclusions locally block further reaction between the oxidant and reactive solute because diffusional transport of penetrating species to the reaction front is restricted to the metal channels between those particles which were previously precipitated. This slows the rate at which the supersaturation necessary for new precipitate nucleation can be achieved. In such a situation, sidewise growth of the existing particles (which required very small supersaturation) rather than the nucleation of new precipitates will occur. If solute content in the initial

alloy is high enough to sustain a sufficient (outward) flux needed to maintain growth of precipitates, the particles would grow together and form a compact reaction product layer which would prevent further internal precipitation. Since this elimination of internal precipitation occurs at the very beginning of the interaction, the reaction product layer is formed at the alloy surface.

Critical solute content in the initial alloy or critical volume fraction of internal precipitates is considered in order to find a criterion for the transition from internal to external oxidation. Let us now return to Eq. (7.37), and let V_A and V_p represent the molar volumes of the solvent metal A and precipitating compound BF_v , respectively. Then the volume fraction of the internal precipitates in the reaction zone, g , equals

$$g = \varphi \times \left(\frac{V_p}{V_A} \right) = \alpha \times N_B^{(o)} \left(\frac{V_p}{V_A} \right). \quad (7.54)$$

The enrichment factor α may be calculated from Eq. (7.37) for known values of $\Phi = \frac{D_F}{D_B}$, γ , and $N_F^{(s)}$ (see Eq. (7.33)).

Under the case of interest here, when the outward diffusion flux of oxidizable solute B exceeds the inward flux of penetrating element F, i.e., $N_B^{(o)} \times D_B \gg N_F^{(s)} \times D_F$, which corresponds to the second limiting case of the Wagnerian system behavior, the product $\gamma\sqrt{\Phi} \ll 1$ in Eq. (7.37), and therefore

$$\alpha \cong \frac{2v}{\pi} \times \left[\frac{N_B^{(o)} \times D_D}{N_F^{(s)} \times D_F} \right]. \quad (7.55)$$

Wagner stated [12] that when volume fraction of precipitates, g , reaches a critical value, g^* , the transition from internal precipitation to formation of reaction product layer at the alloy surface should occur. Combining the last two equations gives the transition criterion as

$$N_B^{(o)} > \frac{\pi g^*}{2v} \times N_F^{(s)} \times \frac{D_F \times V_A}{D_B \times V_p}, \quad (7.56)$$

which enables prediction of how changing exposure conditions will affect the solute content required to produce an external reaction product layer.

It follows from Eq. (7.56) that those conditions which decrease the inward flux of penetrating element, e.g., lower $N_F^{(s)}$ (or activity of F at the alloy surface), and those which increase the outward flux of oxidizable solute B, e.g., cold working the alloy (increasing (“effective”) D_B by increasing the contribution of mass-transport along high diffusivity paths), will allow the transition to external oxidation at lower solute content in the initial alloy.

Perhaps, the most comprehensive test of the Wagner’s transition criterion (formation of a critical volume fraction of internal precipitates) can be found in the frequently

cited work of Rapp on oxidation behavior of Ag–In alloys [64]. It was established that at 550°C, in pure oxygen at one atmosphere pressure, the transition from internal to external oxidation occurs at the indium content in the alloy of $N_{In}^{(o)} = 0.15$, which is equivalent to an $InO_{1.5}$ volume fraction of 0.30. (The molar volume of the oxide $InO_{1.5}$ is approximately twice the molar volume of Ag (solvent metal) [65].) Then this critical volume fraction value was used to predict the effect of reduced oxygen partial pressure (reduced oxygen solubility, $N_O^{(s)}$) on the indium content in the alloy required for the transition from internal to external oxidation. The agreement between the experimental observations and the theory of Wagner was found to be quite good.

Rapp's experiments also provided an indirect verification of the effect of increased diffusional transport of reactive solute due to cold work on the transition. Alloy specimens containing 6.8 at.% of In were observed to undergo the transition to external oxide formation around scribe marks under exposure conditions which requires 15 at.% In to produce the transition on undeformed surface.

In the same investigation, the transition from internal to external oxidation at a given temperature and oxygen partial pressure was found to depend on the initial surface preparation. For example, in air at 550°C, the transition occurred for mechanically polished alloy samples at $N_{In}^{(o)} = 0.10$, whereas for samples etched in hot concentrated nitric acid at $N_{In}^{(o)} = 0.12$, and for specimens etched electrolytically in 1N HNO_3 at $N_{In}^{(o)} = 0.15$. The apparent retardation of internal oxidation (i.e., the increasing tendency to form external oxide layer) in mechanically polished specimens may reflect an enhanced outward solute transport along short-circuit diffusion paths in the deformed surface layer of the metal. Electrolytical etching, on the other hand, produces the most stress-free alloy surfaces for such experiments.

7.6 INTERNAL PRECIPITATION REACTIONS AS A “RESEARCH TOOL” FOR EVALUATING INTERSTITIAL TRANSPORT IN METALS

The use of internal precipitation as a research tool will be demonstrated by “a case study” related to diffusion bonding of silicon nitride ceramics and nickel-based alloys [66–68].

The type of reaction products which can be formed at an elevated temperature in the diffusion zone between Si_3N_4 —ceramics and any metal (or alloy) depends on the chemical potential (activity) of silicon and, hence, on the activity (fugacity) of nitrogen at the contact surface. When using diffusion couples consisting of dense Si_3N_4 —ceramics and non-nitride forming metal, for example, nickel, the interior of the couple is not in direct contact with the surrounding atmosphere. Nitrogen which is formed by the interfacial reaction cannot escape easily. Nitrogen pressure (fugacity) will be built up at the contact surface. This pressure determines the activity of silicon, and hence the type of reaction products that will form at the metal/ceramic interface.

In Fig. 7.17(A) the calculated stability diagram for the Ni–Si–N system is given. This graph displays which condensed phases of the system are in equilibrium with Si_3N_4 as a function of temperature and partial pressure of nitrogen. The thermodynamic activity of silicon at the metal/ceramic interface is related to the N_2 partial pressure through the equilibrium constant of Si_3N_4 .

No intermetallic compounds were detected in the reaction zone of the $\text{Si}_3\text{N}_4/\text{Ni}$ couple after interaction in vacuum at 1125°C. (Fig. 7.17(B)–(C)). Only Ni–Si solid solution was formed. The maximum Si concentration in the solution in the large central part of the reaction zone was found to be approximately 8 at.%. According to the calculated stability diagram, this implies a nitrogen pressure (fugacity) at the metal/ceramic interface of about 100 bar.

Eventually, nitrogen has to escape from the reaction interface either through channels of connected pores or by interstitial diffusion through the metal–silicon solid solution. In order to complete the analysis given above, it is interesting to make some estimates concerning the nitrogen transport during solid state interaction in the $\text{Si}_3\text{N}_4/\text{Ni}$ system.

It is appropriate to stress at this point that during the sample preparation the metal (Ni) deformed sufficiently at the outer edge to confirm the presence of good contact between the diffusion couple halves and to seal efficiently the interior of the couple from the outside atmosphere (Fig. 7.17(C)). The width of the reaction zone in the sample and (simultaneously) the silicon concentration near the metal/ceramic interface somewhat increase towards the edge. In fact, this is a direct outcome of the mechanism of nitrogen removal from the reaction interface, which in the interior of the couple most likely takes place exclusively by permeation through the metal.

At first sight, the quantity of nitrogen, M_N , which diffuses into the metal per unit area of the $\text{Si}_3\text{N}_4/\text{metal}$ interface (mole/m^2) can be found in a straightforward manner as [45]:

$$M_N = 2 \times \frac{N_N^*}{V_m} \times \sqrt{\frac{D_N \times t}{\pi}}. \quad (7.57)$$

Here, N_N^* is the mole fraction of nitrogen in the Ni-based solid solution at the metal/ceramic interface, V_m is the molar volume, D_N is the diffusion coefficient for nitrogen in the nickel-based solid solution, and t is the reaction time. However, information on nitrogen mass-transport in nickel is scarce [60,69–73]. The published results of direct measurements are rather questionable, and there are some serious doubts as to the reliability of the reported diffusivity and solubility values. In this respect, the study of internal nitridation of Ni-based alloys may provide a framework for evaluating nitrogen permeation through nickel.

For the range of pressures where Sieverts' law [74] is valid, the mole fraction N_N^* (for diatomic gas) is proportional to the square root of the nitrogen fugacity. Eq. (7.57)

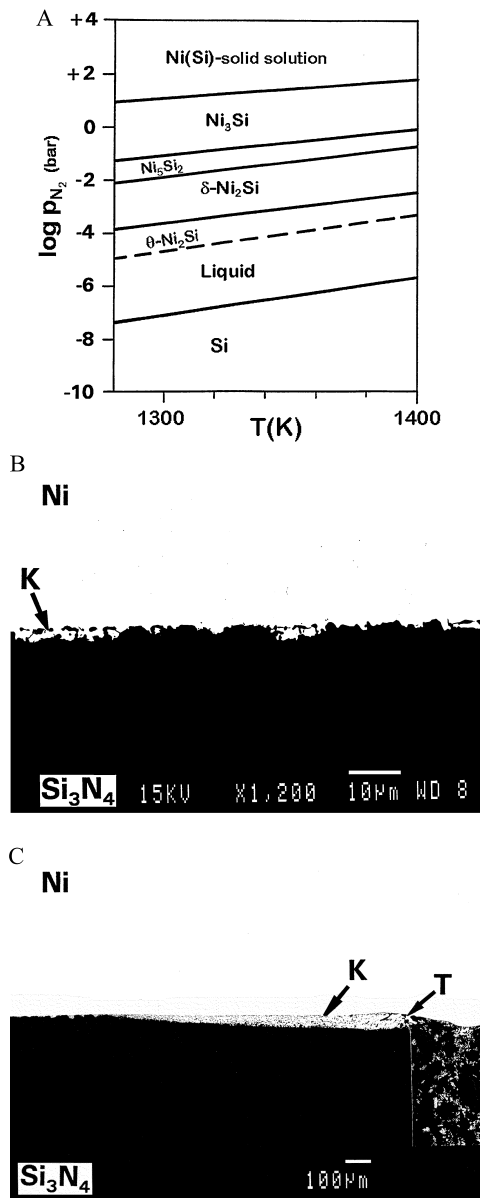


Figure 7.17 (A) Condensed phases in equilibrium with solid Si_3N_4 in the Ni-Si-N system as a function of temperature and nitrogen partial pressure (fugacity) and backscattered electron images of the diffusion zone between dense Si_3N_4 and Ni after interaction at 1125°C for 16 hrs in vacuum: (B) central part of the couple; (C) general view. (Letter K indicates the position of the original interface ("Kirkendall plane") and letter T denotes the "triple point" of the diffusion couple where reaction layers meet ambient atmosphere.)

can be rewritten as:

$$D_N = \left(\frac{2 \times N_N^o \times D_N \times \sqrt{\frac{f_{N_2}}{p^o}}}{M_N \times V_m} \right)^2 \times \frac{t}{\pi}, \quad (7.58)$$

where N_N^o is the mole fraction of nitrogen at the metal surface at standard pressure p^o of 1 bar and f_{N_2} is the nitrogen fugacity that builds up at the $\text{Si}_3\text{N}_4/\text{Ni}$ -contact surface during reaction. The product $N_N^o \times D_N$ is the standard permeability constant for the Ni-solid solution to nitrogen defined at standard pressure. Since the maximum Si concentration in the vicinity of the reaction interface was found to be about 8 at.%, the corresponding value of the nitrogen fugacity at the metal/ceramic interface was estimated from the stability diagram shown in Fig. 7.17(A) as approximately 100 bar.

Unfortunately, it is impossible to measure a concentration profile of nitrogen across the diffusion zone because the concentration of nitrogen in the FCC Ni-based solid solution is below the limit of detection in the analytical technique used (EPMA). There is, however, another way to tackle the problem. From mass balance consideration it is clear that the relation between the amount of nitrogen (M_N) and silicon (M_{Si}) diffusing into the metal across the unit area of the reaction interface is:

$$M_N = \frac{4}{3} M_{\text{Si}}. \quad (7.59)$$

Obviously, this relation pertains only to the situation in the interior of the $\text{Si}_3\text{N}_4/\text{Ni}$ couple. The value of quantity M_{Si} (mole/m²) is equal to the area enclosed by the penetration curve of silicon measured in the central part of the $\text{Si}_3\text{N}_4/\text{Ni}$ couple after annealing at these conditions, divided by the molar volume V_m . In our particular example (annealing for 16 hrs at 1125°C), it was found that

$$M_{\text{Si}} = \frac{1.7 \times 10^{-6}}{V_m} \text{ (mole/m}^2\text{)}. \quad (7.60)$$

Substituting Eq. (7.58) into Eq. (7.59) with (7.60) gives

$$D_N = \left(\frac{2 \times N_N^o \times D_N \times \sqrt{\frac{f_{N_2}}{p^o}}}{\frac{4}{3} \times 1.7 \times 10^{-6}} \right)^2 \times \frac{t}{\pi} \text{ (mole/m}^2\text{)}. \quad (7.61)$$

With respect to the use of internal nitriding as an experimental method for studying nitrogen permeation through nickel, the question which has to be clarified is concerned with the implementation of the Wagner's description itself. It was demonstrated in the previous section that when a moderately stable phase (e.g., chromium nitride) is precipitated out during internal precipitation reaction, the distribution of the various atoms within the diffusion zone can be predicted based on thermodynamic considerations of

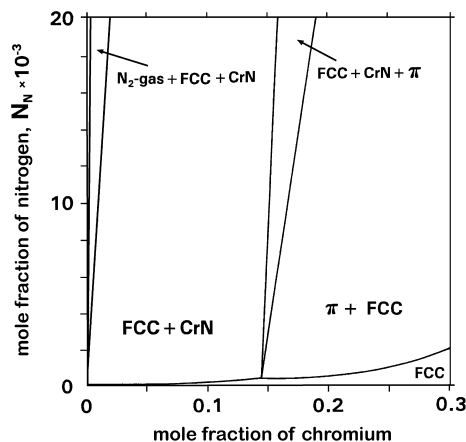


Figure 7.18 Calculated isothermal cross-section through the Ni–Cr–N system at 700°C and external nitrogen pressure of 1000 bar. (π is the ternary phase in the Ni–Cr–N system [35,75].)

the respective systems. In this case, not only is relative stability of the precipitated compound important, but also the interaction between solute and penetrating atoms in the solid solution matrix of the precipitation zone must be taken into account. Nitridation experiments on Ni–Cr alloys at 1125°C under 1–6000 bar of N_2 -pressure gave evidence of “uphill” diffusion of nitrogen through the Ni-based matrix towards the internal precipitation front, which makes it impossible to utilize Wagner’s treatment of internal precipitation.

In general, “uphill” diffusion of the penetrating atoms within the precipitation zone can be predicted from the equilibrium phase diagram, since the shape of the boundary of the solid solution, which is in equilibrium with the internal precipitates, is “responsible” for this phenomenon. The latter can be appreciated just by looking at the isothermal sections through the Ni–Cr–N system at 1125°C given in Fig. 7.9.

As temperature decreases, the solubility of nitrogen in the FCC-phase drops and the precipitated compound (CrN) becomes more stable. In Fig. 7.18 the calculated isothermal cross-section through the Ni–Cr–N phase diagram at 700°C and 1000 bar of nitrogen is given.

From the analysis of the isotherms presented in Figs. 7.9 and 7.18, it can be concluded that with decreasing temperature and increasing external pressure (fugacity) of nitrogen the monovariant equilibrium $FCC + CrN + N_2\text{-gas}$ shifts towards decreasing chromium content in the FCC-phase. The slope of the FCC/CrN boundary becomes smaller and probably even changes sign. This implies that the effect of Cr-atoms on the solubility of nitrogen in the Ni-based lattice under these circumstances is insignificant. High external pressure (activity) applied upon the alloy surface may also sustain a large nitrogen-diffusion flux across the advancing reaction layer. Consequently, it provides

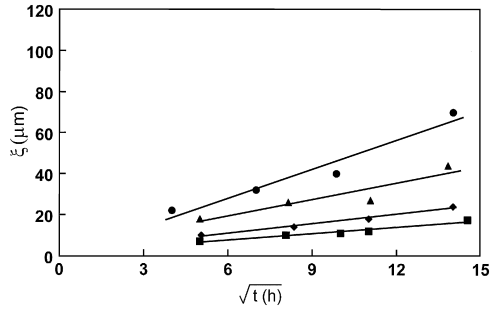


Figure 7.19 Growth of the internal precipitation zone during nitridation of Ni 5 at.% Cr alloy under flowing $\text{NH}_3 + \text{H}_2$ -gas mixture at: (●) 700°C; (▲) 665°C; (◆) 630°C, and (■) 600°C.

conditions for frequent precipitate nucleation (rather than particle growth) throughout the whole nitrided zone.

As explained in Section 7.2, one possible way to create high nitrogen fugacity at the alloy surface that can be equivalent to an actual nitrogen pressure of thousands of bars is to employ a flowing ammonia/hydrogen mixture as a nitriding agent.

When an Ni 5 at.% Cr alloy is exposed at 600–700°C to a flowing ammonia/hydrogen mixture (15 vol.% of NH_3 ; gas flow rate is ~ 70 liter/hr), particles of cubic CrN precipitate within the nickel matrix (see Figs. 7.5 and 7.6). There was no evidence for enhanced precipitation along grain boundaries in any of the samples. The depth of the internal nitridation, ξ , increased parabolically with time as expected for a diffusion-controlled reaction. Fig. 7.19 show plots of internal precipitation depth in the nitrided Ni 5 at.% Cr alloy vs. the square root of exposure time at four nitriding temperatures. It can be seen that the reaction layer thickness increases linearly (within the experimental accuracy) with $\sqrt{t}$, thus confirming the diffusion-controlled uptake of nitrogen by the samples.

The fact that diffusion is the rate-limiting step implies that the transfer of nitrogen atoms from the nitriding medium across the gas/metal interface proceeds very rapidly compared to the inward transport inside the reaction layer. Under these circumstances, the nitrogen concentration (mole fraction) at the metal surface, $N_N^{(s)}$, is equal to the solubility in the base metal (Ni).

Further points are of interest here:

- At 700°C Cr-atoms are relatively immobile within the Ni-based solid solution [76]. This is supported by the results of microprobe measurements reported in [37]. Concentration profiles taken across the nitrided samples revealed that up to the precipitation front the concentration of solute remains practically equal to that in the starting alloy. The latter indicates that no appreciable diffusion of solute atoms takes place in the precipitate-free Ni-based solid solution under these experimental conditions.

- It was found that under conditions used, chromium (solute) is precipitated out completely in the form cubic CrN within the nitrated zone (Fig. 7.6(D)).

It is also reasonable to assume that the diffusion coefficient of nitrogen, D_N , is constant within the precipitation zone and the concentration of interstitially dissolved nitrogen atom decreases linearly across the matrix of the nitrated layer.

These observations make clear that classical Wagner's treatment of the internal precipitation kinetics can also be applied to the nitridation reactions in the systems discussed above. It follows that nitriding kinetics of Ni 5 at.% Cr alloy can be adequately described using the quasi-steady state approximation (i.e., first limiting case of the Wagnerian behavior). Therefore, in the simple concept of a constant equiatomic precipitating nitride composition, the depth of the internally nitrated zone in the samples is a parabolic function of time, and Eq. (7.21) now reads as

$$\xi^2 = \frac{2 \times N_N^{(s)} \times D_N}{N_{Cr}} \times t = 2 \times k_p \times t, \quad (7.62)$$

with k_p being parabolic rate constant of the internal precipitation reaction.

Referring to the last equation, it is clear that the apparent solubility–diffusivity product for nitrogen in nickel, $N_N^{(s)} \times D_N$, can be obtained readily from the rate of internal nitride precipitation. However, the permeability values calculated in this way are pertained only to the nitriding conditions used because of the solubility of the penetrating species (nitrogen) in the nickel ($N_N^{(s)}$ in Eq. (7.62)) is dependent on nitrogen fugacity (activity) at the metal surface. It is important to realize that nitrogen activity at the gas/metal interface produced in the experiment with a flowing $\text{NH}_3 + \text{H}_2$ -gas mixture is also dependent on temperature, provided that initial composition of the mixture, gas flow rate, and geometrical dimensions of the sample are the same. Therefore, a standard permeability (as a material constant) has to be defined in terms of specified temperature and (arbitrarily chosen) standard partial pressure (fugacity) of the penetrating element (nitrogen).

As mentioned above, according to the Sieverts' law, the solubility of a diatomic gas is proportional to the square root of the fugacity of the gas at the metal surface. This simple relation is valid as long as the concentration of the dissolved gas is low, which is true for the case of the dissolution of nitrogen in nickel. Assuming that the activity of nitrogen in nickel exhibits Henrian behavior, the standard permeability, $N_N^{(o)} \times D_N$, can then be expressed as

$$N_N^{(o)} \times D_N = \left(\frac{f_{N_2}}{p^o} \right)^{\frac{1}{2}} \times N_N^{(s)} \times D_N, \quad (7.63)$$

with f_{N_2} being the fugacity of the nitrogen at the gas/metal interface under the experimental conditions and $N_N^{(o)}$ being the nitrogen solubility in nickel at the standard pressure p^o (conventionally 1 bar).

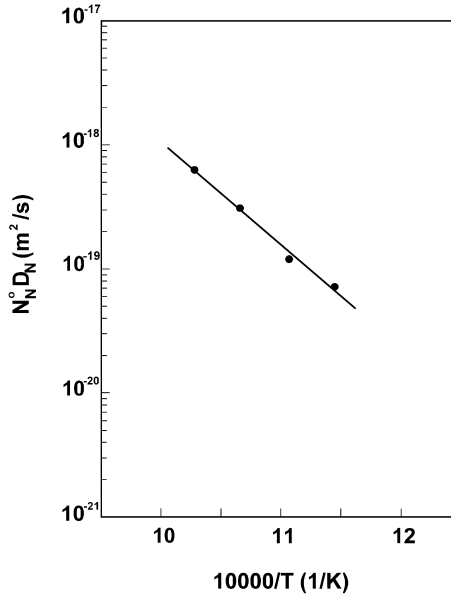


Figure 7.20 Arrhenius plot of permeabilities for nitrogen in nickel, $N_N^{(o)} \times D_N$, at 1 bar of N_2 -pressure obtained from the nitriding experiments on Ni 5 at.% Cr alloy.

Referring to Eq. (7.8), it is clear that the corresponding values of N_2 -fugacity, f_{N_2} , can be calculated readily using, for instance, thermodynamic data listed in [77], and the $N_N^{(s)} \times D_N$ product can be converted into a standard permeability constant, $N_N^{(o)} \times D_N$, at a standard pressure of $p^o = 1$ bar.

In Fig. 7.20 the standard permeation constants of nitrogen in nickel are plotted as functions of the reciprocal temperature.

The representative line drawn in this Arrhenius graph may be expressed by the following equation:

$$N_N^{(o)} \times D_N = 1.66 \times 10^{-10} \exp\left(-\frac{18980}{T}\right) (\text{m}^2/\text{s}), \quad (7.64)$$

with T being the absolute temperature.

Let us return to the original subject of our case study. Assuming as a first approximation that standard permeability value, $N_N^{(o)} \times D_N$, is independent of the Si-content in the FCC Ni-based solid solution, the permeation constant at 1125°C and $p^o = 1$ bar can be found using Eq. (7.64) as approximately 2.2×10^{-16} m²/s. Using Eq. (7.61) this leads to $D_N = 7.0 \times 10^{-14}$ m²/s.

The problem now is reduced to the solution of Fick's second law for diffusion in a semiinfinite solid with the assumption of a constant surface concentration. According

to [48], this is given by an error function:

$$\frac{N_N}{N_N^{(s)}} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D_N \times t}}\right), \quad (7.65)$$

where x is the distance in m.

If the penetration depth of nitrogen, $x = \xi$, is defined as a distance from the Si_3N_4 /metal interface to the point inside the nickel where the $\frac{N_N}{N_N^{(s)}}$ is equal to 0.01, then

$$\frac{\xi}{\sqrt{t}} \approx 60 \mu\text{m} \times h^{-\frac{1}{2}}. \quad (7.66)$$

It is now clear that the microstructure of the interfacial region developed during reaction depends on the thickness of the metal used in the diffusion couple. Our treatment deals with semiinfinite diffusion couples. However, in the case of a couple with an Ni-thin foil in contact with Si_3N_4 , different morphology will be found.

We wish to conclude this part of discussion by emphasizing that so far in the present chapter the main focus was on thermodynamic and kinetic aspects of internal solid-state reactions. As we have seen, by its generality, this combined thermodynamic and diffusion kinetic approach is well-suited to providing a uniform treatment of the subject. It was, however, recognized that a point of view entirely focused on chemical aspects of interaction is somewhat biased since it fails to account for the considerable effect of mechanical stresses induced upon internal precipitation. Therefore, in the next section an attempt is made to explain the significance of the induced stresses for internal precipitation kinetics and morphogenesis of the reacting system. Again, internal nitridation of dilute Ni–Cr alloys will be considered as an example.

7.7 DEFORMATION PHENOMENA ACCOMPANYING INTERNAL PRECIPITATION REACTIONS IN METALS

Research on chemical reactions in the solid-state, which have become well-known as a substantial endeavor among chemists, in fact, also involves many mechanical aspects. Mechanical stress is an unavoidable result of chemical interaction in solids and has to be taken into consideration when the kinetics of solid-state reactions is an issue.

Formation of precipitates in a solid matrix is almost always accompanied by an increase of net volume. For example, in the case of nitriding an Ni 5 at.% Cr ($\text{Ni}_{0.95}\text{Cr}_{0.05}$) solid solution alloy, when solute element (Cr) is precipitated out entirely inside the interaction zone, the total relative volume change according to the equation of the precipitation reaction



is estimated as only 2.7%. However, the local net volume change accompanying the precipitation can be found by realizing that 5.35 cm^3 (one mole) of $\text{Cr}_{0.5}\text{N}_{0.5}$ takes the difference in volume between 10 moles of $\text{Ni}_{0.95}\text{Cr}_{0.05}$ and 9.5 moles of Ni which is 3.59 cm^3 per mole. In other words, 3.59 cm^3 of alloy is replaced by 5.35 cm^3 of nitride (if no relaxation were to take place), and this corresponds to a local volume increase of approximately 49%. (Molar volumes of nickel and Ni–Cr solid solution were calculated with the lattice parameter values of [78]. Data for chromium nitride were taken from [79].

The inevitable consequence of this volume change is matrix deformation around the internal nitride particles precipitated during internal reaction. The stress has to be relieved in some way.

When internal precipitates are coarse and widely spaced, then relief of these stresses may occur by plastic flow within the metal grains in the internal precipitation zone. On the other hand, stress relief may be rather difficult when particles are fine and densely populated.

There is now ample experimental evidence to support the view that the net volume increase during reaction of internal precipitation may result in a number of deformation phenomena, including creep and grain boundary sliding [38,80–88]. The type (or combination) of stress relaxation mechanism that may be operational is determined by a number of interrelated factors affecting size, shape, and number density of precipitates, as well as mechanical properties of the metal matrix inside the internal reaction zone. One might expect that for a particular material system, processing temperature and external activity of the penetrating element are the most critical parameters.

Let us return to our example. In Fig. 7.21 a representative microstructure developed at the surface of an Ni 5at.% Cr alloy after nitriding in flowing ammonia at 700°C is given.

Numerous surface nodules (protuberances) consisting of virtually pure base metal (nickel), free of precipitated material or dissolved chromium, can be seen within the grains. The nodules seem to form indiscriminately over the grain surface during nitriding of the Ni–Cr solid solution. In addition, some of the solvent metal devoid of CrN-internal nitride particles was invariably present along grain boundaries of the alloy.

Close inspection of the sample revealed that the surface of the nitrided alloy is covered with a thin, practically continuous layer of pure nickel (Fig. 7.21(A)). Morphology of the layer suggests that it was formed as a result of the coalescence (and probably ripening) of the Ni-nodules “extruded” from the interior of the nitrided sample to the gas/metal contact surface. The layer of the nodular material (Ni) is also visible in cross-section of the reaction zone (Fig. 7.5(A)).

At some locations the alloy surface after nitriding is slightly stepped and a small opening is apparent at the intersection of the grain boundaries with the surface (Fig. 7.21(A)). The internal nitridation front, however, remains essentially planar throughout a cross-

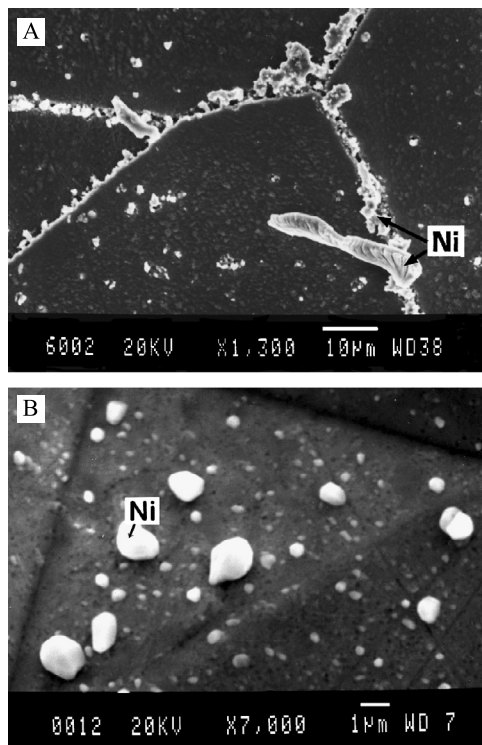


Figure 7.21 Secondary electron images (SEIs) of the surface of Ni 5 at.% Cr alloy nitrided at 700°C for 49 hrs under a flowing $\text{NH}_3 + \text{H}_2$ gas mixture: (A) general view; (B) a magnified area in (A) showing morphology of a continuous layer of virtually pure nickel on surface of the nitrided alloy. Note that “extrusions” of solvent metal (Ni) devoid of precipitating nitride are also present along grain boundaries.

section also across such grains. So, neither the gross surface displacements nor the opening along the grain boundaries detectably influences the nitridation kinetics. It is therefore tempting to assume that despite the relatively low homologous temperature of these nitridation experiments ($T/T_m < 0.56$, T_m = melting point of nickel), grain boundary sliding and the concomitant extrusion of nickel to the alloy surface take place during nitridation. This sliding mechanism, however, cannot explain the appearance of the numerous, virtually pure, Ni-protrusions within the crystallites. Judging from these facts, it is reasonable to believe that transport of the solvent metal (nickel) through the precipitation zone can be mediated by the diffusional creep mechanism.

It is conceivable that the compressive stress developing upon the precipitation reaction may locally reduce the vacancy concentration in the Ni-matrix near the nitridation front.

As a result, a vacancy concentration gradient will build up between the front of the internal precipitates and the alloy surface, which is virtually stress-free. This necessitates

a vacancy flow from the surface to the precipitation front resulting in a counterflow of nickel atoms across the nitrided zone towards the gas/metal interface. In this situation a Nabarro–Herring (volume diffusion) creep mechanism can be operative [89,90].

Before proceeding further with the discussion, one important experimental finding has to be mentioned. Returning to Fig. 7.5(A), one notes that the volume of nickel transported to the metal surface from the interior of the precipitation zone is comparable to the total volume increase associated with the internal nitridation reaction (Eq. (7.67)). It can be seen from the sample cross-section that the Ni-layer deposited at the alloy surface is about 1 μm thick ($\Delta\xi$), whereas the apparent penetration depth of internal nitride formation under these conditions, ξ , is approximately 35 μm .

Following the approach proposed in [84], an upper limit estimate for transport by Nabarro–Herring creep type mechanism based on lattice diffusion of nickel can be obtained. The authors assumed that the compressive stress generated in the vicinity of the internal precipitation front is so high that the vacancy concentration in the matrix (N_V) is negligible compared to the equilibrium value (N_V^0) at the stress-free alloy surface, i.e., $N_V^0 - N_V \approx N_V^0$. Assuming quasi-steady state in the reaction layer, the vacancy (or nickel) instantaneous flux across the matrix of the internal precipitation zone (along the vacancy gradient) can be written as:

$$J_V = -\frac{D_V \times N_V^0}{V_V \times \xi} = -J_{Ni}, \quad (7.68)$$

where ξ is the penetration depth of the internal nitridation, V_V is the molar volume of vacancies, which is equal to the molar volume of nickel, V_{Ni} . With $D_V \times N_V^0 = D_{Ni}^*$ (D_{Ni}^* is the lattice (tracer) diffusivity of Ni), Eq. (7.68) yields

$$J_{Ni} = \frac{D_{Ni}^*}{V_{Ni} \times \xi}. \quad (7.69)$$

On the other hand, the flux of nickel can be described in the quasi-steady state by

$$J_{Ni} = \frac{1}{S} \times \frac{dn_{Ni}}{dt} = \frac{1}{V_{Ni}} \times \frac{d(\Delta\xi)}{dt}, \quad (7.70)$$

where S is the cross-sectional area, n_{Ni} is the number of moles of Ni transported from the reaction front across the precipitation zone, and $\Delta\xi$ the thickness of the virtually pure nickel layer growing at the outer surface of the alloy.

If we assume that the total amount of Ni flowing to the surface is proportional to the relative volume change, taking place during the reaction, the flux of nickel can be expressed as

$$J_{Ni} = \frac{1}{V} \times \frac{\Delta V}{V} \times \frac{d\xi}{dt} = \frac{0.026}{V_{Ni}} \times \frac{d\xi}{dt}, \quad (7.71)$$

with ΔV being the volume change accompanying the precipitation reaction and V the total volume of the reaction zone.

Combining Eqs. (7.69) and (7.71) gives

$$\frac{D_{Ni}^*}{\xi} = 0.026 \times \frac{d\xi}{dt}, \quad (7.72)$$

and, since the parabolic layer growth constant (Eq. (7.62)) is defined as

$$\frac{k_p}{\xi} = \frac{d\xi}{dt}, \quad (7.73)$$

one may conclude that

$$D_{Ni}^* = 0.026 \times k_p. \quad (7.74)$$

The lattice diffusivity of nickel is given in [91] as

$$D_{Ni}^* = 1.9 \times 10^{-4} \exp\left(-\frac{33658}{T}\right) (\text{m}^2/\text{s}). \quad (7.75)$$

Eq. (7.74) then predicts the value of parabolic rate constant, k_p , for instance, at 700°C of approximately $7.0 \times 10^{-18} \text{ m}^2/\text{s}$. This is almost three orders of magnitude less than the value observed in the experiments. From the kinetic measurements (Fig. 7.19 [38]) the parabolic (apparent) rate constant was found to be $\sim 3.4 \times 10^{-15} \text{ m}^2/\text{s}$. Thus, the Nabarro–Herring (lattice diffusion) creep mechanism cannot account for the high rate of nickel transport to the alloy surface even on the extreme assumption of the virtually zero-vacancy concentration in the matrix near the internal nitridation front. In other words, the volume change accompanying internal nitride formation cannot be accommodated by lattice vacancy flow.

It can be argued that at relatively low temperatures diffusional transport of solvent metal may take place also along grain boundaries (Coble creep [92]). The latter seems to be possible when looking at Fig. 7.21: the grain boundaries of the alloy are “decorated” by the nickel devoid of nitride particles. However, contribution of this mechanism is not expected to change the situation significantly, given the very large grain size ($\sim 200 \mu\text{m}$) of the alloys used in the study.

Another alternative has been suggested. The stress accommodation can be mediated by pipe diffusion-controlled creep.

When we extend the above analysis to the diffusional transport of nickel along dislocations, Eq. (7.74) reads:

$$D_P(Ni) \times \rho = 0.026 \times k_p, \quad (7.76)$$

where $D_p(\text{Ni})$ is coefficient of self-diffusivity of Ni-atoms in dislocation core (pipe) and ρ is the dislocation density. Here, $D_p = D_C \times b_C^2$, with b_C^2 being the effective pipe-diffusion cross-section within which the mean diffusion coefficient is D_C .

The data on self-diffusion of nickel along (edge) dislocations were reported by Cannon and Stark [93]. They found that

$$D_C = 1.6 \times 10^{-4} \exp\left(-\frac{20482}{T}\right) (\text{m}^2/\text{s}). \quad (7.77)$$

Assuming the value $b = 5 \times 10^{-10} \text{ m}$ [76] and substituting the experimental value of the parabolic rate constant determined at the 700°C in Eq. (7.76), the dislocation density is calculated as $\sim 3 \times 10^{15} \text{ m}^{-2}$. This is of the same order of magnitude as was suggested (but not demonstrated) to be required to make the pipe diffusion-controlled creep mechanism operative [84].

Thus, looking at the overall picture, one can conclude that pipe diffusion-controlled creep is the dominant mechanism for accommodation of stresses induced during the precipitation reaction.

The question remains how such huge dislocation density can be developed (and sustained) in well-annealed Ni-based alloys.

It has been conjectured that due to the large volume change associated with the internal precipitation, the matrix around the growing particle in the vicinity of the reaction front may, at least initially, deform by slip [84]. This creates enhanced dislocation densities, which can be stabilized by very small, closely spaced internal precipitates.

Reverting to the results of TEM investigation described earlier in Section 7.3 (Fig. 7.6), one can conclude that CrN-precipitates are topotactically (“cube-on-cube”) oriented with respect to the Ni-based matrix, i.e., $(001)_{\text{Ni}} \parallel (001)_{\text{CrN}}$ and $[100]_{\text{Ni}} \parallel [100]_{\text{CrN}}$.

The mismatch between the matching planes of nitride precipitate and Ni-matrix phase can be found as [94]

$$\delta = 2 \times \frac{d_{\text{CrN}} - d_{\text{Ni}}}{d_{\text{CrN}} + d_{\text{Ni}}}, \quad (7.78)$$

where d_{CrN} and d_{Ni} are the lattice parameters of CrN and Ni, respectively.

It was calculated that the mismatch, δ , is $\sim 16.3\%$, which corresponds indeed to one third of the volume difference of 49% found according to Eq. (7.67). That is too large to be absorbed only by transverse dilatational strains in the nitride/nickel interface. Some of the misfit can be accommodated by interface dislocations. The latter implies formation of a semicoherent interface between nitrified particles and Ni-based matrix during internal nitridation of the Ni 5 at.% Cr alloy under the experimental conditions used. The size and distance between the nitride particles found by electron microscopic study prompts us to conclude that the above mentioned dislocation density (of the order of

10^{15} m^{-2}) in which dislocation pipe diffusion is supposed to operate, indeed occurs in the precipitation zone. The high dislocation density developed in the initially annealed alloy is probably stabilized by the tiny, closely spaced internal nitride precipitates and dislocations are, most likely, surface pinned by the particles. As internal nitride precipitation advances, the dislocation pipe network develops at depth providing a path for the sustained diffusional transport of nickel towards the stress-free gas/metal interface throughout the nitridation process.

7.8 CONCLUDING REMARKS

The discussion we went through in this chapter is an example of a much larger topic known as diffusion-controlled solid-state reactions. The formation *ab nihilo* of precipitates of new phase and the development of the microstructure during internal reaction is certainly one of the most fascinating phenomena in solid-state chemistry.

Needless to say, reactions of internal precipitation in metal alloys can be quite complex. Reaction behavior of the system can be rationalized (and in some cases even predicted) by using just pertinent thermodynamic and diffusion data. However, a considerable effect of mechanical stresses induced inside the reaction zone during internal precipitation can vitiate this prediction. Unfortunately, the understanding of stress contribution to the reaction mechanism is still limited, and these mechanical aspects of the interaction cannot, at this moment, be incorporated into the existing theories of the internal precipitation. To this we may add the equally evident (but not fully understood) influence of the defect structure of materials on nucleation of new phases and, hence, on the course of internal precipitation reaction.

It was demonstrated once again that application of the classical treatment of internal precipitation developed by Wagner leads to a simple and straightforward interpretation of the kinetic observations, and its real value lies in providing a complete mechanistic understanding of the internal precipitating reaction under the conditions set up. Even though there are numerous examples for which Wagner's assumptions and analysis do not apply, his theory remains as the starting point for an understanding of this field.

If the conditions established by Wagner are maintained, the derived formulae are always valid. This last statement deserved some further attention since here and there in the literature one encounters attempts to "squeeze" misunderstood data into Wagner theory, which are then followed by the "discovery" that theory is inapplicable to "this case" or by the other less-than-sensible conclusions.

Reactions of internal precipitation are a valuable research tool in evaluating interstitial transport in metals. For properly chosen alloys and experimental conditions, measurements of the depth of internal precipitation can yield reliable values for the product of the solubility and the diffusivity (i.e., permeability) of penetrating element in the base (solvent) metal.

The field of internal reactions is vast and selection of material in this chapter is clearly a subjective one, given a rather limited space available. It is indeed evident that there are several aspects of the internal precipitation reactions which have not been included. These are the cases when: (i) a solute metal forms two (or more) different precipitates corresponding to different oxidation states; (ii) a dilute alloy is simultaneously attacked by two or more different oxidants; and (iii) contribution of short-circuit diffusion in the overall mass transport in the reaction zone is significant. Also internal precipitation in ternary (and higher order) alloys have not been considered here. The author is fully aware of the fact that a series of good papers have been written on these subjects, for example, [10,20,95–98]. It is, however, his experience with students and scientists after a number of years that mathematically correct descriptions of multiple internal precipitation as well as internal reactions involving multicomponent alloys are unwieldy at best, and are still too intricate to be really used.

The material of the present chapter is presented with an open mind, and it is believed that the present text is useful and instructive for those interested and engaged in the field of high-temperature chemistry and metal corrosion.

REFERENCES

- [1] H. Schmalzried, M. Backhaus-Ricoult, *Prog. Solid St. Chem.* 22 (1993) 1–57.
- [2] H. Schmalzried, *Chemical Kinetics of Solids*, VCH Publisher, New York, 1995.
- [3] H.J. Goldschmidt, *Interstitial Alloys*, Butterworths, London, 1967.
- [4] L.B. Pheil, *J. Iron Steel Inst.* 119 (1929) 501–547.
- [5] C.S. Smith, *J. Inst. Metals (London)* 46 (1931) 49–54.
- [6] F.N. Rhines, *Trans. AIME* 137 (1940) 246–290.
- [7] F.N. Rhines, W.A. Johnson, W.A. Anderson, *Trans. AIME* 147 (1942) 205–221.
- [8] F.N. Rhines, A.H. Grobe, *Trans. AIME* 147 (1942) 318–330.
- [9] J.L. Meijering, M.J. Druyvesteyn, *Philips Res. Rep.* 2 (1947) 81–102.
- [10] J.L. Meijering, M.J. Druyvesteyn, *Philips Res. Rep.* 2 (1947) 260–280.
- [11] L.S. Darken, *Trans. AIME* 150 (1942) 157–171.
- [12] C. Wagner, *Z. Elektrochem.* 63 (1959) 772–790 (in German).
- [13] R.A. Rapp, *Corrosion* 21 (1965) 382–401.
- [14] J.H. Swisher, Internal oxidation, in: D.L. Douglass (Ed.), *Oxidation of Metals and Alloys*, ASM, Metal Park, Ohio, 1971, pp. 235–267.
- [15] J.L. Meijering, Internal oxidation in alloys, in: H. Herman (Ed.), *Advances in Materials Science*, vol. 5, Wiley, New York, 1971, pp. 1–81.
- [16] D.L. Douglass, *Oxid. Met.* 44 (1995) 81–111.
- [17] K. Hauffe, *Oxidation of Metals*, Plenum Press, New York, 1965.
- [18] N. Birks, G.H. Meier, *Introduction to High Temperature Oxidation of Metals*, Edwards Arnold, London, 1983.
- [19] P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London, 1988.
- [20] D.J. Young, *High Temperature Oxidation and Corrosion of Metals*, Elsevier, Oxford, 2008.
- [21] D.R. Gaskell, *Introduction to the Thermodynamics of Materials*, Taylor & Francis, London, 1995.
- [22] S.N.S. Reddy, R.A. Rapp, *Met. Trans. B* 11B (1980) 533–534.
- [23] Yong-Kun Li, R.A. Rapp, *Met. Trans. B* 14B (1983) 509–510.

- [24] M. Katsura, *J. Alloys Compd.* 182 (1992) 91–102.
- [25] E.J. Mittemeijer, M.A.J. Somers, *Surf. Eng.* 13 (1997) 483–497.
- [26] H.J. Grabke, *Ber. Bunsenges. Phys. Chem.* 72 (1968) 533–548 (in German).
- [27] E.J. Mittemeijer, J.T. Slycke, *Surf. Eng.* 12 (1996) 152–162.
- [28] H.J. Grabke, *Carburization—A High Temperature Corrosion Phenomenon*, MTI Publication, vol. 52, Materials Technology Institute of the Chemical Process Industries, Inc., St. Louis, 1998.
- [29] F. Gesmundo, F. Viani, Y. Niu, D.L. Douglass, *Oxid. Met.* 42 (1994) 239–247.
- [30] B. Bousfield, *Surface Preparation and Microscopy of Materials*, John Wiley & Sons, Chichester, England, 1992.
- [31] J.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, A.D. Romig Jr., C.E. Lyman, C. Fiori, E. Lifshin, *Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press, New York, 1992.
- [32] D.B. Williams, C.B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, Plenum Press, New York, 1996.
- [33] P.J. Goodhew, Specimen preparation in materials science, in: A.M. Glauert (Ed.), *Practical Methods in Electron Microscopy*, North-Holland Publishing Company, Amsterdam, 1974.
- [34] K.C. Thompson-Russell, J.W. Edington, *Electron Microscope Specimen Preparation Techniques in Materials Science*, The Macmillan Press Ltd, London, 1977.
- [35] A.A. Kodentsov, J.H. Gülpen, Cs. Cserhádi, J.K. Kivilahti, F.J.J. van Loo, *Metall. Mater. Trans. A* 27A (1996) 59–69.
- [36] A.A. Kodentsov, M.J.H. van Dal, Cs. Cserhádi, J.K. Kivilahti, F.J.J. van Loo, *Defect Diffusion Forum* 143–147 (1997) 1619–1624.
- [37] A.A. Kodentsov, M.J.H. van Dal, J.K. Kivilahti, F.J.J. van Loo, *Ber. Bunsenges. Phys. Chem.* 102 (1998) 1326–1333.
- [38] A.A. Kodentsov, M.J.H. van Dal, Cs. Cserhádi, L. Daróczi, F.J.J. van Loo, *Acta Mater.* 47 (1999) 3169–3180.
- [39] A.A. Kodentsov, J.K. Kivilahti, F.J.J. van Loo, *Rare Metals* 25 (2006) 501–511.
- [40] S.I. Sandler, *Chemical and Engineering Thermodynamics*, John Wiley & Sons, New York, 1999.
- [41] L.S. Darken, R.W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill Book Company, New York, 1953.
- [42] J.S. Kirkaldy, L.S. Brown, *Can. Met. Q.* 2 (1963) 89–117.
- [43] A.D. Dalvi, D.E. Coates, *Oxid. Met.* 5 (1972) 113–135.
- [44] J.S. Kirkaldy, D.J. Young, *Diffusion in Condensed State*, Institute of Metals, London, 1987.
- [45] J. Philibert, *Atom Movements. Diffusion and Mass Transport in Solids*, Les Éditions de Physique, Les Ulis, 1991.
- [46] J.E. Verfurth, R.A. Rapp, *Trans. AIME* 230 (1964) 1310–1313.
- [47] W. Eichenauer, G. Müller, *Z. Metallkde*, 53 (1962) 321–324 (in German).
- [48] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975.
- [49] G. Böhm, M. Kahlweit, *Acta Metall.* 12 (1964) 641–648 (in German).
- [50] M. Kahlweit, *Prog. Solid St. Chem.* 2 (1965) 134–174.
- [51] P. Bolsaitis, M. Kahlweit, *Acta Metall.* 15 (1967) 765–772.
- [52] F. Gesmundo, P. Castello, F. Viani, C. Roos, *Oxid. Met.* 49 (1998) 237–260.
- [53] C. Wagner, *J. Colloid Sci.* 5 (1950) 85–97.
- [54] M. Kahlweit, *Advances in Colloid and Interface Science* 5 (1975) 1–35.
- [55] G.R. LaFlamme, J.E. Morral, *Acta Metall.* 26 (1978) 1791–1794.
- [56] E.K. Ohriner, J.E. Morral, *Scripta Metall.* 13 (1979) 7–10.
- [57] J.S. Kirkaldy, *Oxidation of Metal and Alloys*, ASM, Metal Park, Ohio, 1971, pp. 101–114.
- [58] H.-J. Christ, H. Biermann, F.C. Rizzo, H.G. Sockel, *Oxid. Met.* 32 (1989) 111–123.
- [59] Y. Li, J. Morral, *Acta Mater.* 50 (2002) 3683–3691.
- [60] G.C. Savva, G.C. Weatherly, J.S. Kirkaldy, *Metall. Mater. Trans. A* 27A (1996) 1611–1622.

