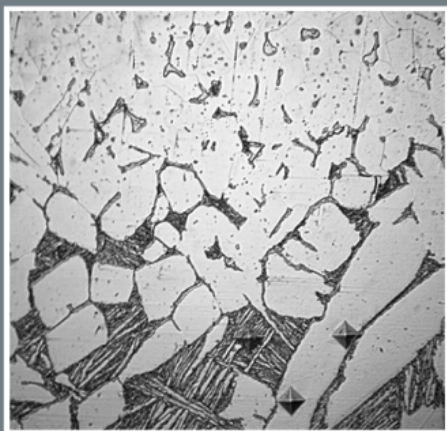




Titanium alloys: modelling of microstructure, properties and applications

Wei Sha and Savko Malinov

Titanium alloys: modelling of microstructure, properties and applications

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Preface

This book is a research monograph, cumulating the experience and results of over ten years' research by the authors. It covers both conventional titanium alloys and titanium aluminides.

Since 1999, the authors have been funded by the UK Engineering and Physical Sciences Research Council (EPSRC), for carrying out the following projects:

- (i) Modelling of the evolution of microstructure during processing of titanium alloys.
- (ii) Computer-based modelling of the evolution of microstructure during processing of gamma Ti–Al alloys.
- (iii) Collaborative research in modelling the evolution of material microstructures.
- (iv) Atomistic simulation of γ/α_2 interfaces and dislocations relevant to lamellar titanium aluminides.

Funding has also been provided by the Queen's University of Belfast, the Royal Society, Royal Academy of Engineering, and Invest Northern Ireland for many smaller projects, most of them jointly with international collaborators. These projects have led to about 100 publications, reflecting research effort in modelling of many correlations in the path of processing parameters to microstructure to properties in titanium alloys. The authors have developed a number of models and computer program packages that are based on experimental results, physical metallurgy theories and different computational approaches.

Computer-based modelling is a fast growing field in materials science, as demonstrated by the large recent literature. The authors have combined expertise in titanium and model development. Therefore, this book fills a gap of the book literature in the application of modelling techniques in titanium research, both hot topics in contemporary materials research, whilst at the same time documenting the latest research in this area. A large chunk of this latest research is from the authors themselves, based on their leading position in this research area, but the book also covers important relevant research by

others. Much of the microstructural modelling is about phase transformations and kinetics.

The book has a clearly defined audience. It is primarily intended for researchers involved with either titanium or modelling, or both. The titanium expert will be able to learn modelling and apply the increasingly important modelling techniques in their titanium materials research and development. The modelling expert will be able to apply their modelling expertise to the remarkable material that is titanium. Combining modelling and titanium into one publication is the idea behind this book which is its strength.

Chapters on modelling will be about using these techniques on titanium only. Computer modellers have lots of options on entire books that are devoted to each of the modelling chapters in the book, but not applied to titanium. The research papers listed at the end of the preface are used in this book, but the underlying structure of the book is based on the techniques of the modelling. It is intended that each chapter can be read largely independently.

Funding from the following is acknowledged:

- EPSRC, for research grants, and for the provision of Synchrotron Radiation Source (SRS) beam time.
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- All co-authors in the papers list at the end of this preface.
- Dr Veneta Yanakieva for her work on IMI 367 alloy.
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Introduction to titanium alloys

Abstract: This is a concise introduction to titanium alloys and focuses on the most relevant aspects for the book, namely the effect of the thermomechanical processing of titanium alloys and aluminides. The chapter includes a section on the most common alloys, as the large number of alloys found in the literature can be very confusing. It includes, for example, Ti-6Al-2Sn-4Zr-6Mo (Ti-6246), which is becoming increasingly important for the aero engine industry.

Key words: titanium alloys, titanium aluminides, thermomechanical processing, properties, applications.

1.1 Introduction

In recent decades, a generic class of titanium-based materials has been developed for a range of applications. Titanium and titanium alloys are currently finding increasingly widespread use in many industries for the production of a variety of components and workpieces due to their desirable and versatile combination of good mechanical and chemical properties. Stimulus for the development of titanium alloys during the past sixty years came initially from the aerospace industry when there was a critical need for new materials with higher strength to weight ratios. The advantages of titanium alloys include: (i) low densities, which fall between those of aluminium and iron and give very attractive strength to weight ratios allowing lighter and stronger structures; (ii) superior corrosion and erosion resistance in many environments, in particular to pitting and corrosion cracking; (iii) high temperature capability in the range of 300–600 °C. They also have high toughness making them useful materials for precision mechanism gears, turbine engine components, and biomedical prosthesis devices. However, titanium alloys possess some disadvantages. One of the most significant disadvantages is their cost.

Today, titanium alloys have many applications, from structural components in the aerospace and automobile industries to corrosion resistance materials in the chemical and marine sectors and medical device manufacturing (Guleryuz and Cimenoglu, 2005; Škorić *et al.*, 2004). It is believed that the expansion of titanium alloys usage will continue for the forthcoming years. Although the titanium materials are still considered as expensive materials, for many applications the cost of titanium alloys can be justified from a material selection viewpoint on the basis of their desirable properties.

The mechanical properties of titanium alloys, such as strength, ductility, creep resistance, fracture toughness and crack propagation resistance, depend

essentially on the microstructure, which is formed during the thermomechanical processing and thermal treatment procedures. It is therefore very important to understand the nature of the phase transformations taking place at different heat treatment conditions.