- [61] W.D. Hopfe, J.E. Morral, *Acta Metall. Mater.* 42 (1994) 3887–3894.
- [62] H. Chen, J.E. Morral, *Acta Mater.* 47 (1999) 1175–1180.
- [63] J.H. Swisher, *Trans. TMS-AIME* 242 (1968) 2433–2439.
- [64] R.A. Rapp, *Acta Metall.* 9 (1961) 730–741.
- [65] R.W.G. Wyckoff, *Crystal Structures*, Interscience Publishers, Inc, New York, 1960.
- [66] E. Heikinheimo, A. Kodentsov, J.A. van Beek, J.T. Klomp, F.J.J. van Loo, *Acta Metall. Mater.* 40 (1992) S111–S119.
- [67] A.A. Kodentsov, J.K. Kivilahti, F.J.J. van Loo, *High Temp. Mater. Sci.* 34 (1995) 137–153.
- [68] A.A. Kodentsov, M.J.H. van Dal, F.J.J. van Loo, Diffusion bonding of Si₃N₄-ceramic to transition metals: interfacial microchemistry, in: A. Bellosi, T. Kosmač, A.P. Tomsia (Eds.), *Proceedings of the NATO Advanced Research Workshop on Interfacial Science in Ceramic Joining*, Bled, Slovenia, November 12–15, 1997, in: NATO ASI Series, vol. 58, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1998, pp. 12–15.
- [69] H.A. Wriedt, O.D. Gonzalez, *Trans. AIME* 221 (1961) 532–535.
- [70] E. Fromm, E. Gebhardt, *Gase und Kohlenstoff in Metallen*, Springer-Verlag, Berlin, 1976 (in German).
- [71] R. Lappalainen, A. Anttila, *Appl. Phys. A* 42 (1987) 263–267.
- [72] R.P. Rubby, D.L. Douglass, *Oxid. Met.* 35 (1991) 259–278.
- [73] A.T. Allen, D.L. Douglass, *Oxid. Met.* 51 (1999) 1–22.
- [74] J.D. Fast, *Interaction of Metals and Gases*, N.V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands, 1965.
- [75] N. Ono, M. Kajihara, M. Kikuchi, *Met. Trans. A* 23A (1992) 1389–1393.
- [76] H. Mehrer (Ed.), *Numerical Data and Functional Relationships in Science and Technology: Diffusion in Solid Metals and Alloys*, vol. 26, Springer-Verlag, Berlin, 1990.
- [77] I. Barin, O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Berlin, 1973.
- [78] P. Nash, *Bull. Alloy Phase Diagrams* 7 (1986) 466–476.
- [79] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data*, ASM International, Materials Park, Ohio, USA, 1985.
- [80] J.R. Mackert, R.D. Ringle, C. Fairhurst, J. Dent. Res. 62 (1983) 1229–1235.
- [81] J.R. Mackert, *Metall. Trans. A* 17A (1986) 746–749.
- [82] F.H. Stott, Y. Shida, D.P. Whittle, G.C. Wood, B.D. Bastow, *Oxid. Met.* 18 (1982) 127–146.
- [83] G.C. Wood, F.H. Stott, D.P. Whittle, Y. Shida, B.D. Bastow, *Corrosion Sci.* 23 (1983) 9–25.
- [84] S. Guruswamy, S.M. Park, J.P. Hirth, R.A. Rapp, *Oxid. Met.* 26 (1986) 77–100.
- [85] H.C. Yi, S.W. Guan, W.W. Smeltzer, A. Petric, *Acta Metall. Mater.* 42 (1994) 981–990.
- [86] G.C. Savva, G.C. Weatherly, J.S. Kirkaldy, *Scripta Mater.* 34 (1996) 1087–1093.
- [87] S.Y. Chang, U. Krupp, H.-J. Christ, *Materials Sci. Eng. A* 301 (2001) 196–206.
- [88] A.A. Kodentsov, M.J.H. van Dal, C. Cserháti, L. Daróczy, F.J.J. van Loo, *Defect Diffusion Forum* 216–217 (2003) 73–76.
- [89] F.R.N. Nabarro, *Report of a Conference on the Strength of Solids*, The Physical Society, London, 1948, pp. 75–78.
- [90] C. Herring, *J. Appl. Phys.* 21 (1950) 437–445.
- [91] A.R. Wazzan, *J. Appl. Phys.* 36 (1963) 3596–3599.
- [92] R.L. Coble, *J. Appl. Phys.* 34 (1963) 1679–1682.
- [93] R.F. Canon, J.P. Stark, *J. Appl. Phys.* 40 (1969) 4366–4373.
- [94] R.W. Cahn, P. Haasen, *Physical Metallurgy*, Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 1983.
- [95] S.W. Guan, H.C. Yi, W.W. Smeltzer, *Oxid. Met.* 41 (1994) 377–387.
- [96] F. Gesmundo, Y. Niu, *Oxid. Met.* 60 (2003) 347–370.
- [97] Y. Niu, F. Gesmundo, *Oxid. Met.* 60 (2003) 371–391.
- [98] Y. Niu, F. Gesmundo, *Oxid. Met.* 62 (2004) 341–355.

CHAPTER 8

Diffusion in Nuclear Materials

Arijit Laik, Gautam Kumar Dey

Bhabha Atomic Research Centre, Mumbai, India

A modern nuclear reactor, being a complex piece of engineering, uses a variety of materials for its construction. Based on their functionalities, these materials can be classified broadly into three classes: *nuclear fuels*, materials that undergo nuclear reactions in the core of the reactor and are primary sources of heat; *cladding materials*, which are used to clad and confine the nuclear fuels, and to prevent radioactive contamination in the reactor; and *structural materials*, which form the part of the outer core and maintain the external structure of the reactors. Materials used in the heat transport system, reactor control mechanism, and other auxiliary systems are also considered as the structural materials. The nuclear fuels are based on uranium, thorium, and plutonium, and can either be in metallic or ceramic form, depending on the type of reactor in which they are used. The clad materials are usually made from aluminium, zirconium, and magnesium based metals and alloys due to their low neutron absorption cross-section and corrosion resistance properties. Most of the structural materials require superior mechanical properties both in ambient and high-temperature conditions, and hence are made of iron and nickel based materials. Various grades of alloy steels, stainless steels, and Ni-based superalloys are used as structural materials in nuclear reactors.

The phenomenon of solid state diffusion is of immense importance to a wide range of nuclear materials from a number of viewpoints. The significance of diffusion is such that it becomes the limiting factor in a number of processes such as fabrication, recrystallization, grain growth, sintering, irradiation enhanced creep, void swelling, embrittlement, fuel-clad interaction, etc. At times, a high rate of diffusion may also lead to conditions for catastrophic failure and hence becomes a safety concern. Therefore, proper understanding of the diffusion processes in all these materials is of utmost importance for safe operation of nuclear reactors, and to a large extent for academic interest. Various defects and impurities in these nuclear materials influence their diffusion properties. Hence, proper assessment of diffusion characteristics, role of defects and impurities, and the mechanisms involved therein becomes essential.

The present chapter deals with the diffusion behavior of different nuclear materials such as nuclear fuels, clad materials, and reactor structural materials. The data available on diffusion properties of these classes of materials will be reviewed. The fundamental aspects which are vital to the diffusion of different species in these materials will be brought out. Different mechanisms of diffusion involved and the influence of the defects

and impurities present in the system will be discussed. The self- and impurity-diffusion coefficients and their temperature dependence in some of the technologically important alloy systems are also included.

8.1 DIFFUSION IN NUCLEAR FUELS

Nuclear fuels are an integral part of nuclear reactors. A wide variety of fuels, ranging from metallic uranium to mixed oxide (U,Pu)O₂ and mixed carbides (U,Pu)C, are used in these reactors. Almost all of today's commercial power reactors, such as pressurized water reactors (PWR), boiling water reactors (BWR), pressurized heavy water reactors (PHWR), and advanced gas-cooled reactor (AGR), use UO₂-based ceramic fuels. Research programmes on metallic fuel development for fast breeder reactors have also gained momentum in recent years. Since the operating temperature and residence time of these fuels are very high in the reactors, diffusion plays a vital role in determining their in-service behavior. Also, since most of the ceramic based fuels are fabricated through the powder metallurgy route, the diffusion characteristics of these fuels decides their fabricability and final properties, especially in the sintering stage. Nevertheless, determination of the diffusion properties of these materials has many experimental difficulties. The main obstacles are the narrow temperature ranges for different allotropic forms in case of metallic fuels and the deviation from stoichiometry in case of oxide based fuels. Another special feature of the nature of diffusion of different species in ceramic based nuclear fuels is that the diffusion rate of the non-metallic elements, i.e., O, C, and N, are orders of magnitude greater than that of the metallic atoms. Besides, the release and diffusion of volatile fission products may lead to formation of pores and bubbles, which ultimately lead to swelling, cracking, and loss of mechanical integrity of the fuel. Hence, due to safety concerns, the study of diffusion behavior of these fission gases and volatile products becomes important.

8.1.1 Difficulties in Diffusion Experiments

The accuracy of diffusion data depends very much on the experimental techniques used for their determination. The most hindering difficulty in conducting experiments for evaluating diffusion properties in nuclear fuels is the radioactivity associated with these materials. This necessitates the use of a glove box, and the experiments need to be conducted in a controlled atmosphere. Also, the threshold of detection of the tracers in radioactive experiments is increased due to the presence of radioactivity in these materials. Some of the practical difficulties in determination of diffusion properties in nuclear materials have been highlighted by Matzke [1]. Further, it is difficult to maintain the composition of the oxide and nitride of fuels. During annealing at high temperatures, for each temperature, a new chemical potential for oxygen (μ_{O}) and hence partial pressure of oxygen ($p(\text{O}_2)$) needs to be maintained to keep the composition constant. However,

the relationship between the change in the partial pressure of nitrogen ($p(N_2)$) and the N/M ratio is not well-known in nitrides of uranium, compared to the relationship between $p(O_2)$ and the O/M ratio in oxides. Also, the change in μ_O is quite large for composition shift from hypo- to hyper-stoichiometry in case of UO_2 [1]. In contrast, the composition of the carbides of U and Pu are not much altered when annealed in vacuum. Another major problem in conducting diffusion experiments in ceramic fuels in particular is that they need to be exposed to very high temperatures for a long time to achieve perceivable diffusion length, since most of them exhibit high and incongruently evaporating properties [1]. Therefore, maintaining a constant composition in the specimens throughout the duration of experiments poses great challenge.

For accurate and reliable data on diffusion properties, it is recommended to conduct experiments on single crystals of the materials on which a radiotracer is deposited. In the case of nuclear fuels one may encounter problems in both of these fronts. Due to the high melting point and reactive nature of these ceramic materials, it is difficult to produce single crystals with acceptable level of purity and size. Besides, formation of a thin layer of a radiotracer on the surface of non-stoichiometric ceramics is not easy. Hence, one has to resort to unconventional techniques, such as electron beam evaporation for this purpose. The diffusional properties of interstitial elements C, O, and N are particularly important in case of ceramic nuclear fuels. Moreover, there exist experimental difficulties in evaluation of these properties due to limited availability of a suitable radiotracer for these elements. For carbon, C^{14} is the only available radioisotope, whereas isotopes of oxygen (O^{18}) and nitrogen (N^{15}) have natural abundance of only 0.2% and 0.37%, respectively.

For generating good quality diffusion data, apart from chemistry, it is also equally important to maintain the nature of phases in the specimens during the course of diffusion experiments. However, it is known that off-stoichiometric oxides of U and Th often exist in two phases at high temperatures. The presence of the second phase contributes to the diffusion properties of the major phase. In case of sub-stoichiometry, metal dioxides (MO_2) may contain metal inclusions and sesquioxides, and on the hyper-stoichiometric side, they may contain higher oxides such as U_4O_9 [1]. Similarly, carbides may contain metal or higher carbides, and nitrides may also contain either metal or two types of sesquinitride. All these difficulties have potential in adversely affecting the quality of the diffusion data, and therefore all measures within practical limits should be adopted to prevent creeping in of errors due to them.

8.1.2 Diffusion in Metallic Fuels

In the metallic form, nuclear fuels may be based on three actinide metals: thorium, uranium, and plutonium. These metals vary a lot in their melting points: 2023 K for Th, 1409 for U, and 913 for Pu. All these elements exhibit allotropic transformations upon heating at high temperatures. Th undergoes only one phase transition from α -phase

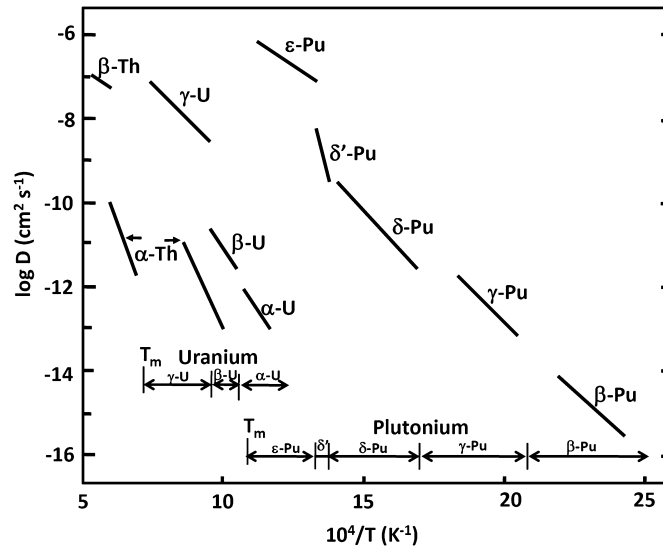
(face-centered cubic) to β -phase (body-centered cubic) at 1633 K, whereas U exists in three crystallographic forms: α (orthorhombic), β (tetragonal), and γ (body-centered cubic). Pu is known to have the largest number of allotropes and exists in six different crystal structures: α (monoclinic), β (body-centered monoclinic), γ (face-centered orthorhombic), δ (face-centered cubic), δ' (tetragonal), and ϵ (body-centered cubic). The existence of so many allotropes and the radioactive and toxic nature of these metals make experiments on evaluation of diffusion properties rather difficult. Since the temperature range of existence of these phases is quite narrow, especially for U and Pu, the evaluated values of activation energy and pre-exponential factors may contain a certain degree of inherent uncertainty.

The self- and impurity-diffusion processes have been studied in various phases of Th, U, and Pu by several researchers. The data available have been reviewed by Matzke [1,2]. Table 8.1 presents a summary of the self-diffusion parameters in these metals. Recently, Neumann and Tuijn [3] also included data on these actinide metals in their compilation of self- and impurity-diffusion data. The fcc phases of Th and Pu showed usual behavior as expected of typical fcc metals. It is known that metals transforming to bcc phase at high temperatures show anomalous diffusion in the bcc phase, for example, Zr and Ti, where the values of the activation energy (Q) and the pre-exponential factor (D_0) are lower than expected. It may be noted that in case of diffusion in the bcc phases in U and Pu, the values of Q and D_0 are also low. Therefore γ -U and ϵ -Pu can be assumed to exhibit anomalous diffusion. The temperature dependence of self-diffusion coefficients is shown in Fig. 8.1. It can be noted that at temperatures of phase change the diffusion coefficient changes drastically. For Th, D increases by 200 times upon transformation from the α to β phase. Also, in the case of U, upon β to γ phase change, D is enhanced by about 150 times. For Pu perhaps the largest change in D occurs upon transformation of δ' -Pu to ϵ -Pu. In case of ϵ -Pu, there exists another unusual observation of decrease in diffusion coefficient upon increase in pressure [4]. This type of anomalous behavior is associated with a negative activation volume. Although an interstitial mechanism of self-diffusion has been assumed for ϵ -Pu, it has not been confirmed [4].

The impurity diffusion coefficients in the bcc phases of Th and U have been summarized and reviewed earlier [1–3]. The data available on the diffusion of various impurity atoms in the matrices of β -Th and γ -U can be summarized in an Arrhenius plot shown in Fig. 8.2. Both of these phases are high-temperature phases; nevertheless, the temperature ranges of existence of these phases are 224 K apart. As in the case of other metals, the interstitial elements O, N, and C show fastest diffusion. It can also be observed that in the case of Th, the diffusion data on almost all the impurity atoms reported, show faster diffusion than self-diffusion rate of Th, whereas, in the case of U, Au and Nb were found to diffuse slower than U. Fe, Co and Ni are also fast diffusing elements in these two bcc phases. In general opinion, the fast diffusion rate of impurity atoms is related to interstitial mode of diffusion. Hence, the substitutional atoms exhibiting fast

Table 8.1 Self-diffusion parameters in various crystallographic phases in actinide metals Th, U, and Pu (after [2])

Metal	Phase	Stability range (K)	D_0 ($\times 10^{-4} \text{ m}^2/\text{s}$)	Q (kJ/mol)
Th	β bcc	1633–2023	0.5	230
	α fcc	< 1633	1.7, 395	324, 300
U	γ bcc	1048–1409	1.19×10^{-3}	112
	β tetragonal	940–1048	1.135×10^{-2}	176
	α orthorhombic	< 940	2.0×10^{-3}	192
Pu	ϵ bcc	753–913	4.5×10^{-3}	66.9
	δ fcc	588–731	5.2×10^{-1}	126.4
	δ f.c. orthorhombic	478–588	3.8×10^{-1}	118.4
	β b.c. monoclinic	398–478	1.7×10^{-2}	108

**Figure 8.1** Temperature dependence for self diffusion in the different phases of Th, U, and Pu. (After Matzke [2].)

diffusion show polarizability towards interstitial diffusion. However, these atoms may have a small amount of interstitial solubility which causes the effective diffusion coefficient to increase. In such a situation, one can assume a mixed mode of diffusion to be operative. In the case of Th and U, although the mechanism of diffusion is usually vacancy-assisted, a strong impurity-vacancy binding energy and a high degree of correlation between the direction of successive jumps are very much probable [2]. Such an assumption is corroborated by enhancement of self-diffusion of U in γ -U phase by

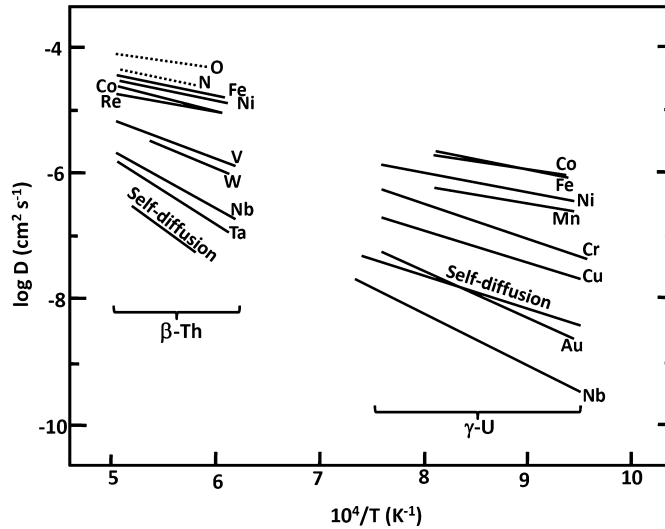


Figure 8.2 Temperature dependence for self- and impurity diffusion in the high temperature body centered cubic phases γ -U and β -Th. (After Matzke [2].)

addition of Co [5]. Further, the slow diffuser Nb was found to retard the self-diffusion of U in γ -U phase, as expected.

Metallic fuels based on U–Mo alloys are being developed for the “reduced enrichment for research and test reactor programme”, to be used in the form of dispersion and monolithic fuel with Al matrix/cladding [6–9]. Interdiffusion studies showed that the magnitude of interdiffusion coefficient ($\tilde{D}$) decreases, while the activation energy (Q) increases with an increase in concentration of Mo [7,8]. For a concentration range $C_{\text{Mo}} = 22\text{--}32$ at.%, the pre-exponential factor D_0 varied between 2.66×10^{-6} and 1.49×10^{-6} m²/s, while the value of Q was between 195 and 200 kJ/mol [8]. Also, marker experiments indicate that the intrinsic diffusion rate of U is 5–10 times higher than that of Mo. The presence of vacancy wind enhances the diffusion rate of U by about 30% and suppresses that of Mo by only 2%. Recent experiments on interdiffusion between U–Mo alloy in γ phase and Zr showed that prominent precipitates of Mo_2Zr occurred on the Zr-rich part of the interdiffusion zone [10]. This promoted an instability, leading to phase separation of the γ -U(Mo,Zr) solid solution [10] within the interdiffusion zone.

8.1.3 Diffusion in Ceramic Fuels

The diffusion properties of ceramic fuels such as oxides, carbides, and nitrides are of utmost importance for their fabrication and from the in-reactor performance point of view. Several reports on evaluation of diffusion characteristics with respect to the

diffusion of metallic and non-metallic atoms in UO_2 , ThO_2 , $(\text{U}, \text{Pu})\text{O}_2$, $(\text{U}, \text{Pu})\text{C}$, UN , and $(\text{U}, \text{Pu})\text{N}$ exist in the literature. The available data have been reviewed by Matzke in several compilations [1,2,11–13].

8.1.3.1 Diffusion in Oxide Based Fuels

A major type of nuclear fuel used in the modern nuclear power reactors is based on UO_2 . The mixed oxide (MOX) type fuel of $(\text{U}, \text{Pu})\text{O}_2$ containing 20–25% PuO_2 has become the standard fuel for liquid metal cooled fast breeder reactors. ThO_2 has been recognized as a fertile material for producing U^{233} in atomic energy programmes of some countries such as India. The crystal structure of UO_2 , ThO_2 , and PuO_2 is of fluorite type and their melting points are high. In these fluorite-type dioxides, the metal atoms, Th, U, and Pu, are slower diffusing than oxygen, as shown in a number of reports [14–18]. Metzke [1,19–21] showed that the temperature dependences for diffusion of Pu in UO_2 and that of Th in ThO_2 are:

$$D_{\text{Pu}}(\text{UO}_2) = 6.5 \times 10^{-5} \exp\left(\frac{-538 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.1)$$

$$D_{\text{Th}}(\text{ThO}_2) = 5 \times 10^{-5} \exp\left(\frac{-625 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.2)$$

The slow nature of diffusion of U and Th is evident from the high values of respective activation energies as shown in these Arrhenius relationships. Also, it may be noted that for diffusion of Th, U, and Pu in ThO_2 , the values of D_0 and Q were very close to each other. Therefore, the difference in ionic radii for Th^{4+} (0.102 nm), U^{4+} (0.097 nm), and Pu^{4+} (0.093 nm) bear little significance for diffusion.

The diffusion rates of metal atoms in these oxides depend strongly upon deviation from stoichiometry. Since the metal ions are slower diffusing, their diffusion is rate-determining for many high temperature processes such as creep, sintering, swelling, and densification. The migration energy for diffusion of U atoms through vacancies in UO_2 was estimated to be about 423 kJ/mole using calculations based on density functional theory [22]. The diffusion coefficient of U for UO_{2+x} increases dramatically with increase in the magnitude of departure from stoichiometry (x). For example, it increases by five orders of magnitude between UO_2 and $\text{UO}_{2.2}$ at 1773 K [1]. This is primarily due to increase in the vacancies in U-sites in UO_{2+x} . In substoichiometric MOX fuels $(\text{U}, \text{Pu})\text{O}_{2-x}$, the diffusion coefficient of Pu decreases with decrease in O concentration from MO_2 to MO_{2-x} . Such a deviation in stoichiometry is accommodated by reduction of Pu^{4+} to Pu^{3+} . However, the diffusion coefficient of Pu goes through a minimum; for example, at 1773 K, the value of D_{Pu} is minimal at $\text{MO}_{1.98}$. Therefore, it was assumed that the mechanism of diffusion is vacancy mode for $\text{O}/\text{M} > 1.98$ and interstitial mode for $\text{O}/\text{M} < 1.98$ [1]. The interdiffusion coefficient of U

and Pu in the mixed oxide system of $\text{UO}_2\text{--PuO}_2$ also attains a minimum value when plotted against the partial pressure of oxygen ($p(\text{O}_2)$) [23]. It is interesting to note that during interdiffusion, the valance of Pu is different from that of U at different partial pressure of O_2 . The O/M ratio, therefore, is composition dependent and hence varies across the interdiffusion zone. In a substoichiometric MOX, $(\text{U}_{1-a}\text{Pu}_a)\text{O}_{2-x}$, the average value of valance of Pu at constant $p(\text{O}_2)$ is given by $\nu_{\text{Pu}} = 4 - 2x/a$ [2]. Therefore, even at constant valance ν_{Pu} the deviation x is a function of a , which manifests as a gradient in the O/M across the interdiffusion zone. The situation is not so severe in case of hyperstoichiometric oxide UO_{2+x} and MOX $(\text{U}_{1-a}\text{Pu}_a)\text{O}_{2+x}$. The U^{4+} in this case can be oxidized to higher valance U^{5+} and U^{6+} , while most of the Pu remains as Pu^{4+} . The temperature dependence also shows an activation energy equivalent to that corresponding to stoichiometric oxides.

Both UO_2 and PuO_2 show large deviation from stoichiometry. Dioxides of U, Th, and Pu can be substoichiometric as (MO_{2-x}) with vacancies at the O-site being the dominant defects. The charge compensation takes place by reduction of the M atoms to lower valance state, e.g., M^{3+} . Hyperstoichiometric UO_{2+x} exists with high valance cations U^{5+} and U^{6+} . In fact, the single phase UO_2 extends to a quite large value of x , i.e., from $\text{UO}_{1.65}$ to $\text{UO}_{2.25}$ at about 2600 K. In case of UO_{2+x} the excess O-ions tend to form clusters by displacing some of the O-ions from their lattice sites [2].

The rate of diffusion of oxygen in the oxide fuels is much larger than that of the metal atoms. For example, the diffusion coefficient of O (D_{O}) is about five orders of magnitude higher than that of metal atoms at 1773 K. The diffusion of O is of importance since it governs the rate of oxidation or reduction of these oxide fuels. Information on diffusion of O in UO_2 [14–16,24], in ThO_2 [25] and PuO_2 [26], exist in the literature. The Arrhenius type relationship for diffusion of O in stoichiometric UO_2 is given by [1]

$$D_{\text{O}}(\text{UO}_2) = 2.5 \times 10^{-5} \exp\left(\frac{-250 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.3)$$

The available data suggests that both O-interstitials and vacancies in the O-sites contribute to the diffusion of O in UO_2 . However, due to unavailability of sufficient data, the mechanism of diffusion of O in case of PuO_2 could not be postulated.

In case of nonstoichiometric oxides $\text{UO}_{2\pm x}$ and $(\text{U,Pu})\text{O}_{2\pm x}$, the diffusion of O takes place through the interstitialcy mechanism (with O-interstitial) and hence is much faster than the diffusion of O in stoichiometric UO_2 [1]. In hyperstoichiometric dioxides MO_{2+x} , the value of D_{O} changes by about five orders of magnitude for a change of x from 10^{-1} to 10^{-5} [14–16]. Similar conditions also exist in case of hypostoichiometric oxides MO_{2-x} [27]. Here, the faster diffusion of O is due to large concentration of vacancies in the O-sites. The low values of the activation energy for diffusion are due to low migration energy for O-vacancies. For the hyperstoichiometric oxides, the

present data do not reveal any evidence of the presence of clusters. However, for substoichiometric oxides, ionic conductivity data suggested interaction of O-vacancies with lower valance cations. Recently, Moore et al. [28] developed a thermodynamic model for diffusion of O in nonstoichiometric UO_2 . They showed that the migration energies for O through vacancy and interstitial defects are 64 and 107 kJ/mol, respectively. They also showed that the activation energy for diffusion goes through a maximum at $\text{O}/\text{U} = 2$, and vacancy migration is the dominant mechanism in the domain $\text{O}/\text{U} < 2$, while interstitial migration dominates when $\text{O}/\text{U} > 2$. Calculations using density functional showed that the migration energy for diffusion of O through interstitial defects in UO_2 is 106 kJ/mol [22] and 109 kJ/mol [29], and that for diffusion through vacancies is 97 kJ/mol [29].

8.1.3.2 Diffusion in Carbide Based Fuels

Carbide based fuels are also used in nuclear reactors because of their high density of heavy metals, high thermal conductivity, and shorter doubling time in fast breeder reactors. The fast breeder test reactor (FBTR) of India has mixed carbide ($\text{UC}+\text{PuC}$) fuel in its core. The reader may refer to the monograph [11] for further details on fuel of fast breeder reactors. The monocarbides UC and PuC are of NaCl-type (cP8) crystal structure. At high temperatures (~ 2500 K) UC shows a large solubility range of $\text{UC}_{0.95}$ to $\text{UC}_{1.9}$. While substoichiometric carbides contain metallic inclusions (U,Pu) apart from the monocarbide, hyperstoichiometric carbides contain precipitates of higher carbides such as MC_2 and U_2C_3 as the second phase. However, the stoichiometric carbide fuels are generally not preferred due to their poor compatibility with the clad material and high rate of swelling.

The diffusion behavior of $\text{UC}_{1\pm x}$ and $(\text{U,Pu})\text{O}_{1+x}$ has been studied extensively [30–34]. The diffusion coefficient of U in the zone refined single crystal monocarbide UC with metallic impurities (< 30 ppm) can be described as [1]:

$$D_{\text{U}}(\text{UC}) = 1.17 \times 10^{-3} \exp\left(\frac{-593 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.4)$$

whereas in the case of polycrystalline UC with higher metallic impurity level (~ 120 ppm) the diffusion coefficient is given by [1]

$$D_{\text{U}}(\text{UC}) = 6.9 \times 10^{-4} \exp\left(\frac{-590 \text{ kJ/mole}}{RT}\right) + 3.6 \times 10^{-9} \exp\left(\frac{-350 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.5)$$

The two terms in the above equation indicate that the Arrhenius plot in this case shows a curvature with a change in slope at around 2400 K. The change in diffusion behavior and lower activation energy at temperatures below 2400 K can be attributed

to the presence of impurity metal atoms which increases the vacancy–impurity atom interaction and hence enhances the diffusivity of U at low temperatures. However, the influence of such vacancy–impurity pair is less at high temperatures and hence the diffusion behavior resembles that of the single crystal material. The reactor grade carbide fuel contains even higher levels of impurities, which keep on increasing during the operation of the reactor. Therefore, the effect of impurity controls the rate of diffusion to a large extent. The effect of impurity atoms such as Fe, Ni, Ta, V, and W in UC matrix has been evaluated [35,36]. Almost all impurities were found to enhance the self-diffusion of U, whereas larger impurity atoms such as Zr and rare earth elements Ce and La may reduce the diffusion coefficient of U. The data indicate that smaller impurity atoms, e.g., Fe, Ni, Ta, V, and W (with ionic radii 20–30% smaller than that of U) enhance the diffusion rate while those with a larger size tend to retard it.

At any given temperature the diffusion coefficient of Pu (D_{Pu}) in mixed carbide (U,Pu)C is larger than that of U (D_{U}) in UC by a factor of 3–5. The reason may be attributed to the smaller size of Pu and slightly larger lattice parameter of (U,Pu)C compared to UC. In a mixed carbide fuel with small grain size and composition (U_{0.8}, Pu_{0.2})C with metallic impurities, the temperature dependence of the diffusion coefficient of Pu can be described as [1]:

$$D_{\text{Pu}}((\text{U}, \text{Pu})\text{C}) = 1.3 \times 10^{-6} \exp\left(\frac{-447 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.6)$$

The diffusion rate of U in higher carbides is greater than that in UC at the same temperature [19]. Data on diffusion coefficient of U in higher carbides also exist in the literature [2,19]:

$$D_{\text{U}}(\text{U}_2\text{C}_3) = 5.9 \times 10^{-8} \exp\left(\frac{-447 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.7)$$

$$D_{\text{U}}(\alpha - \text{UC}_2) = 7 \times 10^{-2} \exp\left(\frac{-548 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.8)$$

$$D_{\text{U}}(\beta - \text{UC}_2) = 1.9 \exp\left(\frac{-625 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.9)$$

Deviation from stoichiometry also has a pronounced effect on the diffusion of metal atoms [36]. Both for UC_{1+x} and (U, Pu)C_{1+x}, the diffusion rate decreases and the activation energy increases with increase in x . The grain boundary diffusions for UC and UC_{1±x} are faster by three to five orders of magnitude, and the activation energy for diffusion through the grain boundaries is about only 55% that of the lattice diffusion [37].

The diffusion of carbon in the UC and $UC_{1\pm x}$ matrices has been reported by some researchers [11,38,39]. In nominally stoichiometric monocarbide UC, the diffusion coefficient of U can be given by the relationship [1]:

$$D_C(UC) = 2.4 \times 10^{-5} \exp\left(\frac{-356 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.10)$$

Recent studies using first principle calculations [40] have shown that the presence of defects in the UC matrix is best accommodated in the C sublattice, and that C and U interstitials are more stable as dumbbells compared to isolated interstitials in the tetrahedral sites [40]. The most probable mechanism of diffusion of C atoms is the dissociation of pair of C–C by jump of a single C-atom to another C-atom to form a new C–C pair. Theoretical calculations showed that the C–C pairs in UC_{1+x} and stoichiometric UC are about 2% at 2400 K [41]. Recent theoretical studies revealed that the C-vacancies, which are present in large fraction in hypostoichiometric UC, do not form vacancy clusters [40].

For nonstoichiometric carbide $UC_{1\pm x}$, the diffusion of C has been studied for wide temperature ranges; there exists a large scatter in the values of activation energies. The mechanisms of C diffusion are suggested to be through vacancies in C-sites, interstitials of C-atoms, C–C pairs, and interstitialcy mechanism. The values of Q for hypostoichiometric $UC_{0.92}$, stoichiometric UC, and hyperstoichiometric $UC_{1.16}$ are 385 kJ/mole, 356 kJ/mole, and 385 kJ/mole, respectively [39]. This shows that D_C varies only slightly with $UC_{1\pm x}$.

8.1.3.3 Diffusion in Nitride Based Fuels

Nitride based fuels are generally used either in the form of mononitrides of uranium (UN) or mixed mononitride ((U,Pu)N). Uranium and mixed mononitrides are being proposed as candidate fuel for next-generation fast reactors. The factors in their favor are primarily due to high melting point (about 3000 K) [42], combined with high conductivity and high uranium density [11,43].

However, these nitrides exist within a narrow solubility range, even at high temperatures. The diffusion coefficient of U in UN has been reported under the condition of partial pressure of nitrogen, $p(N_2) = 1$ bar as [1]:

$$D_U(UN) = 5.4 \times 10^{-7} \exp\left(\frac{-481 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.11)$$

The diffusion behavior of Pu in mixed nitride (U,Pu)N was evaluated under constant partial pressure of N_2 , $p(N_2) = 530$ mbar [44]. The Arrhenius relationship for the

diffusion of Pu is given by [1]:

$$D_{\text{Pu}}((\text{U}, \text{Pu})\text{N}) = 2.5 \times 10^{-3} \exp\left(\frac{-495 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.12)$$

It can be assumed that vacancy mechanism is operative in both materials. The rate of diffusion of heavy metals increases with the partial pressure of nitrogen, for both UN and mixed nitride (U,Pu)N. In case of nitrides, the diffusion coefficient of U and Pu decreases and the value of activation energy for diffusion increases with decrease in the M/N ratio [2], whereas an opposite trend is observed in case of carbides. The reason for such difference in behavior was attributed to the difference in bond characteristics in the two materials. While in mononitrides the bonding is more metallic in character, in case of carbides it is more towards covalent [1].

The diffusion coefficient of N in nitrides is orders of magnitude greater than that of heavy atoms. However, as stated earlier, its measurement may sometimes be erroneous, since suitable stable isotope of N is not available. Literature shows that the activation energy for N in UN is lower than that of U, and varies in the range 230–404 kJ/mol [2]. The diffusion coefficient of N varies with the square root of the partial pressure of nitrogen, which indicates interstitial mode of diffusion [45].

Recent simulations of diffusion processes using molecular dynamics confirmed that the most mobile point defects in UN are U and N interstitial [46]. It was also revealed that U-antisite defects play important role in substoichiometric UN_{1-x} and that U vacancies and U antisites have a major contribution to the self-diffusion of U [46].

8.1.4 Diffusion of Fission Gases

During the operation of nuclear reactors, a considerable proportion of fission products produced are volatile in nature, for example, Kr, Xe, Br, I, Rb, Cs, and Te. These elements, because of their low solubility, tend to either form bubbles within the fuel matrix or diffuse out of the fuel pellets. The release and diffusion of these volatile fission products are of concern because they cause dimensional change by swelling and hence become a performance limiting factor of fuels. Also, because of safety concerns, the study of diffusion nature of these elements in the fuel matrix assumes great importance. A considerable amount of work encompassing both theoretical and experimental aspects on this topic has been carried out in the past, mainly on uranium oxide. The results have been critically reviewed by Matzke [47,48] and Lawrence [49]. The diffusion characteristics of noble fission gases Kr and Xe have been examined in detail using molecular dynamics based numerical modeling [50]. The fission gases are released from the fuel matrix by various mechanisms, of which the most dominant one is diffusion of the gas atoms to the grain boundaries and subsequent migration through these channels to the open surfaces. Therefore, the process can be modeled by postulating the sintered

UO₂ pellet to be an assembly of UO₂ particles having open porosity [51]. One can use Fick's law in its classical form for the diffusion of the gas atoms through the UO₂ matrix. However, while modeling it should be realized that a very small fraction of gas atoms are generated by fission directly. For example, most of Xe formed during operation is produced by β -decay of precursors Te and I. Since the diffusion rates of these precursors are usually higher than that of the rare gases, their mobility should also be considered during modeling [1].

It is well-known by now that Xe atoms diffuse unperturbed in the classical manner only when their concentration is low and the density of defects caused by irradiation is low. As the concentration of the gas atoms and defects increase, the diffusion of the atoms is influenced by atom–atom and atom–defect interactions. At still higher concentrations of gas atoms, bubbles of fission gases are formed within the matrix [1]. Therefore, to handle such a situation, usually one should use *effective diffusion coefficients* for all practical purposes. The use of this parameter should take into account all the factors that influence the migration of fission gas atoms, such as trapping into the defects, formation of gas bubbles, precipitation at grain boundaries, and preexistence of pores. The interior of fuel is far from homogeneous and contains closed porosities, grain boundaries, fission gas bubbles, and solid fission products. The presence of almost all of them causes deviation from the classical nature of diffusion of atoms.

The mechanisms of transport of the gas atoms to the grain boundaries are several: diffusion as simple gas atoms, transport of gas-filled pores and bubbles, sweeping process of moving gas boundaries or dislocations. Gas atoms are released from the grain boundaries to the exterior subsequently through a network of tunnels and via cracks formed within the pellets during power excursion in startup and shutdown of the reactors.

The experimental observation on diffusion of Xe in UO₂ was reported by several workers [52–54]. Also, the diffusion coefficients determined through these experiments were calculated from gas release values, and not from the penetration plots, the scatter was relatively small compared to that expected. The diffusion of Xe gas atoms in UO₂ matrix can be described by the following equation when the gas atom concentration is very low [1]:

$$D_{\text{Xe}}(\text{UO}_2) = 5 \times 10^{-5} \exp \left(\frac{-336 \text{ kJ/mole}}{RT} \right) \text{ m}^2/\text{s}. \quad (8.13)$$

At concentration levels higher than 10^{−5} at.%, the gas–gas and gas–defect interactions start to dominate, which leads to an increase in the activation energy by about 50–80 kJ/mol [1]. A drastic reduction in the *effective diffusion coefficient* of Xe in UO₂ by three orders of magnitude for a change in concentration from 10^{−5} to 10^{−4} at.% has been reported [1,47].

It may be noted that during the course of irradiation, the UO₂ matrix accumulates various other fission products such as Ba, Ce, La, Mo, Nd, Pd, Rh, Ru, Sr, Y, Zr, etc.,

in concentrations depending upon the burnup, which is about 3–8 at.%. The presence of these fission products may lead to a change in the diffusion behavior of the fission gas atoms. Further, at high burnup the O/M ratio of the fuel is increased. It is interesting to note that due to neutron resonance capture, the outer rim of the fuel pellet, which is colder than the central region, has increased Pu-formation compared to the central region. This results in an alteration of the distribution of U-fraction within the fuel pellet. Moreover, Te and Cs occupy lattice sites at low temperatures, whereas they remain as bubbles and precipitates in the high temperature regions. All these disturbances on the local chemistry of the fuel bear strong influence on the transport behavior of the fission gases in the fuel. This has been demonstrated by the modeling work of diffusion in UO_2 [55]. Such reduction in diffusion rate due to trapping of the gas atoms has been observed in ThO_2 [56].

The report on diffusion coefficients of UO_2 was also critically reviewed by Lawrence [49], who commented that high degree of scatter exists in the published values of the diffusion coefficient. The most sensitive factor to which such a high scatter can be attributed to is the deviation from stoichiometry of UO_2 . The findings of Miekeley and Felix [53] showed a difference of about four orders of magnitude in diffusion coefficients when O/U varied between 1.997 and 2.01. The values of the activation energies obtained from in-pile experiments are in general lower than those determined from out-of-pile experiments. This is clearly due to enhancement caused by radiation damage, leading to lowering of the average activation energy required for diffusion in the presence of radiation-induced defects.

8.2 DIFFUSION IN CLAD MATERIALS

Aluminium is widely used as fuel clad material in water cooled, low power research reactors, used for training, materials testing, and isotope production. The fuel in such reactors is usually metallic or of dispersion type in the form of either rod or plate, where the clad temperature is restricted to typically 373 K. The advantage of using aluminium and its dilute alloys as clad material lies in the fact that they possess low neutron absorption cross-section, are corrosion resistant, and can be easily fabricated. However, in power reactors, where the coolant temperature is typically about 573 K, aluminium is not a suitable cladding material, since its strength decreases and creep rate increases drastically in this temperature regime. Zirconium based alloys such as Zircaloy-2, Zircaloy-4, Zr–2.5% Nb and Zr–1% Nb are extensively used in in-core structural components of nuclear power reactors due to their low neutron absorption cross-section, excellent corrosion resistance, adequate mechanical properties such as tensile strength, ductility, and creep properties. Zircaloy-2, Zircaloy-4, and Zr–0.1% Nb alloys are primarily used as cladding material for fuel in various types of thermal reactors. Zr–2.5% Nb alloy is used as the coolant tube material in pressurized heavy water reactors (PHWR) in cold

worked stress relieved condition, due to its higher strength and creep resistant properties. Therefore, Al- and Zr-based alloy systems are the two most important alloy systems with respect to clad materials of nuclear reactors. In reactor operating conditions, these clad materials need to withstand harsh environments which include oxidation, corrosion, irradiation assisted creep, irradiation damage caused by neutrons and fission products, and microstructural changes due to synergistic effect of high temperature and irradiation. In order to understand the above mentioned behaviors of these classes of materials in reactor operating environment, it is necessary to have an adequate knowledge of their diffusion behavior.

8.2.1 Diffusion in Aluminium

Substantial amount of work has been carried out by various researchers on self- and impurity diffusion coefficients in aluminium matrix. The activation energy for self-diffusion of Al was determined to be 141.5 kJ/mol by Lundy and Murdock [57]. The mechanism of diffusion was assumed to be by vacancy exchange [58]. Regarding impurity diffusion measurements for various elements in Al, Du et al. [59] had cited difficulties in carrying out experiments primarily due to formation of near-surface oxide layer [60,61], extremely low solubility in Al [60,62], strong tendencies to form intermetallic compounds [63], and the existence of dislocations [64,65]. In spite of these facts, appreciable data exist on the impurity diffusion in Al, a good number of which have been critically evaluated by Du et al. [59] and Anand et al. [66]. It has been in general observed that the activation energies of the non-transition elements such as Ag, Zn, Cu, Ga, Ge, In, and Sn have activation energies comparable to that of the self-diffusion of Al. However, the diffusion of transition elements such as Ti, V, Cr, Mn, Fe, Co, Zr, Mo, and W in the Al matrix was found to be slower than self-diffusion of Al and therefore has higher activation energies. Such behavior by the 3d transition elements in Al can be explained by the fact that the participation of the 3d electrons in metallic bonding leads to larger effective charged states of these transition elements in conjunction with perturbation of local charge density [58].

Table 8.2 contains the relevant diffusion parameters for the impurity diffusion of various elements in aluminium. One of the earliest data on diffusion of Cr in Al was carried out by Agarwala et al. [67] using a residual activity technique. However, the significantly larger values of impurity diffusion were attributed to diffusion through dislocation short circuiting paths by Peterson and Rothman [68]. They determined the diffusion behavior of Cr in Al single crystals by means of microtome sectioning technique. Rummel et al. [69] measured the diffusion of Cr in Al single crystals using ion implantation as a tracer deposition technique. The experimental procedure of Rummel et al. [69] is proven to avoid the problems associated with the near-surface oxide layer, low solubility, and the formation of intermetallics. The results of Fricke [70] and Bergner and van Chi

Table 8.2 Diffusion parameters of solute elements in aluminium

Solute atom	D_0 (m ² /s)	Q (kJ/mol)	Reference
Ag	1.30×10^{-5}	117.2	[61]
	1.60×10^{-5}	118.9	[89]
Au	1.31×10^{-5}	116.4	[68]
	7.71×10^{-6}	113.0	[61]
	2.71×10^{-5}	121.0	[89]
Cd	1.04×10^{-4}	124.3	[61]
Co	4.68×10^{-2}	174.8	[68]
	5.06×10^{-2}	175.7	[94]
Cr	1.93×10^{-2}	168.4	[69]
	10	282.0	[69]
	5	242.7	[68]
	80	255.3	[70]
Cu	6.4	161.0	[71]
	6.47×10^{-5}	135.0	[68]
	8.4×10^{-6}	136.4	[78]
	1.5×10^{-5}	126.4	[87]
	2.0×10^{-4}	142.3	[88]
	1.0×10^{-5}	127.6	[84]
Fe	6.5×10^{-5}	136.1	[90]
	91	158.7	[60]
	1.35×10^{-2}	192.5	[61]
	1.1	121.6	[62]
	5.3×10^{-3}	183.4	[63]
	7.7×10^{-1}	220.9	[69]
	4.1×10^{-13}	58.2	[72]
	7.7×10^{-1}	220.9	[69]
Ga	4.6×10^{-5}	122.4	[68]
	4.81×10^{-5}	121.3	[68]
In	1.16×10^{-4}	122.6	[76]
Mg	6.3×10^{-6}	113.0	[70]
	1.2×10^{-5}	119.7	[78]
	1.0×10^{-6}	110.9	[84]
	1.2×10^{-4}	130.4	[85]
Mn	6.2×10^{-6}	114.6	[86]
	8.7×10^{-3}	208.2	[69]
	3.8×10^{-2}	221.8	[70]
	2.2×10^{-5}	120.5	[57]
	1.0×10^{-2}	211.4	[76]
	3.2×10^{-2}	217.0	[75]

continued on next page

Table 8.2 (continued)

Solute atom	D_0 (m ² /s)	Q (kJ/mol)	Reference
Ni	2.9×10^{-12}	65.7	[72]
	4.4×10^{-4}	145.8	[74]
Si	1.8×10^{-3}	150.6	[70]
	9.0×10^{-5}	127.8	[78]
	3.5×10^{-5}	123.9	[71]
	2.6×10^{-4}	136.8	[81]
	2.0×10^{-4}	136.0	[82]
Zn	2.6×10^{-5}	120.8	[68]
	4.0×10^{-7}	100.4	[70]
	2.0×10^{-5}	120.7	[74]
	1.2×10^{-3}	116.3	[78]
	9.0×10^{-5}	127.2	[88]

[71] employing semiinfinite diffusion couples with the penetration profile measured by electron probe microanalysis were consistent with those of Rummel et al. [69].

Diffusion of Fe in Al has received much attention due to its technological importance. Hirano et al. [72] were the first to measure Fe diffusion in Al using radioactive tracers and the residual activity technique, followed by investigation by Tiwari and Sharma [64], who researched diffusion of the ⁵⁹Fe isotope in Al polycrystalline specimens, and that by Alexander and Slifkin [61], who did the same in Al single crystals by means of a precision lathe sectioning. Hood [60] evaluated the diffusion behavior of Fe in both single crystal and polycrystalline specimens of Al, employing an ion implantation technique to deposit radioactive ⁵⁹Fe for a tracer-sectioning method. The diffusion of Fe in Al has also been measured by using Mossbauer spectroscopy [62], microtome technique [63], and ion implantation of radiotracers [69]. The pressure dependence of Fe diffusion in Al single crystals was measured by Becker et al. [73] using ion implantation of ⁵⁹Fe radiotracers.

The impurity diffusion of Ni in Al was reported by Hirano et al. [72] and Erdelyi et al. [74]. The data by Erdelyi et al. [74] were measured by the resistometric method, which is a diffusion couple technique without a profile measurement.

Since Mn is a primary alloying element in commercial Al alloys, the diffusion of Mn has been investigated by several researchers. While Fujikawa and Hirano [75] used ⁵⁴Mn radiotracer, Hood and Schultz [76] utilized implanted tracer deposits and measured the impurity diffusion of the stable isotope ⁵⁵Mn and the short-lived radioisotope ⁵⁶Mn in Al single crystals using a microtome sectioning technique. Studies reported earlier by Buckle [77], using a microhardness method, and Lundy and Murdock [57], using a lathe sectioning method, showed high rate of diffusion, which was attributed to the presence of an unidentified impurity in addition to the high dislocation and grain-boundary densities by Hood and Schultz [76].

Since Si is the most common element in commercial Al alloys, its diffusion in fcc Al has been investigated in detail. However, the experimental results of early work [77–80] are not in agreement with those reported later [71,81,82]. In all, the experimental procedure performed by Fujikawa and coworkers [81,82] is accepted as the most reliable.

Several reports on diffusion of Mg in Al exist in the literature [70,77,78,83–86]. Rothman et al. [85] measured the diffusion coefficient of Mg in Al using a microtome sectioning technique. Fujikawa and Hirano [86] carefully investigated the diffusion of ^{28}Mg in nearly single crystal Al by using the photo-nuclear reaction. Doig and Edington [84] obtained the diffusion coefficients of Mg in Al at low-temperatures by measuring the composition profile during the precipitation. These data are considered to be reliable since the problems associated with the initial interface, such as presence of oxide films and high local dislocation densities, were avoided.

Cu is also one of the most important alloying elements in commercial Al alloys, and hence its diffusion behavior in Al has been studied extensively [61,68,77,78,83,84,87–92]. Investigation has been carried out using a variety of techniques including microhardness method [77], profile measurement in diffusion couple [78,83], residual activity measurement [87], resistometric method [88], tracer-sectioning technique [61,68,90–92], γ -spectrometry and X-ray emission microanalysis [89], measurement of solute composition profiles at grain boundaries [84], and inductively coupled plasma-atomic emission spectrometry [93]. Out of these, the data reported by Alexander and Slifkin [61], Peterson and Rothman [68], Beyeler et al. [89], and Fujikawa and coworkers [90–92] seem to be the most reliable.

8.2.2 Diffusion in Zirconium and Its Alloys

8.2.2.1 Self- and Impurity Diffusion in Zirconium

Zirconium undergoes allotropic transformation from hcp (α -Zr) to bcc structure (β -Zr) upon heating at 1136 K. An early report on self-diffusion coefficient in α -Zr exists from the work of Naik and Agarwala [95], who reported low values of activation energy (Q) and pre-exponential factor (D_0), which was quantitatively explained on the basis of dislocations, although the diffusion data in this report exhibited a linear Arrhenius plot. Subsequently, Horvath et al. [96] through their ion-beam sputter-sectioning technique experiments with ^{95}Zr radiotracer penetrations in α -Zr showed a pronounced curvature in the Arrhenius plot. Also, an increase in the self-diffusion of Zr by about five orders of magnitude was observed at the α/β transition temperature, which was explained by the enhancement in the self-diffusion in the β -phase, close to the α/β phase transition, due to the phonon softening and the transition from bcc (more open structure) to hcp (closed packed structure) phase [97].