1.2 Conventional titanium alloys

1.2.1 Microstructure and properties

The physical metallurgy of titanium is both complex and interesting. The metal is stable only at certain temperature ranges. At a temperature of 882 °C, known as the β -transus temperature, pure titanium undergoes a phase transformation from a low temperature stable, modified hexagonal close packed structure (hcp) (α) to a body centred cubic phase (bcc) (β) that remains stable up to the melting point of 1678 °C. The main characteristics for a crystal structure are the plastic deformation capability and diffusion. The diffusion rate depends on the lattice microstructure (Leyens and Peters, 2003). Titanium and its alloys react with several interstitial elements including the gases oxygen, nitrogen and hydrogen. Such reactions may occur at temperatures well below the melting points.

The type of phases present, grain size and grain shape, morphology and distribution of the fine microstructure (for example, $\alpha + \beta$ colonies) determine the properties and therefore the application of titanium alloys. The technical titanium-rich alloys can be classified into these categories: α , near- α , $\alpha + \beta$, near- β , metastable β and stable β , depending on their composition, the ratio of the amounts of the α and β phases, and the position in the pseudo binary β -isomorphous phase diagram. The subclasses near- α and near- β refer to alloys with compositions which place them near to $\alpha/(\alpha + \beta)$ or $(\alpha + \beta)/\beta$ phase boundaries, respectively.

α and near- α titanium alloys have mainly α structure and depending on the processing conditions may have different microstructural grain morphologies, ranging from equiaxed to acicular (martensitic). These classes of titanium alloys are preferred for high temperature applications. β titanium alloys contain a balance of β stabilisers to α stabilisers which is sufficient to ensure that a fully β phase microstructure can be retained on fast cooling (slow cooling, in furnace, for instance, causes β -phase decomposition). In this condition, the metastable β alloys are generally thermodynamically unstable. This can be used as an advantage (for cold deformation before ageing, for example) by allowing some decomposition reactions (α precipitation) during an ageing treatment in order to provide secondary strengthening. As a result, the metastable β titanium alloys generally have higher strength, higher toughness and improved formability at room temperature as compared to the α and $\alpha + \beta$ titanium alloys, although the

processing parameters to achieve these properties are sometimes critical. The metastable β alloys are heat treatable to very high strength usually by solution treatment plus quenching followed by ageing. The highest strength among titanium alloys can be reached with such heat treatment combined with cold deformation.

1.2.2 The most popular alloys

Over the recent decades, many titanium-based materials have been developed for different ranges of applications.

Ti-6Al-4V presently is the most widely used, high-strength titanium alloy. It finds a large application in the aerospace industry and in medicine, for medical prostheses. It is also used in the automotive, marine and chemical industries (Boyer *et al.*, 1994). The control and optimisation of the morphology of the α phase is one of the important issues in the use of the alloy. Thermomechanical processing is a very useful method of improving the microstructure, e.g. controlling the size and the aspect ratio of the α lamellar phase, optimising the phase ratio of α to β phases, and controlling the morphology of the β phase. Hot deformation of the Ti-6Al-4V alloy in the β phase field results in relatively large prior- β grains, α phase is formed during cooling and martensite may be formed on rapid quenching. When processing in the $\alpha + \beta$ phase field, a much finer $\alpha + \beta$ structure can be obtained, because the primary α phase limits the growth of β phase. When processing in the β phase field, the microstructural evolution may include the mechanical deformation of the equiaxed β grains and possible dynamic or metadynamic recrystallisation during processing, and the β to α phase transformation when cooling after deformation.

Commercial titanium alloy Ti-6Al-2Sn-4Zr-2Mo (usually in its modified version Ti-6Al-2Sn-4Zr-2Mo-0.08Si) is one of the most commonly used high temperature titanium alloys. It has an attractive combination of tensile strength, creep strength, toughness and stability for long-term applications at temperatures up to 425 °C. It is used for gas turbine components and in other applications where this good combination of properties is required. At the same time, it has poor tribological properties that are typical of most of the titanium alloys. It has low surface hardness and wear resistance. These disadvantages of the material limit its application.

Ti-6Al-2Sn-4Zr-6Mo is becoming increasingly important for the aero engine industry. This heat-treatable α - β alloy is designed to combine the elevated temperature characteristics of Ti-6Al-2Sn-4Zr-2Mo with higher strength levels.

Ti-8Al-1Mo-1V was developed for gas turbine engine applications and especially for compressor blades and wheels. It has the highest modulus of all the commercial titanium alloys.

Ti-10V-2Fe-3Al is a high-strength titanium alloy. Its major advantages

are its excellent forgeability, high toughness in air and saltwater environments and its high hardenability. It is used in the aerospace industry.

The commercial alloy β 21s has a higher strength to weight ratio (specific strength) over other common engineering materials. It is specifically designed for oxidation resistance, elevated temperature strength, creep resistance and thermal stability. This alloy is also resistant to corrosion from aircraft hydraulic fluids (e.g. Skydrol) at all temperatures. It is applicable for metal matrix composites because it can be rolled to foil, is compatible with fibres, and is stable until 816 °C. Commercial applications include aerospace components and prosthetic devices. For the latter application, with appropriate thermal mechanical processing, the modulus of β 21s is comparable to that of bone. β 21s also possesses excellent hydrogen embrittlement resistance, which has contributed to its chemical and offshore oil uses.