The origin of the nonlinear behavior in the Arrhenius plot for Zr is not well established. The effect of dislocations on diffusion properties has been discussed by Schultz and Hood [98] and Peterson [99]. Le Claire and Rabinovitch [100–102] showed through

their analysis that the effect of dislocation on diffusion is not appreciable if $(Dt)^{1/2}$ is about five times the dislocation spacings. Stassis et al. [103] have shown anomalies of the phonon dispersion curves in their investigation of the temperature dependence of the vibrational modes of α -Zr using inelastic-neutron-scattering. A downward curvature observed in the α -Zr self-diffusion denoted a decrease in the diffusion coefficient at temperatures near the α - β phase transition; however, such behavior is in contrast to that expected by assuming a phonon softening mode. It was pointed out by Hood [104] that the data reported by Horvath et al. [96] on diffusion in α -Zr in the temperature range 950–1130 K may have a solute enhancement effect. Therefore, the explanation for the curvature in the α -Zr Arrhenius plot was that since Fe is an ultra-fast impurity, its presence of about 20 ppm in the Zr samples [96] caused a solute-enhanced diffusion process in these samples. This enhancement in diffusion ceased at lower temperatures, when impurity Fe precipitates out of the solution [104]. Strong interaction between Fe impurities with vacancies has been experimentally observed in electron microscopic studies [105].

Some 3d transition elements such as Fe, Co, and Ni exhibit ultra-fast diffusion in the α -Zr matrix. The solutes at high temperatures were found to have diffusion coefficients which are about seven to eight orders of magnitude greater than those corresponding to self-diffusion in α -Zr [106]. In the cases of Fe [107] and Co [108] these elements show a downward curvature in the Arrhenius plot similar to the self-diffusion behavior. However, this is not the case with Ni [109] where no curvature can be noticed. The low activation energy for Fe diffusion in high temperature range is consistent with the atomic-size effect, and a kind of interstitial mechanism was assumed to be responsible for such high diffusion coefficients. A rapid increase in the effective activation energy, as the temperature falls below 900 K, may be associated with a tendency for the Fe atoms to precipitate forming some kind of second phase structure. Kidson [108] studied the diffusion in single crystals with different orientations and polycrystals of α -Zr using ^{60}Co and ^{58}Co isotopes. He presented the results as two linear Arrhenius plots, one above and the other below 923 K and attributed the break in diffusion coefficients to the low Co solubility in α -Zr below 923 K. It is possible to present these results as a curved Arrhenius plot similar to that obtained for the α -Zr self-diffusion.

Several workers have reported experimental results on the diffusion of impurity elements in α -Zr. A compilation of self- and impurity diffusion parameters in Zr is presented in Table 8.3. In most of these works the data are available in very narrow temperature ranges, close to the α/β phase transition, in samples with a high, or even unknown, impurity content. However, in order to understand their diffusion behavior properly, data should be available for extended ranges of temperature in relatively pure Zr host. Diffusion experiments on Ti [110], Hf [111], Pb [112], and Au in α -Zr matrix with an impurity content similar to that used in self-diffusion measurements were found to follow the curvature of the self-diffusion, with low diffusion parameters Q and D_0

Table 8.3 Parameters for self- and impurity diffusion in zirconium

Diffusion species	Diffusion phase	D_0 (m^2/s)	Q (kJ/mol)	Reference
Zr	α	5.06×10^{-12}	91.96	[124]
Zr	β	1.00×10^{-8}	112.8	[124]
Zr	β	2.40×10^{-8}	125.8	[138]
Zr	β	4.80×10^{-12}	86.5	[139]
Zr in single crystal	α	2.10×10^{-11}	112.8	[140]
Zr in single crystal	α	1.84×10^{-2}	319.0	[132]
Zr	α	$3.28 \times 10^{-23} - 1.04 \times 10^{-18}$		[96]
Ag	α	1.7×10^{-6}	204	[141]
Ag	β	2.5×10^{-8}	128	[141]
Al	β	5.6×10^{-6}	220.1	[121]
Cr	β	4.53×10^{-7}	137.8	[142]
Cr	α	1.0×10^{-5}	156.4	[143]
Cu	β	1.0×10^{-5}	155.0	[141]
Fe	β	5.3×10^{-7}	104.3	[144]
Mo	β	2.0×10^{-8}	147.7	[145]
Nb	α	1.88×10^{-4}	259.7	[146]
Nb	β	2.7×10^{-9}	116.8	[147]
Sn	α	2.0×10^{-12}	92.1	[122]
Sn	β	8.5×10^{-7}	169.5	[148]
U	β	3.6×10^{-4}	242.8	[149]

in the low temperature regime and high diffusion parameters in the high temperature regime. Since the atomic radius of those elements (Ti: 0.1462 nm, Hf: 0.158 nm, Pb: 0.175 nm, Au: 0.1442 nm) is similar to Zr atomic radius (0.1602 nm), a substitutional diffusion behavior is expected. The diffusion coefficients were found to be within a band of almost one order of magnitude, with the exception of the Ti diffusion [97].

A close analysis of the diffusion characteristics in β -Zr phase showed that the self- and impurity diffusion coefficients also exhibited nonlinear behavior in the Arrhenius plot. However, unlike the diffusion in the α -Zr phase, at higher temperatures, the diffusion coefficients are greater than the values extrapolated from low temperature diffusion coefficients. Such behavior is commonly termed as “anomalous diffusion”, primarily due to a curved plot of $\ln D$ versus $1/T$. Several explanations have been put forward by researchers over the years for these experimental observations. Some of these possible explanations are discussed here:

The curved nature of the Arrhenius plot prompts one to assume a change of the mechanism of diffusion in different temperature regimes. For example, the mechanism of diffusion can be postulated to occur due to a combination of monovacancies and

divacancies [113]. The diffusion coefficient can be represented as

$$D = D_{01} \exp(-Q_1/RT) + D_{02} \exp(-Q_2/RT) \quad (8.14)$$

where Q_1 and Q_2 represent the activation energies due to monovacancies and divacancies, respectively. However, such a model suffered from the drawback that it could not explain the isotope effect, since divacancy contribution would require a decrease in the isotope effect.

It was believed that the presence of oxygen impurity produces excess vacancies in Zr, thereby enhancing the rate of diffusion [114]. Even the presence of 100 ppm of O at high temperatures, which is difficult to avoid, is enough to produce a high concentration of structural vacancies. However, various experiments on diffusion in Zr containing 100 to 700 ppm of oxygen showed that the diffusion coefficient is independent of the concentration of oxygen.

The enhancement of diffusion was attributed to the participation of dislocations in Zr and its alloys by Kidson [115]. Naik and Agarwala [116] evaluated the enhancement factor assuming a dislocation density as 10^{13} lines/m², which yielded results that agreed well with the experimental results. However, such a high dislocation density is quite unlikely to exist at high temperatures. Aaronson and Shewmon [117] showed that the activation energy for migration of monovacancies is almost zero when the bcc phase is cooled to temperatures close to the transformation temperature, since the elastic constant $(C_{11} - C_{12})/2$ approaches zero at this temperature.

Sanchez and de Fontaine [118,119] proposed a model for anomalous diffusion in the β -phase of Zr-based alloys due to the presence of ω -embryos. The activated configuration of atomic structure at the saddle point of the $\langle 111 \rangle$ direction in the bcc phase is known as the ω -embryo. The formation of large population of such ω -embryos at temperatures close to the transition temperature causes a substantial reduction in the activation energy, thereby enhancing the diffusion coefficient in this temperature regime.

The anomalous behavior of self-diffusion of β -Zr was, to a large extent, explained by Kohler and Herzig [120]. They have proposed a model based on soft phonon without involving the presence of the ω -embryos. It is well known that the phonon spectra in these systems exhibit soft modes with wave vectors $q = 2/3 \langle 111 \rangle$ and $q = 1/2 \langle 110 \rangle$. While the former is associated with the β -to- ω transformation, the latter relates to the β -to- α transformation. Softening of the modes essentially leads to a lowering of the energy barrier associated with atomic displacements. These modes contribute to large fluctuations in the displacement coordinate, leading to small activation energies and correspondingly high diffusion coefficients.

The diffusion behavior of Al and Zr was investigated by Laik et al. [121] in the β -Zr phase in the temperature range 1203–1323 K by employing single-phase diffusion couples of pure Zr/Zr–2.8 wt.% Al. The activation energy for interdiffusion was found to

Table 8.4 Diffusion coefficients in zirconium based alloys

Diffusing element	Host alloy	Diffusion coefficients (m ² /s)		Reference
		α -Zr	β -Zr	
C	Zircaloy-2	$1.40 \times 10^{-7} \exp\left(\frac{-158.0 \text{ kJ/mol}}{RT}\right)$	$2.45 \times 10^{-5} \exp\left(\frac{-149.4 \text{ kJ/mol}}{RT}\right)$	[128]
Ce	Zircaloy-2	$1.52 \times 10^{-10} \exp\left(\frac{-124.3 \text{ kJ/mol}}{RT}\right)$	$2.86 \times 10^{-7} \exp\left(\frac{-129.1 \text{ kJ/mol}}{RT}\right)$	[127]
Cr	Zircaloy-2	$2.91 \times 10^{-10} \exp\left(\frac{-148.4 \text{ kJ/mol}}{RT}\right)$	$6.31 \times 10^{-6} \exp\left(\frac{-213 \text{ kJ/mol}}{RT}\right)$	[125]
Fe	Zircaloy-2	$2.56 \times 10^{-12} \exp\left(\frac{-112.8 \text{ kJ/mol}}{RT}\right)$	$1.30 \times 10^{-6} \exp\left(\frac{-195.6 \text{ kJ/mol}}{RT}\right)$	[125]
Nd	Zircaloy-2	$1.3 \times 10^{-10} \exp\left(\frac{-125.3 \text{ kJ/mol}}{RT}\right)$	$4.57 \times 10^{-7} \exp\left(\frac{-134 \text{ kJ/mol}}{RT}\right)$	[127]
Ni	Zircaloy-2	$1.0 \times 10^{-11} \exp\left(\frac{-122.4 \text{ kJ/mol}}{RT}\right)$	$7.30 \times 10^{-7} \exp\left(\frac{-199.5 \text{ kJ/mol}}{RT}\right)$	[126]
Sn	Zircaloy-2	$3.31 \times 10^{-10} \exp\left(\frac{-153.2 \text{ kJ/mol}}{RT}\right)$	$2.8 \times 10^{-5} \exp\left(\frac{-233.2 \text{ kJ/mol}}{RT}\right)$	[126]
C	Zr-2.5% Nb	$5.68 \times 10^{-7} \exp\left(\frac{-159.0 \text{ kJ/mol}}{RT}\right)$	$1.70 \times 10^{-5} \exp\left(\frac{-158 \text{ kJ/mol}}{RT}\right)$	[128]
Zr	Zr-1% Nb		$3.83 \times 10^{-9} \exp\left(\frac{-109.9 \text{ kJ/mol}}{RT}\right)$	[129]
Zr	Zr-3% Nb		$3.0 \times 10^{-9} \exp\left(\frac{-106.9 \text{ kJ/mol}}{RT}\right)$	[129]
Zr	Zr-1% Nb		$5.07 \times 10^{-9} \exp\left(\frac{-127.2 \text{ kJ/mol}}{RT}\right)$	[129]
Zr	Zr-3% Nb		$9.75 \times 10^{-9} \exp\left(\frac{-127.2 \text{ kJ/mol}}{RT}\right)$	[129]

decrease linearly with an increase in Al concentration. The activation energy and pre-exponential factor for impurity diffusion of Al in β -Zr was determined as 220.1 kJ/mol and 5.56×10^{-6} m²/s, respectively (Table 8.3). Upon comparing the values of these two parameters with those of other elements, for example, Co, Mn, Sn, V, Be, Fe, Ag, and Ta for diffusion in the β -Zr phase, both values were found to be on the higher side [121].

8.2.2.2 Diffusion in Zirconium Based Alloys

The most important Zr-based alloys that are used extensively in the nuclear industry are Zircaloy-2 and Zircaloy-4 – in both Sn is the major alloying element. Therefore, the effect Sn on the diffusion properties of these alloys is important primarily because many vital in-pile degradation mechanisms such as oxidation, creep and hydriding are related to the diffusion behavior of these alloys. The effect of Sn on the self-diffusion of Zr in the Zn-Sn alloys has been the focus of various studies by Federov and Zhomov [122], Lyashenko et al. [123], and Gruzin et al. [124]. Table 8.4 contains a compilation of the diffusion parameters in Zr-based alloys in the α and β phases based on work of various researchers [106,125–129]. It was reported that the diffusivity of Sn in Zr-Sn alloys decreases with increase in Sn content up to about 973 K [122,124]. Beyond this temperature, the diffusion coefficient of Sn again starts increasing with increase in Sn content. The activation energy for diffusion of Sn also increases from 91.5 kJ/mol to 170.6 kJ/mol up to a concentration of 1.97 at.% Sn. Such an increase in the activation energy can be attributed to the fact that addition of Sn impurity in Zr causes a rise in the stiffness of the matrix. Studies on the diffusion of Zr in the β -phase of Zircaloy-2 have also been reported [130]. When comparing these results with pure Zr and Zr-Sn

alloy, it was observed that up to 1473 K the diffusion coefficients are lower in Zr–Sn alloy and Zircaloy-2. Also, the diffusion coefficients in Zircaloy-2 are higher than those in Zr–Sn alloy, and correspondingly the activation energy in Zircaloy-2 is lower. This can be explained by the fact that presence of β -soluble elements like Fe and Ni leads to enhancement of diffusion.

Apart from Sn, other alloying elements in Zircaloy-2 and Zircaloy-4 are Fe, Ni, and Cr. The diffusion behavior of Fe, Ni, Cr, and Sn in Zircaloy-2 was studied by Pande et al. [125,126]. The activation energies for diffusion of Fe, Ni, Cr, and Sn were found to be 112.7, 122.4, 148.9, and 153.2 kJ/mol, respectively, in the α -Zr phase. It was noticed that unlike the temperature dependence of Fe and Cr in the α and β phases of pure Zr, the Arrhenius plots indicate three distinct regions: low temperature α -phase in the range 923–1053 K, β -phase 1253–1523 K, and the intermediate transition range of 1053–1253 K. While in the former two ranges, the temperature variation can be described using linear relationships, in the latter range (1053–1253 K) the plot of $\ln D$ versus $1/T$ deviates from linearity. The temperature dependence of diffusion coefficients of Cr and Fe in the α and β phases in Zircaloy-2 can be represented using the following equations [106]:

$$D_{Cr/\alpha}(923 - 1053 \text{ K}) = 2.91 \times 10^{-10} \exp\left(\frac{-148.9 \text{ kJ}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.15a)$$

$$D_{Cr/\beta}(1253 - 1523 \text{ K}) = 6.31 \times 10^{-6} \exp\left(\frac{-213.3 \text{ kJ}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.15b)$$

$$D_{Fe/\alpha}(923 - 1053 \text{ K}) = 2.56 \times 10^{-12} \exp\left(\frac{-112.7 \text{ kJ}}{RT}\right) \text{ m}^2/\text{s}, \quad (8.15c)$$

$$D_{Fe/\beta}(1253 - 1523 \text{ K}) = 1.03 \times 10^{-6} \exp\left(\frac{-195.5 \text{ kJ}}{RT}\right) \text{ m}^2/\text{s}. \quad (8.15d)$$

The values of the activation energy (Q) and pre-exponential factor (D_0) for the constituent elements of Zircaloy-2 are in general higher than those of the self-diffusion of Zr [106]. Such a conclusion can also be drawn from the studies by Federov and Zhomov [130]. It is interesting to note that the transition of the diffusion coefficients in the α and β phases is not sharp at a particular temperature. The transition extends over the range 1053–1253 K. This can be due to the presence of the second phase particles in Zircaloy which alters the diffusion behavior of these alloys significantly. However, the overall diffusion coefficient in this transition region can be described as a weighted average of diffusion coefficients in the corresponding α - and β -Zr phases. The diffusion coefficient can be calculated using the following relationship:

$$D = C_\alpha D_\alpha + C_\beta D_\beta \quad (8.16)$$

where C_α and C_β are the corresponding compositions of the two phases.

A few discrepancies in the diffusion coefficients of the alloying elements in Zircaloy were noticed. The diffusion coefficient of Ni in Zircaloy-2 was also later determined by Hood and Schultz [109]. They showed that the diffusion coefficient of Ni in Zr at 893 and 1120 K was 1.7×10^{-14} and 8.1×10^{-12} m²/s, respectively. However, these values were about four orders of magnitude higher than those reported by Pande and Agarwala [126]. It was also noted that the diffusion coefficients of substitutional elements were lower than those of the self-diffusion coefficients. The slower diffusing rate of Ni was attributed to the complex behavior with other alloying elements. The difference in the values of diffusion coefficient could be due to the difference in impurity levels in the matrix and also due to the different profiling techniques used in different studies. It has been discussed earlier that the presence of a very small amount of Fe as impurity in Zr can have profound influence on the diffusion behavior.

Reports also exist for the studies on diffusion behavior of various fission products in Zr alloys. For example, Paul and Agarwala [127] reported studies on diffusion of Cs and Nd in the α and β phases of Zircaloy-2. The diffusivity values for both these elements were similar and quite low. Also, the activation energies in the α and β phases are not quite different, unlike for Sn and Fe. In both these cases of diffusion of Cs and Nd, linearity was observed in the α and β phases, but not in the transition range. The diffusion coefficient in the transition range can be described as:

$$\log(D) = C_{\alpha} \log(D_{\alpha}) + C_{\beta} \log(D_{\beta}) \quad (8.17)$$

where D_{α} and D_{β} are the diffusion coefficients and C_{α} and C_{β} are the composition of the α and β phases, respectively.

It is interesting to learn about the diffusion behavior of interstitial impurity elements in the Zr-based alloys specifically with respect to the anomalous diffusion. Research has also been carried out in this direction. Agarwala and Paul [128] reported studies on diffusion of C in Zr. They reported that the values of Q and D_0 are 158.0 and 149.4 kJ/mol, and 1.41×10^{-7} and 2.457×10^{-5} m²/s in the α and β phases, respectively. Even in the case of diffusion of C a nonlinear relationship was observed in the transition temperature range as explained earlier for other solute elements, and the diffusion coefficient can be calculated in the transition range using the relationship in Eq. (8.17). An interstitial diffusion mechanism was assumed in this case. Further, it was observed that the diffusion coefficient in the β -Zr phase is about two to three orders of magnitude greater than that in α phase. A linear relationship exists between the values of activation energy for diffusion of other interstitial elements such as O, N, and H and C. Based on this relationship, the activation energy for diffusion of C was estimated to be 145.5 kJ/mol.

The diffusion of He in Zr is also of technological importance. Lewis and Farrell [131] determined the diffusion coefficient of He between 10^{-18} and 10^{-16} m²/s at

temperatures higher than 700 K and assumed a substitutional mechanism of diffusion to be operative. However, Hood [132] argued that in the open structure host metal, specific atoms may occupy the interstitial sites. The diffusivity values of He is similar to those of O and Cr in the equivalent temperature range, and hence He can therefore be assumed to diffuse by the interstitial mechanism.

Zirconium–niobium system is a very important alloy system in nuclear technology, since at least two alloy compositions are very widely used in nuclear reactors. Apart from Zircaloy-2 and Zircaloy-4, Zr-1% Nb alloy is also used as a cladding material. Also, the Zr-2.5% Nb alloy is used as the pressure tube material in tube type reactors, such as the CANDU. The studies by Ryakova and Gruzin [133] and Lyashenko et al. [123] on self-diffusion of Zr in Zr–Nb alloys showed a reduction in the self-diffusion coefficient of Zr due to the presence of Nb. However, the pre-exponential factor was found to increase due to the presence of Nb. The studies by Agarwala and Paul [128] on diffusion behavior of C in Zr-2.5 at.% Nb yielded the values of Q and D_0 as 144.6 kJ/mol and $4.68 \times 10^{-7} \text{ m}^2/\text{s}$ in the α phase and 158.0 kJ/mol and $1.7 \times 10^{-5} \text{ m}^2/\text{s}$ in the β phase. As can be seen, although the activation energies in the two phases are nearby, the values of D_0 vary by two orders of magnitude. Also, the activation energy for diffusion of C in the β -phase is almost the same as the self-diffusion in Zr. However, this does not imply that the diffusion of C is anomalous in nature, since C diffuses by interstitial mechanism as has been emphasized earlier.

Various authors have also reported on the diffusion of Zr and Nb across the α/β interphase boundaries in Zr-2.5% Nb alloys [134–136]. It was reported [134] that the diffusion coefficient for diffusion across the interphase boundary is six orders of magnitude greater for the α phase and about three to four orders of magnitude greater in the β phase, compared to the values in bulk diffusion in these phases. The diffusion of Nb across the interphase boundaries was found to be affected by the microstructural stability whereas diffusion of Zr remained unaffected [135,136]. This can be explained since Zr is the major element in these alloys. Since the growth of the α/β interphase boundaries is affected by the diffusion of Nb across the boundaries, it is expected to influence the diffusion behavior of Nb more than that of Zr.

The diffusion of Ni in the α -Zr phase was evaluated by Hood and Schultz [109]. The values of diffusion coefficient of Ni in α -Zr at 894 K and 1121 K were 1.1×10^{-13} and $8.9 \times 10^{-12} \text{ m}^2/\text{s}$, respectively. The values in Zr-2.5% Nb host are about two orders of magnitude lower than those in pure Zr. Tiwari et al. [129] carried out studies on self- and solute diffusion in Zr- x % Nb alloys ($x = 1\text{--}3\%$). Their study showed that in the β phase the values of Q and D_0 for diffusion of Zr are 109.9 kJ/mol and $3.83 \times 10^{-9} \text{ m}^2/\text{s}$, respectively, and those for diffusion of Nb are 127.2 kJ/mol and $5.07 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. The activation energy of Nb is larger than that of Zr in the β phase. It was also showed that addition of Nb enhances the diffusion process in Zr. The correlation factor for diffusion of Nb in β Zr-1% Nb alloy was found to be 0.92 by Tiwari et

al. [129]. Contrary to these results, studies by Herzig and Kohler [137] on diffusion behavior in β Zr–Nb system showed an decrease in diffusion coefficient of Nb in Zr. Addition of Nb showed to cause a continuous decrease in the curvature in the Arrhenius plot.

8.3 DIFFUSION IN STRUCTURAL MATERIALS

A nuclear reactor system consists of a large number of subsystems apart from the core. These include the pressure vessel to hold the core and coolant, mechanical support for the core components, piping for the coolant, and the control and shutdown mechanism. The requirement for the materials that are used in these applications might vary to some extent depending upon the reactor type, but should possess some basic properties. Mechanical strength, such as strength, ductility, and impact strength, and creep resistance must be adequate under operating conditions. In case of thermal reactors, materials used for in-core components should have low neutron absorption cross-section. However, this is not of much significance in case of fast reactors. These materials should not be susceptible to radiation damage such as embrittlement, void swelling, and corrosion. Primarily two classes of materials, viz., iron and nickel based alloys, are used in most of the structural components due to their suitable properties. Austenitic stainless steels of various grades are used in different applications in nuclear reactors such as piping, pumps, core barrel, and shroud, thermal shields and piping for coolant. They are also quite extensively used in fuel reprocessing plants and in the back-end of the fuel cycle. Ferritic stainless steels are also used, though to a lesser extent, in reactors. They find application mainly where moderate resistance to chemical attack is required and applications which require lower coefficient of expansion and higher thermal conductivity. These steels are easier to weld and fabricate and are less susceptible to stress–corrosion cracking, compared to austenitic stainless steel. Low alloy carbon steels are also an important class of reactor materials and are used in pressure vessels, piping, and other components where high corrosion resistance is not required.

Nickel based alloys, due to their high strength and resistance to oxidation and creep at high temperatures, are used in various applications in nuclear reactors. Various grades of Inconels are used in steam generator tubes and reactor vessel penetrations because they are less prone to intergranular corrosion and stress corrosion cracking. Hastelloys (containing 15–30% Mo besides Cr and Fe) possess excellent resistance to high temperature corrosion and hence are candidate materials for use under severe conditions of molten salt breeder reactors.

8.3.1 Self-Diffusion in Iron

A lot of work has been carried out by various researchers on self-diffusion characteristics of iron. The oldest evaluation of self-diffusion coefficient in Fe dates back to 1948 when

Birchenall and Mehl reported the values of activation energy (Q) and pre-exponential factor (D_0) as 323 kJ/mol and $3.4 \text{ m}^2/\text{s}$, respectively [150]. These values seem to be quite high compared to those evaluated recently by Iijima et al. [151], who reported the values of Q and D_0 as 252 kJ/mol and $2.76 \times 10^{-4} \text{ m}^2/\text{s}$, respectively. It should be pointed out here that the older data reported on diffusion coefficients lack reliability primarily due to two reasons: firstly, due to the techniques which were used in these studies, inherent errors are present in the measurements, and secondly, to some extent due to use of specimens of low purity. Later on, the influence of the magnetic transition on diffusion properties were realized by Borg and Birchenall [152] and Biffington et al. [153], following which the topic was investigated extensively by various researchers [154]. Most of these studies were carried out for low temperature diffusion using the sputter-microsectioning technique. However, since the topic is not of much significance in the present discussion, the readers are directed to a comprehensive review on the topic by Iijima and Hirano [155].

The measurement of self-diffusion by Iijima et al. [151], Lubbehusen and Mehrer [156] and Hettich et al. [157] using sputter-microsectioning technique showed that the self-diffusion coefficient of Fe varied between 10^{-22} – $10^{-15} \text{ m}^2/\text{s}$ in the temperature range 750–1200 K. The value of activation energy was found to increase below the Curie temperature as compared to that of the paramagnetic ferrite phase. The values of Q and D_0 , in the range of temperature from Curie point to α – γ transition temperature, are 250 kJ/mol and $2.76 \times 10^{-4} \text{ m}^2/\text{s}$, respectively [151]. The self-diffusion behavior was also studied in the δ -Fe phase by Buffington et al. [153], James and Leak [158], and Walter and Peterson [159]. The values of Q and D_0 were found to be 296 kJ/mol and $9.21 \times 10^{-3} \text{ m}^2/\text{s}$, respectively. The diffusion coefficient in the δ -Fe phase was found to be higher by factor of 1.3–1.7 when compared with the values of diffusion coefficient in paramagnetic α -Fe, extrapolated to high temperature range.

8.3.2 Impurity Diffusion in Iron

8.3.2.1 Diffusion of Chromium in Iron

Chromium is the most common alloying element in iron and is used to impart strength as well as corrosion and oxidation resistance properties in iron. Hence, the impurity diffusion behavior of Cr in Fe has been of interest, and therefore has been worked upon by various researchers. While Bowen and Leak [160] and Huntz et al. [161] used the residual activity method, Braun and Feller-Kniepmeier [162] used diffusion couples and EPMA to determine the diffusion coefficients of Cr in Fe. Lee et al. [163] used the sputter-microsectioning technique to determine the diffusion coefficients. All these studies, using various techniques, seem to be in agreement, and the diffusion coefficient of Cr was found to vary approximately between 5×10^{-15} and $5 \times 10^{-20} \text{ m}^2/\text{s}$ in the temperature range 900–1200 K. These studies [160–162] also suggested that the

influence of short-range magnetic spin ordering in diffusion of Cr in the paramagnetic regime of α -Fe is negligible as in the case with self-diffusion of Fe [151].

8.3.2.2 Diffusion of Nickel in Iron

Being the most widely used austenite stabilizer, Ni is a very important alloying element of iron. Studies on diffusion behavior of Ni in Fe were carried out by Hirano et al. [164] and Borg and Lai [165] using residual activity method, and by Cermak et al. [166] using the sputter-microsectioning at low temperatures and microtome sectioning method for high temperature measurements. The diffusion coefficient was found to vary between 10^{-15} and 5×10^{-21} m²/s in the temperature range 800–1200 K. The diffusion coefficients determined by various researchers were found to be in agreement. However, the activation energy for diffusion of Ni was lower than that for self-diffusion in α -Fe. At high temperatures, the data of Hirano et al. [164] matched with that of Cermak et al. [166].

8.3.2.3 Diffusion of Molybdenum and Manganese in Iron

Oikawa [167,168] presented a compilation of the experimentally determined diffusion parameters for impurity and interdiffusion in Fe-based systems. In the austenitic phase, the order of diffusion coefficients is $D_{\text{Mo}} > D_{\text{Mn}} \approx D_{\text{Cr}} > D_{\text{Fe}} > D_{\text{Ni}}$, while in the paramagnetic ferritic phase the order is $D_{\text{Mo}} \approx D_{\text{Mn}} > D_{\text{Cr}} \approx D_{\text{Ni}} > D_{\text{Fe}}$ [155]. For the diffusion of Mo in δ - and α -Fe phases, the pre-exponential factor is 6.63×10^{-5} m²/s and the activation energy is 224.2 kJ/mol, while for the γ -Fe phase the values of these parameters are 3.6×10^{-6} m²/s and 239.8 kJ/mol, respectively [167,168]. The corresponding values for diffusion of Mn are 7.56×10^{-5} m²/s and 224.5 kJ/mol for the ferrite phase, and 1.78×10^{-5} m²/s and 264.2 kJ/mol for the austenite phase, respectively [167,168].

8.3.3 Diffusion in Iron–Nickel System

Addition of Ni into stainless steel primarily stabilizes the austenite phase and hence is used in almost all austenitic and duplex stainless steels. The work by Million et al. [169] on diffusion of ⁵⁹Fe and ⁶³Ni in Fe–Ni alloys of wide composition range, measured within 1258–1578 K using residual activity method, showed that the diffusion coefficient of both the components increased in log-scale with increase in the concentration of Ni. The diffusion coefficient of Fe was systematically higher than that of Ni. However, near the composition Ni₃Fe, the short-range ordering has a pronounced effect on the thermodynamic factor and hence causes an enhancement of the interdiffusion coefficient [169,170]. The work by Kohn et al. [171] revealed that the intrinsic diffusion coefficient of Fe is larger than that of Ni at 1473 K ($D_{\text{Fe}} > D_{\text{Ni}}$). The study by Nakagawa et al. [172] on the interdiffusion behavior in the Fe–Ni system, in the temperature range

1123–1373 K using diffusion couples, showed that the interdiffusion coefficient assumes a low value at a composition around Fe–30 at.% Ni at low temperatures. Later on Goldstein and coworkers [173,174] measured the diffusion coefficient of Ni in martensites of the Fe–Ni system at temperatures as low as 573 K using scanning transmission electron microscope (STEM). Their results also showed a kink in the Arrhenius plot for diffusion of Ni in the temperature range 673–773 K.

8.3.4 Diffusion in Ferritic Stainless Steels

The stainless property is imparted to steels by alloying it with a minimum of 12 wt.% Cr. Being a ferrite stabilizer, Cr enhances the stability of ferrite in the presence of low concentration of C to form a technologically important class of materials called ferritic stainless steel. The diffusion properties of the Fe–Cr system have been extensively investigated with respect to both lattice and grain boundary diffusion. The studies by Ray and Sharma [175] and Kucera et al. [176] on the ferritic phase in the composition range 9–20 wt.% Cr and 0–11.8 wt.% Cr, respectively, showed that the diffusion coefficient of Fe increases with the concentration of Cr. Their work also indicated a pronounced effect of magnetic transformation in the ferrite phase on the diffusion of Fe. It was also reported that the presence of interstitial impurities such as C and N in the ferritic phase also enhances the lattice diffusion of Fe in alloys containing Fe–3 to 7.8 wt.% Cr [177]. This effect of enhancement of diffusion of Fe is even stronger for grain boundary diffusion [177]. Such an effect can be attributed to a reduction in the activation energy of Fe due to presence of C and N. In the composition range 30–70 at.% Cr in the Fe–Cr binary alloys, it was shown by Paxton et al. [178,179] that values of the activation energy and pre-exponential factor for diffusion of Fe and Cr pass through a minimum at about 30% Cr and a maximum at about 70% Cr. Although there exists a report on interdiffusion studies in the Fe–Cr system [180], the values of the interdiffusion coefficients were noticed to be considerably lower than the tracer diffusion coefficients.

8.3.5 Diffusion in Austenitic Stainless Steels

Austenitic stainless steels, specifically of type 304L and type 316, are extensively used in nuclear power plants. These materials are used in steam generator tubes of pressurized water reactors [181]. Also, the modified 316 LN grade of stainless steel finds application as the fuel clad material in sodium-cooled fast breeder reactors. Patil et al. [182] determined the diffusion behavior of the elements Mo, Zr, Co, Mn, Cr, and Fe in type 316 stainless steel. Their study showed that the diffusion coefficients are ordered as $D_{\text{Mo}} > D_{\text{Zr}} > D_{\text{Co}} > D_{\text{Mn}} > D_{\text{Cr}} > D_{\text{Fe}}$ at temperatures above 1368 K [155]. Mo was found to have a very high diffusivity in the austenitic stainless steel matrix and hence was classified as a fast diffuser in type 316 stainless steel. It may be noted that addition of Mo imparts void-swelling properties in stainless steel and hence is used in the clad material of fuels of fast breeder reactors. Patil et al. [182] also established an empirical linear

relationship between $\ln D_0$ and Q in type 316 stainless steel, which can be expressed by the equation

$$\ln D_0 = 7.47 \times 10^{-2} Q - 29.5 \quad (8.18)$$

where D_0 and Q are expressed in m^2/s and kJ/mol , respectively. Both coefficients in this relationship are consistent with the vacancy mechanism of diffusion, and hence it was assumed to be the most dominant mode of diffusion in this alloy. Iijima and Hirano [155] presented a collection of diffusion parameters in various Fe–Cr–Ni alloy systems.

For diffusion of Fe and Cr in type 304 stainless steel, the activation energies are 281 kJ/mol and 245 kJ/mol , respectively, and the pre-exponential factors are 5.8×10^{-5} and $8.0 \times 10^{-6} \text{ m}^2/\text{s}$, respectively [183,184]. Thorvaldsson and Salwen [185] estimated the diffusion coefficient of Cr at low temperature regime in the range 873–973 K using microanalysis of the Cr-depleted zone of sensitized 304 stainless steel. The activation energies for the diffusion of Fe, Cr, and Mo in type 316 stainless steel are 229, 243, and 143 kJ/mol , respectively; while the pre-exponential factors for these elements are 1.18×10^{-6} , 6.3×10^{-6} , and $1.68 \times 10^{-8} \text{ m}^2/\text{s}$, respectively [182,186,187]. Assassa and Guiraldenq [188] studied the effect of concentration of Si on the diffusion properties of Fe, Cr, and Ni in 316 type stainless steel. Their study showed that the activation energy for grain boundary diffusion was the lowest at 1 wt.% Si.

The use of Alloy 800, containing typically Fe–20.6% Cr–32.3% Ni, is ever increasing in the nuclear industry due to its superior mechanical and corrosion resistance properties and low cost compared to Ni-based superalloys. The steam generator tubes of the Indian pressurized heavy water reactors (PHWRs) being built in recent years are of Alloy 800. The studies by Paul et al. [189–191] and Federov et al. [192] provide information on the diffusion rates of Fe, Co, Ni, and Cr in this material. The activation energy for these elements varied in the narrow range 242–260 kJ/mol , in the temperature regime 1070–1500 K, the order being $Q_{\text{Fe}} > Q_{\text{Ni}} > D_{\text{Co}} > Q_{\text{Cr}}$. However, the order of diffusivity was found as $D_{\text{Ni}} > D_{\text{Co}} > D_{\text{Cr}} > D_{\text{Fe}}$ [155].

The diffusion behavior of the constituent elements changes in nature in fine-grained materials compared to coarse-grained material, primarily because of increased contribution of diffusion through the grain boundaries. In case of stainless steel such behavior can be observed in the work reported by Perkins et al. [183]. It was shown that in the matrix of Fe–17% Cr–12% Ni the order for diffusion coefficients is $D_{\text{Cr}} > D_{\text{Fe}} > D_{\text{Ni}}$ for lattice diffusion in all temperature regimes, whereas for grain boundary diffusion the order is $D_{\text{Ni}} > D_{\text{Cr}} > D_{\text{Fe}}$ below 1123 K and $D_{\text{Fe}} > D_{\text{Cr}} > D_{\text{Ni}}$ above 1123 K [155].

8.3.6 Diffusion in Nickel

8.3.6.1 Self-Diffusion in Nickel

The earliest work on self-diffusion of Ni was reported by Hoffman et al. [193] and Reynold et al. [194] using ^{63}Ni radioisotope tracer. While Hoffman et al. [193] reported

an activation energy of 279.7 kJ/mol and pre-exponential factor of 1.27×10^{-4} m²/s in the temperature range 1151–1521 K, Reynold et al. [194] reported an activation energy of 267.1 kJ/mol and pre-exponential factor of 4.0×10^{-5} m²/s in the temperature range 1373–1448 K. The contribution of divacancy on self-diffusion was pointed out by Seeger et al. [195,196]. However, since the temperature range of measurement was rather narrow, the contribution of divacancy seems overestimated. Bakker [197] in his work estimated the self-diffusion of Ni in a moderate temperature range of 1253–1670 K, using the method of residual activity measurement of ⁶³Ni radioisotope. The activation energy and pre-exponential factor were computed as 285 kJ/mol and 1.77×10^{-4} m²/s, respectively. His work also confirmed the presence of a curvature in the Arrhenius plot of Ni. Subsequently, Maier et al. [198] extended the measurement of self-diffusion at lower temperature range 813–1193 K by adopting the sputter-microsectioning method and reported the values of the activation energy and pre-exponential factor as 281 kJ/mol and 1.33×10^{-4} m²/s, respectively, which are not much different from those estimated at high temperatures. In their work, Maier et al. [198] also estimated the isotope effect for self-diffusion of Ni and found that the contribution of divacancy increases at high temperatures. Later Neumann and Tolle [199] estimated that individual contribution of monovacancy and divacancy to the diffusion of self-diffusion of Ni. According to them, the divacancy mechanism has about 23% contribution to the total diffusion at temperatures near the melting point. The total diffusion coefficient can be described as [155]:

$$D = D^{1V} + D^{2V} = D_0^{1V} \exp(-Q^{1V}/RT) + D_0^{2V} \exp(-Q^{2V}/RT). \quad (8.19)$$

The parameters in Eq. (8.19) were estimated to be $D_0^{1V} = 8.5 \times 10^{-5}$ m²/s, $Q^{1V} = 277$ kJ/mol, $D_0^{2V} = 1.35 \times 10^{-5}$ m²/s and $Q^{2V} = 400$ kJ/mol.

8.3.6.2 Impurity Diffusion in Nickel

The primary alloying elements in Ni-based alloys relevant to nuclear technology are Cr, Fe, Ti, Nb, Al, Co, Mo, Ta, V, and W. These alloying elements are commonly used in Ni-based superalloys, which are mainly used at high temperatures. The diffusion behavior of these elements in Ni has been studied by various researchers. The diffusion parameters have been summarized in Table 8.5. It may be noted that in most of these studies, the diffusion coefficients were calculated using suitable radioisotope tracer, followed by serial sectioning and by using diffusion couples.

8.3.6.3 Diffusion in Nickel Based Alloys

Ni-based alloys possess unique combination of properties such as high temperature strength, creep resistance, and oxidation resistance, which make them suitable materials for a host of applications in nuclear power plants. Alloying Ni with Cr makes it

Table 8.5 Parameters for impurity diffusion in nickel

Solute	Temperature range (K)	Experimental method	D_0 ($\times 10^{-4} \text{ m}^2/\text{s}$)	Q (kJ/mol)	Reference
Al	914–1212	Vapor deposition; SIMS	5.06	260.0	[200]
Co	855–1255	^{57}Co electroplated; residual activity	0.55	265.5	[201]
Co	1323–1648	Ni/Ni–4.85%Co couple; EPMA	1.8	282.0	[202]
Cr	1223–1423	^{51}Cr electroplated; residual activity	8.52	292.1	[203]
Cr	1323–1648	Ni/Ni–5.06%Cr couple; EPMA	5.2	289.0	[202]
Cu	1327–1632	^{64}Cu ; lathe	0.57	258.3	[204]
Cu	1123–1323	^{64}Cu electroplated; residual activity	0.66	255.4	[87]
Cu	1080–1613	Cu serial sectioning	0.61	255.0	[205]
Fe	1409–1629	Ni/Fe couple; EPMA	0.22	252.9	[206]
Fe	1478–1669	^{59}Fe electroplated; grinding	1.0	269.4	[207]
Mo	1323–1623	Ni/Ni–2.97%Mo couple; EPMA	1.3	283.0	[208]
Mo	1173–1573	Ni/Ni–6.5%Mo couple; EPMA	1.15	281.3	[209]
Nb	1116–1527	diffusion couple; EPMA	1.3	261.7	[71]
Nb	1173–1500	Ni/Ni–3%Nb couple; EPMA	0.88	257.0	[209]
Ta	1117–1532	Ni/Ta couple; EPMA	0.4	257.5	[71]
Ta	1173–1573	Ni/Ni–3%Ta couple; EPMA	0.22	251	[210]
Ti	1323–1648	Ni/Ni–3.41%Ti couple; EPMA	14.1	275	[202]
V	1073–1573	^{48}V salt sol.; residual activity	0.87	278.4	[211]
W	1423–1623	Ni/Ni–1.94%W couple; EPMA	2.1	303.0	[212]

stronger and improves high temperature oxidation resistance properties. Ni alloys very easily with Co and Cu because of their complete solid solubility in nickel. Also, the ternary system of Ni–Cr–Fe forms the base of different commercial superalloys, for example, Alloy 600, Alloy 690, and Alloy 625, which are extensively used in high temperature applications such as steam generator tubings and various in-core components in boiling and pressurized water reactors, and in vitrification of high level nuclear waste.

Nickel–Copper Alloys. Various grades of commercial alloy Monel (Ni–30–40% Cu), which is corrosion resistant, are used in applications such as steam generator tubes and tube sheet. Studies on tracer diffusion behavior in Ni–Cu alloys, using radioisotopes ^{63}Ni and ^{64}Cu , have been reported by Monma et al. [204]. The diffusion coefficients of both Ni and Cu were found to increase with increase in Cu concentration. One of the widely adopted methods to study the intrinsic diffusion of the constituent elements is by measuring the shift in the position of the markers, due to Kirkendall effect, put at the original interface of the two end members of diffusion couples. Heumann and Grundhoff [213] used the equations developed by Levasseur and Philibert [214] to determine the concentration dependent intrinsic diffusion coefficients. Cornet and Calais [215,216] generalized and extended the use of the analysis made by Levasseur and Philibert [214]. Iijima et al. [217] also studied the diffusion in Ni–Cu diffusion couples using CrO markers and analyzed the results using the method developed by Cornet and Calais [215,216]. It was found that the values of intrinsic diffusion coefficients determined in the studies by Heumann and Grundhoff [213] and Iijima et al. [217] are in agreement. However, on the Cu-rich side, the values of the interdiffusion coefficient ($\bar{D}$) and the intrinsic diffusion coefficients of Ni and Cu (D_{Ni} and D_{Cu}) determined by Iijima et al. [217] seem to be on the higher side. The ratio of diffusivities $D_{\text{Cu}}/D_{\text{Ni}}$ was found to be 4.6 and 2.5 for concentrations of 30 and 80 at.% Cu, respectively [155].

Nickel–Chromium Alloys. Tracer diffusion coefficients of Ni and Cr were determined in Ni–Cr binary alloys by Monma et al. [218] and Ruzickova and Million [203] using radiotracers ^{63}Ni and ^{51}Cr . Monma et al. [218] selected composition ranges up to 30 at.% Cr in the temperature range 1373–1677 K, while the studies by Ruzickova and Million [203] were carried out in the range 1223–1473 K for compositions up to 47.7 at.%. Both works reported that diffusion coefficients of Ni and Cr decrease with increase in Cr content and reach a minimum at the concentration of 35 at.% Cr. The ratio $D_{\text{Cr}}/D_{\text{Ni}}$ was found to vary between 1.5 and 2.0 in the temperature range of study. The activation energies Q_{Ni} and Q_{Cr} ranged between 280 and 290 kJ/mol. Monma et al. [218] showed that in the concentration range 0–30 at.% Cr, $Q_{\text{Cr}} > Q_{\text{Ni}}$, whereas, according to Ruzickova and Million [203], $Q_{\text{Ni}} > Q_{\text{Cr}}$ in the same concentration range. However, in the concentration range 37–47 at.% Cr, $Q_{\text{Cr}} > Q_{\text{Ni}}$ [203]. The studies by Moulin et al. [219] on lattice and grain boundary diffusion of Ni and Cr on alloy Ni–20 at.% Cr, containing varying concentration of carbon (0.0015, 0.06, and 0.01%) showed that the concentration of carbon does not have any effect on the lattice diffusion of both Ni and Cr. Delaunay et al. [220] worked on the effect of doping the alloy with a small amount of rare earth metals such as yttrium. They showed that addition of 350 ppm of Y on Ni–20 at.% Cr alloy results in reduction in the lattice as well as grain boundary diffusion coefficients in this alloy.

Nickel–Chromium–Iron Alloys. As stated earlier, Ni-based Ni–Cr–Fe alloys are widely used as heat resistant materials. However, some of these alloys suffer from stress–corrosion–cracking and intergranular fracture in the environment of service. As a solution to this, suitable heat treatments were devised and various modifications to the alloy chemistry were proposed. The diffusion behavior of the constituent elements plays an important role in these modifications [181]. Chen et al. [221] determined the lattice and grain boundary diffusion coefficients of ^{51}Cr in Inconel 600M containing Ni–16 wt.% Cr–7 wt.% Fe–2 wt.% Mo and 0.004 and 0.015 wt.% C, in the temperature range 858–1346 K, using the sputter-microsectioning technique. Their work showed that an increase in concentration of C effectively reduces the lattice diffusion of Cr. An increase in carbon content also has a similar effect on the grain-boundary diffusion of Cr. This tendency is in qualitative agreement with the results observed in Ni–20 at.% Cr and 0.0015–0.06 at.% C [219]. Such behavior indicated an interaction process between Cr and C at the grain boundaries. Kale et al. [222] reported interdiffusion studies in the fcc solid solution phase of the Ni–Cr–Fe system in the composition range Ni–2–30% Cr and 0–51% Fe at temperature 1223 K. It was shown that the ternary interdiffusion coefficients are of the order $10^{-16} \text{ m}^2/\text{s}$. The direct interdiffusion coefficients $D_{\text{CrCr}}^{\text{Fe}}$ and $D_{\text{NiNi}}^{\text{Fe}}$ are positive, whereas the diagonal interdiffusion coefficients $D_{\text{NiCr}}^{\text{Fe}}$ and $D_{\text{CrNi}}^{\text{Fe}}$ are negative.

REFERENCES

- [1] H.J. Matzke, in: R.P. Agarwala (Ed.), *Diffusion Processes in Nuclear Materials*, North Holland, Amsterdam, 1992, p. 9.
- [2] H.J. Matzke, *J. Less Comm. Metals* 21 (1986) 537–564.
- [3] G. Neumann, G. Tuijn, *Self-Diffusion and Impurity Diffusion in Pure Metals*, Handbook of Experimental Data, Pergamon, Amsterdam, 2009.
- [4] D. Calais, J.A. Cornet, *Mem. Sci. Rev. Met.* 69 (1972) 493.
- [5] N.L. Peterson, S.J. Rothman, *Phys. Rev. A* 136 (1964) 842.
- [6] D. Keiser, S. Hayes, M. Mayer, C. Clark, *JOM* 55 (2003) 55–58.
- [7] K. Huang, Y. Park, D.D. Keiser Jr., Y.H. Sohn, *J. Phase Equil. Diff.* 34 (2013) 307–312.
- [8] K. Huang, D.D. Keiser Jr., Y.H. Sohn, *Metall. Mater. Trans. A* 44 (2013) 307–312.
- [9] J.L. Snelgrove, G.L. Hofman, M.K. Mayer, C.L. Trybus, T.C. Weincek, *Nucl. Eng. Des.* 178 (1997) 119–126.
- [10] S. Neogy, M.T.S.A. Laik, D. Srivastava, S.K. Jha, G.K. Dey, *Philos. Mag. Lett.* 94 (2014) 163–171.
- [11] H.J. Matzke, *Science and Technology of Advanced LMFBR Fuels*, A Monograph on Solid State Physics, Chemistry and Technology of Carbides, Nitrides and Carbonitrides of Uranium and Plutonium, North Holland, Amsterdam, 1986.
- [12] H.J. Matzke, in: P. Vincenzini (Ed.), *Ceramics Today–Tomorrow’s Ceramics*, Elsevier, 1991, p. 2961.
- [13] H.J. Matzke, *Ceramics International* 17 (1991) 31.
- [14] H.J. Matzke, *J. Nucl. Mater.* 3 (1961) 267 and 311.
- [15] J. Belle, *J. Nucl. Mater.* 30 (1969) 3.
- [16] J.F. Marin, P. Contamin, *J. Nucl. Mater.* 30 (1969) 16.
- [17] R. Lindner, F. Schmitz, *Z. Naturforsch.* 169 (1961) 1373.