Other titanium alloys described in this book include Timetal 205. The chemical compositions of the alloys are shown in Table 1.1.

1.3 Titanium aluminides

The aluminides of titanium (titanium aluminides) are ordered intermetallic alloys, and are one special class of titanium alloys. Ti–Al alloys are different compared to conventional titanium alloys because they are principally chemical compounds alloyed to enhance strength and formability. Aluminides have higher operational temperatures than conventional titanium alloys, but are more expensive and generally have lower ductility and formability. With the increasing demands for high temperature structural materials with high strength-to-weight ratios, there has been a great increase in the research and development of alloys based on titanium aluminides such as TiAl, Ti_3Al and Ti_3AlNb , because of their attractive and unique set of specific properties, such as high melting temperature, exceptionally high proof strength at elevated temperatures (Winstone, 2001), hardness, high modulus and modulus retention with temperature, creep resistance at high temperatures, and good oxidation resistance (Sun *et al.*, 2002). These alloys are characterised by their high oxidation and corrosion resistance of at least up to 800 °C. However, the practical use of these titanium aluminides has been limited. The main reasons for this are their lack of ductility and toughness, and poor fracture resistance, at ambient temperatures. In addition, cost remains a negative factor. Nevertheless, they offer the promise of a light, strong, and chemically stable material for structural applications at high temperatures, in the aerospace, automobile and turbine power generation industries. Intermetallic compound Ti_3Al (α_2 -phase) with superstructure is the main component of a number of single- or two-phase alloys, for example $\text{Ti}_3\text{Al}/\text{TiAl}$ (α_2/γ -phases).

The γ -based titanium aluminide intermetallics have been considered as one of the most promising candidate materials, for examples in advanced

Table 1.1 Characteristics and typical chemical composition in weight percent of some popular titanium alloys

Alloy	Type	β -transus (°C)	Al	Mo	V	Nb	Zr	Fe	Cr	Sn	O	Si	H	C	N
Ti-8Al-1Mo-1V	near α	1040	8.02	1.04	0.98	–	–	0.08	–	–	0.085	–	0.0035	0.01	0.004
Ti-6Al-2Sn-4Zr-2Mo	near α	995±15	6.13	1.95	–	–	3.97	0.07	–	1.93	0.065	0.11	0.0045	–	0.002
Ti-6Al-2Sn-4Zr-6Mo	$\alpha + \beta$	932	6	6	–	–	4	0.15	–	2	0.1	–	0.0125	–	0.015
Ti-6Al-4V	$\alpha + \beta$	1000±15	6.59	–	4.1	–	–	0.18	–	–	0.19	–	0.002	–	0.005
Ti-10V-2Fe-3Al	near β	790–805	3.06	–	9.95	–	–	1.93	–	–	0.09	–	0.002	0.02	0.009
β 21s	meta-stable β	807	3	14.12	–	3.48	–	0.32	–	–	0.15	0.14	0.0963	0.016	0.024
Ti metal 205	β	780	–	14–16	–	–	–	–	–	–	–	–	–	–	–
Ti-46Al-1.9Cr-3Nb	γ	–	31.3	–	–	7.0	–	–	2.5	–	0.07	–	0.0024	–	–

aerospace engine and airframe components. The remaining part of this section will focus on this type of aluminide. Efforts to enhance ductility and improve other mechanical properties have been concentrated on microstructural control with a variety of micro-alloying additions including B, Cr, Mn, Mo, Nb, Si, V, Ta, and W. TiAl alloys usually have the form of lamellar structures composed of γ -TiAl and α_2 -Ti₃Al phases. They have higher specific strength than Ni based superalloys (Lipsitt *et al.*, 2001), but their tensile strength is not as high and further improvement of their strength is necessary for them to replace Ni based alloys. It is known that refinement of the lamellar size is a promising way of improving the yield strength of TiAl alloys.

Industrial multiphase γ -TiAl alloys have a wide set of phases, which include disordered α (ordinary hcp structure) and β (ordinary bcc structure) phases, ordered α_2 (Ti₃Al with the DO₁₉ structure based on hcp lattice) and γ (near-cubic face-centred tetragonal L1₀ crystal structure), and ordered body-centred cubic B2 phase.

TiAl-based alloys generally start solidification as the β phase and go through the α single-phase region and α to $\alpha + \gamma$ and $\alpha + \gamma$ to $\alpha_2 + \gamma$ reactions, producing an $\alpha_2 + \gamma$ two-phase structure. Thus, different two-phase structures can be obtained by manipulating these phase transformation reactions. Mechanical properties can be tailored to meet the needs for a special application component by controlling the alloy microstructure.

Duplex (DP) and fully lamellar (FL) microstructures are two typical microstructures. Gamma titanium aluminides usually have a lamellar microstructure that consists of equiaxed polycrystalline grains and densely packed lamellae within the grains. The lamellae consist of two phases, α_2 and γ . The α_2 plates are thinner than the γ plates and are interspersed between the many γ plates. Because they have slower diffusion rates than conventional titanium alloys, the titanium aluminides feature enhanced high-temperature properties, in strength retention, creep, stress rupture, and fatigue resistance.

The phase transformation involving the ordering of disordered α -Ti phase with formation of ordered α_2 (Ti₃Al) and γ (TiAl) phases at different temperatures in TiAl-based alloys is of major importance in manufacturing these materials, as it controls the grain size and spacing of γ and α_2 lamellae, and hence the yield strength and other mechanical properties. Because of its importance, the α to $\alpha_2 + \gamma$ transformation has been studied in great depth from both technological (Hu, 2001) and scientific (Yamaguchi *et al.*, 2000) points of view.

The fully lamellar microstructure is currently regarded as the most attractive because the overall balance of properties is reasonably good. The presence of lamellae can have a significant effect on the mechanical properties due to the high density of semi-coherent lamellar boundaries, which affects subsequent dislocation motion and fracture behaviour. The mechanical behaviour of γ alloys changes with both the volume percentage of the various phases and

grain morphologies. Two main microstructural parameters – grain size and lamellar thickness, of both α_2 and γ phases – compete to contribute to the tensile and toughness properties. The influence of lamellar thickness on yield strength (Cao *et al.*, 2000), deformation and fracture, and creep behaviour (Wen *et al.*, 2000) has proved to be crucial.

Oxygen and nitrogen have significant effect on alloy strength properties. As the amount of oxygen and nitrogen increases, the toughness decreases until the material eventually becomes quite brittle.

Much improved service properties, including ductility, may be achieved with titanium aluminides by forging and extrusion at temperatures high enough for the alloys to have the α structure, thermomechanical processing and heat treatment. Development of the new methods of such a treatment should be based on scientific data about phase transformations in these materials.

1.4 Modelling

The development of titanium alloys, including titanium aluminides targeted for specific applications, has been an important task in the manufacturing industry. Traditionally, such alloys and processes are designed empirically, i.e. with a mixture of experience and intuition. This is both costly and time consuming. It is now highly desirable to develop advanced computer-based models for the design of alloy compositions in an increasingly theoretical and less empirical manner. These models will be based upon the general theories of thermodynamics and phase transformation.

Accurate prediction of microstructural evolution is essential to control the microstructure, to understand processing–microstructure–property relationships, and to tailor manufacturing conditions. It is important to understand the correlation among processing parameters, microstructure and properties, which would allow the optimisation of the processing parameters and alloy composition in order to achieve the desired combination of properties for any particular application. At present, this is one of the most challenging areas in the field of research on titanium alloys. The relationship between the processing parameters and the mechanical properties for titanium alloys has so far mainly been studied empirically. The idea of computer modelling and simulation of the different processes taking place during processing of titanium alloys and of the correlation between processing parameters and mechanical properties is very attractive and highly desirable. Computer modelling of these alloys is a promising way to optimise the processing parameters.

Describing and understanding phenomena and correlations in materials by modelling and simulation is becoming popular and effective. Materials modelling and simulation have proven their ability to address a variety of problems ranging from development of fundamental knowledge to solving real practical and industrial problems. There is a huge amount of work devoted to materials modelling (Guo *et al.*, 2004).

The titanium manufacturing industry will benefit from improvement in microstructure control leading to more consistent and less scattering of properties, therefore gaining improved competitiveness in worldwide markets. The aerospace and offshore industries will benefit from improved materials properties and a wider selection of materials due to more advanced processing technology. Microstructure modelling will contribute to the scientific understanding of microstructural evolution as a whole, which will also have long-term benefit to the improvement of titanium products for other applications including both aerospace and non-aerospace, the latter including applications in civil engineering and a whole range of other applications. Therefore, mechanical and construction industries will also benefit. Moreover, the established modelling methods are also applicable to other alloy systems.

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Abstract: The first part of the chapter discusses *in situ* high temperature microscopy, using two popular commercial titanium alloys as examples. An optical microscope equipped with a high temperature stage is used with both normal and florescence lighting. The second part describes optical microscopy and scanning electron microscopy conducted on Ti-46Al-1.9Cr-3Nb alloy before and after heat treatments. Heat treatment has led to the formation of a fully lamellar microstructure. The third and final part extends to transmission electron microscopy and energy-dispersive spectroscopy of this alloy before and after heat treatment.

Key words: high temperature, optical microscopy, titanium aluminides based on TiAl, microstructure, scanning/transmission electron microscopy.

2.1 High temperature microscopy of surface oxidation and transformations

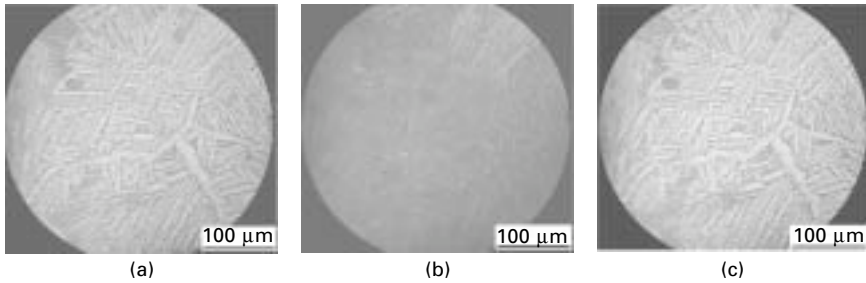
Titanium alloys are desirable and essential for many structural applications at elevated temperatures (Winstone, 2001). It is important, especially for high-temperature applications, to understand the nature of the phase transformations taking place under such conditions. Most of the research on the phase transformations in titanium alloys is performed at room temperature on samples quenched after heat treatment. There have been some studies dedicated to *in situ* experimental studies and modelling of the phase transformations in titanium alloys (Chapters 6 and 7). These studies, however, are concerned with the quantitative study of the kinetics and the thermodynamics of the phase transformations but not with the morphology and geometry of the phases present.