- [18] F. Schmitz, A. Marajofsky, Thermodynamics of Nuclear Materials, IAEA, Vienna, 1974.
- [19] HJ. Matzke, J. Phys. (Paris) 34 (1973) 317.
- [20] HJ. Matzke, Amer. Ceram. Soc. 17 (1986) 1.
- [21] HJ. Matzke, Faraday Trans. 83 (1987) 1124.
- [22] M. Dorado, J. Durinck, P. Garcia, M. Freyss, M. Bertolus, J. Nucl. Mater. 400 (2010) 103–106.
- [23] D. Glasser-Leme, HJ. Matzke, Solid State Ionics 12 (1984) 217.
- [24] Z. Hadari, M. Kroupp, Y. Wolfson, J. Appl. Phys. 42 (1971) 534.
- [25] K. Ando, Y. Oishi, J. Nucl. Sci. Technol. 16 (1979) 214.
- [26] R.L. Deaton, C.J. Weidenheft, J. Inorg. Nucl. Chem. 35 (1973) 214.
- [27] A.S. Bayoglu, R. Lorenzelli, Solid State Ionics 12 (1984) 53.
- [28] E. Moore, C. Gueneau, J.P. Crocombette, J. Solid State Chem. 203 (2013) 145–153.
- [29] F. Gupta, A. Pastural, G. Brillant, Phys. Rev. B 81 (2010) 014110.
- [30] W. Chubb, R.W. Getz, C.W. Townley, J. Nucl. Mater. 13 (1964) 63–74.
- [31] H.M. Lee, R.L. Barbett, J. Nucl. Mater. 27 (1968) 275–284.
- [32] C.R.A. Catlow, J. Nucl. Mater. 60 (1976) 151–157.
- [33] B. Lindner, G. Riemer, H.L. Scherff, J. Nucl. Mater. 23 (1967) 222–230.
- [34] HJ. Matzke, J.L. Routbort, H.A. Tasman, J. Appl. Phys. 45 (1974) 5187.
- [35] J.L. Routbort, HJ. Matzke, J. Nucl. Mater. 54 (1974) 1.
- [36] T. Inoue, HJ. Matzke, J. Nucl. Mater. 91 (1980) 1.
- [37] J.L. Routbort, HJ. Matzke, J. Amer. Ceram. Soc. 58 (1975) 81.
- [38] HJ. Matzke, Solid State Ionics 12 (1984) 25.
- [39] H. Matsui, HJ. Matzke, J. Nucl. Mater. 89 (1980) 41.
- [40] M. Freyss, Phys. Rev. B 81 (2010) 014101.
- [41] F. Jeanne, PhD Thesis, Univ. Grenoble, 1972.
- [42] S. Hayes, J. Thomas, K. Peddicord, J. Nucl. Mater. 171 (1990) 300.
- [43] V.J. Tennery, T.G. Godfrey, R.A. Potter, J. Amer. Ceram. Soc. 54 (1971) 327.
- [44] M.H. Bradbury, HJ. Matzke, J. Nucl. Mater. 75 (1978) 68.
- [45] J.W. Droege, C.A. Alexander, U. S. Rep. BMI-1882, 1970.
- [46] A.Yu. Kuksin, S.V. Starikov, D.E. Smirnova, V.I. Tseplyaev, J. Alloys Compd. 658 (2016) 385–394.
- [47] HJ. Matzke, Radiation Effects 53 (1980) 219.
- [48] HJ. Matzke, in: Donnelly (Ed.), Fundamental Aspects of Inert Gases in Solids, Plenum, New York, 1963, p. 401.
- [49] G.T. Lawrence, J. Nucl. Mater. 71 (1978) 195–218.
- [50] J.M. Harp, PhD Thesis, North Carolina State Univ., 2010.
- [51] A.H. Booth, AECL Report DCI-27, 1957.
- [52] HJ. Matzke, Nucl. Appl. 2 (1966) 131.
- [53] W. Miekeley, F. Felix, J. Nucl. Mater. 42 (1972) 297.
- [54] J.C. Carter, E.J. Drisoll, T.S. Elleman, Phys. Stat. Sol. A 14 (1972) 673.
- [55] D.A. MacInnes, P.W. Winter, J. Phys. Chem. Sol. 49 (1988) 143.
- [56] HJ. Matzke, J. Nucl. Mater. 21 (1967) 190.
- [57] T.S. Lundy, F.S. Murdock, J. Appl. Phys. 33 (1962) 1671.
- [58] J. Friedel, in: J. Friedel, A. Guinier, W.A. Benjamin (Eds.), Metallic Solid Solutions, 1963.
- [59] Y. Du, Y.A. Chang, B. Huang, W. Gong, Z. Jin, H. Xu, Z. Yuan, Y. Liu, Y. He, F.Y. Xie, Mater. Sci. Engg. A 363 (2003) 140–151.
- [60] G.M. Hood, Phil. Mag. 21 (1970) 305.
- [61] W.B. Alexander, L.M. Slifkin, Phys. Rev. B 1 (1970) 3274.
- [62] S. Mantl, W. Petry, K. Schroeder, G. Vogl, Phys. Rev. B 27 (1970) 5313.
- [63] D.L. Beke, I. Godeny, I.A. Szabo, G. Erdelyi, F.J. Kedves, Philos. Mag. A 55 (1987) 425.
- [64] G.P. Tiwari, B.D. Sharma, Philos. Mag. 24 (1971) 739.

- [65] J.S. Netchajev, A.A. Zsuhovickii, *Fiz. Metall. i Metalloved.* 51 (1981) 326.
- [66] M.S. Anand, B.M. Pande, R.P. Agarwala, in: R.P. Agarwala (Ed.), *Diffusion Processes in Nuclear Materials*, North Holland, Amsterdam, 1992, p. 149.
- [67] R.P. Agarwala, S.P. Murarka, M.S. Anand, *Acta Metall.* 12 (1964) 871.
- [68] N.L. Peterson, S.J. Rothman, *Phys. Rev. B* 1 (1970) 3264.
- [69] G. Rummel, T. Zumkley, M. Eggersmann, K. Freitag, H. Mehrer, *Z. Metallkd.* 85 (1995) 122.
- [70] W.G. Fricke, in: K.R. van Horn (Ed.), *Aluminum*, vol. 1, Properties, Physical Metallurgy and Phase Diagrams, American Society for Metals, Metals Park, Ohio, 1967.
- [71] D. Bergner, N. van Chi, *Wiss. Zeitschrift Padagogischen Hochschule* 15 (1977) 15.
- [72] K.I. Hirano, R.P. Agarwala, M. Cohen, *Acta Met.* 10 (1962) 857.
- [73] C. Becker, G. Erdelyi, G. Hood, H. Mehrer, *Defect and Diff. Forum* 66–69 (1989) 409.
- [74] G. Erdelyi, D.L. Beke, F.J. Kedves, I. Godeny, *Philos. Mag. B* 38 (1978) 445.
- [75] S. Fujikawa, K. Hirano, *Mater. Sci. Forum* 13–14 (1978) 539.
- [76] G.M. Hood, R.J. Schultz, *Philos. Mag.* 23 (1971) 1479.
- [77] B. Buckle, *Z. Elektrochem.* 49 (1943) 238.
- [78] A. Beerwald, *Z. Elektrochem.* 45 (1939) 789.
- [79] R.F. Mehl, F.N. Rhines, K.A. von den Steinen, *Metals Alloys* 13 (1941) 13.
- [80] W. Roth, *Metall. Tech.* 14 (1960) 979.
- [81] K. Hirano, S. Fujikawa, *Kakuriken Kenkyu Hokoku (Tohoko Daigaku)* 9 (1976) 291.
- [82] S. Fujikawa, K. Hirano, *Metall. Trans. A* 9 (1978) 1811.
- [83] R.M. Brick, A. Phillips, *Trans. AIME* 124 (1937) 331.
- [84] P. Doig, J.W. Edington, *Philos. Mag.* 28 (1973) 961.
- [85] S.J. Rothman, N.L. Peterson, L.J. Nowicki, L.C. Robinson, *Phys. Status Solidi B* 63 (1974) K29.
- [86] S. Fujikawa, K. Hirano, *Mater. Sci. Engg.* 27 (1977) 25.
- [87] M.S. Anand, S.P. Murarka, R.P. Agarwala, *J. Appl. Phys.* 36 (1965) 3860.
- [88] S. Ceresara, *Phys. Status Solidi* 27 (1968) 517.
- [89] M. Beyeler, M.F. Maurice, R. Seguin, *Mem. Sci. Rev. Met.* 67 (1970) 295.
- [90] S. Fujikawa, K. Hirano, *Defect Diff. Forum* 66–69 (1989) 447.
- [91] S. Fujikawa, S. Ushino, *Kakuriken Kenkyu Hokoku (Tohoku Daigaku)* 24 (1991) 128.
- [92] S. Ushino, S. Fujikawa, K. Hirano, *Keikinzoku* 41 (1991) 433.
- [93] A. Combe, J. Cabane, *Analisis* 20 (1992) 28.
- [94] G.M. Hood, R.J. Schultz, *J. Armstrong, Phil. Mag. A* 47 (1983) 775.
- [95] M.C. Naik, R.P. Agarwala, *Acta Met.* 15 (1967) 1521.
- [96] J. Horvath, F. Dymont, H. Mehrer, *J. Nucl. Mater.* 126 (1984) 206–214.
- [97] R.A. Perez, H. Nakajima, F. Dymont, *Mater. Trans.* 44 (2003) 2–13.
- [98] R.J. Schultz, G.M. Hood, *J. Nucl. Mater.* 135 (1985) 292.
- [99] N.L. Peterson, *Comm. Solid State Phys.* 8 (1978) 93.
- [100] A.D. LeClaire, A. Robinovitch, *J. Phys. C* 14 (1981) 3863.
- [101] A.D. LeClaire, A. Robinovitch, *J. Phys. C* 15 (1982) 3455.
- [102] A.D. LeClaire, A. Robinovitch, *J. Phys. C* 16 (1983) 2087.
- [103] C. Stassis, J. Zarestky, D. Arch, O.D. McMasters, B.N. Harmon, *Phys. Rev. B* 18 (1978) 2632–2642.
- [104] G.M. Hood, *J. Nucl. Mater.* 135 (1985) 292–295.
- [105] M. Griffiths, R.W. Gilbert, *J. Nucl. Mater.* 150 (1987) 169.
- [106] R.P. Agarwala, *Diffusion and Defect Studies in Zirconium and Some of Its Alloys*, Trans Tech Publication, Switzerland, 2004.
- [107] H. Nakajima, G.M. Hood, R.J. Schultz, *Philos. Mag. B* 58 (1988) 319–337.
- [108] G.V. Kidson, *Philos. Mag. A* 44 (1981) 341–355.
- [109] G.M. Hood, R.J. Schultz, *Mater. Sci. Forum* 15–18 (1987) 475–480.
- [110] G.M. Hood, H. Zou, R.J. Schultz, E.H. Bromley, J.A. Jackman, *J. Nucl. Mater.* 217 (1994) 229–232.

- [111] G.M. Hood, H. Zou, R.J. Schultz, J.A. Roy, J.A. Jackman, *J. Nucl. Mater.* 189 (1992) 226–230.
- [112] R.A. Perez, F. Dymont, *Appl. Phys. A* 68 (1999) 667–671.
- [113] A. Seeger, H. Mehrer, in: A. Seeger, D. Schumacher, W. Schilling, J. Diehl (Eds.), *Vacancies and Interstitials in Metals*, North Holland Publishing Co., Amsterdam, 1970, p. 1.
- [114] G.V. Kidson, *Can. J. Phys.* 41 (1963) 1563.
- [115] G.V. Kidson, *Diffusion in body centered cubic metals*, in: J.A. Wheeler, F.R. Winslow (Eds.), *Proc. Intl. Conf. Gatlinburg*, Amer. Soc. for Metals, 1964, p. 329.
- [116] M.C. Naik, R.P. Agarwala, *J. Phys. Chem. Solids* 30 (1969) 2330.
- [117] H.I. Aaronson, P.G. Shewmon, *Acta Met.* 15 (1967) 385.
- [118] J.M. Sanchez, D. de Fortaine, *Phys. Rev. Lett.* 35 (1975) 227.
- [119] J.M. Sanchez, D. de Fortaine, *Acta Met.* 2635 (1978) 1083.
- [120] U. Kohler, C. Herzig, *Philos. Mag. A* 58 (1988) 76.
- [121] A. Laik, K. Bhanumurthy, G.B. Kale, *J. Nucl. Mater.* 305 (2002) 124–133.
- [122] G.B. Federov, F.I. Zhomov, *Metallurgiya i Metallovedenie Chistykh Metallov* 1 (1959) 162.
- [123] V.S. Lyashenko, V.N. Bykov, L.V. Pavlinov, *Fiz Metall. i Metalloved.* 8 (1959) 40.
- [124] P.L. Gruzin, V.S. Emelyanov, G.G. Ryabova, G.B. Federov, In: *2nd Inter. Conf. Peaceful Uses of Atomic Energy*, Geneva, 1958, p. 187.
- [125] B.M. Pande, M.C. Naik, R.P. Agarwala, *J. Nucl. Mater.* 28 (1968) 324.
- [126] B.M. Pande, R.P. Agarwala, *J. Nucl. Mater.* 42 (1972) 324.
- [127] A.R. Paul, R.P. Agarwala, *Thermodynamics of Nuclear Materials*, IAEA, Vienna, 1975.
- [128] R.P. Agarwala, A.R. Paul, *J. Nucl. Mater.* 58 (1975) 25.
- [129] G.P. Tiwari, B.D. Sharma, V.S. Raghunathan, R.V. Patil, *J. Nucl. Mater.* 46 (1973) 35.
- [130] G.B. Federov, F.I. Zhomov, *Metallurgiya i Metallovedenie Chistykh Metallov Sb. Nauch. Rabot* 3 (1961) 43.
- [131] M.B. Lewis, K. Ferrell, *Nucl. Instr. Meth. B* 16 (1986) 163.
- [132] G.M. Hood, *J. Nucl. Mater.* 159 (1988) 149.
- [133] G.G. Ryakova, P.L. Gruzin, *Metallurgiya i Metallovedenie Chistykh Metallov* 3 (1961) 120.
- [134] M.J. Iribarren, F. Dymont, *J. Nucl. Mater.* 167 (1989) 148.
- [135] R. Piotrkowski, F. Dymont, *J. Nucl. Mater.* 137 (1986) 94.
- [136] R. Piotrkowski, *J. Nucl. Mater.* 183 (1991) 221.
- [137] C. Herzig, U. Kohler, *Mater. Sci. Forum* 15–18 (1985) 301.
- [138] G. Kidson, J. McGurn, *Can. J. Phys.* 39 (1961) 1146.
- [139] J.I. Federer, T.S. Lundy, *Trans. Met. Soc. AIME* 227 (1963) 592.
- [140] F. Dymont, C.M. Libanati, *J. Mater. Sci.* 3 (1968) 349.
- [141] Y. Iijima, O. Taguchi, *J. Mater. Sci. Lett.* 14 (1995) 486.
- [142] R.V. Patil, G.P. Tiwari, B.D. Sharma, *Philos. Mag. A* 44 (1981) 717.
- [143] G.M. Hood, R.J. Schultz, *J. Nucl. Mater.* 200 (1993) 141.
- [144] J. Trampenau, C. Herzig, *J. Phys.: Condens. Matter.* 2 (1990) 9345.
- [145] A.R. Paul, M.S. Anand, M.C. Naik, R.P. Agarwala, in: *Inter. Conf. Vacancies and Interstitials in Metals*, Jülich 1, 1968, p. 105.
- [146] G.M. Hood, H. Zou, R.J. Schultz, N. Matsuura, *Defect and Diffusion Forum* 143–147 (1997) 55.
- [147] G. Neumann, V. Tolle, *Z. Metallk.* 82 (1991) 741.
- [148] B. Chelluri, D. Lazarus, C.A. Wert, *Phys. Rev. B* 23 (1981) 4849.
- [149] G.B. Federov, E.A. Smirnov, F.I. Zhomov, V.N. Gusev, S.A. Paraev, *Met. Metalloved. Chist. Met.* 9 (1971) 30.
- [150] J. Askil, *Tracer Diffusion Data for Metals, Alloys and Simple Oxides*, IFI/Plenum, New York, 1970.
- [151] Y. Iijima, K. Kimura, K. Hirano, *Acta Met.* 36 (1988) 2811.
- [152] R.J. Borg, C.E. Birchenall, *Trans. Met. Soc. AIME* 218 (1960) 980.
- [153] E.S. Buffington, K. Hirano, M. Cohen, *Acta Met.* 9 (1961) 434.

- [154] R.J. Borg, *Diffusion in Body Centered Cubic Metals*, ASM, Metals Park, Ohio, 1965.
- [155] Y. Iijima, K. Hirano, *Diffusion in iron, steels and some nickel alloys*, in: R.P. Agarwala (Ed.), *Diffusion Processes in Nuclear Materials*, North-Holland, Amsterdam, 1992.
- [156] M. Lubbehusen, H. Mehrer, *Acta Met. Mater.* 38 (1990) 283.
- [157] G. Hettich, H. Mehrer, K. Maier, *Scripta Met.* 11 (1977) 795.
- [158] D.W. James, G.M. Leak, *Philos. Mag.* 14 (1966) 701.
- [159] C.M. Walter, N.L. Peterson, *Phys. Rev.* 178 (1969) 922.
- [160] A.W. Bowen, G.M. Leak, *Met. Trans.* 1 (1970) 1695.
- [161] A.M. Huntz, M. Aucouturier, P. Lacombe, *Compt. Rend. Acad. Sci. C* 265 (1967) 554.
- [162] R. Braun, M. Feller-Kniepmeier, *Phys. Stat. Sol. (a)* 90 (1985) 553.
- [163] C.G. Lee, Y. Iijima, K. Hirano, *Mater. Trans. JIM* 31 (1990) 255.
- [164] K. Hirano, M. Cohen, B.L. Averbach, *Acta Met.* 9 (1961) 440.
- [165] R.J. Borg, D.Y.F. Lai, *Acta Met.* 11 (1963) 861.
- [166] J. Cermak, M. Lubbehusen, H. Mehrer, *Z. Metallk.* 213 (1989) 213.
- [167] H. Oikawa, *Tech. Rep., Tohoku Univ.* 47 (1982) 67.
- [168] H. Oikawa, *Tech. Rep., Tohoku Univ.* 48 (1983) 7.
- [169] B. Milloin, J. Ruzickova, J. Velisek, J. Vrestal, *Mater. Sci. Engg.* 50 (1981) 43.
- [170] J.I. Goldstein, R.E. Hanneman, R.E. Ogilvie, *Trans. Met. Soc. AIME* 233 (1965) 812.
- [171] A. Kohn, J. Levasseur, J. Philibert, M. Wanin, *Acta Met.* 18 (1970) 163.
- [172] Y. Nakagawa, Y. Tanji, H. Morita, H. Hiroyoshi, H. Fujimori, *J. Magn. Magn. Mat.* 10 (1979) 145.
- [173] A.D. Romig Jr., J.I. Goldstein, *Met. Trans. A* 12 (1981) 243.
- [174] C. Narayan, J.I. Goldstein, *Met. Trans. A* 14 (1983) 2437.
- [175] S.P. Ray, B.D. Sharma, *Acta Met.* 16 (1968) 981.
- [176] J. Kucera, B. Million, J. Ruzickova, V. Fildyana, A. Jakobova, *Acta Met.* 22 (1974) 135.
- [177] A.M. Huntz, P. Lacombe, *Can. Met. Quart.* 13 (1974) 155.
- [178] H.W. Paxton, T. Kunitake, *Trans. Met. Soc. AIME* 218 (1960) 1003.
- [179] R.A. Wolfe, H.W. Paxton, *Trans. Met. Soc. AIME* 230 (1964) 1426.
- [180] P.J. Alberry, C.W. Haworth, *Met. Sci.* 8 (1974) 407.
- [181] R.S. Dutta, *J. Nucl. Mater.* 393 (2009) 343–349.
- [182] R.V. Patil, G.P. Tiwari, B.D. Sharma, *Mater. Sci.* 14 (1980) 525.
- [183] R.A. Perkins, R.A. Padgett Jr., N.K. Tunali, *Met. Trans.* 4 (1973) 2535.
- [184] V. Linnenbom, M. Tetenbaum, C. Cheek, *J. Appl. Phys.* 26 (1955) 932.
- [185] T. Thorvaldsson, A. Salwen, *Scripta Met.* 18 (1984) 739.
- [186] R.V. Patil, B.D. Sharma, *Met. Sci.* 16 (1982) 389.
- [187] A.F. Smith, *Met. Sci.* 9 (1975) 375.
- [188] W. Assassa, P. Guiraldeng, *Met. Sci.* 12 (1978) 123.
- [189] A.R. Paul, M.C. Naik, K.N.G. Kaimal, *Mater. Sci. Tech.* 7 (1991) 8.
- [190] A.R. Paul, M.C. Naik, K.N.G. Kaimal, *Phys. Stat. Sol. (a)* 128 (1991) 9.
- [191] M.C. Naik, A.R. Paul, K.N.G. Kaimal, K.S. Venkataswarlu, *J. Mater. Sci.* 25 (1990) 1640.
- [192] G.B. Federov, E.A. Smirnov, E.I. Zhomov, *Met. Metalloved. Chistykh Metal. Sb. Nauch. Rabot* 4 (1963) 110.
- [193] R.E. Hoffman, F.W. Pikus, R.A. Ward, *Trans. AIME* 206 (1956) 483.
- [194] J.E. Reynolds, B.L. Averbach, M. Cohen, *Acta Metall.* 5 (1957) 29.
- [195] A. Seeger, G. Schottky, D. Schumacher, *Phys. Stat. Sol.* 11 (1965) 363.
- [196] A. Seeger, D. Schumacher, *Mater. Sci. Engg.* 2 (1967) 31.
- [197] H. Bakker, *Phys. Stat. Sol.* 28 (1968) 569.
- [198] K. Maier, H. Mehrer, E. Lessmann, W. Schule, *Phys. Stat. Sol. (b)* 78 (1976) 689.
- [199] G. Neumann, V. Tolle, *Philos. Mag. A* 54 (1986) 619.
- [200] W. Gust, M.B. Hintz, A. Lodding, H. Odelius, B. Predel, *Phys. Stat. Sol. (a)* 64 (1981) 187.

- [201] B. Million, *Z. Metallk.* 63 (1972) 484.
- [202] S.B. Jung, T. Yamane, Y. Minamino, K. Hirao, H. Araki, S. Saji, *Mater. Sci. Lett.* 11 (1992) 1333.
- [203] J. Ruzickova, B. Million, *Mater. Sci. Engg.* 50 (1981) 59.
- [204] K. Monma, H. Suto, H. Oikawa, *J. Japn. Inst. Metals* 28 (1964) 197.
- [205] O. Taguchi, Y. Iijima, K. Hirano, *J. Japn. Inst. Metals* 48 (1984) 20.
- [206] M. Badia, A. Vignes, *Acta Metall.* 17 (1969) 177.
- [207] H. Bakker, J. Backus, F. Waals, *Phys. Stat. Sol. (b)* 45 (1971) 633.
- [208] Y. Minamino, H. Yoshida, S.B. Jung, K. Hirao, T. Yamane, *Defect and Diff. Forum* 143–147 (1997) 257.
- [209] M.S.A. Karunaratne, R.C. Reed, *Defect and Diff. Forum* 1237–1240 (2005) 420.
- [210] M.S.A. Karunaratne, P. Carter, R.C. Reed, *Mater. Sci. Eng. A* 281 (2000) 229.
- [211] S.P. Murarka, M.S. Anand, R.P. Agarwala, *Acta Metall.* 16 (1968) 69.
- [212] T. Takahashi, Y. Minamino, T. Asada, S.B. Jung, T. Yamane, *J. High Temp. Soc.* 22 (1996) 121.
- [213] T. Heumann, K.J. Grundhoff, *Z. Metallk.* 63 (1972) 173.
- [214] J. Levasseur, J. Philibert, *Phys. Stat. Sol.* 21 (1967) K1.
- [215] J.F. Cornet, D. Calais, *J. Phys. Chem. Solids* 33 (1972) 1675.
- [216] J.F. Cornet, *J. Phys. Chem. Solids* 35 (1974) 1247.
- [217] Y. Iijima, K. Hirano, M. Kikuchi, *Trans. Jap. Inst. Metals* 23 (1982) 19.
- [218] K. Monma, H. Suto, H. Oikawa, *J. Japan Inst. Metals* 28 (1964) 188.
- [219] P. Moulin, A.M. Huntz, P. Lacombe, *Acta Met.* 27 (1979) 1431.
- [220] D. Delaunay, A.M. Huntz, P. Lacombe, *Scripta Met.* 13 (1979) 419.
- [221] T.F. Chen, Y. Iijima, K. Hirano, K. Yamaguchi, *J. Nucl. Mater.* 169 (1989) 285.
- [222] G.B. Kale, K. Bhanumurthy, S.K. Khera, M.K. Asundi, *Mater. Trans. JIM* 32 (1991) 1034.

CHAPTER 9

The Growth of Silicides and Germanides

Dominique Mangelinck

IM2NP, CNRS, Aix Marseille Université, France

9.1 INTRODUCTION

Metallic silicides are used as contact materials on source/drain and gate in MOS structure for more than 40 years. They are fabricated by reactive diffusion between a metal or a metallic alloy thin film and the Si (Ge) substrate, and there have been many studies to understand these reactions.

Indeed one of the challenges of nanoelectronics is to create a contact on the active zones of transistors or memories which has to be reliable and fully compatible with both the fabrication processes and the other materials constituting the transistor. The metallic silicides obtained by reaction between a metal and silicon can fulfill these constraints by increasing the level of integration and decreasing the contact resistance. Another crucial advantage of the silicides is that they can be integrated in the devices by the Salicide process (Self-Aligned Silicidation) [1]. Based on the reaction between a metal film and the silicon substrate, this process allows increasing the integration level by forming selectively the silicide on the active parts of the transistor and avoiding photolithography steps. In advanced technologies, i.e., 65 nm and below, the nickel monosilicide phase (NiSi) is used to replace TiSi_2 and CoSi_2 . NiSi has indeed many advantages: it consumes less silicon, has a low resistivity ($\sim 14 \mu\Omega\text{-cm}$), is independent of linewidth, and forms at low temperatures below 400°C [2]. The major drawback is, however, that NiSi is not the Si-richest phase in the Ni–Si phase diagram: the high resistivity NiSi_2 phase is the richest one. Enlarging the temperature range where NiSi_2 does not form at the expense of NiSi is a major concern. It has been shown that a few Pt atoms (typically, 5 to 10 at.%) to an Ni film could stabilize the low resistivity NiSi phase by retarding the NiSi_2 formation of 150°C [3]. This was associated with a better resistance to morphological degradation and has allowed for a better integration of NiSi as a material of contacts for nanometric transistors [4]. The Salicide process using an Ni(Pt) alloy, instead of pure Ni, has been introduced in sub-90 nanometer CMOS technologies to improve the integration of NiSi process. NiPtSi phase with high Pt concentration (10 at.%) is now in volume production for 28 nm process of CMOS application as contact material in nanometric transistors. These silicides offer interesting opportunities for contacting nanodevices, but controlling contacts at the nanoscale requires a very good understanding of reactions at the nanoscale.

A considerable amount of work has been done on the formation [5–7], stress [8], and properties [9,10] of these silicide films with thickness in the range of a few hundreds of nanometers. The reactions in thin films (typically above 50 nm) [5] are usually characterized by sequential growth, the absence of some equilibrium phases, and sometimes by the growth of metastable phases, while the simultaneous parabolic growth of all the equilibrium phases is usually observed in bulk interdiffusion couples. However, the fundamental mechanisms of the silicide formation are still not fully understood, especially for small film thicknesses (<50 nm) where growth may be mainly controlled by the interfacial reaction; furthermore, for these small thicknesses, other phenomena like nucleation, lateral growth [11], stress [12–14], texture [15], and transient phase formation with very short lifetime [2] should certainly play an important role.

Beyond the 32 nm CMOS technology node, the silicide film used in the source and drain regions for electrical contact will be at most 15 nm thick. Recent results for ultra-thin nickel silicide films [16–18] show that an entirely new phase formation sequence can be observed when the nickel film thickness drops below a critical thickness of 4 nm. The increasing importance of interface energy due to the reduction of the layer thicknesses results in a strong texture of the phases that form. Even thermodynamically unstable phases can form due to epitaxial stabilization, as evidenced for θ -Ni₂Si [16–18]. One of the major issues with such extremely thin silicide films concerns a severely deteriorated morphological stability because of capillary effects. Indeed, thin films of NiSi often suffer from poor morphological stability and start to agglomerate at 500°C as a result of the low melting point of NiSi at 992°C. Since the agglomeration of thin films is driven by a minimization of interface energy, it is expected that thinner films will agglomerate faster, i.e., have a lower agglomeration temperature. However, this holds true only if the as-deposited Ni film thickness remains larger than 5 nm, while for thinner layers the resulting nickel-silicide layer is much more resistant to agglomeration and exhibits an extraordinary morphological stability up to 800°C [16–18]. This was attributed to the formation of an epitaxial nickel-silicide layer.

Recently the availability of Atom Probe Tomography (APT) to measure in 3D the atomic composition has allowed important findings concerning the formation of silicides [19]. This instrument is the only analytical microscope capable of producing 3D maps of the chemical specie distribution with an atomic resolution. The development of laser-assisted atom probe tomography (APT) allows nowadays the analysis of not only metals but also of both semiconductor and insulator materials. A focused ion beam equipped with high resolution scanning electron microscopy enables the preparation of site-specific samples with complex combinations of several materials. These improvements have significantly advanced the characterization of semiconductor materials and devices by APT, including progress in the Ni silicide formation for advanced MOS structures. Indeed, the capability of APT to map out elements in devices at the atomic

scale with high sensitivity can meet the characterization requirements of semiconductor devices such as the determination of elemental distributions for each device region.

Germanides thin films are actually of interest for their use in integrated microelectronic devices as ohmic contacts [20–24]. Indeed, they can be useful for low power consumption or high speed devices as MOSFET transistor [20–24] due to the high mobility of both holes and electrons in germanium compared to silicon. The understanding of Ge metallization is thus important for the very large scale integration (VLSI). The tendency to shrink MOS devices, and thus to shrink the silicide thickness, requires a better understanding of the first stages of reaction for nanometric Ni films deposited on various Ge substrates, in particular germanides, which are growing and their kinetics.

This chapter does not aim to be an extensive review of the work on silicides and germanides. Its goal is to provide some basis to understand the mechanisms of formation of these intermetallic compounds. It will be mainly focused on the Ni silicide and germanide since they are used in microelectronics today and have been thus largely studied.

In this chapter, some mechanisms of Ni silicide formation have been studied by *in situ* techniques (X-ray diffraction, X-ray reflectivity, differential scanning calorimetry, X-ray photoemission spectroscopy) coupled with other *ex situ* techniques and in particular APT. The effects of alloy elements on the Ni silicide formation are presented together with mechanisms for both the dopant and the alloy element redistribution. The formation of silicides and the redistribution of the elements have also been studied in transistors by APT.

9.2 EXPERIMENTAL PROCEDURE

Although several deposition techniques can be used to deposit the metal film on Si or Ge, such as electron beam evaporation, chemical vapor deposition, or molecular beam epitaxy, magnetron sputtering is the most commonly used technique in the microelectronics industry. Before deposition, the substrate is dipped in a 5% HF solution in order to remove the native oxide that can hinder the reaction. Most of the results reported here were obtained for Ni and Ni(Pt) thin film deposited by magnetron sputtering on (100)Si substrates. The deposition was performed in a sputtering deposition setup with a base pressure of $\sim 10^{-7}$ mbar using 99.9999% pure Ar gas flow and Ni or Ni(Pt) target. The wafer was rotating during deposition to improve the homogeneity of the layer.

The reaction between film and substrate was mainly followed by *in situ* X-ray diffraction (XRD), *in situ* X-ray reflectivity (XRR), and differential scanning calorimetry (DSC). XRD measurements were performed using a diffractometer equipped with a Cu tube ($\lambda_{\alpha} = 0.15405$ nm) and a temperature chamber. Both isothermal and ramp annealing were performed in a vacuum in the 10^{-5} mbar range, and the XRD spectra were continuously recorded in the Bragg–Brentano geometry. In the case of ramp an-

nealing in situ XRD analysis was performed after ramping from room temperature to 130–150°C with a rate of 30°C/min. The temperature was then increased by 4–5°C per step and kept constant during the XRD measurements that typically lasted from one to two minutes. In situ XRR measurements were performed under vacuum (10^{-6} mbar) at the BM05 beamline of European Synchrotron Radiation Facilities (ESRF). XRR spectra were recorded during isothermal anneals after ramping from room temperature to the expected temperature at a rate of 20°C/min.

DSC has already been shown to be a very powerful technique to analyze the first stages of thin film reactions [11,25–28]. In order to obtain detectable DSC signals, samples were usually made of self-supported multilayers that generate more interfaces where the reactions of interest take place and thus more reacting materials. However, the presence of multiple interfaces and/or the absence of substrate can modify the solid-state reaction mechanisms. In our work, Ni or Ni(Pt) were deposited on both sides of a thinned Si(001) wafer (100 μm) in order to decrease the signal due to the substrate during DSC measurements [29,30]. After deposition, the thickness of the layer on each side of the wafer was checked using XRR. The two layers were found to have the same thickness within a few nm. The DSC thermograms were obtained using a Perkin-Elmer Pyris Diamond apparatus. Samples were heated from 50 to 700°C with heating rates ranging from 10 to 100°C/min. A continuous flow of high purity Ar was applied in the cell.

Atom Probe Tomography (APT) is a powerful technique to analyze materials in three dimensions at the atomic scale [31–34]. This technique allows reconstructing, atom by atom, a small piece of matter (typically $50 \times 50 \times 100 \text{ nm}^3$) in the three directions of the real space and is unique for its (a) spatial resolution in three dimensions (0.2 nm achievable), (b) analytical sensitivity (10 ppm), (c) high detection efficiency (>30%), and (d) ability to detect all elements. The ideal atom probe specimen is a long needle whose final radius of curvature is between 50 and 100 nm with a shank angle in the range of 10° . This geometry allows getting a high electric field on the specimen tip and at the same time a fast heat release during laser assisted experiments. Samples for APT analysis (tips) were prepared by focused ion beam, with a dual-beam (FIB-SEM) system, FEI Helios dual-beam-FIB, using the lift-out technique, and annular milling using a Ga^+ ion beam. Tips were prepared with a direction either perpendicular or parallel to the sample surface. APT analyses were performed using a LEAP 3000X HR instrument. This instrument is able through the use of local electrode, high pulse rate, ultra-fast laser, and reflectron to achieved high throughput data acquisition both in voltage and laser pulse mode with high mass resolution (>1000 at FWHM, >300 at FW1%M) and a field of view superior to 150 nm. The conventional analyses were carried out at 50 K, with a laser (532 nm wavelength) pulse frequency of 100 kHz, using a laser power between 0.5 and 0.6 nJ, and an evaporation rate of 0.5 ion per pulse, under a vacuum pressure lower than $5 \cdot 10^{-11}$ torr. Data reconstruction was done with

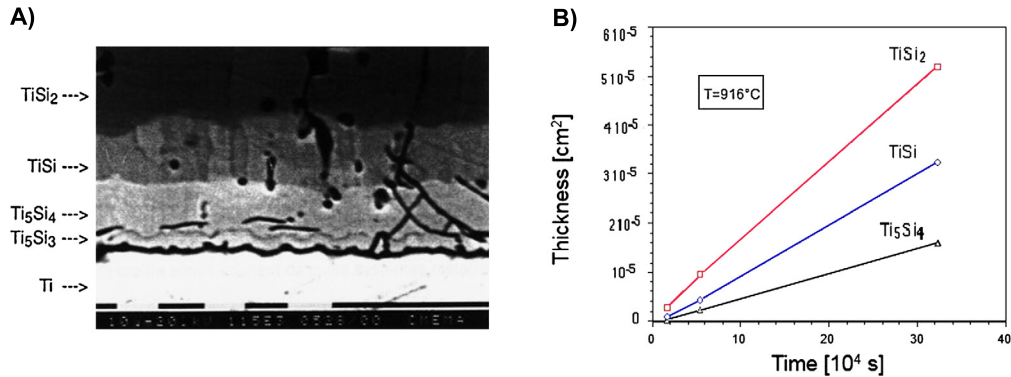


Figure 9.1 (A) SEM image of a bulk diffusion couple between Ti and Si annealed at 916°C . (B) Square of the thickness versus time for the Ti silicides [36].

the IVAS software incorporating standard reconstruction algorithms. The IVAS software enables the visualization and powerful analysis to extract 1D, 2D, and 3D quantitative information.

9.3 GROWTH OF SILICIDES: BULK DIFFUSION COUPLE VERSUS THIN FILM

9.3.1 Growth of Silicide in Diffusion Couple

The abundant literature on the growth of silicide has been summarized in several reviews [5,7] and is characterized by two dominant features: (a) most of the measurements of diffusion were made during reactive diffusion, namely during the formation of a silicide by reaction of a metal, or another silicide with Si, and (b) most of this work concerns thin films. This latter aspect maximizes the effect of grain boundary transport. While the silicide formation has been mainly studied in thin films because of the applications in microelectronics, there is comparatively less work done on bulk diffusion couple [35].

However, bulk diffusion couples are very instructive for the understanding of silicide formation as exemplified in the following.

Fig. 9.1(A) shows an SEM image of a bulk diffusion couple between Ti and Si annealed at 1200°C for 15 hours. A comparison with the binary Ti/Si phase diagram shows that all the phases stable at this temperature are present as layers of uniform thickness. For the relatively high temperature and time used for diffusion couple, the interface is expected to be at equilibrium and a diffusion couple can be used to determine the phase diagram.

Fig. 9.1(B) shows that the square of the thickness varies linearly with time as expected for a growth controlled by diffusion. The silicides are thus growing with constant

ratio between their thicknesses. The growth rate of a given silicide in a diffusion couple depends of the interdiffusion coefficient in this silicide but also of the interdiffusion coefficients in the other silicides [36]. From the growing rate of the silicides, one can determine the interdiffusion coefficients in the silicides [36].

9.3.2 Link Between Silicide Growth in Diffusion Couple and in Thin Films

The abundant research on the growth of silicide was mainly carried out on a few hundreds of nanometer thin films [5,7,35]. In addition to the interest for application, this facilitates measurements because in films up to about 0.5 μm thick, at the temperatures and scales at which growth is observed to occur, phases generally form sequentially, which greatly simplifies the interpretation of growth kinetics.

Experimentally, a metal film is deposited on a silicon substrate and the change in the metal (and Si) profile(s) is measured after various heat treatments. Rutherford backscattering spectrometry (RBS) is almost ideally suited for this purpose [37], at least for thicknesses between 10 nm and 1 μm . As illustrated in Fig. 9.2, it yields at the same time the composition of the phases that are formed and, provided one knows the crystallographic structure or the density, the thickness of the growing layers. From the measurement of the thickness as a function of time, the growth rate for a given temperature can be obtained (Fig. 9.2(B)) and by plotting an Arrhenius diagram of the growth rate, i.e., the $\log(\text{growth rate})$ versus the inverse of temperature, an activation energy for the growth can be determined (Fig. 9.2(C)). More recently in situ measurement during the heat treatment has also been used to measure the kinetics of silicide and germanide formation. These methods rely on measuring a physical parameter that changes during the phase formation such, e.g., resistance, heat release, amount of diffracting materials, and thickness by the measurement of sheet resistance, differential scanning calorimetry, X-ray diffraction, and X-ray reflectivity, respectively. Isothermal or constant heating rate can be used, the later allowing us to obtain the activation energy [35,38,39]. This mode of experimentation is much less time consuming than the previous ones and allows a more precise analysis of the sequence and kinetics even for phases with complex behavior as will be exemplified latter in this chapter.

As already pointed out, there exists an apparent difference in behavior between thin films and their equivalent bulk couples, such as the absence of certain phases [40] or the general observation of sequential formation in thin films instead of the simultaneous formation often reported for bulk couples. These two differences will be commented in Section 9.4.

Most of the time, when plotted properly as L^2 vs. t (with L being the thickness of the growing layer and t the time), the slope gives the growth constant k and measurements at different temperatures yield the activation energy. For isothermal heat treatments, the growth rate k is usually constant, indicating that most of the kinetics of the metal/silicon reactions are controlled by diffusion processes as in a bulk diffusion couple (Fig. 9.2(B)).

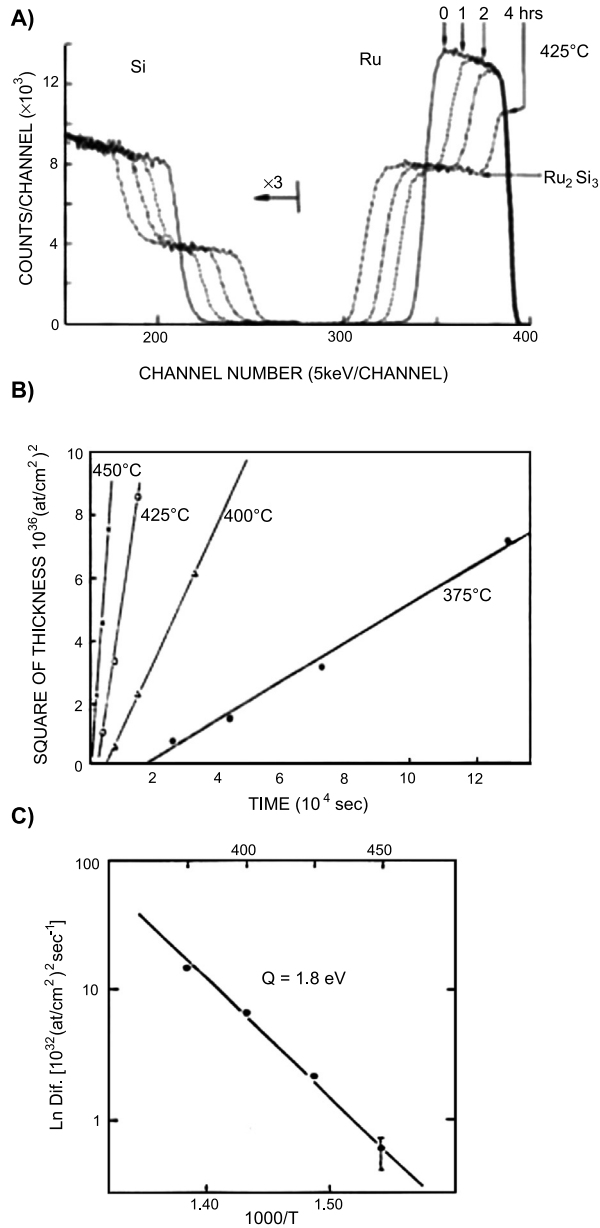


Figure 9.2 (A) Backscattering spectra showing the progressive formation of Ru_2Si_3 at 425°C. (B) The square of the thickness of growing layers of Ru_2Si_3 plotted as a function of time. (The vertical axis is calibrated in backscattering units: atoms/cm². The actual thickness is obtained through division of these units by the atomic density – 7.3×10^{22} atoms/cm³.) (C) Arrhenius plot of the slopes in (B). The activation energy 1.8 eV gives the correct expression for the kinetics of growth of Ru_2Si_3 , but its relation to specific diffusion processes is complex. Reprinted with permission from [145].

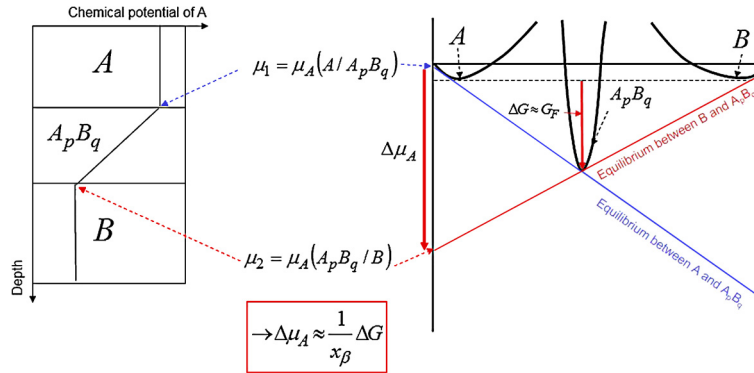


Figure 9.3 Relationship between the variation of the chemical potential in a stoichiometric compound and its Gibbs free energy of formation.

However, the relationship between the growth rate and the diffusion coefficients is not straightforward. Since growth occurs quite often at low temperatures with respect to the melting points of the different phases, grain boundary diffusion plays a role. There are thus potentially two mobile elements and two sets of paths (lattice and grain boundaries), hence one may ultimately have to separate four different diffusion coefficients and four activation energies. Luckily some simplifications may be allowed. For an analysis of the growth conditions to obtain thin film silicides, see [5].

One has also to be careful when analyzing the results. Because many silicides exist only within very narrow limits of composition, and, when this is not precisely true, within poorly known limits of composition, growth results cannot be properly interpreted in terms of Fick's law (that is true also for many other intermetallic compounds). It is more appropriated to consider diffusion in terms of a modified Nernst–Einstein equation

$$J_A = c_A \left(\frac{D_A}{k_B T} \right) \frac{\partial \mu_A}{\partial z}, \quad (9.1)$$

where the flux of A atoms, J_A , is expressed as the product of the concentration of A atoms, c_A , their mobility (D_A/kT), and $d\mu_A/dz$, the gradient of chemical potential (i.e., the force on these atoms). Ideally, D_A here is equal to D_{A^*} , the tracer diffusion coefficient in the formed compound. For the sake of simplicity and as schematically shown in Fig. 9.3, $d\mu_A/dz$, the gradient of chemical potential, is taken equal to $\Delta G_A/L$ with ΔG_A being the free energy change per moving A atom (from the free energy – or heat – of formation of the compound, at least in elemental A – B reactions):

$$J_A = c_A \left(\frac{D_A}{k_B T} \right) \frac{\Delta G_A}{L}. \quad (9.2)$$

Moreover, the use of the gradient of chemical potential would require complete knowledge of the free energies versus composition for the whole A/B system, and would become meaningful only if it were possible to determine the varying value of D_A as a function of the chemical potential of A within the compound.

If both the A and B atoms contribute to the formation of an A_mB_n compound, addition of two equations [5,41] such as the one above yields an overall diffusion coefficient equal to Darken's [42]:

$$D_{A,B} = \frac{p}{p+q} D_B + \frac{q}{p+q} D_A. \quad (9.3)$$

For a phase growing alone from the reaction between A and B elements, one obtains

$$L^2 = k_D t. \quad (9.4)$$

With the following expression for the growth rate k_D , if growth occurs by the motion of A atoms only (this is usually the case as explained later):

$$k_D = 2 \left(\frac{\Delta G}{k_B T} \right) \left(\frac{D_A^0}{p} \right) \exp \left(\frac{-Q}{k_B T} \right). \quad (9.5)$$

Here, ΔG for solid state reactions can be taken as the heat of formation of the compound $A_p B_q$ per mole (Fig. 9.3), and Q as the activation energy for the diffusion of A atoms in $A_p B_q$.

Gas and d'Heurle [5,35,43] have presented a compilation of the different results for diffusion controlled growth of silicides (Fig. 9.4). They pointed out that an important difference between thin film and bulk diffusion couple is the relatively high rates of formation and quite low activation energies for diffusion controlled growth of thin films. Indeed, they [5,35,43] found the following relations between the rate of formation, activation energy (Q), and melting temperature (T_m):

$$- \text{rate of formation at } 0.4T_m = 10^{-14} \text{ cm}^2/\text{s}, \quad (9.6)$$

$$- Q/R = 11.5T_m. \quad (9.7)$$

The relation between the rates of formation, their activation energies, and melting temperatures indicates correlation between diffusion parameters and melting temperatures than have been established and used for diffusion in different materials [44]. For example, in the case of pure metals, one has:

$$- \text{for lattice diffusion [45]: } D_L \text{ at } 0.4T_m = 10^{-21} \text{ cm}^2/\text{s} \text{ and } Q_L/R = 18T_m, \quad (9.8)$$

$$- \text{for grain boundary diffusion [45,46]:}$$

$$D_{GB} \text{ at } 0.4T_m = 10^{-10} \text{ cm}^2/\text{s} \text{ and } Q_{GB}/R = 10-12T_m. \quad (9.9)$$

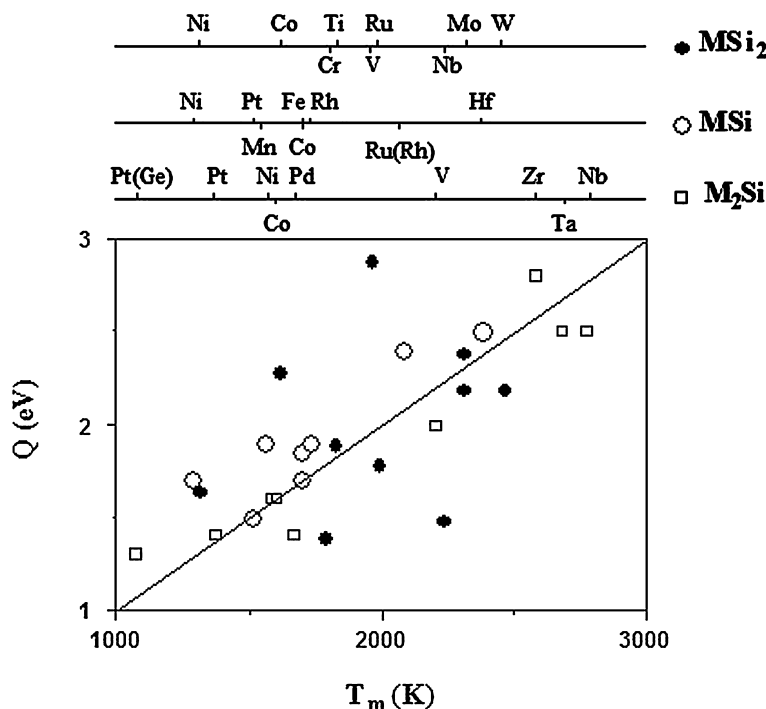


Figure 9.4 Activation energy for “diffusion controlled” silicide formation as a function of the silicide melting temperature. Squares correspond to metal rich silicides; open circles to monosilicides; black points to disilicides. Reprinted with permission from [43].

Many reasons may explain this increase in diffusion rates during solid state reaction: (i) the influence of the driving force which in reactive diffusion is the formation of the new phase; (ii) the fact that the growing layer is in contact with pure metal and Si and may thus grow with compositions limits in excess of the equilibrium ones. Such a departure from stoichiometry may correspond to structural defects (antisites or vacancies) which may enhance diffusion; and (iii) the role of extended defects (e.g., silicide grain boundaries) which may increase the mass transport through the silicide layer. In order to get a better understanding of diffusion processes during silicide formation, it is thus important to determine the influence of these different factors.

As expected for the usual polycrystalline nature of silicide thin film, it appears that the rate of formation and the activation energies measured for “diffusion controlled” silicide formation should be more representative of a grain boundary diffusion mechanism than of lattice diffusion. One should be careful since diffusion mechanisms in silicides may be more complex than diffusion mechanisms in pure metals.

Lattice diffusion in intermetallics [47,48] depends on the structure and can be influenced by changes in composition. In fact, for each intermetallic one should take

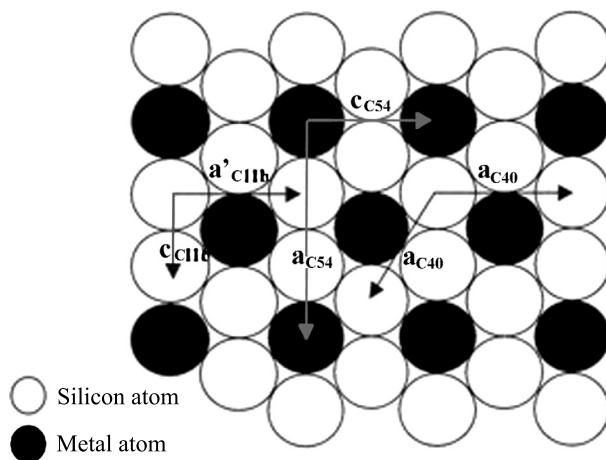


Figure 9.5 Illustration of the “Cu₃Au rule” for diffusion in intermetallic.

into account the possibility of having structural defects (structural vacancies or antisites) and the disorder associated with diffusion [49]. A general trend of diffusion studies in intermetallics is that most of the compounds studied admit large departure from stoichiometry. However, this is generally not the case of silicides (which are often line compounds).