It is possible to study the material's microstructures by applying *in situ* microscopic investigations. Kobayashi *et al.* (2001) studied the phase transformations in Ti-10%Zr alloy during continuous cooling and isothermal holding using hot-stage optical microscopy. High-temperature microscopy was also applied to study the reverse martensite transition in titanium–zirconium alloys.

In this section, we will introduce and describe *in situ* study of the phase transformations and changes on the titanium alloys' surface during high temperature exposure using high-temperature microscopy.

2.1.1 Surface oxidation and deoxidation

Figure 2.1 shows how the surface microstructure of the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy changes during continuous heating at different temperatures.



2.1 Microscopic images taken at different temperatures during continuous heating (25 °C/min) of etched Ti-6Al-2Sn-4Zr-2Mo alloy, showing the appearance of an oxidised surface layer at about 750 °C, which disappears upon further heating to 950 °C. (a) 600 °C; (b) 750 °C; (c) 950 °C.

The sample was etched chemically before the experiment and the microstructure was developed. The initial microstructure was typical for the alloy, containing α lamellae colonies. There is no change in the microscope image when the alloy was heated to 600 °C (Fig. 2.1a). The images at room temperature and at 600 °C are identical for both Ti-6Al-2Sn-4Zr-2Mo-0.08Si and Ti-6Al-4V alloys. With the continuing heating process, a gradual change of the brightness of the samples is observed. This implies that processes of oxidation took place on the samples' surface. The most oxidised surface is observed at about 750 °C (Fig. 2.1b). However, further increase of the temperature leads to disappearance of the surface oxidised layer and the microscopic image returns to the initial image (see Fig. 2.1c). This effect has been observed in many samples and mainly when a standard purity helium (99.996%) atmosphere was used for reducing sample oxidation. The oxidation usually starts at around 650 °C and disappears at around 900 °C. In most of the samples, there are no changes upon cooling.

The process of oxidation takes place because the high-temperature optical microscope stage is not a vacuum device and the helium purity is not sufficient to completely prevent the oxidation. Two possible reasons for the disappearance of the surface oxidation are:

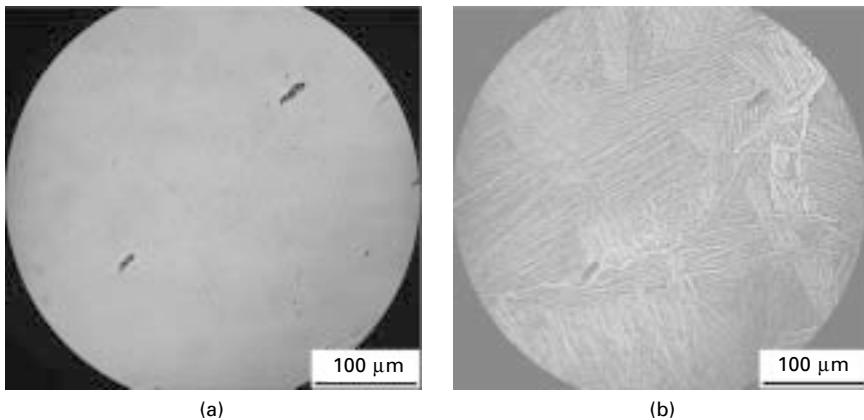
- The increase in temperature leads to an increase of the diffusivity of oxygen. Hence, when the temperature is high (> 850 °C), oxygen from the surface diffuses to the sample core, tending towards homogenisation. This effect would result in a decrease of the oxygen level in the surface layer, if there is not an adequate oxygen supply from the environment.
- The oxides formed on the sample surface in the temperature range of 650–750 °C are Ti_3O and Ti_2O . The ranges of existence of these oxides are not well determined even for the binary Ti-O system. However, it is known that they are not stable at high temperatures. These ordered oxides

are formed and decomposed through second order transitions (α Ti $\leftrightarrow$ Ti₂O and Ti₂O $\leftrightarrow$ Ti₃O). The temperatures for these transitions are not yet well established. For the binary Ti-O alloys, these temperatures are suggested at around 600 °C. For the titanium alloys, the temperature may be increased due to the alloying elements.

2.1.2 Thermal etching

$\alpha \leftrightarrow \beta$ phase transformations were not detected during continuous heating and cooling when etched samples were used, even when oxidation was not apparent. Further experiments were conducted starting with polished but unetched samples. Because the samples were unetched, their microstructure was not observable at room temperature (Fig. 2.2a). However, when these samples were heated to about 680–750 °C, their microstructure gradually became visible (Fig. 2.2b). This effect was observed in all unetched samples. Usually the microstructure was developed at around 680–720 °C when a heating rate of 25 °C/min was applied, and at higher temperatures when faster heating rates were used.