In silicide and intermetallic, quite often the atoms of only one atomic species are mobile under the experimental growth conditions (all the more true as the temperature is low, as is usually the case for thin film reactions). Marker experiments used to determine the moving species during silicide formation are described in [5]. In general, it is found that metal atoms constitute the dominant mobile species in metal-rich silicides, and Si atoms in silicon-rich ones. This is especially true of a series of silicides (TiSi₂, VSi₂, NbSi₂, TaSi₂, CrSi₂, MoSi₂, and WSi₂), which are built in the same fashion with each metal atom surrounded by 10 Si atoms, and no metal nearest neighbors (as in L12 structures typified by Cu₃Au). In all of these the Si atoms are greatly more mobile than the metal atoms [5,49]. This observation has been generalized as the “Ordered Cu₃Au Rule” [5,50], according to which generally in A_mB_n compounds with m/n equal to or greater than 2, the majority atoms (A) are much more mobile than the atoms of the minority species (B). As illustrated in Fig. 9.5, this is related to the structures where the A atoms can migrate on a continuous network of A lattice sites, whereas the migration of the B atoms requires that these occupy A sites with an increase in activation energy for diffusion that should be commensurate with the heat of ordering (or of compound formation, per B atom).

Diffusion will thus be favored if the structure of the compound is such that one of the elements may diffuse on its own sublattice: this is more likely for the majority

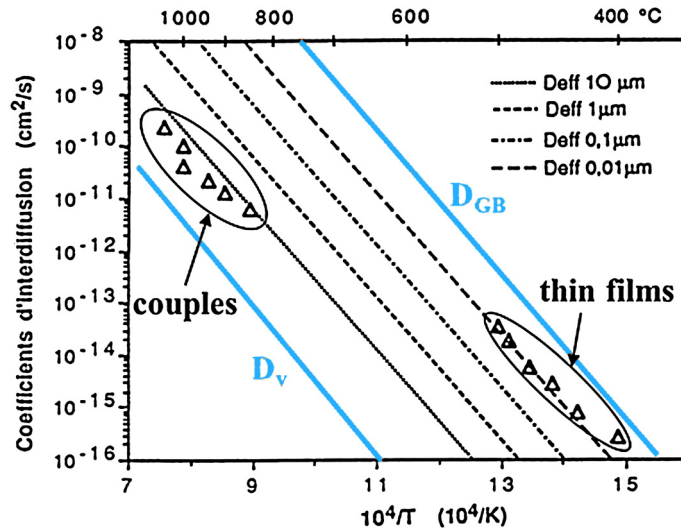


Figure 9.6 Comparison of the efficient diffusion coefficient (D_{eff}) (deduced from self-diffusion measurement by taking into account the mobility of both elements and the grain size) and the Nernst–Einstein diffusion coefficient ($D_{\text{N.E.}}$) deduced from reactive diffusion experiments. Different grain sizes (ranging from 10 to 0.1 μm) are used to calculate D_{eff} [36].

element that can diffuse on its own sublattice by near neighbor jumps while the minority element has to go through a “high energy” position (antisite).

The similarity between the relations between the rate of formation, the activation energy (Q), and the melting temperature (T_m) for silicide formation in thin film and for grain boundary in metals is in accordance with a strong contribution of grains boundary diffusion linked to the thin film microstructure.

This was further evidenced by the work of Barge et al. [51]. They evaluated the different factors affecting diffusion during silicide formation by comparing the kinetics of growth of thin films and bulk diffusion couples with the diffusion parameters (lattice and gb diffusion coefficients) measured by classical diffusion methods. Fig. 9.6 [51] shows an Arrhenius plot of the interdiffusion coefficient in CoSi_2 obtained from bulk diffusion couples and from thin films. The values for the bulk diffusion couples were obtained from the solid state reaction in Co/Si diffusion couples annealed between 850 and 1100 $^\circ\text{C}$. The three stable phases Co_2Si , CoSi , and CoSi_2 were found to grow simultaneously, according to diffusion controlled kinetics. The results were analyzed with the Nernst–Einstein equation taking into account the interdiffusion diffusion fluxes and the free energy changes driving the formation.

The interdiffusion coefficients for a thin film were obtained from the work of Lien et al. [52]. As expected, the values for the thin film correspond to a much lower temperature than those for bulb diffusion couples. Fig. 9.6 shows that the values at high

temperatures (bulk samples) are not aligned with those determined in thin films, at much lower temperatures.

In Fig. 9.6, lattice and grain boundary (gb) diffusion coefficients are also reported. They were determined using classical techniques based on the penetration of radioactive isotopes (^{60}Co and ^{68}Ge) in bulk polycrystalline CoSi_2 samples. ^{68}Ge was used in lieu of a Si radiotracer and D_l and D_{gb} were deduced from the penetration profiles using Fick's laws). Measurements of grain boundary and lattice diffusion in bulk CoSi_2 lead to the following results: (a) Co and Si have similar diffusion coefficients in the lattice as well as in the gb, (b) for both elements the ratio between gb and lattice diffusion coefficients is about 10^6 , and (c) these coefficients are not affected by defects due to departures from stoichiometry (Co- or Si-rich CoSi_2). Fig. 9.6 shows that the values for the bulb diffusion couple are closer to the lattice diffusion coefficient while those for thin film are closer to the grain boundary diffusion coefficient.

In order to compare these diffusion coefficients to those deduced from the growth of CoSi_2 (DNE), the motion of both Co and Si and the contribution of lattice and gb diffusion have thus need to be taken into account. The last contribution is approximated by the use of an effective diffusion coefficient:

$$D_{\text{eff}} = D_L + \frac{\delta}{2d} D_{GB} \rightarrow D_{\text{eff}} = (2D_L^{\text{Co}} + D_L^{\text{Si}}) + \frac{\delta}{2d} (2D_{GB}^{\text{Co}} + D_{GB}^{\text{Si}}). \quad (9.10)$$

This coefficient is plotted as a function of the grain size in Fig. 9.6 and is compared to the diffusion coefficient deduced from the Nernst–Einstein equation for a diffusion couple and thin film. A very reasonable agreement is obtained between the two sets of coefficients, provided that a grain size of $10\text{ }\mu\text{m}$ is assumed for bulk couples and $0.01\text{ }\mu\text{m}$ for thin films, which correspond to the actual experimental values. This agreement between the two sets of data implies that the effective diffusion coefficients during growth are not enhanced by the creation of point defects which have been shown to occur under some circumstances [53,54]. This might be due to the absence of defect creation or to the dominance of grain boundary diffusion which may be insensitive to such defect creation.

The comparison further requires that attention be paid to two factors. The first one is that the laws of growth are slightly different for a phase growing simultaneously with two others (bulk) and one phase growing alone (thin films). The second factor is the grain size of the various samples, which varies with the temperature of reaction. Once this is done, excellent agreement is obtained between the two sets of measurements. Moreover, it is shown that knowing the grain size, it is possible to calculate quite accurately the growth rate from the respective isotope diffusion coefficients both for lattice and grain boundaries of Co and Si in CoSi_2 .

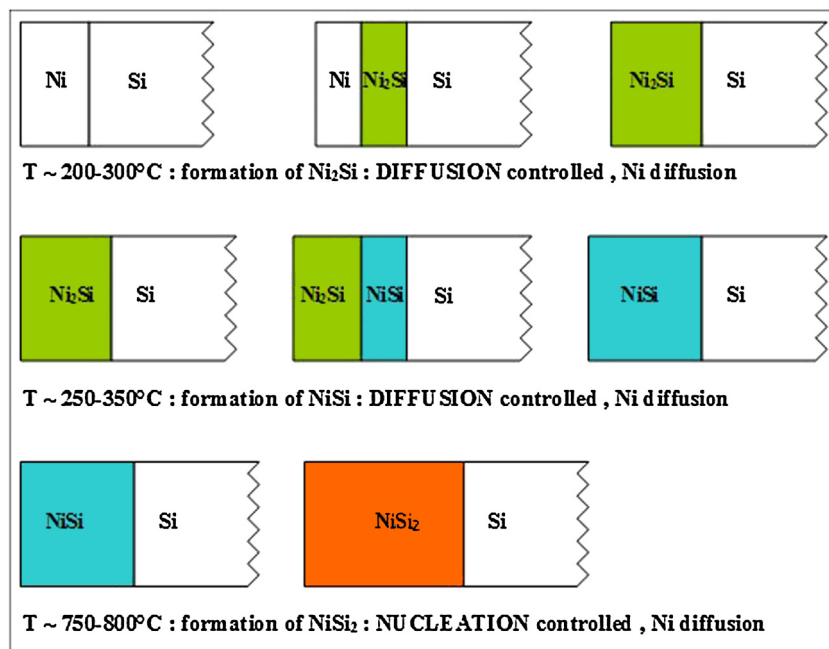


Figure 9.7 Schematic of the Ni silicide formation in thin film.

9.4 MECHANISMS OF FORMATION OF NI SILICIDES AND GERMANIDES

As pointed out before, there are differences between the growth of silicide and germanide in thin film and in bulk diffusion couples. In order to illustrate these difference and recent advances in the field, we will now present results on the formation of Ni silicides and germanides, since these systems (Ni/Si and Ni/Ge) have been the most studied and constitute typical examples of thin film reactions.

Numerous studies were carried on Ni thin film reaction with silicon in order to clarify the silicide formation mechanisms both for its interest of application and as a characteristic system for reactive diffusion [55,56]. Most of the studies on the reaction between a pure Ni thin film and the Si substrate have shown that the following sequence of phases occurs during the reaction (Fig. 9.7): $\delta\text{-Ni}_2\text{Si}$ appears as the first phase and grows at low temperature (from 250°C) until full consumption of the Ni metallic film. The NiSi phase grows then at the expense of the $\delta\text{-Ni}_2\text{Si}$ phase and is stable in a temperature range up to 700–800°C. The third phase NiSi_2 grows after NiSi at a temperature normally higher than 700°C since it has difficult nucleation [40].

If one compares to the Ni–Si phase diagram, only three phases are formed in thin film while six silicides are stable at low temperature. Several phases are thus missing, and

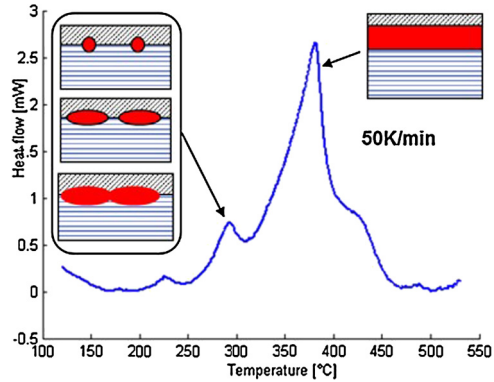


Figure 9.8 DSC thermogram obtained for the reaction between 50 nm Ni film and the α -Si/Si(100) substrate. The insert indicates the mechanisms responsible for the peaks corresponding to the growth of Ni_2Si .

the phases appear sequentially instead of the simultaneous formation observed usually in bulk diffusion couples.

In addition to the three phases commonly observed in most of the experimental works (δ - Ni_2Si , NiSi , and NiSi_2), it was shown that during the deposition of Ni film on an Si substrate, an Ni-Si intermixed layer is usually formed at the interface between the Ni film and the Si substrate [57,25]. Moreover, other studies performed on Ni thin films between 10 and 100 nm using in-situ X-ray diffraction (XRD) have shown the formation of a transient phase [58–61]. This transient phase was first identified as Ni_3Si_2 [2] but a deeper analysis based on pole figures leads to the identification of θ - Ni_2Si [18,62]. In the Ni-Si phase diagram, θ - Ni_2Si is only stable around 825°C, while in thin films, it can thus be metastable since it has been observed at a lower temperature (around 300°C).

The reaction between Ni thin films and Si substrate is thus characterized by the following points: lack of some stable phases, growth of a metastable phase, sequential formation. These points are representative not only of the Ni/Si system, but more generally of the silicide formation in thin film.

In the following, we will bring some explanations for these behaviors even if the first phase formation, the sequential phase growth, and the reason behind the missing phases during the Ni silicide formation are still not fully understood.

9.4.1 Lateral Growth

In [29], DSC was used to clarify the different steps of the first Ni silicide to appear in the sequence (δ - Ni_2Si).

Fig. 9.8 shows the DSC thermograms obtained with a heating rate of 50 K/min for a 50 nm Ni film on amorphous Si. Four peaks are observed and correspond to

different steps of the silicide formation. This illustrates the potential of DSC to reveal the initial steps of reaction at an interface. It should be stressed that in the present case this information is obtained from a single reacting interface on an Si substrate while the former DSC experiment results were obtained from self-supported metal/Si multilayers. In order to identify the origin of these peaks, samples were prepared by stopping the DSC experiments after each peak and phase identification was performed by XRD. The two peaks indicated by arrows were attributed to the growth of δ -Ni₂Si. In addition, integration of these peaks gives approximately the Gibbs free energy of formation of Ni₂Si (−49 kJ/g atoms) [63].

Two DSC peaks are thus associated with the formation of one phase (δ -Ni₂Si) and correspond to two steps of growth for a phase formation. In accordance with earlier results [11,29,30,64–66], the first DSC peak corresponds to the nucleation of Ni₂Si and its subsequent lateral growth up to a continuous layer as indicated by the insert. The second peak results from the one-dimensional thickening of this continuous layer up to the full consumption of the film.

Following the model developed by Coffey et al. [11], by assuming the nucleation of the new phase at the interface and its lateral growth, the volume fraction can be expressed by:

$$\frac{dX_v}{dt} = \left(\frac{dX_a}{dt} \right) \frac{L}{L_{\max}} + \left(\frac{dL}{dt} \right) \frac{X_a}{L_{\max}}, \quad (9.11)$$

where L is the thickness of M₂Si, $L_{\max}$ is the maximum thickness that M₂Si grows to (for sequential growth in thin film, $L_{\max}$ is proportional to the Ni thickness through the atomic volume of Ni and Ni₂Si), dL/dt is the one-dimensional growth rate, X_a is the area fraction of M₂Si in a plane parallel to the plane of the original layer, dX_a/dt is the change in the area fraction as a function of time.

The lateral growth of the precipitates takes place in two dimensions and saturates when the precipitates enter in contact with each other. For an isotropic growth at the interface, the saturation can be taken into account via the concept of extended volume [67]. For simplicity, it was assumed that the nucleation barrier was low and that a fixed density of nucleation sites (n) existed at the interface. Moreover, the precipitates were chosen to be cylinders with an initial height L_0 and radius r_0 . The area fraction when the precipitates of cylindrical shape (radius r) are in contact is given by:

$$X_A = 1 - \exp(-n\pi r^2). \quad (9.12)$$

The lateral growth rate of these precipitates was also assumed to be limited by the reaction at the interface and can be expressed as follows:

$$\frac{dr}{dt} = K_{LG} = K_{LG0} \exp\left(-\frac{E_{LG}}{k_B T}\right), \quad (9.13)$$

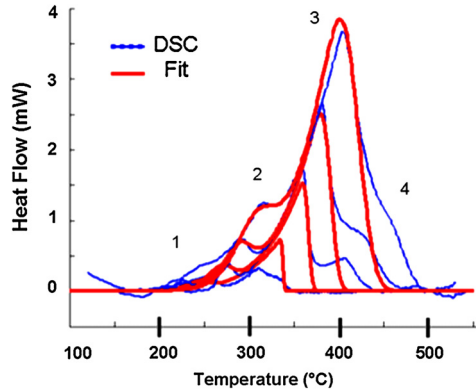


Figure 9.9 Reaction between Ni (50 nm) on α -Si (300 nm) bilayer deposited on a (100)Si substrate: Comparison between the DSC thermograms obtained with four heating rates (10, 25, 50, 100 K/min) and a simulation based on a numerical integration of the model (Eq. (9.11)). The simulated curve was convoluted with a Gaussian to take into account the DSC instrumental function. Reprinted with permission from [146].

Table 9.1 Values of the parameters used in Eqs. (9.11)–(9.13) to describe the lateral growth of Pd_2Si and Ni_2Si

System	L_0 [nm]	r [nm]	N [site/nm ²]	K_{i0} [cm/s]	E_i [eV]
Ni/ α -Si	7	5	3×10^{-5}	13	0.85
Pd/(001)Si	5	20	5×10^{-4}	15	0.85

where k_B is the Boltzmann constant, T is the temperature, K_{LG0} and E_{LG} are the preexponential factor and the activation energy of the lateral growth of the precipitates.

The thickening of the precipitates was modeled using the Deal and Grove model that will be detailed later.

A comparison of DSC with simulation using the above model and finite differences is shown by the red lines in Fig. 9.9(B).

The modeled kinetic parameters are given in Table 9.1 for lateral growth. These parameters provide a good fit between experiments and simulation for the four heating rates and in situ XRD isothermal measurements. For comparison, the values for the formation of Pd_2Si obtained from similar experiments (XRD and DSC) are also reported in Tables 9.1 and 9.2.

The values for the interdiffusion coefficient (K_D) are in fair agreement with values from the literature [7,35]. The growth of Ni_2Si and Pd_2Si does not obey a pure parabolic (diffusion controlled) law, but is more likely a linear-parabolic one. The interface mobilities are usually difficult to measure, and only the combination of in situ XRD and DSC allows determining their values in this case. It should be noticed that the mobilities of the interface are relatively close to each other in the Ni and Pd systems.

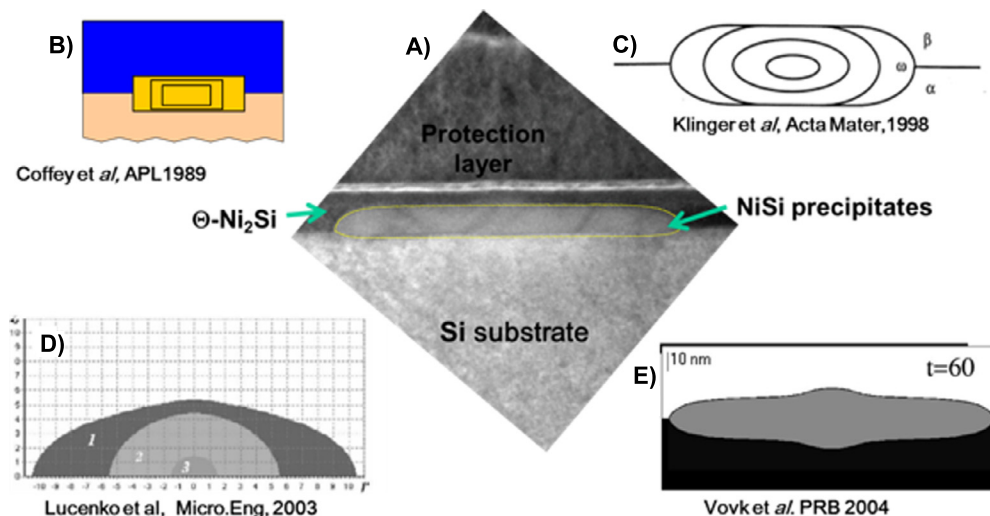


Figure 9.10 NiSi precipitate at the $\theta\text{-Ni}_2\text{Si}/\text{Si}(100)$ interface together with different models of lateral growth.

The mobility corresponding to lateral growth is also not very far from the mobility for normal growth. More studies on other systems should be done to confirm this tendency.

A further evidence of the lateral growth was obtained recently: El Kousseifi et al. [68] found the presence of a low density of NiSi particles at the $\theta\text{-Ni}_2\text{Si}/\text{Si}(100)$ interface during the reaction of Ni(10%Pt) film with Si substrate.

Fig. 9.10(A) shows the TEM images with the NiSi precipitates located at the interface between the $\theta\text{-Ni}_2\text{Si}$ and the Si substrate: the length of the particles was measured and varies between 130 and 380 nm while the thicknesses of the middle of NiSi particle varies between 13 and 17 nm, respectively.

The size of the NiSi particle observed in this study is very large compared to the typical critical size of a nucleus. Indeed, the formation of a critical nucleus requires fluctuations in composition [67] and this should limit the critical size to a few nm^3 . An estimate with typical Gibbs free energies (a few tens of kJ/mol) and typical interface energies (a few hundreds of mJ/m^2) gives also a few nm^3 . The situation observed in Fig. 9.10(B) is thus certainly not the first stage of nucleation but a later stage where the growth of the nucleus has already started. Moreover, the TEM images show that the ratio between the length and the thickness of the nuclei varies between 10 and 20. In addition, one can notice from the image in Fig. 9.10(A) that the particle did not consume the whole $\theta\text{-Ni}_2\text{Si}$ phase in thickness. This indicates a fast lateral growth compared to the normal growth of the NiSi nuclei. Fig. 9.10(A) shows that the position of the NiSi particle is asymmetrical toward the $\theta\text{-Ni}_2\text{Si}/\text{Si}$ interface. Indeed, the lateral growth of NiSi particles is more developed on a side of $\theta\text{-Ni}_2\text{Si}$ phase compared to Si

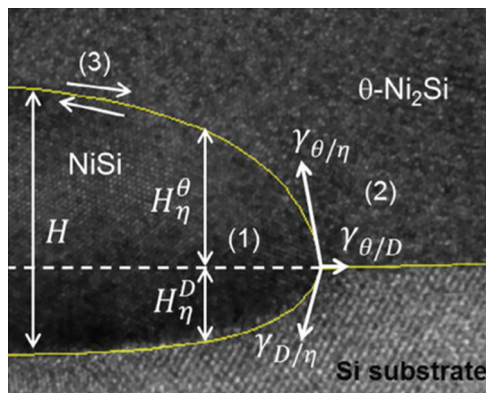


Figure 9.11 HR-TEM image of the NiSi particle obtained on the 250°C annealed Ni(10% Pt) sample observed in cross-section along the $\langle 110 \rangle_{\text{Si}}$ direction. The different parameter used in the Klinger model [73] modified to take into account the atomic volumes are indicated. The yellow line corresponds to the fit. Reprinted with permission from [68]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

substrate. This asymmetrical shape can be explained by the mass conservation during the reaction ($\theta\text{-Ni}_2\text{Si} + \text{Si} \rightarrow 2\text{NiSi}$).

Several experimental studies [11,29,64,65,69–71,19] found the presence of a discontinuous phase as the first results of the reaction between the two other phases. However, the shape of the entire particle was not reported in these studies; thus, it was not possible to compare these experimental results with existing models [11,71–73]. The TEM results provide a direct observation of the particle shapes, which are similar to the shape proposed in these models (Fig. 9.10). They also highlight that the formation of the NiSi phase begins by the nucleation and lateral growth at the $\theta\text{-Ni}_2\text{Si}/\text{Si}$ interface during the reaction of Ni (10 at.% Pt) films with Si.

Indeed, even the very simple shape (cylindrical particles) assumed in the Coffey model [11] is similar to the shape observed in Fig. 9.10(A) because NiSi particles can be approximately assimilated into cylinders. However, the TEM results provide more information on the shape, which can then be more quantitatively compared to the following models. The models of Lucenko [72] and Vovk [71] need numerical calculation and require several unknown parameters. Klinger model [73] leads to an analytical solution that is easy to handle, so it was chosen to fit the particle shapes by El Kousseifi et al. They have extended Klinger model to take into account the change in volume associated with different atomic volumes of the silicides and were able to fit the shape of NiSi precipitates.

The good agreement between the model and the experiments (Fig. 9.11) allows us to validate the assumptions of the model, i.e., lateral growth with conservation of mass, mechanical equilibrium at the triple junction, and diffusion along the interfaces driven

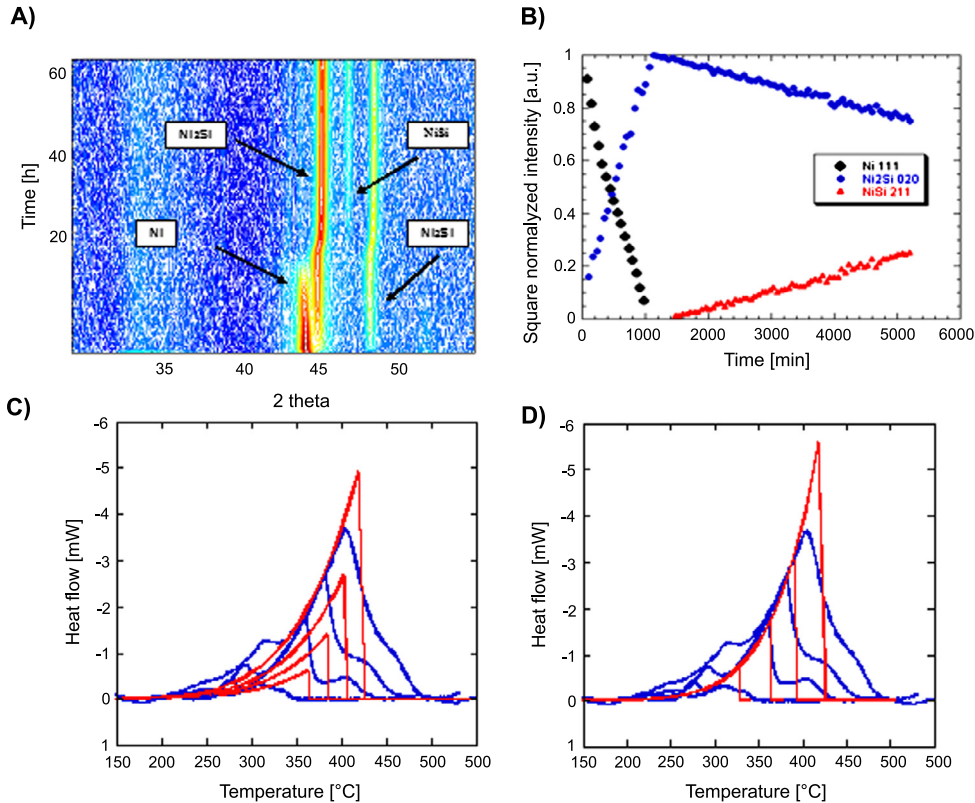


Figure 9.12 Reaction between Ni (50 nm) on α -Si (300 nm) bilayer deposited on a (100)Si substrate. (A) XRD intensity as a function of diffraction angle and time during an isothermal heat treatment at 210°C; (B) Variation of the square of the normalized intensities of the Ni 111, Ni₂Si 020 and NiSi 211 X-ray diffraction lines as a function of annealing time; (C) Comparison of the DSC thermograms and a simulation based on a diffusion controlled growth; (D) Comparison of the DSC thermograms and a simulation based on a reaction controlled growth. Reprinted with permission from [29].

by the gradient of curvature. For the diffusion, the mobility for both Si and Ni at the interface was determined to be 10^{22} at/(sJ) because they allow obtaining the precipitates diameter to be measured experimentally. These mobilities have dimensions of at/(sJ) instead of at/(m sJ) because the flux is a surface (or interface) flux with dimensions of at/(m s).

9.4.2 Normal Growth

The thickening of the precipitates was modeled by taking into account DSC thermograms obtained with four heating rates (10, 25, 50, and 100 K/min) and isothermal in situ XRD measurements such as the one in Fig. 9.12. Fig. 9.12(A) shows the variation

with time of the square of the normalized XRD intensities of the Ni 111, Ni₂Si 020, and NiSi 211 lines for an isothermal heat treatment at 210°C for the same 50 nm Ni film on amorphous Si. The formation of δ -Ni₂Si and NiSi is sequential: δ -Ni₂Si grows at the expense of Ni, and NiSi starts to grow only when Ni is totally consumed. In Fig. 9.12(A), the square of the XRD intensities varies linearly with time indicating that, for this heat treatment, the growth of δ -Ni₂Si and NiSi appears to be controlled by diffusion, in agreement with former reports [35].

Taking into account the results obtained by in situ XRD, the DSC peaks (dL/dt) were first modeled according to a diffusion controlled growth (Fig. 9.12(B)) but it was not possible to fit all the ramps using the same kinetic parameters (D_0 and Q) for normal growth [74]. Fig. 9.12(D) shows that a reaction controlled growth allows reproducing the peaks for the normal growth. In order to further improve the fit, the linear parabolic law in its derivative form was thus used (Fig. 9.9). The kinetic parameters controlling the growth of the M₂Si layer have thus been extracted from experimental data using a model that considers both interfacial reactions and atom diffusion through the growing M₂Si layer, i.e., the Deal and Groves growth law (linear-parabolic law for isotherm) [75]:

$$\frac{dL}{dt} = \frac{KD}{LK + D} \frac{\Delta G}{k_B T}. \quad (9.14)$$

L is the thickness of the M₂Si layer and k_B the Boltzmann constant. ΔG , the driving force of the growth, was assumed to be constant over the small experimental range of temperature. K_{NG} is the average effect of reactions at both interfaces, and D is the effective effect of both M and Si diffusion on the M₂Si layer growth. K_r and D could be obtained using the DSC measurement only, but for better reliability, equation (9.14) with the same parameter values was used to fit all XRD and DSC measurements. Indeed, XRD and DSC measurements were performed under different conditions (isotherm and temperature ramp annealing, respectively) and are related to different physical/chemical properties (Ni₂Si crystal structure for XRD and formation enthalpy for DSC). Since both D and K are thermally activated, Eq. (9.14) can be integrated only for an isothermal heat treatment. For isochronal treatments, numerical integration should be used. The values of K_r and D were obtained respectively by fitting the DSC experiments with an interface controlled growth law and XRD experiments with a parabolic law. They were then slightly adjusted in order to obtain the best fit for both XRD and DSC with Eq. (9.14). The final values are:

$$K = 0.25 \exp\left(\frac{-0.8}{k_B T}\right) \text{ cm/s} \quad \text{and} \quad D = 1.67 \exp\left(\frac{-1.5}{k_B T}\right) \text{ cm}^2/\text{s}. \quad (9.15)$$

As shown above, it is needed to use the linear parabolic law to fit the XRD and the DSC measurement of the normal growth of Ni₂Si. We will now discuss in more details this law and its implication in microelectronics.

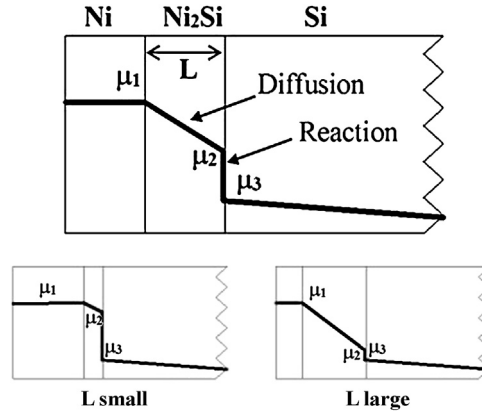


Figure 9.13 Schematic of the mechanisms involved in the linear parabolic growth.

The linear parabolic law is obtained by considering two phenomena that can control the growth (Fig. 9.13).

The first one is the diffusion across the growing Ni_2Si . If one considers that Ni is the main diffusing species [76] and that the chemical potential gradient is constant in Ni_2Si , the flux due to diffusion is proportional to $D \cdot (\mu_2 - \mu_1)/L$, where D is the interdiffusion coefficient, L the thickness of Ni_2Si , μ_1 and μ_2 are respectively the chemical potentials of Ni at the Ni/ Ni_2Si interface and at the Ni_2Si /Si interface in Ni_2Si . The second phenomenon is the interfacial reaction for which the flux is proportional to $K \cdot (\mu_3 - \mu_2)$, where K is the interfacial rate constant and $(\mu_3 - \mu_2)$ the difference in chemical potential at the moving interface. By equating these two fluxes and applying the law of conservation of matter, one obtains the Deal and Groves law [75] in its differential form:

$$\frac{dL}{dt} = \frac{KD}{KL + D} \frac{\mu_3 - \mu_1}{k_B T} = \frac{1}{\frac{L}{K_D} + \frac{1}{K_I}}, \quad (9.16)$$

where K_D and K_I are the diffusion and interface growing rates.

This law was also used to fit the growth of the Pt silicides measured by in situ XRD, sheet resistance and DSC, and will be detailed here.

The consumption of the reactant layers was obtained by the conservation of matter from the above equation and the molar volumes of the different phases. In thin films, the surface where the reaction takes place is constant, and thus the variation in volume is proportional to the variation in thickness for the layer. For XRD measurement, no large changes in texture were observed: the normalized XRD intensities were thus assumed to be proportional to the volume and thus to the thickness. For DSC, the heat flow is proportional to the volume (thickness) variation with time. For the sheet resistance measurements, the procedure developed by Zhang et al. [39,77] was followed,

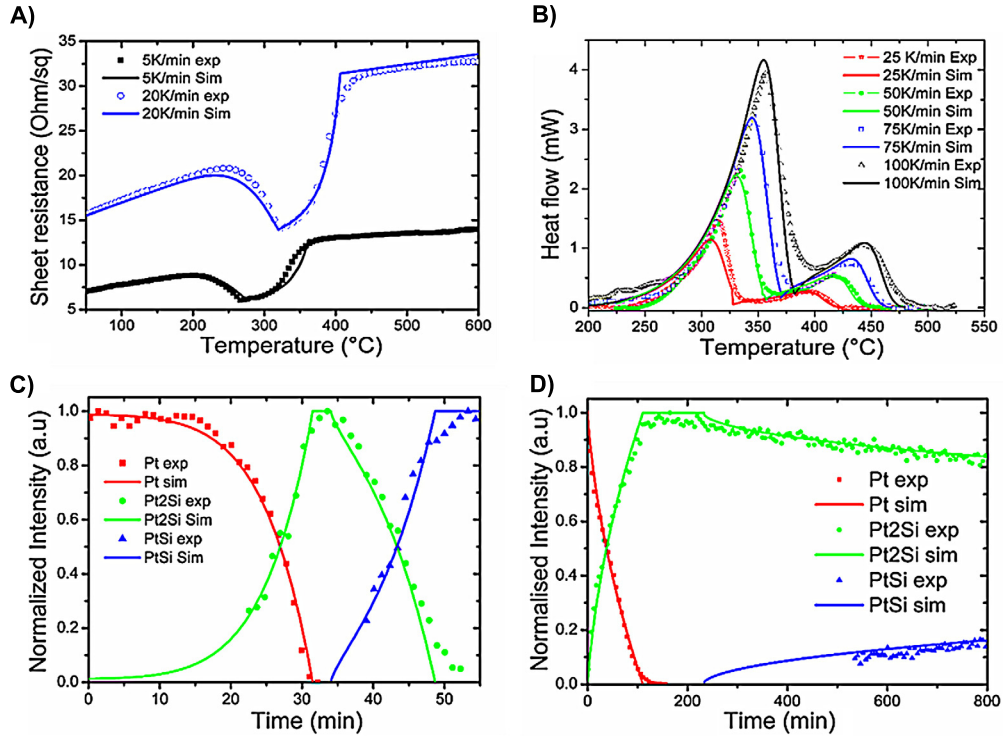


Figure 9.14 Simulation of the in situ experiments: the continuous lines corresponding to the simulation are superimposed onto the in situ experimental data obtained for 50 nm of Pt deposited on undoped Si substrates: (A) sheet resistance as a function of temperature, (B) DSC signal versus sample temperature measured during sample annealing following a ramp of 25, 50, 75, and 100°C/min, (C) integrated intensity of the (111) Pt, (112) Pt₂Si, and (020) PtSi XRD peaks as a function of the annealing time during annealing using steps of 4°C/min, and (D) the integrated intensity of the (111) Pt, (112) Pt₂Si, (002) Pt₂Si, and (020) PtSi XRD peaks as a function of the annealing time during the isothermal annealing at 200°C. Reprinted with permission from [147].

i.e., the resistivity of the different phases was assumed to vary linearly with temperature. The layer thickness was assumed to be uniform and the sheet resistance of the sample was expressed as: $1/R_{\text{sample}} = 1/R_{\text{metal}} + 1/R_{\text{silicide}}$. The contribution of the substrate was neglected since the resistivity of Si should be high at low temperatures at which the silicidation takes place and since the oxide layer is expected to insulate the substrate. The same kinetic parameters were used to fit simultaneously all the in situ measurements in order to have the best average agreement with the experience (Fig. 9.14). These simulations were superimposed to the experimental results in Fig. 9.14 and the values for the interface mobility and the diffusion growth rate are reported in Table 9.2. The error for the activation energies (Table 9.2) is approximately 0.05 eV.

Table 9.2 Values of the parameters used in Eq. (9.7) to describe the normal growth of Pd₂Si and Ni₂Si

System	Silicide	K_0 [cm/s]	E_r [eV]	D_0 [cm ² /s]	E_d [eV]
Ni/a-Si	δ -Ni ₂ Si	0.25	0.8	2	1.5
Pd/(001)Si	Pd ₂ Si	2	0.8	0.05	1.2
Pt/(001)Si	Pt ₂ Si	0.8	0.8	30	1.5
Pt/(001)Si	PtSi	0.2	0.8	10	1.7

To simulate the growth of PtSi, one has to take into account that the growth of PtSi starts after the formation and the relaxation of Pt₂Si. Thus a starting time for isotherm (XRD) or a starting temperature for isochrones (DSC, Rs) or steps annealing (XRD) was introduced in the simulation to take into account both the initial growth of Pt₂Si and the time delay for the growth of PtSi. Note that good agreement is obtained between experiment and simulation based on growth controlled by interfacial reaction and diffusion through the growing layer. It was not necessary in our experiment to use a simulation with Avrami kinetics as reported recently by Faber et al. [78]. The values obtained by the simultaneous fit of all the in situ measurement were $0.2 \exp(-0.80 \text{ eV}/kT) \text{ cm/s}$ and $10 \exp(-1.70 \text{ eV}/kT) \text{ cm}^2/\text{s}$ for the interface mobility and diffusion growth rate, respectively. The activation energy for diffusion growth rate is in accordance with Faber [78]. Given the difference in the in situ techniques and the experimental uncertainties linked to these techniques, one can consider that the simulation with the simple model based on diffusion in the growing phase and the reaction at the interface is quite good.

The values (D_0 and E_D) obtained for the interdiffusion coefficient are in fair agreement with literature values [7,35]. However, it should be noticed that the activation energy of K (interface rate) is lower than that of D (interdiffusion coefficient). Although one might at first expect the contrary, this is in accordance with previous results obtained for the growth of oxides or intermetallic compounds [79].

The growth of the silicide is thus controlled not only by the usual phenomenon of diffusion but also by the reaction at the interface. These results (Figs. 9.12 and 9.14) show that, with the relatively fast heating ramp used in DSC, the growth is mainly limited by the interfacial reaction while isothermal heat treatment at relatively low temperature leads to a growth controlled by diffusion. This can be understood if one takes into account the two limiting cases of Eq. (9.16). If the thickness of the growing phase is much inferior to a transition thickness defined by $L_t = \frac{D}{K}$, the growth will be mainly controlled by the interfacial reaction while in the other case it will be controlled by diffusion. The relation between L_t and the temperature T_t is the following:

$$L_t = \frac{D_0}{K_0} \exp\left(\frac{-(E_D - E_i)}{k_B T_t}\right) \quad \text{or} \quad T_t = \frac{E_D - E_i}{k_B \ln\left(\frac{D_0}{L_t K_0}\right)}. \quad (9.17)$$

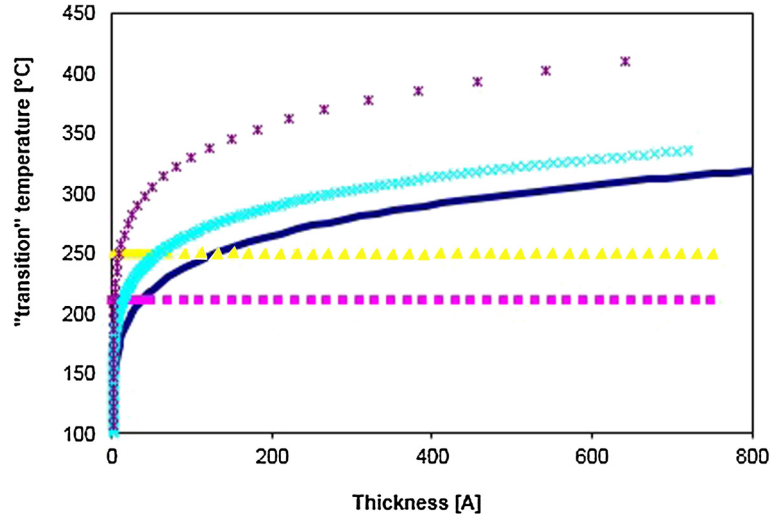


Figure 9.15 Variation of T_t as a function of L_t for Ni_2Si showing the two domains of growth: interfacial reaction and diffusion. The variation of the thickness as a function of temperature for two of the DSC ramps (10 and 100 K/min) and two of the XRD isotherms (210 and 260°C) is also shown. Reprinted with permission from [29].

Fig. 9.15 shows the variation of T_t as a function of L_t for Ni_2Si . In this figure, two domains can be defined: one where the growth is mainly controlled by interfacial reaction and one where it is mainly controlled by diffusion. It should be emphasized that the growth is always controlled by both phenomena but will be mainly controlled by one of them if the measurement is performed far from the boundary between the two domains. The variation of the thickness as a function of temperature for two of the DSC ramps (10 and 100 K/min) and two of the XRD isotherms (210 and 260°C) has also been schematically reported in Fig. 9.15. It can be seen that the XRD experiment at the lowest temperature is mainly in the diffusion controlled domain while the DSC experiment with the 100 K/min ramp is clearly in the interface-controlled domain. In a general manner our results show that the interface-controlled regime will dominate at low thickness and high temperature. This is quite important in microelectronics where the thickness of films is continuously decreasing and where heat treatments are performed using fast heating ramps (rapid thermal process, flash annealing). The knowledge of the interface mobilities is also important to understand the sequential growth of the silicide and germanide as will be detailed in the next part of this chapter. However, one should be aware before using a very simple view of the growth such as the interface/diffusion controlled model that there might be quite a lot of phenomena (nonequilibrium defects, grain growth, change of texture, etc.) that can influence the growth, especially when heat treatments are performed very far from equilibrium or quasi-equilibrium.

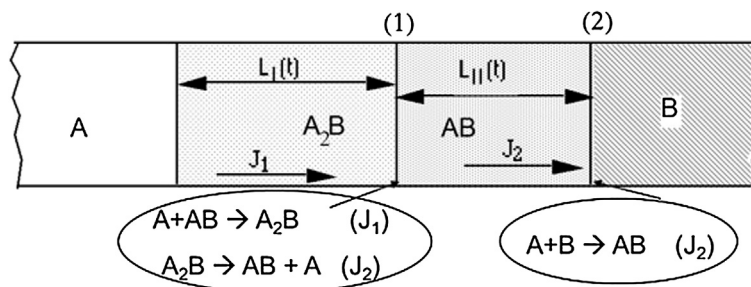


Figure 9.16 Schematic of the growth of two phases assuming that the main diffusion species is A.

9.4.3 Sequential Versus Simultaneous Growth

As illustrated in Fig. 9.16 (Ni/Si reactions), one specific characteristic of the reaction in thin films is the sequential growth: namely, that when, for example, nickel thin films react with silicon, the second phase to form, NiSi, does not appear until all the nickel has been consumed in the formation of Ni₂Si. Examination of the interfaces with TEM indicate that the Ni₂Si/Si interface remains sharp during the growth of Ni₂Si, so that the observed absence of NiSi is a real physical phenomenon, not an illusion based on the failure to use sufficiently sensitive means of investigation.

Many explanations have been given for the sequential growth [80,81], including a model for sequential growth based on the kinetic competition between two phases in which the Deal and Grove law was applied.

D'Heurle and Gas [5,43] gave a simpler version that will be presented here.

To understand the sequential formation, one has to consider the simultaneous formation of two phases. When two phases grow together, the situation becomes more complex since the kinetics of growth of each phase will depend not only on the characteristics of this phase (kinetics of reaction, diffusion coefficient) but also on the characteristics of all the phases present in the A/B diffusion couple. Let us, for example, consider a system where two phases (A₂B and AB) with the same atomic volume form simultaneously, and let us suppose that only the same element A is mobile in both phases (Fig. 9.16).

In these conditions the growth of A₂B happens at the A₂B/AB interface by the reaction $A + AB \rightarrow A_2B$ while the growth of AB happens at both A₂B/AB and AB/B interfaces. At the first interface the reaction $A_2B \rightarrow AB + A$ gives free A atoms which will cross AB to give the reaction $A + B \rightarrow AB$ at the AB/B interface. If one calls J_1 and J_2 the respective fluxes of A in A₂B and AB, one finds for the growth of A₂B and AB:

$$\begin{aligned}\frac{dL_1}{dt} &= \Omega(J_1 - J_2) \\ \frac{dL_2}{dt} &= \Omega(-J_1 + 2J_2).\end{aligned}\tag{9.18}$$

This system of equations shows the coupling existing between the growth rates of different phases. As the fluxes J_1 and J_2 may be controlled by different processes (reaction at interfaces or diffusion), the growth in the case of simultaneous formation can be complex [82].

For the sake of simplification, we shall again consider the growth of two phases A_2B and AB between A and B , where only A is assumed to be mobile (see Fig. 9.16).

Using the Nernst–Einstein relation (Eq. (9.2)) to define J_1 and J_2 gives:

$$\begin{aligned}\frac{dL_1}{dt} &= \frac{\alpha}{L_1} - \frac{\beta}{L_2} \\ \frac{dL_2}{dt} &= -\frac{\alpha}{L_1} + 2\frac{\beta}{L_2},\end{aligned}\tag{9.19}$$

$$\begin{aligned}\text{with } \alpha &= D_1 \Delta G_1 / RT \\ \beta &= D_2 \Delta G_2 / RT.\end{aligned}$$

Note that Eq. (9.19) is valid only if the atomic volumes are equal in all phases.

Although the relative magnitudes of L_1 and L_2 can vary, according to these relations neither L_1 nor L_2 can become zero since whenever these two quantities become small, dL_1/dt and dL_2/dt tend towards infinity. While the mathematics of Fick's law or of the Nernst–Einstein relation mandate that diffusion should be infinitely fast when the thickness of a growing layer is infinitely small (obviously a physical impossibility), when the reaction rate is in control, this is no longer true. In particular, it has been shown [80] that the competition between reaction rate and diffusion controls can explain the sequential growth in thin film. As a simple approach, one may consider that the flux J_2 through AB is limited to a constant value (reaction limited) if the thickness of AB is small.

$$\frac{dL_2}{dt} = -\frac{\alpha}{L_1} + 2K_2.\tag{9.20}$$

In order for the phase AB to grow, dL_2/dt should be greater than zero. One obtains the following relation:

$$L_1 = L_{1c} > \frac{\alpha}{2K_2}.\tag{9.21}$$

AB will not grow until L_1 has reached a critical value L_{1c} , whose magnitude increases when: (a) diffusion through A_2B increases, and (b) the reaction rate limiting factor in AB becomes smaller (more rate limiting).

In thin film, the metal will be fully consumed before A_2B reaches the critical thickness that is of several hundreds of nanometers. For example, for the growth of Ni_2Si and $NiSi$, one obtain a critical thickness of Ni_2Si of about 200–300 nm.

To illustrate the sequential versus simultaneous growth, we will now compare Ni silicide and Ni germanide formation.

Germanide formation has been much less studied than the silicide one. Only a few systems were studied (for a short review, see [82]), but in a recent work, Gaudet et al. [82] have performed a systematic study of the reaction of 30 nm thin film of 20 transition metals (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, and Cu) with Ge substrates using in situ XRD with synchrotron radiation. Fig. 9.17 shows the formation sequence for thin films of these 20 elements on either Ge(100) or amorphous Ge (α -Ge). Gaudet et al. observed many dissimilarities between the phase sequences reported in the literature and their in situ results concerning the formation of the first phase.

During in situ XRD, several phases were detected only over relatively short temperature windows. As the phase formation sequences are typically determined using anneal-and-quench experiments in which the temperature interval between measurements is of the order of 25°C or more, some phases could have been inadvertently missed in anneal-and-quench experiments. Furthermore, the nature of the substrate, the film thickness, and the annealing conditions varied considerably in these investigations. It is therefore not surprising that different phase sequences have been reported in the literature.

In most of the 20 systems, the germanides usually grow sequentially during thin film reactions, meaning that only one phase would grow at the expense of another at a given time. However, in a few of these systems (Pt–Ge, Ta–Ge, and Ni–Ge), several germanides can coexist. For Fe, Co, and Ti, the formation can be either sequential or simultaneous, depending on the substrate nature: for Fe and Co, the formation is sequential on crystalline Ge and simultaneous on amorphous Ge while it is the opposite for Ti.

The results of Gaudet et al. are in agreement with the former observation by Nemouchi et al. [83] that Ni_5Ge_3 grows simultaneously with NiGe during the reaction of 50 nm of Ni. These authors have done a complete analysis of the kinetics of simultaneous formation that will be presented now.