The alloy microstructure was observed due to the effect of thermal etching. The thermal etching is based on the difference in the thermal expansions of the phases present. As a result, the topography of the sample surface is changed and the microstructure becomes visible. A small effect is also possible from concurrent surface evaporation. However, the surface evaporation would result in irreversible changes on the sample topography, whereas in the present case a tendency to reverse flattening of the sample surface upon further heating is observed (see next section).

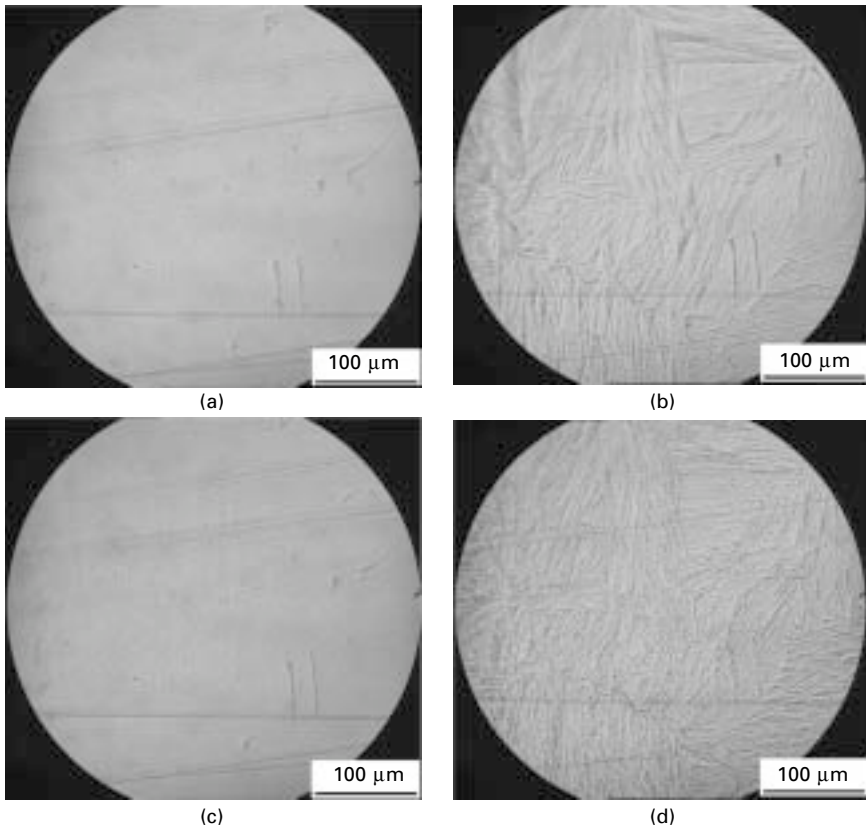


2.2 Microscopic images at (a) room temperature and (b) 680 °C of unetched Ti-6Al-4V alloy, showing the development of the microstructure at high temperatures as a result of thermal etching.

2.1.3 Phase transformations

Figure 2.3 traces one case when in the Ti-6Al-4V alloy the $\alpha \leftrightarrow \beta$ phase transformations were observed and monitored *in situ*. Such observations are experimentally possible when surface oxidation is avoided. The oxidation can be avoided by (i) use of helium with very high purity ($> 99.9999\%$); (ii) protection of the sample surface with heat-resistant glass and (iii) applying higher heating/cooling rates ($60\text{ }^{\circ}\text{C/min}$). Following these experimental conditions, a number of successful cases when the phase transformations were detectable were obtained.

Starting with an initial unetched structure (Fig. 2.3a), when the sample was heated up to $800\text{ }^{\circ}\text{C}$ (Fig. 2.3b), the α lamellae microstructure was detectable due to the thermal etching. Further increases in temperature led to



2.3 Microscopic images taken at different temperatures during continuous heating and cooling ($60\text{ }^{\circ}\text{C/min}$) of an unetched Ti-6Al-4V alloy, showing the change of the sample surface topography as a result of $\alpha \leftrightarrow \beta$ phase transformations. (a) $20\text{ }^{\circ}\text{C}$ (initial structure); (b) $800\text{ }^{\circ}\text{C}$ (during heating); (c) $1100\text{ }^{\circ}\text{C}$ (maximum temperature); (d) $800\text{ }^{\circ}\text{C}$ (during cooling) and $20\text{ }^{\circ}\text{C}$ (final structure).

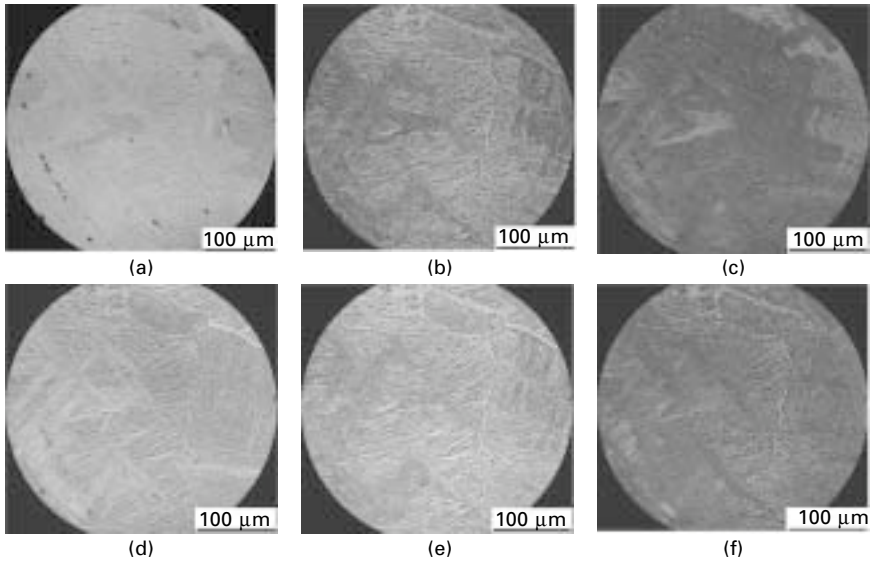
more contrast and clear microstructure. However, when the temperature was increased to above β -transus (about 1000 °C), the topography of the sample gradually became smoother (see Fig. 2.3c). This implies that the α to β phase transformation took place upon continuous heating. The lamella α microstructure transformed to β grains. The sample surface did not return to a completely flat surface but the tendency for flattening was clear when the temperature was increased to above 1000 °C.

The set of microscopic images upon cooling shows the reverse effect of gradual change of the surface back to fine lamellae microstructure (see Fig. 2.3d). This implies that the β to α phase transformation took place upon cooling, with formation of the α -lamellae microstructure. One indirect proof that the change of the topography was a result of the above transformation was that the thickness of the lamellae colonies observed in Fig. 2.3d was the same as the thickness of the α -lamellae microstructure after cooling with the applied cooling rate (60 °C/min). This was checked by polishing and chemical etching of the sample after the experiment. Moreover, the gradual change of the topography from smooth (Fig. 2.3c) to fine lamellae (Fig. 2.3d) took place upon cooling from 1000 to 800 °C. No change of the microscopic image was observed upon further cooling from 800 °C to room temperature, and the images at 800 °C and at room temperature (after cooling) were identical (Fig. 2.3d). This implies that the β to α phase transformation took place and was completed in the temperature range of 1000 to 800 °C. This observation is in agreement with differential scanning calorimetry data (Chapter 7). It should be mentioned that Fig. 2.3 shows only the selected points of the *in situ* observed morphology of the β to α transformation in the Ti-6Al-4V alloy. The transformation was monitored in detail upon continuous cooling for the entire temperature range.

2.1.4 Isothermal experiments

Figure 2.4 illustrates experiments with a Ti-6Al-4V unetched sample performed in isothermal conditions. Starting with the polished sample, when the sample was heated to 700 °C, the microstructure became visible (Fig. 2.4a) due to the above discussed effect of thermal etching. With time, the sample gradually became darker (Fig. 2.4c), then lighter (Fig. 2.4d,e) and then darker again (Fig. 2.4f), implying different stages of oxidation. The change of the sample brightness is caused by two concurrent processes, namely (i) change of the thickness of the surface oxidised layer and (ii) change of the type of the oxide (Ti_6O , Ti_3O , Ti_2O). Further isothermal holding at 700 °C results in the sample surface totally oxidised and the microstructure disappeared.

No change of the topography due to the possible processes of ageing was observed. The ageing processes are too slow (compared to the oxidation) and they cannot cause a change of the topography.



2.4 Microscopic images taken after different periods of time during isothermal exposure of unetched Ti-6Al-4V alloy at 700 °C, tracing the kinetics of the surface oxidation. (a) 0 min; (b) 1 min; (c) 3 min; (d) 15 min; (e) 30 min; (f) 60 min.

2.1.5 Summary

The behaviours of Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys were monitored both in continuous heating and cooling and in isothermal conditions applying *in situ* high-temperature microscopy. The effects of surface oxidation and subsequent deoxidation of the sample surfaces were observed. In conditions of continuous heating the oxidation started at about 650 °C and disappeared at about 900 °C. In isothermal conditions, the oxidation was continuous, until oxidation of the sample surface was complete. The morphology of the α – β phase transformations was observed and monitored *in situ* in continuous heating and cooling conditions. Such observation was possible due to the effect of thermal etching.

2.2 Gamma titanium aluminide

2.2.1 Introduction

TiAl-based alloys with two-phase structures consisting of the major γ and the minor α_2 phases are the most intensively studied intermetallic materials among aluminides and their alloys. There are two reasons for this. Firstly, their low density (about 4 g/cm³), relatively high melting point (>1450 °C), high yield strength (to about 1000 MPa), adequate ductility (to 5% room-

temperature elongation), and reasonably good oxidation resistance are very attractive for structural applications (Yamaguchi *et al.*, 2000). Secondly, TiAl-based alloys can be processed very similarly to traditional metals and alloys through conventional manufacturing processes such as ingot melting, casting, forging, precision casting and machining using almost conventional equipment. In this respect, it is essential that TiAl-based alloys have some ductility even at room temperature and thus are readily castable using standard titanium casting processes.