Based on a few reports about nickel–germanium reactions, the kinetics reactions have the same estimate order of Ni–silicide [84] with Ni as the major mobile species. It is usually found that the growth of thin film nickel germanides is sequential with two phases in the sequence: the first one is an Ni-rich phase, then the monogermanide NiGe grows. If the available reports agree on the second and final phase (NiGe), they are different in the reports for the first phase. Some authors report orthorhombic Ni_2Ge [85–87] while others monoclinic Ni_5Ge_3 [88] or hexagonal Ni_3Ge_2 [89]. The contro-

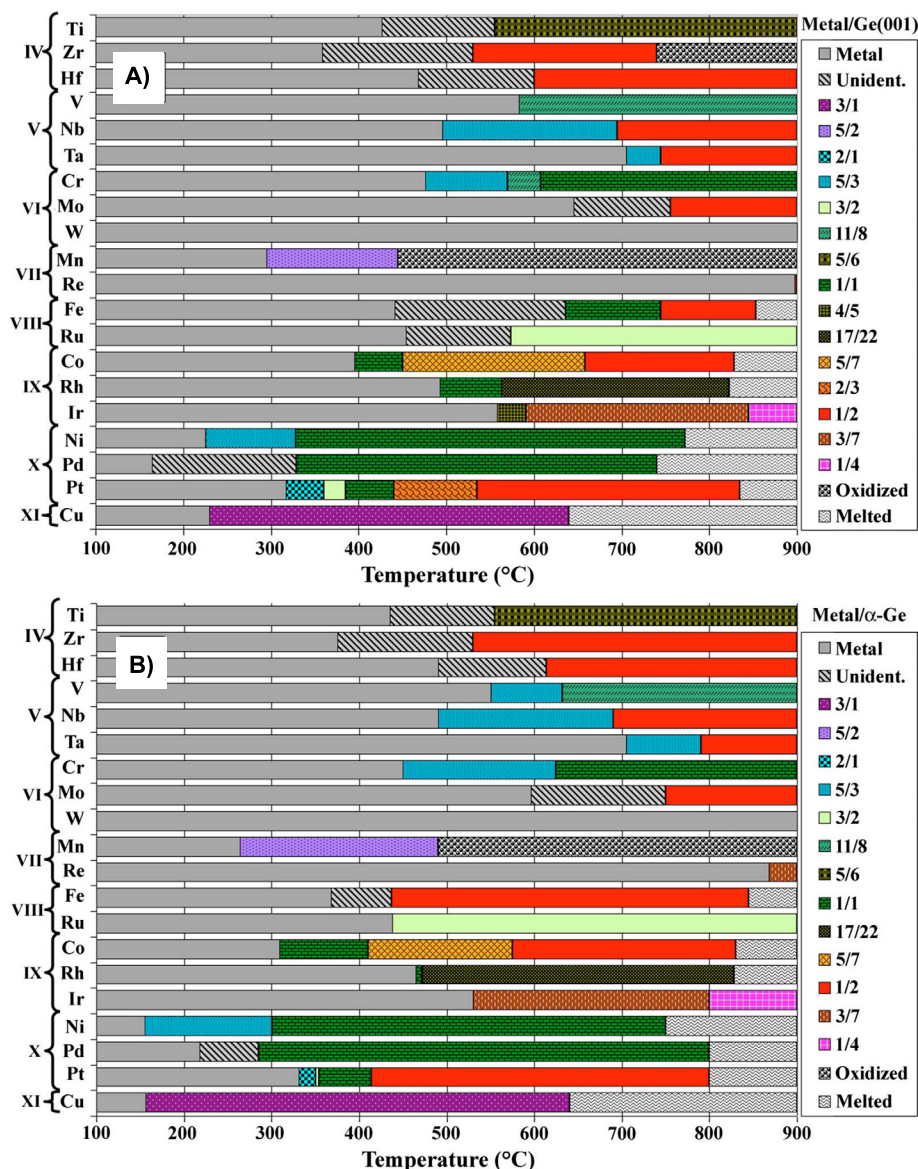


Figure 9.17 Phase sequence of the reaction of 30-nm-thick transition metal films capped with a 5-nm-thick α -Ge overlayer deposited on (a) Ge(001) and (b) α -Ge during a 3°C s^{-1} ramp annealing in purified He. Metal-to-germanium ratios in each germanide phase are indicated in the color-coded legend. Reprinted with permission from [82].

versy of the first Ni-rich phase comes from several reasons: (i) these three compounds are close in Ni proportion (less than 10% between Ni_2Ge and NiGe) so it difficult to

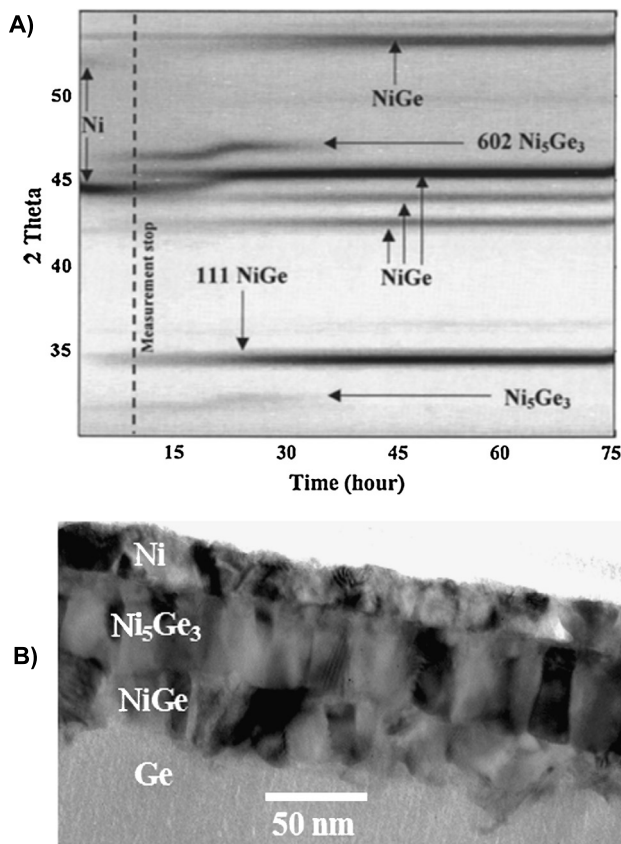


Figure 9.18 (A) In situ X-ray diffraction measurements of 50 nm Ni films deposited on amorphous Ge annealed at 250°C using Bragg–Brentano geometry, (B) TEM examination and EELS analysis after an annealing at 180°C during 110 min. Reprinted with permission from [83].

identify by mass detection; (ii) their crystallographic structure gives the same strongest lines for X-ray or electron diffraction due to closed unit cell parameters.

Nemouchi et al. [83] have studied the formation of nickel germanides obtained by solid state reaction between a 50 nm Ni film and amorphous Ge (Fig. 9.18). They found that the first phase is Ni₅Ge₃ by XRD and TEM, and then followed the phase formation by in situ XRD.

Fig. 9.19 shows the integrated intensities for the Ni₅Ge₃ and NiGe as a function of time for annealing at 150°C. The simultaneous formation Ni₅Ge₃ and NiGe is observed until the Ni film is fully consumed (about 20 hours) and then NiGe grows at the expense of Ni₅Ge₃.

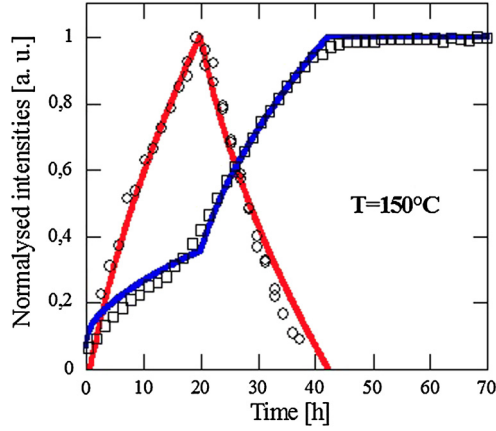


Figure 9.19 Normalized integrated intensities for Ni_5Ge_3 and NiGe as a function of time for an annealing at 150°C . Reprinted with permission from [83].

In order to fit the peak intensity evolution, the growth of the germanides was assumed to be controlled by diffusion and reaction [43,90]:

$$\begin{aligned}\frac{dL_1}{dt} &= a_{11} \frac{D_1}{L_1 + D_1/K_1} - a_{12} \frac{D_2}{L_2 + D_2/K_2} \\ \frac{dL_2}{dt} &= a_{21} \frac{D_1}{L_1 + D_1/K_1} - a_{22} \frac{D_2}{L_2 + D_2/K_2},\end{aligned}\quad (9.22)$$

where D_1 , D_2 , K_1 , and K_2 are the interdiffusion coefficients and the interface coefficients for Ni_5Ge_3 and NiGe , respectively.

If one further assumed that Ni is diffusing much faster than Ge in the germanides and that germanides are stoichiometric, the a_{ij} coefficients are given by:

$$\begin{aligned}a_{11} &= 1/2\Phi_1, & a_{12} &= \Omega_1/2\Omega_1\Phi_2, \\ a_{21} &= 3\Omega_2/2\Omega_1\Phi_1, & a_{22} &= 5/2\Phi_2,\end{aligned}$$

where

$$\begin{aligned}\Phi_1 &= [4G(\text{Ni}_5\text{Ge}_3) - 3G(\text{NiGe})]/RT, \\ \Phi_2 &= [-4G(\text{Ni}_5\text{Ge}_3) + 5G(\text{NiGe})]/RT.\end{aligned}$$

$G(\text{Ni}_5\text{Ge}_3)$ and $G(\text{NiGe})$ are the free energies of formation of the germanides and are equal [63] to 3000 and 3200 J/at.gr, respectively. Eqs. (9.22) are valid for the simultaneous growth of Ni_5Ge_3 and NiGe . When Ni has been totally consumed, the growth of NiGe and shrinkage of Ni_5Ge_3 can be simply obtained by setting a_{11} and a_{21} to zero in Eqs. (9.22). In order to reduce the number of fitting parameters, the ratio D_2/K_2 was

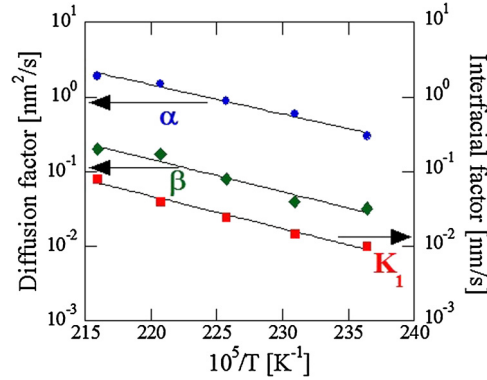


Figure 9.20 Arrhenius plot of the kinetics parameters for the growth of NiGe and Ni₅Ge₃.

supposed to be very small and neglected for the simulation (i.e., a pure diffusion controlled growth was assumed for NiGe). Indeed, if during the first stage of the growth of NiGe the growth law is difficult to establish because of the scattering of the data, the thickness is clearly proportional to the square root of the time during the second stage, meaning that the growth is controlled by diffusion. However, it was very difficult to fit the growth of Ni₅Ge₃ by a diffusion control growth and thus a diffusion–reaction law was used. In the simulation, the maximum thicknesses for NiGe and Ni₅Ge₃ were calculated by considering that all the Ni was transformed into NiGe and Ni₅Ge₃ or into NiGe at the end of the reaction.

Using this phase competition model, Nemouchi et al. fit the XRD in-situ measurements (Fig. 9.19) applying the equation system (Eqs. (9.22)) and obtained the reaction rate of Ni₅Ge₃ and NiGe for each annealing temperature. Fig. 9.20 shows the values obtained for α_1 , α_2 , and K_1 as a function of the reciprocal temperature. The diffusion factors (α_1 and α_2) and the interface factor follow an Arrhenius law with the following dependency:

$$D_1 = 10^{-7} \exp\left(\frac{-0.8 \text{ [eV]}}{k_B T}\right) [\text{cm}^2/\text{s}],$$

$$D_2 = 10^{-7} \exp\left(\frac{-0.9 \text{ [eV]}}{k_B T}\right) [\text{cm}^2/\text{s}],$$

$$K_1 = 30 \exp\left(\frac{-0.9 \text{ [eV]}}{k_B T}\right) [\text{cm}^2/\text{s}].$$

This means that, in the temperature range examined in this study, only one phenomenon is responsible for mass transport in the growing layers and for what happens at the interfaces. It should be mentioned that, from the definition we used, the inter-

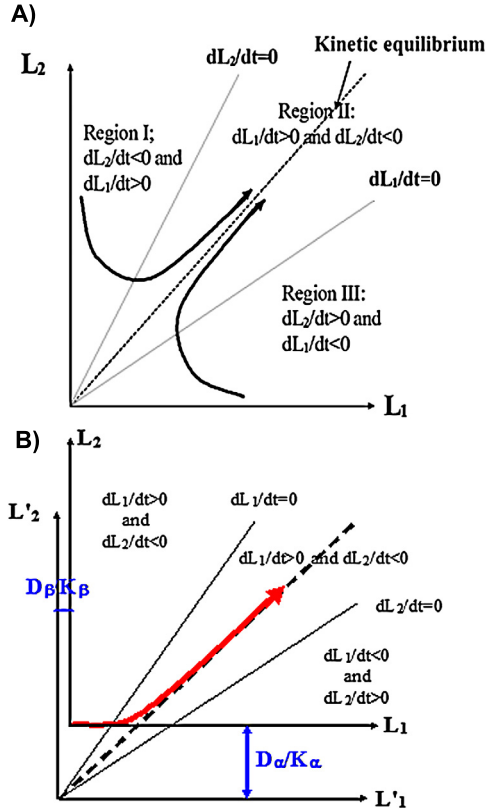


Figure 9.21 Variation of the thickness for two growing phases: (A) with a diffusion control growth, (B) with a growth controlled both by diffusion and interface.

diffusion coefficient doesn't take into account the thermodynamic factor (Φ/RT) that is in the range from 3 to 10.

As the representation proposed by Johnson and Martin [90,91] is very useful to understand reactive diffusion, it will be explained in some details now. Fig. 9.21 shows the thickness of phase 2 as a function of the thickness of phase 1 for a diffusion control growth of the two phases corresponding to the following equations:

$$\begin{aligned} \frac{dL_1}{dt} &= a_{11} \frac{\alpha}{L_1} - a_{12} \frac{\beta}{L_2} \\ \frac{dL_2}{dt} &= -a_{21} \frac{\alpha}{L_1} + a_{22} \frac{\beta}{L_2}, \end{aligned} \quad (9.23)$$

$$\begin{aligned}\text{with } \alpha &= D_1 \Delta G_1 / RT \\ \beta &= D_2 \Delta G_2 / RT.\end{aligned}$$

Three regions can be defined and are delimited by the two lines where $dL_1/dt = 0$ and $dL_2/dt = 0$.

In the upper region (region I), L_2 is large and L_1 is small. Consequently, $a_{21}\alpha/L_1$ is large and $a_{22}\beta/L_2$ is small, and thus dL_2/dt is negative and dL_1/dt is positive. Phase 2 thus shrinks while phase 1 is growing. The reverse is true in the lower region (region III): phase 1 shrinks while phase 2 is growing. In the medium region (region II), both phases are growing. The dotted line corresponds to a “kinetic equilibrium” where both phases are growing proportionally to the square root of time. In bulk diffusion couple, one may assume that the kinetic equilibrium holds.

Let us now consider the case where both phases follow the Deal and Grove law. The differential equations for the growth of the two phases are now:

$$\begin{aligned}\frac{dL'_1}{dt} &= a_{11} \frac{\alpha}{L'_1} - a_{12} \frac{\beta}{L'_2} \\ \frac{dL'_2}{dt} &= -a_{21} \frac{\alpha}{L'_1} + a_{22} \frac{\beta}{L'_2},\end{aligned}\tag{9.24}$$

$$\begin{aligned}\text{with } L'_1 &= L_1 + \alpha/K_1 \\ L'_2 &= L_2 + \beta/K_2.\end{aligned}$$

Eqs. (9.24) are similar to Eqs. (9.23) if one replaces L by $L' = L + \alpha/K$ (Fig. 9.21(B)) and the same regions as in Fig. 9.21(A) can be defined. However, L_1 or L_2 could be mathematically negative in some region: of course, this has no physical sense and the thickness should thus be null there. In other words, the thickness of phase 1 has to reach a critical value before phase 2 can grow.

The representation defined by Johnson and Martin [90,91] has been plotted in Fig. 9.22 for the Ni/Si and Ni/Ge system. It can be seen that there is a critical thickness that Ni_5Ge_3 has to reach before that NiGe can grow. From the present measurement, this critical thickness is around 10–15 nm. This is quite different than the usual sequential formation observed during the silicide formation in thin film. For example, during the reaction of Ni thin film with Si, there is a critical thickness for the Ni-rich silicide (Ni_2Si) before NiSi can grow. This critical thickness has been estimated [80] to be of 150–200 nm. However, several factors (difference in substrate, presence of impurities, etc.) have been shown to change the sequential growth of the silicide to a simultaneous growth (see [43] for a review).

For example, Gaudet et al. [82] found that simultaneous growth of the germanide for Pt, Ta, and Ni all on α -Ge and Ge(100), for Fe and Co films on α -Ge, and Ir films on Ge(100).

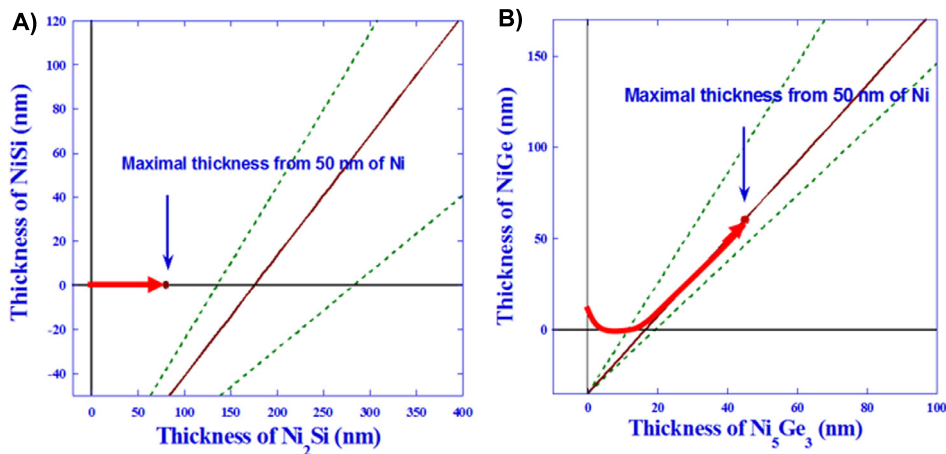


Figure 9.22 Variation of the thickness for two first growing phases in (A) the Ni/Ge system, (B) the Ni/Si system.

The critical thickness depends on the ratio between the diffusion factor and the interface factor. Ni germanide is growing at lower temperatures (around 100°C) than Ni silicide, and the large diffusion coefficient in the germanide compared to the one in silicides might induce an interface controlled growth. This difference in diffusion coefficient comes partly from the low activation energies of the germanides (0.8–0.9 eV) compared to the silicides (1.5–1.7 eV). The low activation energies may be explained to some extent by the low melting point of the germanides.

On the other hand, the origin of the interface coefficients is not well-known: they may be due to several phenomena, including reaction at the interface, transfer of atoms through the interface, stress or defect relaxation. Both the diffusion and interface coefficients might be affected by the substrate crystalline or by the presence of impurities. However, knowledge of the interface coefficient is important to understand and control the intermetallics formation in nanometric scale. The activation energies for the interface factor (0.9 eV) and for the diffusion coefficient (0.8 eV) for Ni_5Ge_3 are comparable. This is another difference with the Ni silicide for which the activation energy for the interface was smaller than that for diffusion in the case of Ni_2Si [29].

9.4.4 Stress During the Formation of Silicide

It has been shown that silicide formation is accompanied by stress and concomitant relaxation of this stress [8,12,92,93]. The presence of strain and stress fields can affect transistors performance [94,95] and thus impact microelectronic devices. Thermoelastic stress due to the difference in dilation behavior between silicide and Si is also playing

an important role in devices [96]. In this chapter, we will focus on the stress associated with the formation of the silicide and not on the thermoelastic stress.

The formation of a new phase from the initial reactants implies a considerable change in volume. This is thought to be the origin of the stress that develops during growth. For stresses caused by metal oxidation, it is customary to refer to the Pillings–Bedworth relation between the volume of metal and the corresponding volume of oxide.

In a thin film, which is attached to a rigid substrate, the volume change has to be accommodated by in-plane strain

$$\varepsilon_{//} = -\frac{1}{3} \frac{\Delta V}{V}, \quad (9.25)$$

where $e_{//}$ is the in-plane strain and $\Delta V/V$ the volume change caused by the formation of the new phase. For the precipitation of a compound A_pB_q from a homogeneous alloy, the overall volume change is

$$\frac{\Delta V}{V} = \frac{V_{A_pB_q} - pV_A - qV_B}{pV_A + qV_B}. \quad (9.26)$$

For silicide and germanide, $\Delta V/V$ is negative, which implies tensile stress buildup in the precipitates.

In thin film reactions, however, the problem is quite different because the reaction takes place at a specific interface. Let us consider, for example, the growth of Ni_2Si from the reaction of Ni with Si. Since Ni is the most mobile diffusing species in Ni_2Si , the reaction occurs at the $\text{Ni}_2\text{Si}/\text{Si}$ interface. Thus the volume change is

$$\frac{\Delta V_S}{V} = \frac{V_{\text{Ni}_2\text{Si}} - V_{\text{Si}}}{V_{\text{Si}}}, \quad (9.27)$$

which is positive. One expects therefore a compressive stress to develop in agreement with experimental observations. In particular, the Ni_2Si phase formation induces a compressive intrinsic stress that relaxes after the complete formation of Ni_2Si phase in the case of pure nickel film [59]. A similar reasoning can be presented for many silicides [93], whether they grow via metal motion or Si motion like MoSi_2 ; then the stress may be related to the relative volumes of metal and silicide. In a vast majority of cases compressive strains are predicted in agreement with experimental observations.

This agreement is nevertheless only qualitative. Indeed, the volume change $\frac{\Delta V_S}{V}$ which appears in Eq. (9.27) is very large: in the case of Ni_2Si growth, it is 66%, which would yield a biaxial stress much higher than the theoretical critical shear strength. Experimentally, the initial stress in the silicide is of the order of -2 GPa and cannot account for the volume change. Plastic relaxation is thus expected to take place.

Indeed, a stressed system with a sufficient temperature tends to relax. The relaxation phenomenon has been studied extensively by Frost and Ashby in metals [97] and

described by Ito et al. in the bulk CoSi_2 silicide [98]. However, thin film exhibits a particular microstructure, which probably makes its relaxation different than in the bulk. The relaxation mechanisms in polycrystalline metal films can be used to understand relaxation in the case of silicides. In general, the relaxation mechanism depends on the temperature which is expressed relative to the melting temperature of the material. Moreover, the relaxation depends also on the applied stress on the material and capacity to maintain its structure, which is determined by the material shear modulus. Finally, it depends on the microstructure of the material. In fact, the microstructure is an important factor for relaxation because of the particular microstructure and small dimensions involved in thin films, the relaxation can be distinguished from the bulk relaxation. Furthermore, the relaxation can be divided into two main categories: relaxation can be based on the movement of dislocations, or the movement (or redistribution) of matter [99]. During silicidation, several stress related processes occur simultaneously: the development of growth stress related to the phase formation, the development of thermal stress in both the parent phase, which is being consumed, as well as in the growing daughter phase and the thermally activated relaxation of the generated stresses. F.M. d'Heurle, and S.-L. Zhang [8,92] developed a phenomenological model which accounts reasonably well for the observed behavior. The model describes the evolution of the force as a result of competing stress buildup due to volume change and stress relaxation. The force arising from the former occurs at a rate given by the growth rate, while the latter depends on the stress relaxation mechanism at work. The key ideas of the model were that the dominant diffusing species governs the normal growth of the phase while the relaxation requires mobility of both fast and slow diffusing species (for example, by a creep mechanism along grain boundaries, i.e., Cobble creep), and therefore requires higher temperature. Both growth and relaxation were thus considered as a thermally activated process; a Newtonian viscous flow relaxation was assumed with a relaxation time t . In short, the stress at location z (measured from the growing interface) within the silicide film is the instantaneous growth stress σ_0 , which has relaxed by an amount related to the time when this particular slice dz was formed. This model was able to reproduce the behavior during Pd silicide formation as shown in Fig. 9.23. However, Fig. 9.24 shows that Ni_2Si relaxation is faster than the growth of Ni_2Si , whereas it should be the on the contrary according to the model of Zhang and d'Heurle. This might be due to the sequential formation of NiSi after Ni_2Si but similar behavior was also observed for the formation of Pd_2Si on $\text{Si}(100)$ [93] while no Pd silicide forms after Pd_2Si . Moreover, it was shown that the stress relaxation is faster for Pd_2Si on $\text{Si}(100)$ than on $\text{Si}(111)$ [100]. This was attributed to the epitaxy of Pd_2Si on $\text{Si}(111)$ rather than to different relaxation mechanisms [100]. The real situation is thus more complex than the simple model.

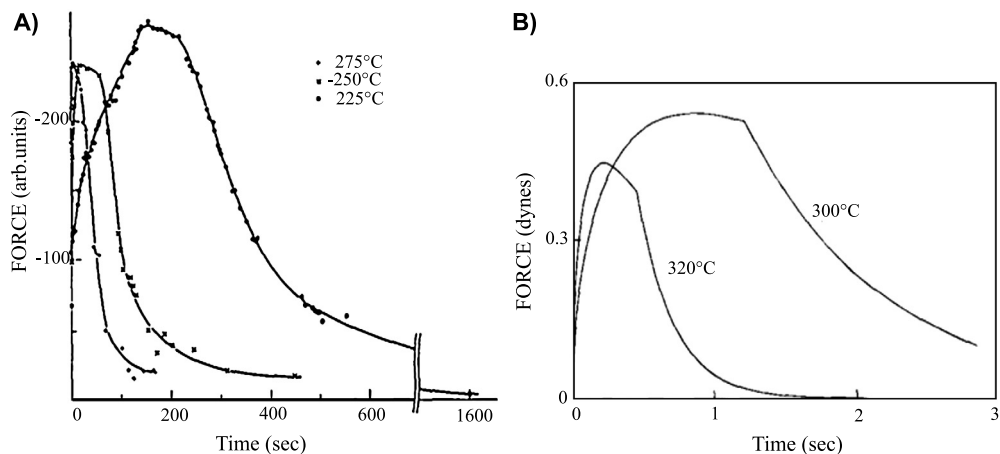


Figure 9.23 Stress during the formation of silicide: (A) The force F_c observed during the formation of Pd_2Si at different temperatures. (B) The evolution is qualitatively similar to that obtained in by the model of Zhang and d'Heurle [99_92Zha]. Reprinted with permission from [92].

The stress can also have a direct influence on the formation of the silicide. Indeed, the formation of NiSi by reactive diffusion was found to be related to the stress in the Ni_2Si phase.

Fig. 9.24 shows the evolution of XRD peaks during an in situ XRD measurement at 210°C of a 50 nm Ni film on a-Si . The square of the normalized area of the XRD peaks is plotted as a function of time. The $(112)\text{Ni}_2\text{Si}$ and $(112)\text{NiSi}$ peaks situated around 48° and 47° were found to be characteristic of the Ni_2Si and NiSi phase, respectively. Since the XRD intensity is proportional to the crystalline volume, the intensities are directly related to the layer thickness. The good linear fit of the experimental points (Fig. 9.24(A)) shows that the growth of Ni_2Si and NiSi is mainly controlled by diffusion for this heat treatment in accordance with former results. An important feature of Fig. 9.24(A) is that the start of the growth of NiSi doesn't coincide with the end of the growth of Ni_2Si and thus with the complete consumption of the Ni film. There is a time delay of about 20 min at this temperature. Similar behavior was observed for heat treatment at other temperatures (180, 200, and 220°C). Arrhenius behavior was found for the time delay with an activation energy of 1.2 eV, indicating that the time delay is associated with a thermally activated phenomenon.

The presence of a time delay is not in accordance with the sequential formation usually reported in thin film. Indeed, in the classical scheme of sequential growth, NiSi should start to grow as soon as Ni_2Si has consumed the entire Ni layer. Fig. 9.24(A) shows also that the relative variation of the $(200)\text{Ni}_2\text{Si}$ spacing is mainly occurring during the time delay between the end of Ni_2Si growth and the start of NiSi growth. No significant shift in the lattice spacing of NiSi was found.

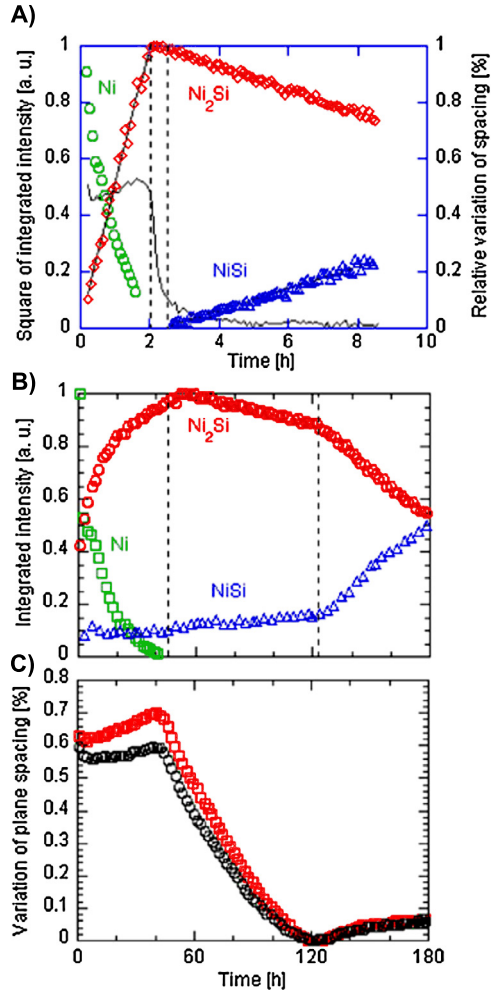


Figure 9.24 Stress relaxation and phase formation during annealing at 210°C of (A) a 50 nm Ni/300 nm α -Si on 100Si: square of the XRD integrated intensity and perpendicular strain for Ni_2Si as a function of the annealing time, (B)–(C) a 50 nm Ni5%Pt film on 100Si: (B) variation of the integrated intensity of the XRD peaks as a function of the annealing time and (C) variation of the perpendicular strain for the 020 and 211 peaks of Ni_2Si phase as a function of the annealing time. Reprinted with permission from [14].

Similar behavior was also observed in another system, i.e., Ni(Pt) films on (100)Si (Fig. 9.24(B)–(C)). In this case NiSi grows simultaneously with Ni_2Si phase. The growth of the Ni_2Si phase (for time below 60 hours) is complex and is partly linked to the redistribution of Pt as will be detailed later. After 60 hours, the maximum intensity of the Ni_2Si diffracted peak is reached and the formation of Ni_2Si is complete. Then, the

Ni_2Si thickness is almost constant and NiSi grows slowly. The rapid growth of NiSi at the expense of Ni_2Si occurs only after this time delay of about 60 hours, i.e., for time greater than 120 hours. Similarly to the case of pure Ni film on amorphous Si , this time delay is related to the relaxation of Ni_2Si .

It appears thus as a time delay between the end of the Ni_2Si growth and the start of the growth of NiSi at the expense of Ni_2Si . The time delay may thus be interpreted as an incubation time usually observed for nucleation. However, in the case of Ni(Pt) on $(100)\text{Si}$, NiSi is already present and does not need to nucleate. One should thus conclude that the time delay is not only a nucleation incubation time but also more likely due to the kinetics of growth. As the time delay is related to a change in the Ni_2Si lattice parameter, it is most probably due to the stress development and relaxation during the growth of silicides.

Johnson and Martin [91] have theoretically shown that stress can modify the formation kinetics of one phase (or two phases) growing by reactive diffusion between two other phases. They took into account the effect of stress on the stability of the phases as well as on the diffusion in the growing phases. Stress can also affect interdiffusion, point defects and interface mobility, and thus the formation of NiSi . The influence of stress on the formation of NiSi can have important consequences for the application of this silicide in microelectronics. Indeed, silicides are usually formed in different zones of the devices where the stress can be different. For example, they are confined in two directions in source and drain, while in gate the confinement is only in one direction. Stress is also used in some devices to enhance the mobility of electrons and holes.

9.4.5 Transient Phase

The classical phase sequence described above can be complicated by the appearance of “transient” phases [2,62]. These phases nucleate, grow, and vanish during the formation of another phase. This behavior is clearly different than the classical behavior for thin film reactions, which are characterized by sequential growth: during the reaction, only three phases coexist, the two consumed phases and the growing phase [101]. Despite the fact that simultaneous and sequential growths can both be explained considering classical diffusion and reaction kinetics, the rapid consumption of the transient phases, while Ni (decreasing) and $\delta\text{-Ni}_2\text{Si}$ (growing) are still present, is not well understood. Transient phase formation may influence the properties, as well as the formation, of the stable phases. For example, it has been shown that the $\theta\text{-Ni}_2\text{Si}$ growth can improve the stability of ultra-thin NiSi films [18], and thus, can improve the integration of NiSi in the CMOS technology as electrical contacts on sub-32 nm transistors. Several phases [58,102] such as $\theta\text{-Ni}_2\text{Si}$, Ni_3Si_2 and $\text{Ni}_{31}\text{Si}_{12}$ have been proposed to be transient during Ni/Si reaction.

Fig. 9.25(A) shows the XRD peak intensities as a function of diffraction angle (2θ) and temperature during ramp annealing of a 60 nm pure Ni film on $(100)\text{Si}$. The peaks

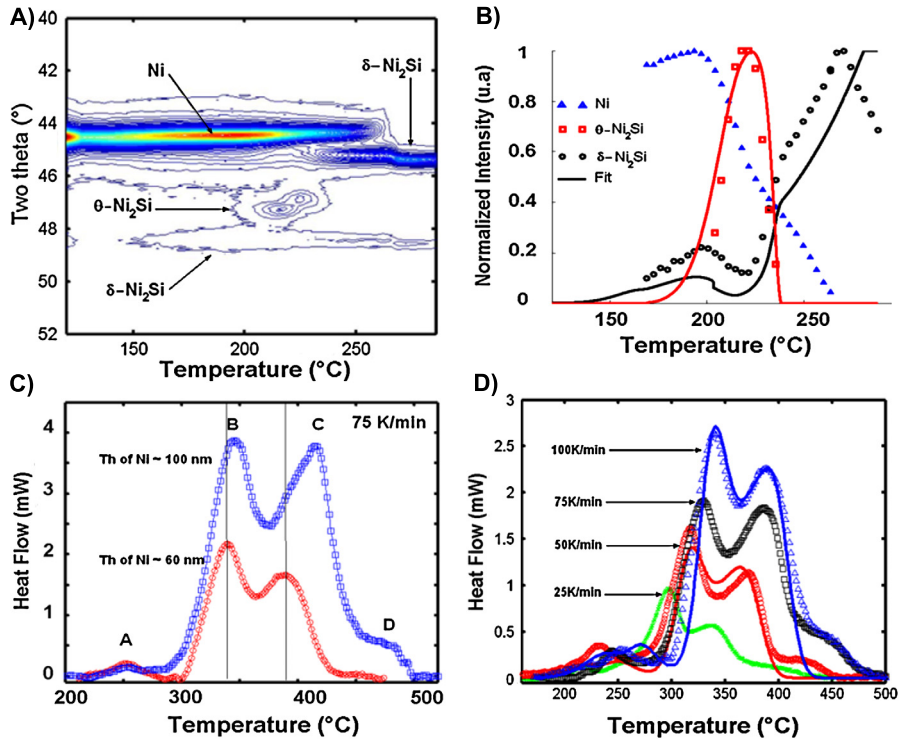


Figure 9.25 In situ XRD measurement: (A) iso-intensity lines and (B) integrated intensities. DSC signal vs sample temperature (C) for 60 and 100 nm Ni films with a ramp of 75 °C/min (D) for 60 nm Ni films following a ramp of 25, 50, 75, and 100 °C/min. The continuous lines correspond to the simulation. Reprinted with permission from [101].

at 45° and 48° correspond to the δ -Ni₂Si phase, while the 44.5° peak corresponds to the Ni film. The transient phase is characterized by a peak at 47° that can be attributed to the θ -Ni₂Si [62,103]. The normalized intensities of δ -Ni₂Si and θ -Ni₂Si are plotted in Fig. 9.25(b) as functions of time: they should be representative of the volume fraction of these phases as no large change in texture was observed. One can see that θ -Ni₂Si grows and disappears with fast kinetics. The formation of δ -Ni₂Si is characterized by 4 regions: the first region with a slow increase, followed by a decrease in the volume fraction. Then δ -Ni₂Si is growing fast, and finally the growth rate is decreasing. The evolution of the volume fraction for both phases is not similar to the common observation where the volume fraction is continuously increasing with possible change in the growing rate [29,83,101]. It should be pointed out that such a behavior was also observed in other cases including an Ni(6%Pd)/Si(100) film [104].

DSC traces for two thicknesses 60 and 100 nm of Ni film during the heating rate 75 K/min are shown in Fig. 9.25(C). For the two thicknesses, we observe four peaks,

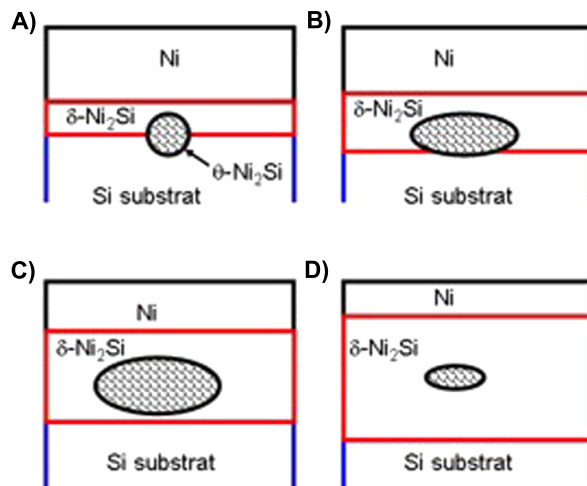


Figure 9.26 Schematic of the model for the behavior of the transient phase. This model was used to simulate the DSC and XRD experiment. Reprinted with permission from [101].

labeled A, B, C, and D. Two main peaks (B and C) are present: peak B has a width that is roughly equal to the resolution of the DSC and should thus correspond to a very sharp peak. Peak C has a more classical shape [11,28,29], and XRD diagram indicates the presence of θ -Ni₂Si, δ -Ni₂Si, and Ni phases for B peak. For C and D peaks, XRD diagram shows the presence of δ -Ni₂Si and NiSi phase, respectively. The second peak is related of θ -Ni₂Si phase formation and consumption. The evolution of this peak shows that the formation of θ -Ni₂Si is not limited by diffusion or reaction. Moreover, we observe that A and B peaks are present at the same temperatures for two thicknesses. On the contrary, C and D peaks change the formation temperature following the thickness. Fig. 9.25(D) shows the DSC thermograms obtained for the 60 nm Ni on (100)Si with the following ramping rates: 25, 50, 75, and 100 K/min. Two main peaks are present: the first one has a width that is roughly equal to the resolution of the DSC and should thus correspond to a very sharp peak. The second peak has a more classical shape [11, 28,29].

A model has been developed to understand and to simulate the XRD and DSC experiments and is based on the following steps: (i) growth of δ -Ni₂Si (Fig. 9.26(A)) until a critical thickness at which θ -Ni₂Si starts to grow laterally, (ii) growth of θ -Ni₂Si (Fig. 9.26(B)): θ -Ni₂Si is expected to grow laterally because the lateral growth should be faster than the normal growth. The lateral growth of θ -Ni₂Si consumes part of δ -Ni₂Si. During the growth of θ -Ni₂Si, the δ -Ni₂Si is still growing by diffusion of Ni through the place not covered by θ -Ni₂Si. (iii) Consumption of θ -Ni₂Si (Figs. 9.26(C)–(D)): at some time, θ -Ni₂Si will enclose δ -Ni₂Si and thus will separate θ -Ni₂Si from the

Si substrate. When θ -Ni₂Si is enclosed by δ -Ni₂Si, it becomes unstable and thus will decompose to form δ -Ni₂Si.

To validate the model, simulations of the XRD and DSC results were performed using the following assumption based on the Coffey's model [11]:

- The growth of δ -Ni₂Si is controlled by diffusion;
- θ -Ni₂Si grows in the shape of a cylinder with a kinetics controlled by the interface;
- θ -Ni₂Si start to shrink when it is enclosed by δ -Ni₂Si;
- The consumption of θ -Ni₂Si leads to the formation of δ -Ni₂Si.

The simulations that are superimposed to the experimental results in Fig. 9.25 show good agreement between the model and the experiments as they allow reproducing the main characteristics of the results. A more complex model was also developed by another group [62].

9.4.6 Texture in Silicides and Germanides

Except for a few specific cases (CoSi₂/Si(111), NiSi₂/Si(111), Pd₂Si/Si(111), etc.) [105], silicides do not grow as perfect epitaxial layers on Si. The crystallographic orientations of silicide grains and/or islands are better described with pole figures which describe crystallographic orientations present in the sample. It has been shown that silicide layers grown by solid-state reaction may develop very peculiar textures called "axiotaxy" [15]. In particular, it has been established that the NiSi phase formed from 5 to 30 nm-thick Ni films on Si(001) and Si(111) exhibits an axiotaxial texture [15,106]. This recently discovered type of texture is characterized by the alignment of planes in the film and in the substrate which share the same interplanar spacing (Fig. 9.27). This preferred alignment of planes across the interface manifests itself as a fiber texture lying off-normal to the sample surface, with the fiber axis perpendicular to the planes that are aligned at the interface (Fig. 9.27(B)). Axiotaxy is believed to be responsible for abnormal grain growth at the early stages of agglomeration [107] in which axiotaxial grains consume randomly oriented grains, since their interfacial energy is lower (Fig. 9.27(C)). It was also shown recently that the difference in texture induced by different orientations of the crystalline Si substrate strongly affects the reaction pathways, thereby altering the phase formation sequence upon annealing [108].

9.5 ALLOY ELEMENTS

Alloy elements have been used in several cases to improve the properties of silicides. This is particularly true for the Ni silicides. NiSi has been largely used since the beginning of 65 nm technology node and is currently used for 45 nm node and below. It is obtained by solid-state reaction between metal and silicon using the self-aligned silicide process called SALICIDE [109]. In the currently developed process, the silicidation is performed in two stages. Ni-rich silicides [2] are formed during a first heat treatment

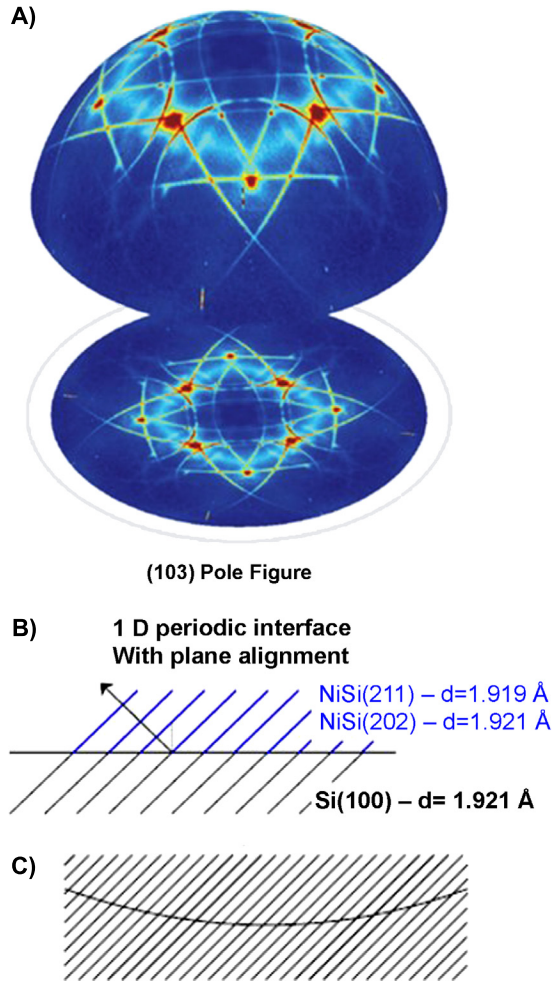


Figure 9.27 Axiotaxy: (A) Illustration of the projection method (left) used to obtain the NiSi(112) pole figure (right) for a 60-nm NiSi layer formed by annealing in ultrahigh vacuum. (B) Schematic of the 1D matching between the NiSi plane and the Si plane. (C) Illustration of the possible bending of the interface for axiotaxy. Reprinted with permission from [15].

at relatively low temperature (around 300°C), then a selective etch is used to remove any unreacted metal. The low resistivity NiSi phase is formed during a second low temperature anneal (about 400°C). However, NiSi phase can be transformed at high temperature (700–800°C) to the high resistivity NiSi₂ phase [110] which is a major disadvantage for its integration in devices. The addition of alloying elements in the Ni layer has been shown to influence both the silicide nucleation and growth [111,112].

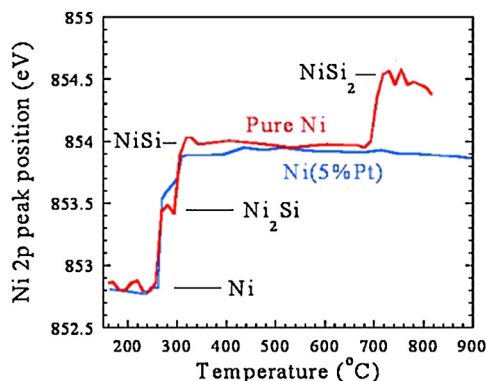


Figure 9.28 Variation of the Ni 2p XPS peak position (binding energy) with the temperature during in situ annealing of Ni (red line) and Ni(Pt) (blue line) films on (100)Si inside the XPS system. Reprinted with permission from [3]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

9.5.1 Role of Pt on the Nucleation of NiSi₂

Pure Ni and Ni(5%Pt) films with a thickness ranging from 20 to 50 nm were deposited onto (100) Si wafers by sputter deposition using pure Ni and Ni(Pt) alloy targets. The formation of various silicides at different temperatures was monitored by *in situ* X-ray photoelectron spectroscopy (XPS) during thermal annealing. The pressure was kept below 10^{-8} torr inside the chamber and a heating rate of $2^{\circ}\text{C}/\text{min}$ was applied. The XPS spectra around the Ni 2p, Si 2p, and Pt 4f peaks were recorded every 2 min using a monochromatic Al K α X-ray source.

Fig. 9.28 shows the variation of the Ni 2p XPS peak position (binding energy) with temperature during *in situ* annealing of Ni and Ni(Pt) films [3]. As XPS is surface sensitive, a change in the Ni peak position is observed when the silicide front reaches the surface. The temperature at which this occurs is dependent on the film thickness and on the heating rate. There are clearly four plateaus for pure Ni films which correspond to Ni, δ -Ni₂Si, NiSi, and NiSi₂, respectively. The binding energy and the temperature corresponding to the onset of each of the plateaus are in accordance with previous studies on Ni silicides [113]. The formation of δ -Ni₂Si occurs around 250°C , and NiSi starts to form when the entire Ni film has been transformed into δ -Ni₂Si [114]. The formation of NiSi₂ occurs around 700 – 750°C through nucleation [41]. In the presence of Pt, the binding energy corresponding to Ni 2p is slightly different from that obtained for pure Ni silicide. However, the major difference in the two curves in Fig. 9.28 is the length of the NiSi plateau which shows that NiSi is stable at temperatures up to 900°C in the presence of Pt. This is well above the nucleation temperature of about 750°C for pure NiSi₂.

The increase in the stability can be explained on the basis of changes in the interfacial energies and the free energy for silicide formation. The formation of NiSi_2 on crystalline Si substrate is controlled by nucleation [40]. Nucleation of a phase occurs when the decrease in free energy (ΔG) of a reaction (here $\text{NiSi} + \text{Si} \rightarrow \text{NiSi}_2$) just exceeds the increase in the interfacial energy ($\Delta\sigma$) associated with the creation of the new phase ($\Delta\sigma = \sigma(\text{NiSi}_2/\text{Si}) + \sigma(\text{NiSi}_2/\text{NiSi}) - \sigma(\text{NiSi}/\text{Si})$). The critical activation free energy for nucleation in such cases is proportional to a quantity $\Delta\sigma^3/\Delta G^2$.

Addition of alloy elements may influence both $\Delta\sigma$ and ΔG terms. The effect of alloy addition on the stability of the Ni mono- and disilicide can be examined as follows [3,115]. Adding a small amount of solute results in a decrease of the Gibbs energy, and thus to a stabilization of the silicide. In addition, for a given concentration of the alloy element, the decrease in the Gibbs energy is likely to be higher for an element with high solubility than for an element with low solubility. As NiSi and PtSi have the same crystallographic structure (orthorhombic, type MnP) and a small difference in their lattice parameters (within 15%), a pseudo-binary solid solution may form for the full range of concentration. The decrease in $G(\text{NiSi})$ induced by the formation of the $\text{NiSi}(\text{PtSi})$ solid solution is thus expected to be relatively high. On the other hand, the solubility of Pt in NiSi_2 seems to be low and the change in $G(\text{NiSi}_2)$ is likely to be small. One can thus reasonably expect a smaller decrease in free energy for the reaction $\text{NiSi} + \text{Si} \rightarrow \text{NiSi}_2$ due to the presence of Pt. Pt can also induce changes in the texture of the silicides [116] and thus changes in $\Delta\sigma$.

9.5.2 Role of Pt on the Kinetics of Formation

Based on the results shown above [3], NiSi with added Pt is now the reference silicide to create contacts in today's advanced integrated circuits. The Self Aligned Silicide (Salicide) process using a Ni(Pt) alloy, instead of pure Ni, has been introduced in sub-90 nanometer CMOS technologies to improve the NiSi process integration. Firstly, only 5% of Pt were used, and now NiPtSi phase with higher Pt concentration (10 at.%) is in volume production for 28 nm process of CMOS application as contacts in nanometric transistors. The presence of Pt in the Ni film is changing the silicide formation at low temperature and the redistribution of Pt can impact the properties of silicides. In the following, the formation of the Ni silicides will be described and some effects of the redistribution of Pt on this formation will be presented.

Fig. 9.29 shows the results obtained from an in situ XRD experiment performed during an isothermal annealing at 210°C on Ni(5%Pt) film deposited on Si(100) substrate [117]. In this figure, the integrated intensity of the XRD peaks corresponding to Ni(Pt), $\delta\text{-Ni}_2\text{Si}$, and NiSi phases has been reported as a function of the time. One important thing to notice is the presence of NiSi phase at the very beginning of the annealing. This phase grows simultaneously with the $\delta\text{-Ni}_2\text{Si}$ phase. These results were

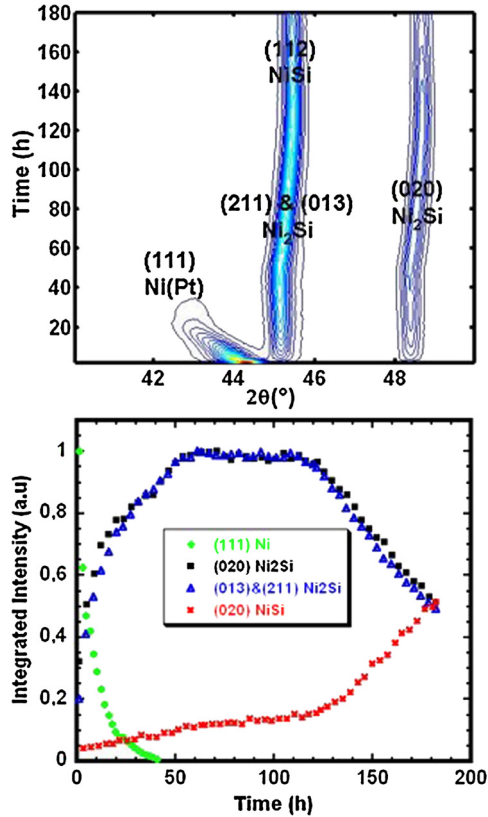


Figure 9.29 In situ XRD during isothermal annealing at 483 K as a function of annealing time of a 50 nm thick layer of Ni5%Pt on Si(100) (A) iso-intensity lines (B) integrated intensities. Reprinted with permission from [117].

confirmed by TEM analysis showing that three layers were present at the same time, corresponding to NiSi, δ -Ni₂Si, and Ni(Pt). The evolution of the kinetics is quite complex and five regions can be defined:

(a) Up to 20 hours, the intensity of Ni(Pt) peaks decreases rapidly, the δ -Ni₂Si phase grows with a parabolic increase contrary to NiSi phase that grows slowly and linearly with time.

(b) Between 20 and 40 hours, the slope of the square intensity of δ -Ni₂Si peak decreases; it means that the formation kinetics is delayed.

(c) Between 40 and 60 hours, the Ni(Pt) film is consumed totally, but the δ -Ni₂Si growth continues. This growth is probably linked to the grain growth of the δ -Ni₂Si phase, once formed.

(d) Between 60 and 120 hours, the peak intensity of the δ -Ni₂Si phase decreases slowly and a slight increase for the peak intensity of the NiSi phase is observed.

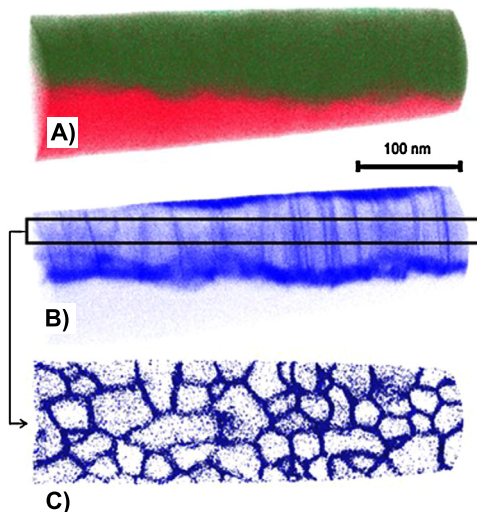


Figure 9.30 APT reconstruction of a large ($120 \times 120 \times 400$ nm) analysis volume collected from the Ni silicide structure: (A) shows the Si (red dots) and Ni atoms (green dots); (B) shows the location of the Pt atoms (blue dots). Pt enrichment is observed at the top of the structure (corresponding to the unreacted Ni layer) and at the interface between silicide and silicon regions; (C) a 20 nm slice in depth through the Ni_2Si region significant grain boundary enrichment of Pt (2 at% Pt iso-concentration surfaces shown) can be seen. In one single APT analysis it is now possible to capture many (~ 50) of these columnar features. Reprinted with permission from [148]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

(e) The last region corresponds to the consumption of $\delta\text{-Ni}_2\text{Si}$ to form NiSi which grows faster than in the other regions.

An APT analysis performed on the same sample ($\text{Ni}(5\%\text{Pt})/\text{Si}(100)$) annealed at 300°C for 1 hour is shown in Fig. 9.30. Ni and Si atoms (Fig. 9.30(A)) and Pt atoms (Fig. 9.30(B)) are represented as dots. One can notice that the large volume analyzed in Fig. 9.30 allows statistical information at the atomic scale to be obtained from one dataset. From the composition measurements, three regions have been identified, in addition to the Si substrate: (i) the unreacted Ni(Pt) film; (ii) the $\delta\text{-Ni}_2\text{Si}$ phase with a thickness of approximately 60 nm; (iii) the NiSi phase that forms large islands at the $\delta\text{-Ni}_2\text{Si}/\text{Si}$ interface. As shown in Fig. 9.30(B), Pt atoms are present in all phases but they are not distributed in the same way in the different phases. A high concentration of Pt is found in the Ni(Pt) layer that has not reacted during the isothermal treatment: this is the result of a snow-plow effect in which Pt atoms have been rejected from the $\delta\text{-Ni}_2\text{Si}$ layer during its formation. In the $\delta\text{-Ni}_2\text{Si}$ phase, Pt is present in a majority in the grain boundaries as it can be seen in Fig. 9.30(C) that represents a top view of a 20 nm slice of the $\delta\text{-Ni}_2\text{Si}$ phase. Only the Pt atoms corresponding to a concentration higher than 1.5 at.% were plotted. In this phase, Pt is preferentially present at the

grain boundaries, acting as a marker to identify grains and reveals the classical columnar structure of the δ -Ni₂Si phase. NiSi phase is located between the δ -Ni₂Si phase and the Si substrate as large islands. Pt atoms are accumulated at this interface but they are not incorporated into the NiSi grains. This APT analysis corresponds to an intermediary step in the NiSi formation and helps to understand what happens during this formation. The effect of Pt on the growth mechanisms can be related to its redistribution: the simultaneous growth of δ -Ni₂Si and NiSi should result from a kinetic competition [43]. The redistribution of Pt at interfaces during the nickel silicide formation delays the δ -Ni₂Si formation kinetics, changes the reaction rates at interfaces, and can be the reason of the simultaneous growth of δ -Ni₂Si and NiSi. The accumulation of platinum at the interfaces Ni(Pt)/ δ -Ni₂Si and δ -Ni₂Si/NiSi can act as diffusion barriers for nickel and probably also decrease the interface mobility. The presence of Pt at the grain boundaries of δ -Ni₂Si may also decrease the growth rate of this phase. It is necessary to know the redistribution steps to understand the kinetics modifications. More precisely, accurate knowledge of the location and concentration of Pt atoms allows obtaining a better understanding of the effect of this alloy element on this Ni silicide formation. In this respect, a very nice method has been shown by Demeulemeester et al. using in situ RBS [118].

9.5.3 Role of Pt on the Formation Sequence

The addition of a larger quantity of Pt into the Ni film can lead to a more drastic change in Ni silicide formation as will be shown in the following.

Fig. 9.31(A) shows the X-ray reflectivity (XRR) spectra recorded during an isothermal annealing ($T = 230^\circ\text{C}$) of Ni(13%Pt) film on (100)Si. The first XRR scan was performed at room temperature and exhibits two modulations. The XRR simulation has shown that these two modulations correspond to the deposited Ni(13%Pt) layer (thickness around 40 nm) and a thinner layer (around 4 nm) with a density in-between those of Ni₂Si and NiSi. This means that a silicide layer already forms during the deposition process. During annealing, the different modulations evolve with time; the presence of oscillations means that the growth occurs in a layer mode and that the roughness is quite low (less than 1 nm). To analyze the in situ XRR spectra, an inverse fast Fourier transform (IFFT) method was developed [119]. Fig. 9.31(C) shows the IFFT of the XRR spectra of Fig. 9.31(A). It represents the evolution of the distance between the interfaces of the stack versus annealing time. One can follow the evolution of 3 main peaks, indicating that only two layers are present and evolve during the annealing: the first corresponds to an increasing thickness (labeled L_{NiSi}), the second to a decreasing thickness ($L_{\text{Ni(Pt)}}$), and the third to the total thickness of the stack (L_{Tot}) that increases. This result shows that only one phase is growing at the expend of the Ni(13%Pt) layer. This is also confirmed by the simulation and fitting procedure that was applied on some

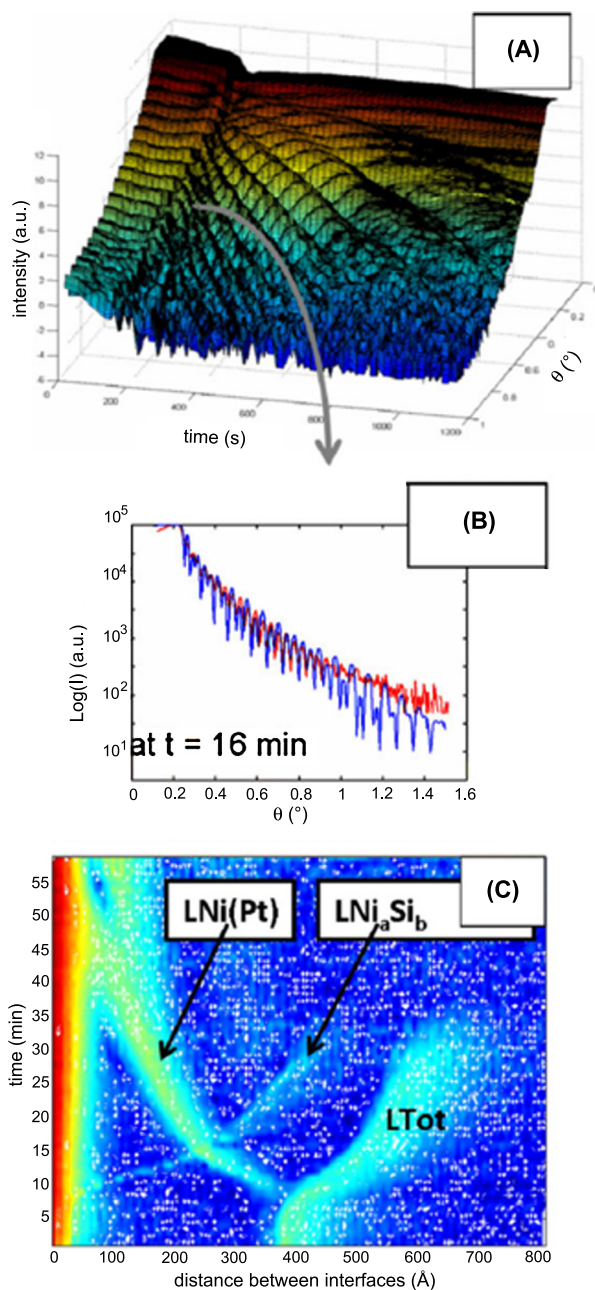


Figure 9.31 (A) XRR curves recorded on 45 nm Ni(13% Pt)/Si(100) during an isothermal anneal at 230°C ($\lambda = 0.73\text{\AA}$); (B) Experimental and simulated XRR curves at $t = 16$ min; the simulation is made with a two layer model; (C) IFFT of the in situ XRR curves. Each horizontal line corresponds to the IFFT of one XRR curve. Reprinted with permission from [119].

selected XRR curves (see Fig. 9.31(B)) using a two-layer model (the growing silicide and the consuming metal).

Fig. 9.31(C) shows that in-situ XRR allows us to follow the thickness evolution of the different layers during the reaction, and an important point is that using the IFFT analysis, the layer thicknesses of the growing and consumed phases are directly measured without any physical assumption. Consequently, it allows a unique in-situ determination of the Pilling and Bedworth ratio (PBR), providing valuable information about the first phase to form during the reaction. Indeed, the PBR ratio is defined as $PBR = \frac{1}{a} \frac{V(M_aSi_b)}{V(M)}$, where $V(M)$ and $V(M_aSi_b)$ represent the molecular volumes of the metal and silicide, respectively. As the reaction occurs on a sample of constant surface, the volume ratio is equal to that of the thickness: the PBR ratio can thus be calculated directly from the measured thickness on the IFFT diagram and was determined to be 1.8 ± 0.1 . This value [120], together with XRD measurements, suggests that the first phase to grow must be the already observed hexagonal θ -Ni₂Si phase with about 42% Si, the NiSi-silicide being then formed by its consumption. Therefore, the first growing silicide switches from δ -Ni₂Si to θ -Ni₂Si when increasing the Pt concentration from 5% to 13%. Furthermore, the θ -Ni₂Si kinetics pass from a transient behavior for a pure Ni film to the first growing phase for Ni(13%Pt) alloy. This may have some important role in the properties of the silicides and in particular on the morphological stability [121].

9.5.4 Role of the Intermixed Layer on the First Phase

In addition to the work by Putero et al., other publications have shown that the nature of the first Ni silicide may depend on several parameters. For pure Ni film thickness of less than 6 nm, θ -Ni₂Si was obtained as the first phase in the phase formation sequence instead of δ -Ni₂Si [18]. In the presence of 5 at.% Pt, δ -Ni₂Si still appears as the first phase and the θ -Ni₂Si phase was suppressed from the phase formation sequence. When the percentage of Pt in the Ni film was increased from 5 at.% to 10 at.% to improve the yield of the contacts, θ -Ni₂Si was found to replace δ -Ni₂Si as the first phase [119,122]. In particular, the reaction between 11 nm Ni(10 at.% Pt) with Si substrate was found by Panciera et al. [123] to lead to the formation of θ -Ni₂Si as the first phase. This was evidenced by transmission electron microscopy [18,102,122] where an epitaxial relationship between θ -Ni₂Si and the Si(100) substrate was revealed. The formation of θ -Ni₂Si as the first phase can thus be related to the thickness of the metal layer and/or the Pt concentration in the alloy. Indeed, as mentioned before, the pure Ni thickness greatly influences the onset of the phase according to De Keyser et al. [18, 121] measurements. Moreover, taking into consideration the percentage of Pt in the Ni film, Demeulemeester et al. [124] has shown that for Pt concentration less than 7at.%, δ -Ni₂Si is the first phase to form. Therefore, one may wonder what controls the

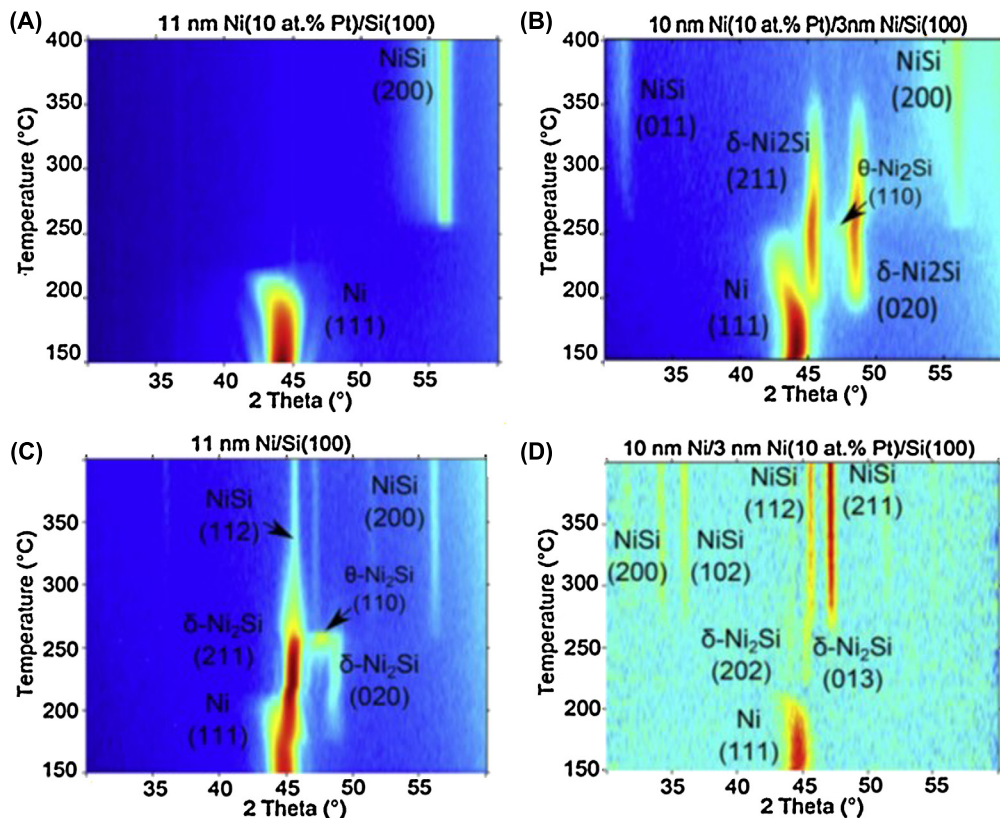


Figure 9.32 In situ XRD using step annealing for (A) 11 nm Ni(10 at.% Pt)/Si(100), (B) 10 nm Ni(10 at.% Pt)/3 nm Ni/Si(100), (C) 11 nm Ni/Si(100) and (D) 10 nm Ni/3 nm Ni(10 at.% Pt)/Si(100). Reprinted with permission from [125].

formation of the first phase: the thickness of the deposited film or the concentration of Pt in this film?

In a recent work, El Koussiefi et al. [125] provided some insight to this question by showing that Pt can modify the intermixed layer formed during deposition and influence the nature of the first Ni silicide to form during the reaction.

Fig. 9.32 shows that a 3 nm thick layer inserted at the interface can change the phase sequence and especially the first phase formation. Indeed, a 3 nm pure Ni inserted between the Ni(Pt) film and the Si substrate changed the phase sequence of the 10 nm Ni(10 at.% Pt) film and induced δ -Ni₂Si as the first phase as for the 11 nm pure Ni reaction with Si substrate. Even more intriguing, the insertion of a 3 nm Ni (10 at.% Pt) layer in-between a pure Ni film and Si led to the formation of the metastable θ -Ni₂Si phase instead of the stable δ -Ni₂Si phase. To summarize, for the Ni (10 at.% Pt)/3 nm Ni/Si and Ni/Si samples, δ -Ni₂Si is the first phase to grow (Fig. 9.32) in contrast to

the Ni(10 at.% Pt)/Si and Ni/3 nm Ni(10 at.% Pt)/Si samples where θ -Ni₂Si is the first phase obtained (Fig. 9.32).

D'Heurle and Gas [5] have argued that the first phase to grow is the fastest. Although this statement holds in general, Fig. 9.32 shows that θ -Ni₂Si or δ -Ni₂Si form at the same temperature range: there should not be a large difference between the growth kinetics of the two phases that can change the appearance of the first phase during the formation sequence. A more suitable possibility is that the formation of the first phase is limited by the nucleation which might depend on the composition of the intermixed layer.

Indeed, it has been reported several times [25] that, in the first steps of the reaction and/or deposition, a thin layer of an amorphous intermixed layer is formed at the metal/Si interface. This intermixed layer can grow up to a given critical thickness, for which the nucleation of the first crystalline phase starts [5]. In particular, after Ni deposition by magnetron sputtering, a 4 nm amorphous intermixed layer of Ni and Si was formed between the substrate and the Ni film. Its composition in Si was determined to vary from 33 to 45 at.% [123]. Furthermore, this intermixed layer has been investigated in detail in the case of 11 nm Ni (10 at.% Pt), where the Si gradient was maintained and an incorporation of 4 at.% Pt was observed [123]. As the thickness of the intermixed layer is very similar in all cases, our results indicate that only the composition of the intermixed layer controls the formation of the first phase and specifically the Pt concentration in the intermixed layer. As the Si concentration in the intermixed phase varies between 33 and 45 at.%, these concentrations correspond to the composition of δ -Ni₂Si (33 at.%) on the metal side of the intermixed phase and to the one of the Ni rich θ -Ni₂Si on the silicon side. The formation of the intermixed layer allows thus the nucleation of θ -Ni₂Si or δ -Ni₂Si without (or with very little) change in composition. The nucleation of δ -Ni₂Si is thus expected to take place in the intermixed layer close to the metal layer and the one of θ -Ni₂Si close to the Si substrate as indicated in.

Fig. 9.33 shows that the concentration of Pt in the intermixed layer is larger, close to the metal where δ -Ni₂Si is expected to nucleate. From the classical nucleation theory, the nucleation barrier depends on the variation of the interfaces energies ($\Delta\sigma$) and the volume energies of the newly formed phase (ΔG) as

$$\Delta G^* = (\Delta\sigma)^3 / (\Delta G)^2.$$

The presence of Pt may change this variation. The epitaxy of θ -Ni₂Si on Si(100) should favor the nucleation of θ -Ni₂Si even if this phase is metastable in the Ni-Si phase diagram at low temperature. An additional contribution to the nucleation of θ -Ni₂Si is that the intermixed layer has the same composition gradient as θ -Ni₂Si (34 to 45 at.%).

Pt incorporation into the phases can also change the energy for phase formation: since the solubility of Pt is expected to be larger in δ -Ni₂Si than in θ -Ni₂Si, this should increase the driving force value of the θ -Ni₂Si formation energy and favors its formation. Although the change in energy induced by Pt incorporation is difficult to quantify,

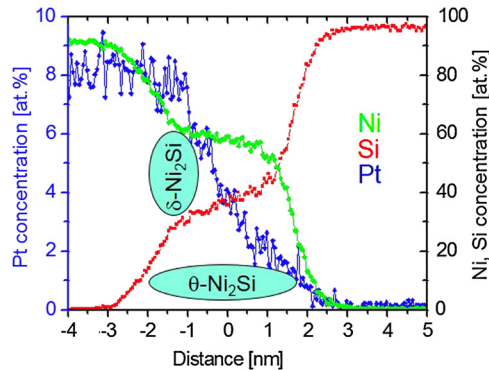


Figure 9.33 Depth profile obtained by APT in the as deposited 11 nm Ni(10 at.% Pt)/Si(100). The location of the nucleation of δ -Ni₂Si and θ -Ni₂Si is indicated [123].

it should be substantial since it induces the growth of θ -Ni₂Si as the first phase for the Ni (10 at.% Pt) alloy. Therefore, when Pt is incorporated in the intermixed layer, δ -Ni₂Si will have nucleation difficulties while the presence of Pt makes the θ -Ni₂Si phase more stable and increases its driving force ($G_\theta - G_a$) for nucleation. Moreover, Pt incorporation into the intermixed layer was found to be maximally close to the metal layer [123]. As this corresponds to the position where δ -Ni₂Si is expected to nucleate (i.e., one can argue that Pt plays an important role in hindering the δ -Ni₂Si nucleation at this interface (metal layer/intermixed layer) since its concentration is maximum there.

In conclusion, the deposition of the 3 nm interfacial layer allows controlling the composition of the intermixed layer and thus the nucleation (formation) of the first phase. These findings could have a strong impact on the self-aligned silicide process used for contact production in microelectronics industry, since the modification of the intermixed layer composition allows the selection of the desired compounds.

9.6 DOPANT AND SILICIDE

Downscaling is a key challenge for the microelectronics industry. In this context, ultra-shallow source/drain junctions (USJs) with low resistivity must be fabricated [126] to sustain the development of complementary metal–oxide semiconductor (MOS) devices. The interaction of dopants with Ni-silicides is also of crucial importance for integrated silicon technology [127]. During the formation of the different silicide phases, part of the doped Si of the device junctions is actually consumed, involving the redistribution of the dopants in the silicides and in the Si substrate [128]. This redistribution can have important consequences on the electrical properties of the device [129]. Dopant redistribution at the silicide/Si interface can affect the junction electrical properties, and the dopants may also change the contact resistance due to their influence on the silicide

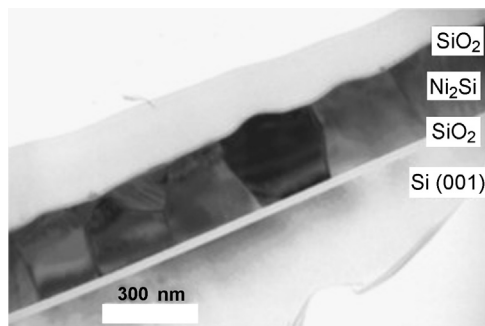


Figure 9.34 TEM cross-section view of the sample used to measure the diffusion of As in Ni_2Si . Reprinted with permission from [135].

formation [130]. Consequently, the redistribution of dopants during Ni silicide formation has been mainly studied by secondary ion mass spectrometry (SIMS) [131–133]. It has been reported that As is snowplowed (As is pushed into Si by the moving interface) during the formation of the near-noble metal silicides Ni_2Si and NiSi . It is therefore essential for technological applications to understand and control the dopant redistribution at silicide/Si interfaces. However, the fundamental mechanisms controlling this redistribution are still not fully understood. Ternary phase diagrams have been shown to be a useful tool to predict the redistribution of dopants and the stability of silicide/doped silicon structures [134]. The solubility and the diffusion of dopants in silicides must also be known to control the dopant behavior. Little data of dopant solubility and diffusion in silicides are available in the literature and they have been determined mainly in thin polycrystalline silicide films where grain boundaries play an important role [35].

9.6.1 Diffusion of As in $\delta\text{-Ni}_2\text{Si}$

The sample structure used for this study can be seen in the TEM image (Fig. 9.34) and consists of 20 nm SiO_2 /256 nm Ni_2Si /30 nm SiO_2 /Si(001) [135]. An SiO_2 layer was first deposited on Si(001) by low pressure chemical vapor deposition (LPCVD) at 730°C to act as a diffusion barrier. Ni_2Si was obtained by deposition of a 150 nm-thick Si layer by LPCVD at 550°C and a 175 nm thick Ni layer by sputtering followed at 350°C. The sample was then annealed at 700°C during 2 h in order to stabilize the silicide grain size, and a second oxide layer was deposited by LPCVD at 380°C. This process enabled us to form a stable $\delta\text{-Ni}_2\text{Si}$ layer with quasi-columnar grains (Fig. 9.34). An As dose of 5×10^{15} at cm^{-2} was implanted through this oxide at 120 keV. In order to study As diffusion, sample pieces were annealed at temperatures between 400 and 700°C for different time under vacuum. The concentration profiles were measured before and after annealing by SIMS, using AsCs_2^+ .

Fig. 9.35 shows the As concentration profiles before and after annealing at 650°C for 1, 4, and 16 h. Before annealing, the implantation profile has a Gaussian distribution, and after annealing, three different regions, separated by dashed lines in Fig. 9.35(A), can be observed. The first region, on the left, corresponds to the original Gaussian implantation peak, the second region, in the middle, corresponds to a small negative concentration gradient, and the third region, on the right, exhibits a positive concentration gradient and ends with a concentration peak at the interface with the bottom oxide layer. After annealing, both region 1 and 3 become broader until region 2 almost disappears after 16 h annealing. This evolution of the dopant concentration profile can be explained by simultaneous fast diffusion at the interfaces with the top and bottom oxide layers and slow diffusion in the bulk of the grains [136]. The broadening of the Gaussian implantation peak in region 1 can be explained by slow lattice diffusion. The smaller gradient observed in region 2 corresponds to fast diffusion in the grain boundaries (GB) that act as diffusion short circuits. This phenomenon causes the presence of a diffusion tail in the concentration profile that is identical to what is commonly observed in the type B kinetic regime of Harrison [137]. Diffusion occurs fast enough in the grain boundaries so that the interface with the bottom oxide layer is already enriched with As after 1 h heat treatment. The broadening of region 3, observed after 4 and 16 h heat treatment corresponds to slow diffusion from the bottom interface to the bulk of the grains. The different diffusion fluxes are represented by the black arrows in Fig. 9.35(B).

The diffusion coefficients in the grains and the GBs have been determined for this system using two-dimensional (2D) finite element simulations based on the Fisher model geometry [135]. The profiles measured after heat treatment at 650°C are compared to the simulated profiles in Fig. 9.35(C). The diffusion coefficients used to fit the measured profiles are shown in the insert. Similar experiments were performed for the same system for different time and temperatures, and the data are summarized in Fig. 9.35(C). It is shown that lattice diffusion is characterized by a preexponential factor $D_{0v} \sim 1.5 \times 10^{-1} \text{ cm}^2 \text{ s}^{-1}$ and an activation energy $Q_v \sim 2.72 \pm 0.10 \text{ eV}$. In the case of GB diffusion, the triple product of the As segregation coefficient (s), the GB width (δ) and the diffusion coefficient (D_{gb}) is found to be $s\delta D_{gb} = 9.0 \times 10^{-3} \exp(-(3.07 \pm 0.15) \text{ eV}/kT) \text{ cm}^3 \text{ s}^{-1}$ assuming diffusion takes place in Harrison's kinetic regime of type B. The higher activation energy for the GBs diffusion than for lattice diffusion may be due to the preferential segregation of another element or to an enrichment in Si of the GBs.

9.6.2 Precipitation of As in θ -Ni₂Si

One should be very cautious when using SIMS to study dopant redistribution during silicidation. Indeed, the concentrations measured by SIMS can be affected by artifacts in the vicinity of interfaces [138]. Moreover, as other one-dimensional profiling methods,

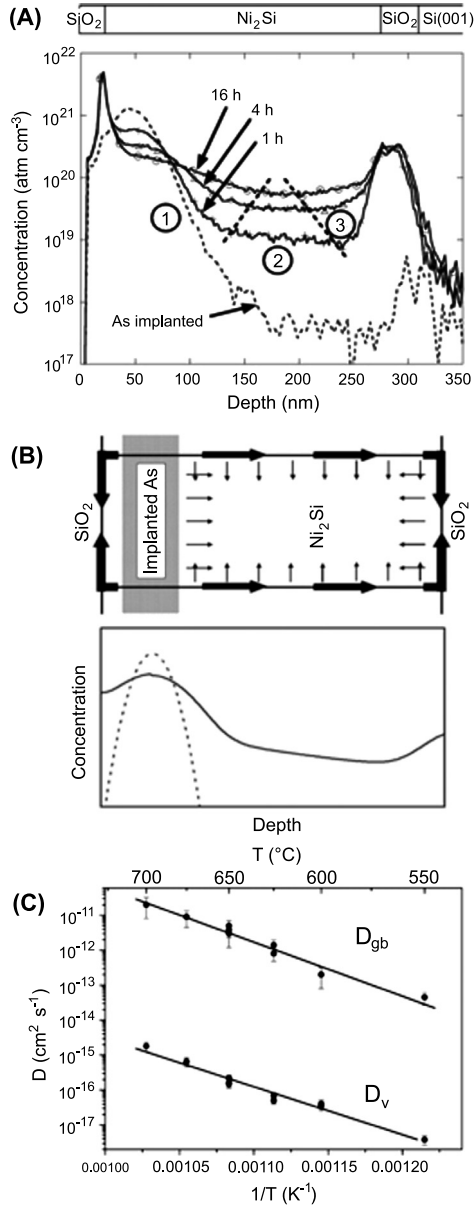


Figure 9.35 (A) Comparison between the measured profiles and the profiles obtained by 2D simulations. The thick lines correspond to the simulated profiles, and the dashed lines indicate the three different regions of the profile. The values of D_v and D_{gb} used in the simulation are presented in the insert. (B) Schematic view of the atom fluxes and concentration profiles. The diffusion is considered to be fast in the GBs and at the interfaces. (C) Arrhenius plot of the diffusion coefficients used in the fitting procedure of profiles measured after different annealing times at temperatures ranging from 550 to 700°C. Reprinted with permission from [135].

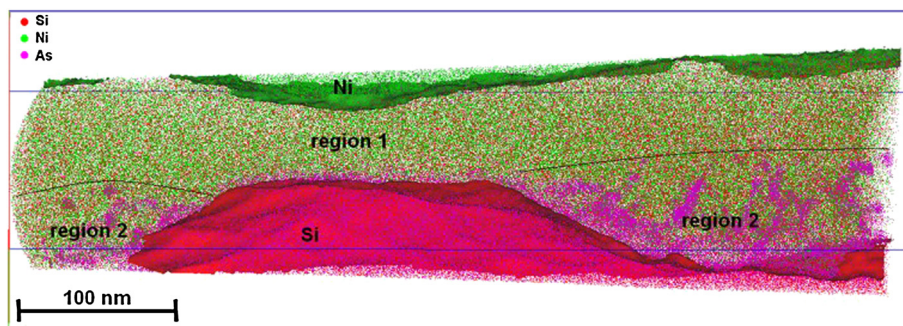


Figure 9.36 APT reconstructed volume of the sample after in situ XRD heat treatment stopped at 290°C. The iso-concentration surfaces correspond to a Si (red) and Ni (green) concentration of 95 at.%, and show the Si/silicide and silicide/Ni interfaces, respectively. The As-rich clusters are located in the q-Ni₂Si phase. Reprinted with permission from [146]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

SIMS is mostly efficient for characterizing stacked continuous layers. In contrast, APT measurements are quantitative at interfaces and can provide concentrations without calibration in three dimensions, often at the subnanometer scale.

This example deals with the effect of the formation of the transient phase on the redistribution of As during the reaction of Ni with an As-doped Si(001) substrate. The sample preparation is described in Section 2.2. In situ XRD was used to study the phase formation sequence and to define the heat treatment allowing us to obtain the maximum volume fraction of the transient phase in the sample (maximum intensity of the corresponding XRD peak). For APT, the sample preparation and analysis conditions are described in Section 9.1.

Fig. 9.36 shows a $120 \times 120 \times 180 \text{ nm}^3$ reconstructed volume where Ni, Si, and As atoms are represented by green, red, and purple dots, respectively. In Fig. 9.36, iso-concentration surfaces corresponding to concentration of 95% of Ni and Si are represented to visualize respectively the Ni/silicide and silicide/Si interfaces and to show that these interfaces are not flat. Arsenic-rich clusters can be observed and correspond to an As concentration of 5at.%. They were probably formed during annealing at 290°C, with the formation of Ni silicides. These clusters are not distributed homogeneously in the Ni silicide layers. In addition to the Si substrate and the unreacted Ni film, two regions with different As distribution can be identified: in region 1, As is in solution within one Ni silicide, while the As-rich clusters are contained in region 2 that corresponds to another Ni silicide. The composition of each region was determined by the analysis of the mass spectrum of the specific regions. The first Ni-rich region (region 1, Fig. 9.36) contains 67 at.% of Ni and corresponds thus to the $\delta\text{-Ni}_2\text{Si}$ phase which is in contact with both the unreacted Ni and the Si substrate. On the opposite, the second Ni-rich region (region 2, Fig. 9.36) is located at the interface between $\delta\text{-Ni}_2\text{Si}$ and Si.

The concentration of Ni in this second region is approximately 60 at.%, and it contains the As rich clusters. This second silicide should thus correspond to the transient θ -Ni₂Si phase. This assumption was also confirmed by the XRD result, and similar results were obtained in different APT analyses.

Different methods were used to determine the composition of these clusters (clusters identification, radial concentration, proxigram, and 1D depth profile): the average As concentration in the clusters was found to be in the range of 10%. The increase of As concentration is concomitant with a decrease of the Ni concentration, while the Si concentration does not show any significant difference between the clusters and the matrix. This suggests that As atoms substitute Ni in the clusters. In conclusion, arsenic clusters, with an average composition of Ni_{0.5}Si_{0.4}As_{0.1}, were found to be located in the transient phase and not in the δ -Ni₂Si layer. Additional results [61,139] show that the silicide/Si interface exhibits a large roughness, and that arsenic accumulates at this interface.

9.7 FORMATION OF SILICIDE IN TRANSISTORS

In microelectronic devices, the presence of stress, defects, and confinement may have an effect on the silicide formation mechanism, as well as on the alloying element and dopant redistribution and segregation. It is thus essential to know the distribution of elements in three dimensions, to quantify the interface segregation and the silicide compositions in real MOSFET. Despite the large number of studies on Ni silicides, the chemical analysis of a real transistor remains a great challenge. APT has the capability to perform such an analysis with a subnanometer spatial resolution. However, it should be pointed out that such analysis remains highly complex because of the experimental difficulties linked to the APT tip preparation and analysis from a real device.

Fig. 9.37 shows an example of an APT analysis of an N-MOS transistor gate taken from a static random access memory (SRAM) cell [140]. The analyzed device is a 28 nm transistor taken from 0.15 μm^2 SRAM unit cell fabricated with the standard process flow of 300 mm production wafers. The transistor fabrication was performed by following the standard gate-first procedure, i.e., a hafnium based gate-oxide film, a metal layer, and a poly-Si gate were deposited on a P-doped channel. The sample was then patterned and etched by conventional lithography and dry etching. Implantation of As was followed by a spike annealing at 1065°C for activation. Ni-silicide contacts were formed from a 15 nm Ni(10 at.% Pt) film by two rapid thermal annealing at 280°C (RTA1) and 390°C (RTA2) separated by a selective etch.

Several methods of sample preparation based on FIB were tried, and finally the one based on deprocessing the wafer just below the first metal level was chosen [141]. The APT measurement was performed using the conditions described above.

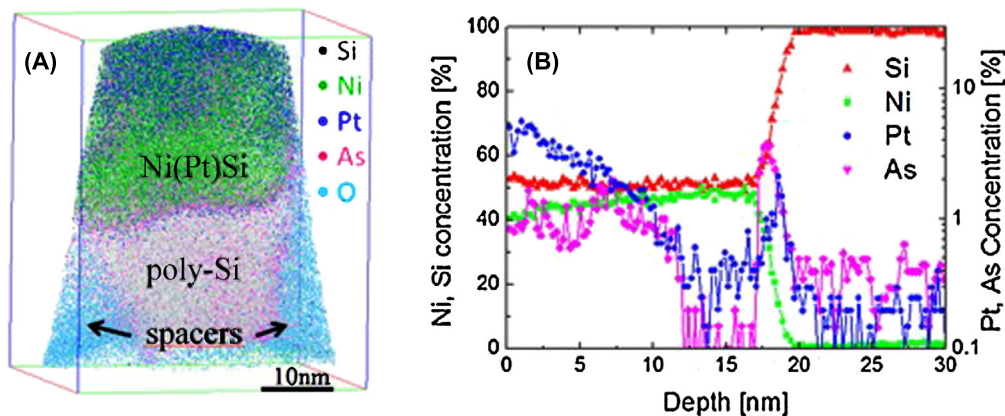


Figure 9.37 (A) Atom map of N-MOS gate showing the Ni silicide, poly-Si, and the spacers. (B) 1D composition profiles calculated in a 10 nm diameter cylindrical region perpendicular to the NiSi/Si interface. Reprinted with permission from [146]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this chapter.)

Fig. 9.37(A) shows a $50 \times 50 \times 60 \text{ nm}^3$ reconstructed volume in which Ni, Si, Pt, As, and O atoms are represented by green, gray, blue, pink, and light-blue dots, respectively. Four distinct regions (Ni(Pt)Si, poly-Si, and the two Si oxide spacers) can be observed. APT analysis shows that Pt and As are accumulated at the NiSi/Si interface and both are not homogeneously distributed in the NiSi contact; in particular, Pt is mainly present in the upper part of the silicide, while As is distributed in form of clusters.

One-dimensional composition profiles (Fig. 9.37(B)) calculated from the 3D volume show that the contact composition corresponds to NiSi phase with Pt atoms substituting Ni atoms. The main features of these profiles are a Pt gradient within the NiSi phase (decreasing from surface to the poly-Si gate) and an accumulation of As and Pt at the NiSi/gate interface with a concentration of 5 and 2 at.%, respectively [140]. The Pt distribution in the final Ni(Pt)Si is different from that observed in the literature. Indeed, several studies report that the Pt is accumulated in the middle of the Ni(Pt)Si final film [118,117,142,143]. Contrary to previous studies, our measurement was performed on a real transistor, implying that these differences in the Pt redistribution could be due to “transistor effects” like confinement induced stress. However, the same feature was obtained for analysis performed on test zones on the same wafer and having undergone the same SALICIDE process leading to the conclusion that the specific redistribution of Pt was due to the SALICIDE process itself, and especially to the unusual phase sequence that take place in presence of Ni(10 at.% Pt) alloy [144]. These results reveal that monitoring the silicide formation and characteristics in real devices is a key parameter for a realistic understanding and control of the device performance.

9.8 CONCLUSION

Recent results on the mechanisms of formation of silicides and germanides have been reviewed. These mechanisms include nucleation, lateral growth, diffusion/interface controlled growth, simultaneous/sequential growth. The redistribution of dopants and alloy elements during the silicide formation have been studied by several techniques including in situ techniques (XRD, XRR, XPS, DSC) for the kinetics measurements and APT for the 3D distribution of the species at the atomic scale. From these measurements, several mechanisms and models have been proposed and fitted to the experimental results in order to determine kinetics parameters and to validate the models. Such analysis allows us to gain understanding of the solid-state reaction in thin films and to better control these reactions for making contacts in microelectronics devices.

ACKNOWLEDGEMENTS

The author would like to acknowledge M. Bertoglio, I. Blum, E. Bourjot, G. Clugnet, M. Descoins, B. Duployer, M. El Koussiefi, T. Luo, F. Panciera, C. Perrin-Pellegrino, M. Putero from IM2NP, M. Gregoire, M. Juhel, R. Pantel from STMicroelectronics, F. Nemouchi, V. Carron from CEA-LETI, E. Ziegler from ESRF, S.K. Lahiri, P.S. Lee, K.L. Pey from IMRE, B. Gault from McMaster University, D. Larson, T. Kelly, R. Ulfing, from former IMAGO company and all the people who have contributed to the works presented in this chapter. Numerous and enlightening discussions with F.M. d'Heurle, K. Hoummada, P. Gas, A. Portavoce, and B. Pichaud are highly appreciated. This work was financially supported by the French National Agency (ANR) through Nanoscience and Nanotechnology Program (TAPAS Project No. ANR-08-027-01) and by the French CNRS and CEA METSA network (FR3507).

REFERENCES

- [1] J.P. Gambino, E.G. Colgan, Silicides and ohmic contacts, *Mater. Chem. Phys.* 52 (2) (Feb. 1998) 99–146.
- [2] C. Lavoie, F.M. d'Heurle, C. Detavernier, C. Cabral Jr., Towards implementation of a nickel silicide process for CMOS technologies, *Microelectron. Eng.* 70 (2–4) (Nov. 2003) 144–157.
- [3] D. Mangelinck, J.Y. Dai, J.S. Pan, S.K. Lahiri, Enhancement of thermal stability of NiSi films on (100) Si and (111) Si by Pt addition, *Appl. Phys. Lett.* 75 (12) (Sep. 1999) 1736–1738.
- [4] P.S. Lee, K.L. Pey, D. Mangelinck, J. Ding, D.Z. Chi, L. Chan, New silicidation technology with Ni(Pt) alloy for MOSFETs, *IEEE Electron. Device Lett.* 22 (12) (Dec. 2001) 568–570.
- [5] F.M. d'Heurle, P. Gas, Kinetics of formation of silicides: a review, *J. Mater. Res.* 1 (1) (Feb. 1986) 205–221.
- [6] R. Tung, J. Gibson, J. Poate, Formation of ultrathin single-crystal silicide films on Si – surface and interfacial stabilization of Si–NiSi₂ epitaxial structures, *Phys. Rev. Lett.* 50 (6) (1983) 429–432.
- [7] S.S.L.M.A. Nicolet, *Formation and Characterization of Transition-Metal Silicides*, vol. 6, Academic Press, NY, 1983.
- [8] F.M. d'Heurle, O. Thomas, Stresses during silicide formation: a review, *Defect Diffus. Forum* 129–130 (1996) 137–150.
- [9] F. Nava, K.N. Tu, O. Thomas, J.P. Senateur, R. Madar, A. Borghesi, G. Guizzetti, U. Gottlieb, O. Laborde, O. Bisi, Electrical and optical properties of silicide single crystals and thin films, *Mater. Sci. Rep.* 9 (4) (Feb. 1993) 141–200.

- [10] K. Maex, M. van Rossum, Properties of Metal Silicides, IEE, London, 1995.
- [11] K. Coffey, L. Clevenger, K. Barmak, D. Rudman, C. Thompson, Experimental-evidence for nucleation during thin-film reactions, *Appl. Phys. Lett.* 55 (9) (Aug. 1989) 852–854.
- [12] P. Gergaud, O. Thomas, B. Chenevier, Stresses arising from a solid state reaction between palladium films and Si(001) investigated by in situ combined X-ray diffraction and curvature measurements, *J. Appl. Phys.* 94 (3) (Aug. 2003) 1584–1591.
- [13] C. Rivero, P. Gergaud, M. Gailhanou, O. Thomas, B. Froment, H. Jaouen, V. Carron, Combined synchrotron X-ray diffraction and wafer curvature measurements during Ni–Si reactive film formation, *Appl. Phys. Lett.* 87 (4) (Jul. 2005) 41904.
- [14] D. Mangelinck, K. Hoummada, Effect of stress on the transformation of Ni₂Si into NiSi, *Appl. Phys. Lett.* 92 (25) (Jun. 2008) 254101.
- [15] C. Detavernier, A.S. Ozcan, J. Jordan-Sweet, E.A. Stach, J. Tersoff, F.M. Ross, C. Lavoie, An off-normal fibre-like texture in thin films on single-crystal substrates, *Nature* 426 (6967) (Dec. 2003) 641–645.
- [16] Z. Zhang, S.-L. Zhang, B. Yang, Y. Zhu, S.M. Rossnagel, S. Gaudet, A.J. Kellock, J. Jordan-Sweet, C. Lavoie, Morphological stability and specific resistivity of sub-10 nm silicide films of Ni_{1-x}Pt_x on Si substrate, *Appl. Phys. Lett.* 96 (7) (Feb. 2010) 71915.
- [17] J. Lu, J. Luo, S.-L. Zhang, M. Ostling, L. Hultman, On epitaxy of ultrathin Ni_{1-x}Pt_x silicide films on Si(001), *Electrochem. Solid State Lett.* 13 (10) (2010) H360–H362.
- [18] K. De Keyser, C. Van Bockstael, R.L. Van Meirhaeghe, C. Detavernier, E. Verleysen, H. Bender, W. Vandervorst, J. Jordan-Sweet, C. Lavoie, Phase formation and thermal stability of ultrathin nickel-silicides on Si(100), *Appl. Phys. Lett.* 96 (17) (Apr. 2010) 173503.
- [19] K. Hoummada, E. Cadel, D. Mangelinck, C. Perrin-Pellegrino, D. Blavette, B. Deconihout, First stages of the formation of Ni silicide by atom probe tomography, *Appl. Phys. Lett.* 89 (18) (Oct. 2006) 181905.
- [20] M. Kobayashi, A. Kinoshita, K. Saraswat, H.-S.P. Wong, Y. Nishi, Fermi level depinning in metal/Ge Schottky junction for metal source/drain Ge metal-oxide-semiconductor field-effect-transistor application, *J. Appl. Phys.* 105 (2) (Jan. 2009) 23702.
- [21] S.Y. Zhu, R. Li, S.J. Lee, M.F. Li, A.Y. Du, J. Singh, C.X. Zhu, A. Chin, D.L. Kwong, Germanium pMOSFETs with Schottky-barrier germanide S/D, high-kappa gate dielectric and metal gate, *IEEE Electron. Device Lett.* 26 (2) (Feb. 2005) 81–83.
- [22] J.Y. Spann, R.A. Anderson, T.J. Thornton, G. Harris, S.G. Thomas, C. Tracy, Characterization of nickel germanide thin films for use as contacts to p-channel germanium MOSFETs, *IEEE Electron. Device Lett.* 26 (3) (Mar. 2005) 151–153.
- [23] J.A. Kittl, K. Opsomer, C. Torregiani, C. Demeurisse, S. Mertens, D.P. Brunco, M.J.H. Van Dal, A. Lauwers, Silicides and germanides for nano-CMOS applications, *Mater. Sci. Eng. B* 154–155 (Dec. 2008) 144–154.
- [24] S.-L. Zhang, Nickel-based contact metallization for SiGe MOSFETs: progress and challenges, *Micron. Eng.* 70 (2–4) (Nov. 2003) 174–185.
- [25] L. Clevenger, C. Thompson, Nucleation-limited phase selection during reactions in nickel amorphous-silicon multilayer thin-films, *J. Appl. Phys.* 67 (3) (Feb. 1990) 1325–1333.
- [26] K. Barmak, K. Coffey, D. Rudman, S. Foner, Phase formation sequence for the reaction of multilayer thin-films of Nb/Al, *J. Appl. Phys.* 67 (12) (Jun. 1990) 7313–7322.
- [27] C. Michaelsen, K. Barmak, T.P. Weihs, Investigating the thermodynamics and kinetics of thin film reactions by differential scanning calorimetry, *J. Phys.-Appl. Phys.* 30 (23) (Dec. 1997) 3167–3186.
- [28] E. Emeric, C. Bergman, G. Glugnet, P. Gas, M. Audier, Formation of a decagonal quasicrystalline film by reactive diffusion in Al/Co multilayers, *Philos. Mag. Lett.* 78 (2) (Aug. 1998) 77–85.
- [29] F. Nemouchi, D. Mangelinck, C. Bergman, P. Gas, U. Smith, Differential scanning calorimetry analysis of the linear parabolic growth of nanometric Ni silicide thin films on a Si substrate, *Appl. Phys. Lett.* 86 (4) (Jan. 2005) 41903.

- [30] K. Hoummada, A. Portavoce, C. Perrin-Pellegrino, D. Mangelinck, C. Bergman, Differential scanning calorimetry measurements of kinetic factors involved in silicide process, *Appl. Phys. Lett.* 92 (13) (Mar. 2008) 133109.
- [31] T.F. Kelly, M.K. Miller, Invited review article: atom probe tomography, *Rev. Sci. Instrum.* 78 (3) (Mar. 2007) 31101.
- [32] T.F. Kelly, D.J. Larson, K. Thompson, R.L. Alvis, J.H. Bunton, J.D. Olson, B.P. Gorman, Atom probe tomography of electronic materials, in: *Annual Review of Materials Research*, vol. 37, 2007, pp. 681–727.
- [33] M.K. Miller, A. Cerezo, M.G. Hetherington, G.D.W. Smith, *Atom Probe Field Ion Microscopy*, Oxford University Press, Oxford, 1996.
- [34] B. Gault, M.P. Moody, J.M. Cairney, S.P. Ringer, *Atom Probe Microscopy*, Springer-Verlag, New York, 2012.
- [35] P. Gas, F.M. d’Heurle, Diffusion in silicide, in: D.L. Beke (Ed.), *Diffusion in Semiconductors and Non-Metallic Solids*, Springer Verlag, Berlin, 1998.
- [36] T. Barge, Formation de siliciures par réaction métal-silicium: rôle de la diffusion, PhD thesis, Aix-Marseille III, 1993.
- [37] W.K. Chu, J.W. Mayer, M.-A. Nicolet, *Backscattering Spectrometry*, Academic Press, New York, 1978.
- [38] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* 29 (11) (Nov. 1957) 1702–1706.
- [39] S.-L. Zhang, F.M. d’Heurle, Kinetic studies of intermetallic compound formation by resistance measurements, *Thin Solid Films* 256 (1–2) (Feb. 1995) 155–164.
- [40] F.M. d’Heurle, Nucleation of a new phase from the interaction of two adjacent phases: some silicides, *J. Mater. Res.* 3 (1) (Feb. 1988) 167–195.
- [41] E.G. Colgan, F.M. d’Heurle, Kinetics of silicide formation measured by in situ ramped resistance measurements, *J. Appl. Phys.* 79 (8) (Apr. 1996) 4087–4095.
- [42] L. Darken, R.W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953.
- [43] P. Gas, F.M. d’Heurle, Formation of silicide thin films by solid state reaction, *Appl. Surf. Sci.* 73 (Nov. 1993) 153–161.
- [44] M.F. Ashby, D.R.H. Jones, *Engineering Materials 1*, Pergamon Press, 1980.
- [45] J. Philibert, *Diffusion et transport dans les solides*, Editions de Physique, Les Ulis, 1985.
- [46] G. Martin, B. Perrailon, Diffusion intergranulaire. La diffusion intergranulaire, *J. Phys. Colloq.* 36 (C4) (Oct. 1975), pp. C4-165–C4-190.
- [47] H. Bakker, *Self-Diffusion in Homogeneous Binary Alloys and Intermediate Phases*, Springer, Berlin, 1990.
- [48] H. Mehrer, *Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Processes*, Springer Science & Business Media, 2007.
- [49] S. Zirinsky, W. Hammer, F. d’Heurle, J. Baglin, Oxidation mechanisms in WSi_2 thin films, *Appl. Phys. Lett.* 33 (1) (1978) 76.
- [50] F.M. d’Heurle, P. Gas, C. Lavoie, J. Philibert, Diffusion in intermetallic compounds: the ordered Cu_3Au rule, its history, *Z. Met.* 95 (10) (Oct. 2004) 852–859.
- [51] T. Barge, P. Gas, F.M. d’Heurle, Analysis of the diffusion controlled growth of cobalt silicides in bulk and thin film couples, *J. Mater. Res.* 10 (5) (May 1995) 1134–1145.
- [52] C. Lien, M. Nicolet, C. Pai, S. Lau, Growth of Co-silicides from single-crystal and evaporated Si, *Appl. Phys. – Mater. Sci. Process.* 36 (3) (1985) 153–157.
- [53] D.S. Wen, P.L. Smith, C.M. Osburn, G.A. Rozgonyi, Defect annihilation in shallow p^+ junctions using titanium silicide, *Appl. Phys. Lett.* 51 (15) (1987) 1182.
- [54] N. Stolwijk, H. Bracht, H.-G. Hettwer, W. Lerch, H. Mehrer, A. Rucki, W. Jäger, Defect injection and diffusion in semiconductors, *Mater. Sci. Forum* 155–156 (1994) 475–492.

- [55] W.K. Chu, S.S. Lau, J.W. Mayer, H. Müller, K.N. Tu, Implanted noble gas atoms as diffusion markers in silicide formation, *Thin Solid Films* 25 (2) (Feb. 1975) 393–402.
- [56] J.O. Olowolafe, M.-A. Nicolet, J.W. Mayer, Influence of the nature of the Si substrate on nickel silicide formed from thin Ni films, *Thin Solid Films* 38 (2) (Oct. 1976) 143–150.
- [57] L. Clevenger, C. Thompson, R. Cammarata, K. Tu, Reaction-kinetics of nickel silicon multilayer films, *Appl. Phys. Lett.* 52 (10) (Mar. 1988) 795–797.
- [58] C. Lavoie, C. Coia, F.M. d'Heurle, C. Detavernier, C. Cabral, P. Desjardins, A.J. Kellock, Reactive diffusion in the Ni–Si system: phase sequence and formation of metal-rich phases, in: M. Danielewski, R. Filipek, R. Kozubs, W. Kucza, P. Zieba, Z. Zurek (Eds.), *Diffusion in Materials: Dimat 2004*, Pts 1 and 2, vols. 237–240, 2005, pp. 825–836.
- [59] C. Rivero, P. Gergaud, M. Gailhanou, O. Thomas, B. Froment, H. Jaouen, V. Carron, Combined synchrotron X-ray diffraction and wafer curvature measurements during Ni–Si reactive film formation, *Appl. Phys. Lett.* 87 (4) (Jul. 2005) 41904.
- [60] S. Gaudet, C. Coia, P. Desjardins, C. Lavoie, Metastable phase formation during the reaction of Ni films with Si(001): the role of texture inheritance, *J. Appl. Phys.* 107 (9) (2010) 93515.
- [61] K. Houmada, G. Tellouche, I.D. Blum, A. Portavoce, D. Mangelinck, Arsenic clustering during formation of the transient Ni silicide, *Scr. Mater.* 67 (2) (Jul. 2012) 169–172.
- [62] C. Coia, Metastable Compound Formation During Thin-Film Solid State Reaction in the Ni–Si System: Microstructure and Growth Kinetics, PhD Thesis, Ecole Polytechnique de Montreal, 2008.
- [63] F.R. de Boer, A.R. Niessen, A.R. Miedema, W.C.M. Mattens, R. Boom, *Cohesion in Metals*, Elsevier Science Ltd, Amsterdam, 1988.
- [64] K. Coffey, K. Barmak, D. Rudman, S. Foner, Thin-film reaction-kinetics of niobium aluminum multilayers, *J. Appl. Phys.* 72 (4) (Aug. 1992) 1341–1349.
- [65] C. Bergman, J.L. Joulaud, M. Capitan, G. Clugnet, P. Gas, In situ real-time analysis of the formation of a quasicrystalline phase in Al–Co multilayers by solid-state reaction, *J. Non-Cryst. Solids* 287 (1–3) (Jul. 2001) 193–196.
- [66] E. Ma, L. Clevenger, C. Thompson, Nucleation of an intermetallic at thin-film interfaces – VSi_2 contrasted with Al_3Ni , *J. Mater. Res.* 7 (6) (Jun. 1992) 1350–1355.
- [67] J.W. Christian, *The Theory of Transformation Rates in Metals and Alloys*, Part I, Pergamon, Oxford, 1975.
- [68] M. El Kousseifi, K. Houmada, T. Epicier, D. Mangelinck, Direct observation of NiSi lateral growth at the epitaxial $\theta\text{-Ni}_2\text{Si/Si}(100)$ interface, *Acta Mater.* 99 (Oct. 2015) 1–6.
- [69] G. Lucadamo, K. Barmak, S. Hyun, C. Cabral Jr., C. Lavoie, Evidence of a two-stage reaction mechanism in sputter deposited Nb/Al multilayer thin-films studied by in situ synchrotron X-ray diffraction, *Mater. Lett.* 39 (5) (Jun. 1999) 268–273.
- [70] R. Delattre, O. Thomas, C. Perrin-Pellegrino, C. Rivero, R. Simola, First stage of CoSi_2 formation during a solid-state reaction, *J. Appl. Phys.* 116 (24) (Dec. 2014) 245301.
- [71] V. Vovk, G. Schmitz, R. Kirchheim, Nucleation of product phase in reactive diffusion of Al/Co, *Phys. Rev. B* 69 (10) (Mar. 2004).
- [72] G. Lucenko, A. Gusak, A model of the growth of intermediate phase islands in multilayers, *Microelectron. Eng.* 70 (2–4) (Nov. 2003) 529–532.
- [73] L. Klinger, Y. Bréchet, G. Purdy, On the kinetics of interface-diffusion-controlled peritectoid reactions, *Acta Mater.* 46 (8) (May 1998) 2617–2621.
- [74] F. Nemouchi, Réactivité de films nanométriques de nickel sur substrats silicium–germanium, PhD thesis, Université Paul Cezanne Aix-Marseille III, 2005.
- [75] B.E. Deal, A.S. Grove, General relationship for the thermal oxidation of silicon, *J. Appl. Phys.* 36 (12) (1965) 3770.
- [76] W.K. Chu, Identification of the dominant diffusing species in silicide formation, *Appl. Phys. Lett.* 25 (8) (1974) 454.

- [77] S.-L. Zhang, F.M. d'Heurle, Precisions on reaction monitoring from in-situ resistance measurements: relations between such measurements and actual reaction kinetics, *Thin Solid Films* 279 (1–2) (Jun. 1996) 248–252.
- [78] E.J. Faber, R.A.M. Wolters, J. Schmitz, On the kinetics of platinum silicide formation, *Appl. Phys. Lett.* 98 (8) (2011) 82102.
- [79] J. Philibert, Reactive interdiffusion, *Mater. Sci. Forum* 155–156 (1994) 15–30.
- [80] U. Gösele, Growth kinetics of planar binary diffusion couples: “thin-film case” versus “bulk cases”, *J. Appl. Phys.* 53 (4) (1982) 3252.
- [81] A. Gusak, K.P. Gurov, Peculiarities of intermediate phase nucleation in the process of chemical diffusion, *Solid State Phenom.* 23–24 (1992) 117–122.
- [82] S. Gaudet, C. Detavernier, A.J. Kellock, P. Desjardins, C. Lavoie, Thin film reaction of transition metals with germanium, *J. Vac. Sci. Technol. Vac. Surf. Films* 24 (3) (2006) 474.
- [83] F. Nemouchi, D. Mangelinck, C. Bergman, G. Clugnet, P. Gas, J.L. Lábár, Simultaneous growth of Ni_5Ge_3 and NiGe by reaction of Ni film with Ge , *Appl. Phys. Lett.* 89 (13) (Sep. 2006) 131920.
- [84] E.D. Marshall, C.S. Wu, C.S. Pai, D.M. Scott, S.S. Lau, *Mat. Res. Soc. Symp. Proc.* 47 (1985) 161.
- [85] M. Wittmer, M. Nicolet, J. Mayer, 1st phase to nucleate in planar transition metal–germanium interfaces, *Thin Solid Films* 42 (1) (1977) 51–59.
- [86] Y. Hsieh, L. Chen, E. Marshall, S. Lau, Partial epitaxial-growth of Ni_2Ge and NiGe on $\text{Ge}(111)$, *Thin Solid Films* 162 (1–2) (Aug. 1988) 287–294.
- [87] J. Li, Q. Hong, J. Mayer, L. Rathbun, Interfacial reaction between a Ni/Ge bilayer and silicon (100), *J. Appl. Phys.* 67 (5) (Mar. 1990) 2506–2511.
- [88] J. Patterson, B. Park, K. Ritley, H. Xiao, L. Allen, A. Rockett, Kinetics of $\text{Ni}/\alpha\text{-Ge}$ bilayer reactions, *Thin Solid Films* 253 (1–2) (Dec. 1994) 456–461.
- [89] L.J. Jin, K.L. Pey, W.K. Choi, E.A. Fitzgerald, D.A. Antoniadis, A.J. Pitera, M.L. Lee, D.Z. Chi, C.H. Tung, The interfacial reaction of Ni with (111) Ge , (100) $\text{Si}_{0.75}\text{Ge}_{0.25}$ and (100) Si at 400°C, *Thin Solid Films* 462–463 (Sep. 2004) 151–155.
- [90] W.C. Johnson, G. Martin, Coherency stress effects on the growth kinetics of thin films, *Solid State Phenom.* 3–4 (1988) 247–256.
- [91] W.C. Johnson, G. Martin, Influence of elastic stress on the growth kinetics of planar thin-film binary diffusion couples, *J. Appl. Phys.* 68 (3) (1990) 1252.
- [92] S.-L. Zhang, F.M. d'Heurle, Stresses from solid state reactions: a simple model, silicides, *Thin Solid Films* 213 (1) (May 1992) 34–39.
- [93] O. Thomas, P. Gergaud, C. Rivero, F.M. d'Heurle, Stress development during the reactive formation of silicide films, *Defect Diffus. Forum* 237–240 (2005) 801–812.
- [94] B.M. Haugerud, L.A. Bosworth, R.E. Belford, Mechanically induced strain enhancement of metal–oxide–semiconductor field effect transistors, *J. Appl. Phys.* 94 (6) (2003) 4102.
- [95] S.E. Thompson, M. Armstrong, C. Auth, S. Cea, R. Chau, G. Glass, T. Hoffman, J. Klaus, Z. Ma, B. McIntyre, A. Murthy, B. Obradovic, L. Shifren, S. Sivakumar, S. Tyagi, T. Ghani, K. Mistry, M. Bohr, Y. El-Mansy, A logic nanotechnology featuring strained-silicon, *IEEE Electron. Device Lett.* 25 (4) (Apr. 2004) 191–193.
- [96] S.E. Thompson, M. Armstrong, C. Auth, M. Alavi, M. Buehler, R. Chau, S. Cea, T. Ghani, G. Glass, T. Hoffman, C.-H. Jan, C. Kenyon, J. Klaus, K. Kuhn, Z. Ma, B. McIntyre, K. Mistry, A. Murthy, B. Obradovic, R. Nagisetty, P. Nguyen, S. Sivakumar, R. Shaheed, L. Shifren, B. Tufts, S. Tyagi, M. Bohr, Y. El-Mansy, A 90-nm logic technology featuring strained-silicon, *IEEE Trans. Electron. Devices* 51 (11) (Nov. 2004) 1790–1797.
- [97] H.J. Frost, M.F. Ashby, *Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics*, Pergamon, Oxford, 1982.
- [98] K. Ito, H. Inui, T. Hirano, M. Yamaguchi, Plastic-deformation of single and polycrystalline CoSi_2 , *Acta Metall. Mater.* 42 (4) (Apr. 1994) 1261–1271.

- [99] G.E. Dieter, *Mechanical Metallurgy*, McGraw-Hill International Editions, 1986.
- [100] P. Gergaud, M. Megdiche, O. Thomas, B. Chenevier, Influence of Si substrate orientation on stress development in Pd silicide films grown by solid-state reaction, *Appl. Phys. Lett.* 83 (7) (Aug. 2003) 1334–1336.
- [101] D. Mangelinck, K. Hoummada, I. Blum, Kinetics of a transient silicide during the reaction of Ni thin film with (100)Si, *Appl. Phys. Lett.* 95 (18) (Nov. 2009) 181902.
- [102] K. De Keyser, C. Van Bockstael, C. Detavernier, R.L. Van Meirhaeghe, J. Jordan-Sweet, C. Lavoie, Epitaxial formation of a metastable hexagonal nickel-silicide, *Electrochem. Solid State Lett.* 11 (9) (2008) H266–H268.
- [103] K. Hoummada, I. Blum, D. Mangelinck, A. Portavoce, Composition measurement of the Ni-silicide transient phase by atom probe tomography, *Appl. Phys. Lett.* 96 (26) (Jun. 2010) 261904.
- [104] M. Putero, D. Mangelinck, Effect of Pd on the Ni₂Si stress relaxation during the Ni-silicide formation at low temperature, *Appl. Phys. Lett.* 101 (11) (Sep. 2012) 111910.
- [105] L. Chen, K. Tu, Epitaxial-growth of transition-metal silicides on silicon, *Mater. Sci. Rep.* 6 (2–3) (Mar. 1991) 53–140.
- [106] C. Detavernier, J. Jordan-Sweet, C. Lavoie, Texture of NiSi films on Si(001), (111), and (110) substrates, *J. Appl. Phys.* 103 (11) (2008) 113526.
- [107] D. Deduytsche, C. Detavernier, R.L. Van Meirhaeghe, C. Lavoie, High-temperature degradation of NiSi films: agglomeration versus NiSi₂ nucleation, *J. Appl. Phys.* 98 (3) (Aug. 2005) 33526.
- [108] S. Gaudet, P. Desjardins, C. Lavoie, The thermally-induced reaction of thin Ni films with Si: effect of the substrate orientation, *J. Appl. Phys.* 110 (11) (2011) 113524.
- [109] B.-Y. Tsaur, C.H. Anderson, Metal-oxide-semiconductor field-effect transistors fabricated using self-aligned silicide technology, *Appl. Phys. Lett.* 47 (5) (1985) 527.
- [110] E.G. Colgan, J.P. Gambino, B. Cunningham, Nickel silicide thermal stability on polycrystalline and single crystalline silicon, *Mater. Chem. Phys.* 46 (2–3) (Dec. 1996) 209–214.
- [111] D. Mangelinck, Etude de l'adaptation des parametres cristallins de NiSi₂ et Si par substitution du nickel, PhD thesis, Aix-Marseille III, 1995.
- [112] D. Mangelinck, P. Gas, J.M. Gay, B. Pichaud, O. Thomas, Effect of Co, Pt, and Au additions on the stability and epitaxy of NiSi₂ films on (111)Si, *J. Appl. Phys.* 84 (5) (Sep. 1998) 2583–2590.
- [113] P.J. Grunthaner, Metal/silicon interface formation: the Ni/Si and Pd/Si systems, *J. Vac. Sci. Technol.* 19 (3) (Sep. 1981) 649.
- [114] F. d'Heurle, C.S. Petersson, J.E.E. Baglin, S.J. La Placa, C.Y. Wong, Formation of thin films of NiSi: metastable structure, diffusion mechanisms in intermetallic compounds, *J. Appl. Phys.* 55 (12) (1984) 4208.
- [115] D. Mangelinck, Effect of a third element on the stability of NiSi thin films on Si, *Defect and Diffusion Forum* 249 (2006) 127–134.
- [116] C. Detavernier, C. Lavoie, Influence of Pt addition on the texture of NiSi on Si(001), *Appl. Phys. Lett.* 84 (18) (2004) 3549.
- [117] K. Hoummada, C. Perrin-Pellegrino, D. Mangelinck, Effect of Pt addition on Ni silicide formation at low temperature: growth, redistribution, and solubility, *J. Appl. Phys.* 106 (6) (Sep. 2009) 63511.
- [118] J. Demeulemeester, D. Smeets, C. Van Bockstael, C. Detavernier, C.M. Comrie, N.P. Barradas, A. Vieira, A. Vantomme, Pt redistribution during Ni(Pt) silicide formation, *Appl. Phys. Lett.* 93 (26) (Dec. 2008) 261912.
- [119] M. Putero, L. Ehouarne, E. Ziegler, D. Mangelinck, First silicide formed by reaction of Ni(13%Pt) films with Si(100): nature and kinetics by in-situ X-ray reflectivity and diffraction, *Scr. Mater.* 63 (1) (Jul. 2010) 24–27.
- [120] P. Villars, L.D. Calvert, W.B. Pearson, *Pearson Handbook of Crystallographic Data*, American Society for Metals, 1985.

- [121] C. Van Bockstael, K. De Keyser, R.L. Van Meirhaeghe, C. Detavernier, J.L. Jordan-Sweet, C. Lavoie, Influence of a transient hexagonal phase on the microstructure and morphological stability of NiSi films, *Appl. Phys. Lett.* 94 (3) (2009) 33504.
- [122] F. Panciera, D. Mangelinck, K. Hoummada, M. Texier, M. Bertoglio, A. De Luca, M. Gregoire, M. Juhel, Direct epitaxial growth of θ -Ni₂Si by reaction of a thin Ni(10 at.% Pt) film with Si(100) substrate, *Scr. Mater.* 78–79 (May 2014) 9–12.
- [123] F. Panciera, La sonde atomique tomographique: applications aux dispositifs CMOS avancés sub-45 nm, PhD Thesis, Aix-Marseille Université, France, 2012.
- [124] J. Demeulemeester, D. Smeets, C.M. Comrie, C. Van Bockstael, W. Knaepen, C. Detavernier, K. Temst, A. Vantomme, The influence of Pt redistribution on Ni_{1-x}Pt_xSi growth properties, *J. Appl. Phys.* 108 (4) (Aug. 2010) 43505.
- [125] M. El Kousseifi, K. Hoummada, M. Bertoglio, D. Mangelinck, Selection of the first Ni silicide phase by controlling the Pt incorporation in the intermixed layer, *Acta Mater.* 106 (Mar. 2016) 193–198.
- [126] <http://www.itrs.net/Links/2010ITRS/IRC-ITRS-MtM-v2%203.pdf>.
- [127] M. Wittmer, Dopant diffusion in self-aligned silicide/silicon structures, *J. Electrochem. Soc.* 135 (8) (1988) 2049.
- [128] M. Wittmer, K.N. Tu, Low-temperature diffusion of dopant atoms in silicon during interfacial silicide formation, *Phys. Rev. B Condens. Matter* 29 (4) (Feb. 1984) 2010–2020.
- [129] J. Kedzierski, D. Boyd, P. Ronsheim, S. Zafar, J. Newbury, J. Ott, C. Cabral, M. Jeong, W. Haensch, Threshold voltage control in NiSi-gated MOSFETs through silicidation induced impurity segregation (SIIS), 2003, p. 13.3.1–13.3.4.
- [130] S.-L. Zhang, M. Östling, R. Buchta, U. Smith, J. Linnros, and S.-F. Gong, The influence of substrate doping on silicide formation with tungsten deposited from tungsten hexafluoride, in: *MRS Online Proc. Libr.*, vol. 260, p. N.PAG, Feb. 1992.
- [131] I. Ohdomari, M. Akiyama, T. Maeda, M. Hori, C. Takebayashi, A. Ogura, T. Chikyo, I. Kimura, K. Yoneda, K.N. Tu, Low-temperature redistribution of As in Si during Ni silicide formation, *J. Appl. Phys.* 56 (10) (Nov. 1984) 2725.
- [132] Y.-L. Jiang, A. Agarwal, G.-P. Ru, X.-P. Qu, J. Poate, B.-Z. Li, W. Holland, Nickel silicidation on n and p-type junctions at 300°C, *Appl. Phys. Lett.* 3 (2004).
- [133] M. Wittmer, T.E. Seidel, The redistribution of implanted dopants after metal-silicide formation, *J. Appl. Phys.* 49 (12) (Dec. 1978) 5827.
- [134] D. Mangelinck, J. Cardenas, F.M. d’Heurle, B.G. Svensson, P. Gas, Solid solubility of As in CoSi₂ and redistribution at the CoSi₂/Si interface, *J. Appl. Phys.* 86 (9) (Nov. 1999) 4908–4915.
- [135] I. Blum, A. Portavoce, D. Mangelinck, R. Daineche, K. Hoummada, J.L. Lábár, V. Carron, C. Perrin, Lattice and grain-boundary diffusion of As in Ni₂Si, *J. Appl. Phys.* 104 (11) (Dec. 2008) 114312.
- [136] P. Gas, V. Deline, F.M. d’Heurle, A. Michel, G. Scilla, Boron, phosphorus, and arsenic diffusion in TiSi₂, *J. Appl. Phys.* 60 (5) (1986) 1634, 9/1/1986.
- [137] L.G. Harrison, Influence of dislocations on diffusion kinetics in solids with particular reference to the alkali halides, *Trans. Faraday Soc.* 57 (Jan. 1961) 1191.
- [138] K. Hoummada, D. Mangelinck, C. Perrin, V. Carron, P. Holliger, Measurement of the redistribution of arsenic at nickel silicide/silicon interface by secondary ion mass spectrometry: artifact and optimized analysis conditions, *J. Appl. Phys.* 104 (2) (Jul. 2008) 24313.
- [139] K. Hoummada, G. Tellouche, I. Blum, A. Portavoce, M. Descoins, D. Mangelinck, Direct observation of Ni decorated dislocation loops within As⁺-implanted silicon and arsenic clustering in Ni silicide contact, *Microelectron. Eng.* 107 (Jul. 2013) 184–189.
- [140] F. Panciera, K. Hoummada, M. Gregoire, M. Juhel, N. Bicaïs, D. Mangelinck, Three dimensional distributions of arsenic and platinum within NiSi contact and gate of an n-type transistor, *Appl. Phys. Lett.* 99 (5) (Aug. 2011) 51911.

- [141] F. Panciera, K. Hoummada, M. Gregoire, M. Juhel, F. Lorut, N. Bicaïs, D. Mangelinck, Atom probe tomography of SRAM transistors: specimen preparation methods and analysis, *Microelectron. Eng.* 107 (Jul. 2013) 167–172.
- [142] F. Corni, B. Grignaffini Gregorio, G. Ottaviani, G. Queirolo, J.P. Follegot, Dilute NiPt alloy interactions with Si, in: *Applied Surface Science*, vol. 73, 1993, pp. 197–202.
- [143] O. Cojocar-Mirédin, D. Mangelinck, K. Hoummada, E. Cadel, D. Blavette, B. Deconihout, C. Perrin-Pellegrino, Snowplow effect and reactive diffusion in the Pt doped Ni–Si system, *Scr. Mater.* 57 (5) (Sep. 2007) 373–376.
- [144] F. Panciera, K. Hoummada, M. Gregoire, M. Juhel, D. Mangelinck, Pt redistribution in N-MOS transistors during Ni silicide process, *Microelectron. Eng.* 107 (Jul. 2013) 173–177.
- [145] S. Petersson, R. Anderson, J. Baglin, J. Dempsey, W. Hammer, F. d'Heurle, S. LaPlaca, The thin-film formation of rhodium silicides, *J. Appl. Phys.* 51 (1) (1980) 373.
- [146] D. Mangelinck, K. Hoummada, F. Panciera, M. El Kousseifi, I. Blum, M. Descoins, M. Bertoglio, A. Portavoce, C. Perrin, M. Putero, Progress in the understanding of Ni silicide formation for advanced MOS structures, *Phys. Status Solidi – Appl. Mater. Sci.* 211 (1) (Jan. 2014) 152–165.
- [147] O. Abbes, K. Hoummada, D. Mangelinck, V. Carron, Formation of Pt silicide on doped Si: kinetics and stress, *Thin Solid Films* 542 (Sep. 2013) 174–179.
- [148] D. Mangelinck, K. Hoummada, A. Portavoce, C. Perrin, R. Daineche, M. Descoins, D.J. Larson, P.H. Clifton, Three-dimensional composition mapping of NiSi phase distribution and Pt diffusion via grain boundaries in Ni₂Si, *Scr. Mater.* 62 (8) (Apr. 2010) 568–571.

INDEX

Symbols

δ -Ni₂Si, 392, 418
 ε -phase, 70, 77, 104
 η -phase, 70, 77, 104
 η -phase island, 71
 θ -Ni₂Si, 418, 429

A

Accuracy, 233
Activation energy, 21, 25, 67, 184, 342, 384
 low, 357, 387, 413
Activity coefficient, 102, 298
Activity diagrams, 112, 142
Activity gradients, 103, 114, 142
Adatoms, 55
Alloy compositions, 267, 278, 363
Alloy elements, 381, 421
Alloy surface, 277
 original, 307
Alloying elements, 122, 195, 360, 369, 422, 437
Alloys, 22, 166, 184, 247, 259, 278, 339, 355, 379, 424
 binary, 39, 118, 277, 296, 367
 initial, 315
 multicomponent, 39, 335
 multiphase, 38
 nitrided, 329
 oxidized, 285
 single-phase intermetallic, 233
Aluminium, 339, 352
Ambient environment, 253, 280, 301
Analysis
 microprobe, 255
 quantitative, 210, 286
Analytical electron microscopy (AEM), 210, 272
Antisites, 350, 388
Arrhenius plot, 13, 238, 356, 390
Atom probe tomography (APT), 14, 380, 436
 analyses, 382, 426, 437
Atomic distribution, 1, 15
Atomic fraction, 42, 59, 69, 108, 233
Atomic numbers, 211, 255
Atomic redistribution, 1, 27
Atomic volumes, 60, 80, 176, 394

Auger electron spectroscopy (AES), 22, 210
AuSn, 123

B

Back-stress, 180
Backscattered electron image (BEIs), 209, 228
Bifurcations, 53, 149
Binary system, 62, 104, 113, 118, 124, 150, 166, 215, 224, 231, 241
Black's equation, 177
Blech structure, 178, 187, 198
Boundary conditions, 76, 114, 304
Bubbles, 340, 351
Bulk couples, 384
Bulk diffusion couples, 213, 383, 412

C

Carbides, 257, 341
 higher, 341
Carbon, 117, 211, 231, 277, 283, 341
 diffusion of, 117, 349
Cathode, 173
Cellular precipitation, 39, 77, 84
Channel width, 40, 70
Channels, 40, 67
 empty, 77
Chemical potentials, 38, 45, 58, 102, 111, 128, 399
Chromium, 245, 278, 290, 317, 326, 365
 nitrides, 294, 318
Clad materials, 339
Closed system, 39, 50, 75, 88
Coarsening, 38, 132, 303, 312
Coating, 189
Coefficients of thermal expansion (CTE), 191
 mismatch, 191
Composition, 2, 18, 42, 53, 103, 149, 214, 240, 257, 279, 340, 384, 431
 end-member, 168
 single-phase, 262
Composition range, 104, 263, 366
Composition–structure–property relationships, 207, 262
Compound formation, 95, 389
 intermetallic, 55
Compressive stress, 181, 190, 330, 414

Concentration gradient, 19, 29, 39, 45, 53, 61, 82, 117, 215, 263
 Concentration profiles, 9, 47, 61, 210, 254, 265, 301, 433
 Conductor, 173, 197
 Conductor metal, 108
 Contact line, 133
 Contact surface, 209, 234, 246, 256, 301, 320
 Conventional route, 153, 270
 Cooling, 110, 132, 244
 Copper, 67
 CoSi, 158, 234
 intermetallic, 234
 phase, 158
 Couple
 incremental, 217, 258
 semiinfinite, 242
 Cracks, 251
 Critical nuclei, 45, 98, 396
 Critical size, 87, 396
 Critical thickness, 46, 380, 406
 Crystals, 2, 212, 237, 292
 point defects in, 13

D

Decomposition, 42, 48, 76, 123, 283
 Deformation phenomena, 329
 Deposition, 55, 381, 393, 430
 Differential scanning calorimetry (DSC), 381
 experiments, 394
 thermograms, 382, 420
 Diffusing species, 51, 113, 128, 213, 229, 271, 414
 dominant, 209, 415
 Diffusion, 6, 39, 58, 102, 142, 149, 237, 299, 314, 339, 383, 433
 anomalous, 342, 358
 bulk, 22, 58, 75, 86, 363
 classical, 53, 418
 dopant, 433
 faster, 13, 19, 116, 342
 grains boundary, 390
 interstitial, 29, 321, 343
 intrinsic, 229, 371
 low temperature, 365
 multi-phase, 45, 207
 short-circuit, 238
 uphill, 316
 Diffusion barriers, 10, 43, 116, 194, 427, 433
 Diffusion behavior, 240, 315, 339, 347

Diffusion characteristics, 98, 207, 215, 339, 344, 350, 358
 Diffusion coefficients, 2, 117, 150, 213, 264, 301, 342, 356, 362, 386, 404, 413, 434
 average, 20
 effective, 11, 343, 351, 391
 grain boundary, 371, 391
 impurity, 342, 353
 low temperature, 358
 measurements, 2, 22
 vacancy, 16
 Diffusion couples, 37, 45, 61, 113, 139, 158, 207, 214, 234, 272, 328, 356, 371, 383, 391
 annealed, 262
 approach, 104, 262
 binary, 53, 256
 bulb, 390
 classical, 213, 248
 experiments, 208
 incremental, 120, 219
 method, 207, 240
 multifoil, 221
 polyphase, 248
 semiinfinite, 245, 328
 single-phase, 359
 standard, 37, 53
 technique, 207, 213, 249, 256, 271, 355
 ternary, 241
 thin-film, 123
 Diffusion enhancement, 13, 359
 Diffusion factors, 410
 Diffusion fluxes, 111, 218, 228, 239, 305, 434
 Diffusion interaction, 228, 269
 Diffusion kinetic data, 111, 122
 Diffusion kinetics, 7, 13, 122, 249, 294
 Diffusion measurements, 20, 383
 Diffusion mechanisms, 6, 149, 168, 191, 232, 339, 388
 Diffusion path concept, 115, 300
 Diffusion paths, 3, 29, 85, 113, 137, 241, 299
 short-circuit, 5, 117, 320
 virtual, 137, 299, 314
 Diffusion processes, 194, 221, 339, 350, 363, 384
 Diffusion profiles, 2
 Diffusion rates, 114, 150, 232, 340, 345, 368, 388
 Diffusion zone, 37, 114, 209, 240, 299, 314
 compositions, 210
 multiphase, 254
 quasi-equilibrated, 248

Diffusion zone morphology, 241
 single-layered, 224
 Diffusion-controlled internal precipitation
 reactions, 278
 Diffusion-controlled processes, 214, 238, 253, 277
 Diffusion-controlled reactions, 60, 224, 308, 315,
 325
 Diffusion-grown layers, 239, 254
 Dislocation density, 14, 333
 Displacement curves, 220
 Dissociation, 14, 75, 123, 151, 333, 349, 415
 Dissolution, 22, 41, 108, 297
 Dissolution rate, 108
 Divergence, 51, 61, 88
 Dopants, 432
 Drift, 48, 87, 92, 180, 188
 electromigration-induced, 179
 zero, 88
 Drift terms, 87
 Drift velocity, 87, 176, 200
 Driving forces, 81, 102, 122, 127, 142, 149

E

Electric field, 173, 182, 201
 Electrical resistivity, 176, 184, 201
 Electromigration, 1, 50, 112, 173, 197
 classical, 173
 damages, 176, 198
 Electromigration drift, 179
 Electromigration-induced whiskering, 198
 minimizing, 199
 Electron backscatter diffraction (EBSD), 210, 285
 Electron probe microanalysis (EPMA), 209, 230,
 240, 285, 323, 355, 365
 Electron wind, 57, 173
 End-members, 37, 156, 209, 217, 299
 Equilibrated alloys, 249
 Equilibrium
 local, 22, 103, 240, 251, 282, 307, 314
 metastable, 89, 106
 Equilibrium concentration, 15, 69, 181
 Equilibrium phase diagram, 59, 86, 114, 251, 324
 Equilibrium phases, 256, 380
 Equilibrium solubility, 108
 Error function, 2, 63, 305, 313, 328
 complementary, 21, 305
 Extended defects, 14, 388
 External fluxes, 38, 50, 88

F

Fast diffusion, 4, 43, 67, 434
 Fick's law, 117, 175, 262, 351, 386, 391, 405
 first, 117, 153, 214, 225, 301
 second, 117, 214, 304, 327
 Films, 55, 73, 179, 198, 381, 394, 417, 437
 conducting, 198
 Finite element simulations (FES), 6, 17, 29, 434
 Fisher geometry, 7, 12, 29
 Fisher model, 2, 9, 26
 Fission gases, 350
 Fission products, 350
 Flux equations, 225, 233, 263
 Flux-assisted nucleation (FAN), 88
 Flux-driven grain growth (FDGG), 42, 55
 Flux-driven nucleation (FDN), 88
 Flux-driven phase transformations, 37
 real, 53
 Flux-driven ripening (FDR), 39, 55, 66, 73
 Flux-suppressed nucleation (FSN), 88, 97
 Force of electromigration (FEM), 175
 Formation
 germanide, 384, 406
 intermetallic, 63, 233
 silicide, 384
 simultaneous, 384, 393, 405
 Formation kinetics, 418
 Fuels, 340, 347, 367
 Fugacity, 259, 282, 294, 303, 320
 Furnace
 hot-isostatic-pressure (HIP), 282

G

Gas mixtures, 280, 283
 Gas/metal interface, 282, 291, 318, 325
 Germanides, 381
 Gibbs compositional triangle, 264–265
 Gibbs energy, 47, 92, 226, 424
 Gibbs energy of formation, 228, 231
 Gibbs free energy, 47, 55, 71, 77, 85, 90, 98, 101,
 122, 226, 232, 280, 298, 394
 Gibbs phase rule, 104, 141
 Gibbs potential, 62, 87
 Gibbs–Duhem relation, 154
 Gibbs–Thomson effect, 52
 Grain boundary (GB), 3, 8, 39, 55, 71, 168, 195,
 209, 237, 251, 271, 290, 325, 348, 356
 diffusion, 2, 26, 194, 348, 367, 386, 434
 moving, 209

resistivity, 57
 Grain growth, 27, 55, 67, 73, 339, 403, 425
 abnormal, 199, 421
 Grain rotation, 57
 Grain size, 6, 390
 Grain structures, 57, 199
 Growing layers, 29, 384, 402
 Growing phase, 39, 44, 66, 113, 226, 402, 418
 layer, 42, 234
 Growth
 diffusion control, 410
 diffusion-controlled, 170, 185, 224
 normal, 396
 sequential, 380, 403
 simultaneous, 404
 Growth kinetics, 234, 250, 315, 384, 404, 418, 431
 Growth of silicide, 49, 383
 epitaxial, 49
 in diffusion couple, 383
 Growth of silicides, 392, 418
 Growth processes, 162
 Growth rate, 40, 44

H

Hardness, 262
 Heat treatment, 208, 244, 384, 398, 416, 434
 isothermal, 384, 398
 High-pressure torsion (HPT), 56
 Hillocks, 51, 174, 197

I

Impurity, 23, 257, 339, 366
 concentration, 9, 28
 diffusion, 30, 353
 metallic, 347
 In situ XRD, 395
 Indentation, 262
 Inert markers, 209, 218
 Inert particles, 149, 168, 209, 218
 Initial contact interface, 53, 221
 Integrated diffusion coefficient, 119, 161, 227, 271
 Interaction zone, 209, 221, 269, 307, 328
 Interconnects, 175, 187, 198
 Interdiffusion, 49, 91, 101, 117, 149, 210, 215,
 234, 250, 262, 268, 344, 359, 366, 418
 coefficients, 30, 61, 108, 118, 155, 214, 263,
 344, 366, 384
 fluxes, 214, 262
 zone, 121, 149, 156, 209, 266, 344

Interdiffusivity, 60, 90
 Interface energy, 38, 380, 396
 Interface mobilities, 395
 Interfacial barriers, 45
 Interfacial reactions, 28, 121, 144, 259, 320, 380,
 399
 Interlayer, 178
 Intermediate phase nucleation, 48, 95
 Intermetallic compounds (IMCs), 43, 66, 86, 104,
 123, 144, 164, 184, 207, 233, 271, 381,
 402
 formation, 89
 growth of, 194
 layers, 126, 185, 194
 Intermetallic phases, 224
 Intermixed layer, 430
 Internal nitridation, 281, 287, 316
 Internal oxidation, 277, 302
 region, 314
 Internal precipitates, 287, 301, 310, 318
 Internal precipitation, 277
 kinetics, 278, 304, 326
 reactions, 279, 294, 301, 323, 334
 zone, 285, 302, 314, 329
 Internal reactions, 285, 305, 314, 329
 Interphase boundary, 48, 363
 Interphase interfaces, 213, 232, 240, 255
 Interstitials, 214, 233, 349
 Intrinsic diffusion coefficients, 119, 153, 217, 366
 Intrinsic diffusivities, 119, 154, 223
 Inverse fast Fourier transform (IFFT), 427
 Inward diffusion, 301
 Irradiation, 38, 339, 351
 Isothermal annealing, 401, 424
 Isothermal cross-sections, 230, 251, 260, 272, 296,
 318
 Isothermal section, 113, 135, 241, 314

K

Kinetic equilibrium, 412
 Kirkendall marker plane, 120, 149
 Kirkendall plane, 53, 162, 218, 225
 stable, 220, 271

L

Lamellar structure, 42, 77, 85
 Lateral grain growth, 55
 Lateral growth, 49, 64, 380, 394, 420
 Line-compounds, 224

Liquid channels, 40, 67, 72
 Liquid metals, 182, 201, 345
 Liquid solder, 66, 108
 Liquid state, 107, 182
 Local equilibria, 104, 128, 139, 240, 248, 299, 315
 Low pressure chemical vapor deposition (LPCVD), 433

M

Marker plane, 151, 168, 234
 location of Kirkendall, 150, 168
 Markers, 53, 179, 209, 218, 371, 427
 fiducial, 209, 220
 Mass transport, 114, 173, 188, 190, 237, 388, 410
 Mass-balance requirement, 115, 142
 Material transport, 173, 229
 Melt, 67, 86, 110
 Metal–gas interface, 287
 Metallic films, 198
 Metallic fuels, 340
 diffusion in, 341
 Metallic materials, 173
 Metallic silicides, 379
 Metallic systems, 208, 277
 Metals
 corrosion of, 277
 precipitation reactions in, 278, 328
 solvent, 298, 308, 319, 329
 Metastable phases, 256, 380, 393
 Microstructural evolutions, 149, 161, 169, 279, 285
 Microstructure, 120, 129, 161, 241, 278, 286, 328, 334, 415
 “duplex”, 228
 interfacial, 132
 Migration energy, 14, 345
 Minor alloying, 175, 193, 199
 Mixture, 281, 291, 318, 326
 Molar Gibbs energy diagrams, 107
 Molar volumes, 151, 191, 215, 263, 295, 319, 331, 400
 Molten solder, 39, 66, 109, 138
 Monovacancies, 358, 369
 Morphological evolution, 121, 168
 Morphology, 67, 144, 166, 195, 234, 241, 279, 291, 299, 328
 duplex, 120, 156, 164
 Moving boundary, 108, 314
 Moving interface, 39, 61, 75, 92, 399, 433

Multicomponent systems, 113, 119, 166, 240, 251, 262, 267
 Multiphase diffusion couples, 209, 234, 272
 Multiphase systems, 214

N

Nabarro–Herring creep type mechanism, 331
 Nanocrystalline layers, 5
 Nanocrystalline materials, 2, 12, 29
 Nanocrystals, 1, 12, 29
 Nanograins, 14, 18
 Nanomaterials, 169
 Nernst–Einstein relation, 87, 119, 405
 Ni film, 43, 379, 393, 416
 Ni silicide formation, 380, 393, 427
 Ni-based
 alloys, 321, 369
 superalloys, 339, 368
 Ni₂Si, 394
 Nickel monosilicide phase (NiSi), 49, 379, 392, 415
 NiGe, 406
 NiSi particles, 396
 NiSi phase, 420
 low resistivity, 379, 422
 Nitrided zone, 290, 317, 325, 331
 Nitrides, 257, 329, 340, 349
 Nitriding, 287
 Nitrogen pressure (fugacity), 259, 287, 295, 320
 Nuclear fuels, 339
 Nuclear materials, 339
 Nucleation, 38, 47, 71, 88, 156, 256
 diffusion-controlled, 88
 problems in, 113
 rate of, 303
 suppression of, 47, 98
 Nucleation barrier, 39, 45, 87, 156, 169, 394, 431
 effective, 49, 89
 height of, 39
 Nucleus, 45, 71, 94, 396

O

Open systems, 37, 75, 85
 Ordered alloys, 233
 Ordered phases, 233
 Ordering, 50
 Outgoing fluxes, 75, 88
 Oxidants, 277, 284, 298, 318, 335
 Oxidation of metals, 414

Oxidizable solute, 284, 297, 302, 313, 318

P

Parent phases, 39, 47, 75, 415
 Partial molar volumes, 154, 214
 Penetration depth, 193, 302, 310, 328
 Phase diagram determination, 240
 Phase diagram research, 207, 240, 251
 Phase equilibria, 102, 113, 240, 251, 260
 Phase field boundaries, 250, 272
 Phase formation, 44, 64, 113, 384, 394, 408, 431
 sequence, 45, 406, 421, 429, 436
 Phase growth, 64, 117, 121, 169
 kinetics, 63
 Phase layer, 45, 58, 150, 166, 234
 Phase relations, 230, 243
 Phase transformations, 37, 98, 114
 Phase transition, 37, 341, 356
 Physicochemical approach, 121
 Physicochemical model, 150, 169
 Plastic deformation, 222
 Plating, 125, 129, 195, 208
 Point contact reactions, 37, 49
 Point defect concentration, 1, 29
 equilibrium, 15
 Pores, 5, 340, 351
 Porosity, 79, 235
 Precipitates, 128, 224, 244, 279, 289, 303, 310,
 328, 344, 352, 394
 isolated, 39, 75, 133, 241
 rounded, 287
 Precipitating compound
 equilibrium solubility product of the, 308
 formation of the, 298
 mole fraction of the, 311
 stoichiometry of the, 303
 thermodynamic stability of the, 301
 Precipitation, 75, 108, 285, 298, 308, 313, 329,
 351, 356, 414, 434
 Precipitation front, 292, 303
 internal, 303, 307, 312, 324, 331
 Precipitation reaction, 278, 328
 Precipitation zone, 285, 301
 Preexponential factor, 236, 342, 363
 Pressurized water reactors (PWR), 340, 367, 370
 Product phase, 120, 150, 191, 234
 layers, 121, 229

R

Radiotracers, 24, 341, 355
 Reaction couple, 117, 130, 142, 215, 227, 234,
 241, 252, 259, 299
 Reaction front, 301, 314, 331
 Reaction layers, 101, 114, 228, 239, 253, 301, 324
 interfacial, 139
 Reaction product layer, 39, 225, 236, 241, 253,
 285, 319
 Reaction products, 39, 104, 138, 184, 209, 237,
 250, 259, 285, 320
 Reaction sequence, 114, 127, 140
 Reaction zone, 40, 67, 102, 113, 121, 128, 209,
 213, 234, 272, 285, 314
 morphologies, 242, 245, 249, 259
 Reaction–diffusion process, 161
 Reaction–dissociation equations, 156
 Reactive diffusion, 26, 39, 48, 54, 61, 76, 86, 120,
 210, 379, 411, 416
 initial stage of, 47, 98
 Reactive phase formation, 234
 Reactors, 38, 339, 348, 351, 364
 nuclear, 38, 339, 347, 350, 353, 363
 Recrystallization, 41, 191, 339
 Redistribution, 39, 48, 217, 227, 381, 415, 427,
 432
 diffusive, 39
 dopant, 432
 Relaxation, 75, 329, 402, 415
 Research tool, 207, 320, 334
 Resistance, 179, 364, 379, 384
 creep, 364, 369
 Ripening, 38, 55, 67, 73, 329
 rate, 40, 73
 Rutherford backscattering spectrometry (RBS),
 210, 384

S

Sandwich samples, 248
 Scallop growth, 68
 Scallop–melt, 74
 Scallops, 40, 67, 126
 neighboring, 67
 Scanning electron microscopy (SEM), 125, 144,
 174, 209, 230, 251, 285
 Scanning transmission electron microscopy
 (STEM), 286, 367
 Second diffusion couple (DC2), 264

- Secondary ion mass spectrometry (SIMS), 1, 210, 433
 - Segregation, 23, 52, 82
 - kinetics, 22
 - Selected-area electron diffraction (SAED), 286
 - Self-diffusion, 26, 333, 342, 364, 368
 - behavior, 357, 365
 - coefficients, 22, 154, 271, 342, 356, 364
 - measurements, 357
 - Sequential formation, 384, 393, 404
 - Sequential growth, 380, 394, 404, 416
 - Sever plastic deformation (SPD), 4, 56
 - Sharp concentration gradients, 47, 97
 - Sheet resistance, 384, 400
 - Si monocrystal, 11
 - Silicide films, 380
 - Silicide formation, 380, 383
 - diffusion controlled, 388
 - Silicide nucleation, 49, 422
 - Silicides, 37, 49, 379, 432
 - Silicon nanowires, 49
 - Simulations, 5, 50, 118, 350, 395, 427
 - 3D, 12, 30
 - Single crystals, 341, 353
 - Single diffusion couple (DC1), 264
 - Single intermediate phase, 64
 - Sn coatings, 189
 - Solder, 66, 76, 108, 138
 - Soldering, 66, 75, 130
 - Solid liquid interdiffusion (SLID), 123
 - bonding, 128, 130
 - Solid solution alloys, 215
 - binary, 207, 314
 - ternary, 207
 - Solid solutions, 23, 75, 243, 265, 290, 315, 424
 - binary, 215
 - electromigration in, 51
 - homogeneous, 23
 - marginal, 92
 - supersaturated, 42, 73
 - Solid state diffusion, 139, 149, 339
 - Solid state reactions, 39, 45, 51, 123, 227, 234, 250, 299, 314, 328, 388, 408, 421
 - internal, 277, 285, 328
 - Solubility, 63, 91, 108, 144, 247, 298, 312, 325, 334, 433
 - metastable, 108, 133
 - Solubility product, 298, 312
 - Solubility–diffusivity product, 303, 326
 - Solute, 277, 298
 - average concentration of, 315
 - concentration of, 314
 - enrichment of, 302
 - internally oxidized, 285, 308
 - Solute atom, 301, 306, 325
 - Specimen preparation, 210, 286
 - Specimens, 210, 255, 284, 304, 320, 341, 365
 - Spectrometer, 211, 255
 - Spontaneous whisker growth, 198
 - Stability diagram, 112, 119, 228, 261, 295, 323
 - Stainless steel, 339, 366
 - Stoichiometry, 61, 75, 81, 86, 303, 345, 388
 - Stress, 39, 48, 63, 181, 190, 193, 285, 329, 353, 380, 413
 - relaxation of the, 192, 253, 415
 - tensile, 79, 174, 193
 - thermal, 191, 415
 - thermoelastic, 413
 - Stress generation, 182
 - Stress gradient, 112, 182, 198
 - negative, 180
 - vertical, 58
 - Sublayers, 151
 - Subscale, 278
 - Substrate, 68, 178, 190, 381
 - Supersaturation, 42, 58, 76, 241, 308, 315, 318
 - Surface, 14, 55, 79, 125, 192, 287, 329, 400, 423, 438
 - energy, 47, 52, 55, 71, 92
 - external, 86, 304, 311
 - free, 78, 81, 85, 194
 - segregation, 22
 - tensions, 41, 70, 95
- ## T
- T-phase, 115
 - Ternary alloy systems, 263
 - Ternary compound, 115, 137, 257
 - Ternary isotherm, 114, 241, 296
 - Ternary phase diagrams, 318, 433
 - Ternary phases, 133, 251
 - Ternary systems, 48, 111, 241, 256, 299, 370
 - Texture, 239, 285, 380, 400, 421
 - Thermodynamic activity, 277, 279, 298, 315
 - Thermodynamic assessments, 101, 296
 - Thermodynamic driving force, 64, 85, 90, 116, 122, 154
 - Thermodynamic equilibrium, 2, 240, 251, 296

complete, 103
 global, 117
 local, 214, 250, 314
 Thermodynamic information, 82, 233
 Thermodynamic–kinetic methods, 107, 122
 Thermodynamically stable phases, 104, 113
 Thermomigration, 51, 188
 Thin film, 7, 49, 73, 117, 168, 178, 379, 414
 conductors, 198
 interconnects, 177
 reactions, 49, 117, 382, 389, 406, 414, 418
 Time delay, 416
 TiNi, 243
 Transformations, 38, 42, 47, 52, 60, 85, 129, 342, 359
 allotropic, 341, 356
 Transient liquid-phase (TLP), 123
 Transistors, 379, 418, 437
 nanometric, 379, 424
 Transmission electron microscopy (TEM), 144, 286, 397, 429
 Treatment, 307
 Triple junction (TJ), 2, 397
 diffusion, 3, 12
 Two-phase alloys, 245, 258
 equilibrated, 246
 Two-phase structures, 51, 224

V

Vacancies, 29, 42, 58, 75, 118, 181, 197, 214, 331, 345, 357, 388
 Vacancy concentration, 14, 30, 52, 75, 330
 Vacancy formation, 52
 Void formation, 79, 170, 188, 199
 Kirkendall/Frenkel, 89
 Voids, 42, 48, 76, 174, 184
 evolution of, 178

phases, 42, 86
 presence of pores, 234, 271
 Volume change, 78, 215, 329, 414

W

Wafers, 124, 381, 437
 Wagner diffusivity, 63, 90, 95
 Waiting time, 45, 49
 Walls, 38, 71, 80
 Wavelength dispersive spectrometry (WDS), 211–212
 Whisker grain, 192
 Whisker growth, 190
 continuous, 198
 electromigration-induced, 202
 spontaneous, 191
 Whisker number density, 198
 Whisker root, 190
 Whiskering, 190
 Whiskering phenomenon, 193
 Whiskers, 189

X

X-ray diffraction (XRD), 193, 230, 251, 260, 285, 381, 393, 421
 X-ray reflectivity (XRR), 381
 X-rays, 193, 210, 255, 286, 408

Z

Z-phase, 115–116
 Zirconium, 339, 356
 diffusion of, 360
 self-diffusion of, 356
 Zirconium based alloys
 Zircaloy-2, 360
 Zircaloy-4, 352, 360