The variations in microstructure that can be controlled in these alloys are numerous, but they exist in four broad categories: near γ , duplex (DP), near lamellar (NL), and fully lamellar (FL) microstructures. DP and FL microstructures are two typical microstructures and have been subjected to more intensive investigation than the other two types. When γ/α_2 two-phase alloys with nearly stoichiometric or titanium-rich compositions are prepared by usual melting and casting processes, a polycrystalline FL structure is formed. When these two-phase alloys with a lamellar structure are heated or hot-worked at temperatures higher than 1150 °C in the $\alpha + \gamma$ region, the lamellar structure is destroyed and a DP structure consisting of equiaxed grains with the γ single-phase and the lamellar structure is formed. These two types of microstructure exhibit very different mechanical properties. In general, fine and homogeneous DP structures result in good ductility. The FL microstructures are poor in ductility; however, they are generally superior to the DP structures in other mechanical properties such as fracture toughness, fatigue resistance and high-temperature creep strength.

Mechanical properties of the lamellar microstructures in TiAl-based alloys depend on the lamellar orientation with respect to the loading axis and lamellar microstructural variables such as grain size, thickness and spacing of γ and α_2 lamellae. The structure–property relationships indicate the need for keeping a relatively small grain size (<350 μm) and developing the fully lamellar microstructure with controlled lamellar spacing.

The thermomechanical process routes, which provide control of the grain size and lamellar spacing in FL microstructure, can be classified into the following groups:

- (i) thermomechanical processing, which enables one to obtain FL microstructure during hot working;
- (ii) thermomechanical treatment, when a selected alloy chemistry containing boron as a grain-growth inhibitor is heat-treated to form FL microstructure after hot working; and
- (iii) refinement, which enables both the grain size and lamellar spacing to be controlled, with or without grain-growth inhibitors through post-hot working heat treatment.

The general method for controlling both the grain size and lamellar spacing

through refined fully lamellar (RFL) heat treatment is as follows: the alloy should be heat-treated in the single-phase α field range from T_α , or even better from $T_{\alpha+\beta}$ to 1450 °C within the $\alpha + \beta$ phase field. In this latter regime, α grains are formed but are prevented from growing due to the presence of β -phase particles, so the competition of nuclei formation limits the growth of α grains. Higher temperatures in the range generally result in finer grain sizes. The annealing time is typically 10–20 min. The cooling rate is important for controlling the grain size and the lamellar spacing. In order to minimise coarsening of lamellae, once they are formed the cooling rate should be made as fast as possible (Cao *et al.*, 2000; Wang and Xie, 2000; Wen *et al.*, 2000).

Among the results reported on the effect of the heat treatment on microstructure, there is controversy at present. For example, some believe that microstructure can widely be changed solely by heat treatment, and the nature of phase transformation to FL microstructure depends strongly on both cooling rate and composition of the alloy. This contradicts the opinion of other authors that the effect of cooling rate is not that important for microstructure and that the chemistry (complex alloying effects) controls the grain growth mainly (Hu and Botten, 2002; Zhang *et al.*, 2000).

Controversy concentrates on the influence of heat treatment on two main microstructure parameters, grain size and lamellar spacing. The two parameters are usually related to each other, and the earlier experimental results do not separate the two parameters properly (Cao *et al.*, 2000). One school of opinion suggests that refining lamellar spacing is more important than grain size refining to enhance the mechanical properties. Many papers are devoted to studying only the effect of heat treatment (cooling rate, in particular) on lamellar spacing, although some papers indirectly support that the grain size is determined by how the sample is cooled (Yamaguchi *et al.*, 2000).

The authors who studied the effect of heat treatment on grain size gave varying results on the effect of annealing temperatures, holding time (Cao *et al.*, 2000) and cooling rate (Qin *et al.*, 2000; Wen *et al.*, 2000).

The titanium aluminide alloy described extensively in this book, Ti-46Al-1.9Cr-3Nb (all titanium aluminide compositions are quoted in atomic percent, at.%), is representative of a group of TiAl-based alloys.

2.2.2 Effects of heat treatment on microstructure and grain size

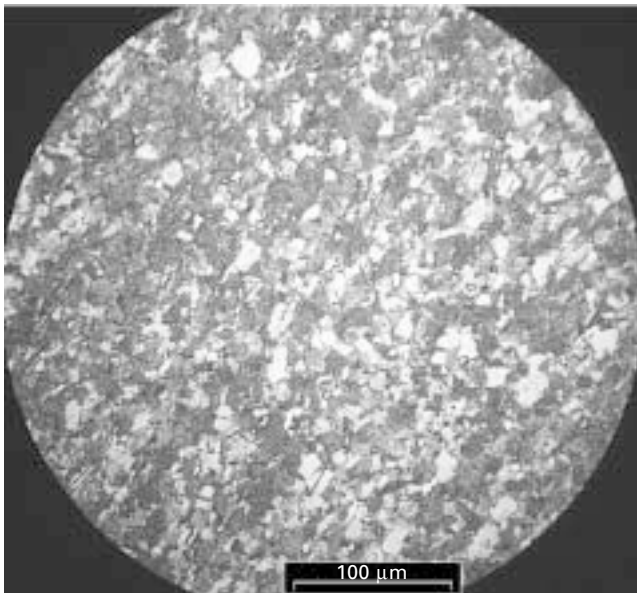
This section will show the heat treatment effect on the grain size of fully lamellar microstructure in Ti-46Al-1.9Cr-3Nb (at.%) at high temperatures (>1400 °C) and clarify the controversy on this subject existing in the literature. Focus is on the current understanding of the phase transformation leading to the fully lamellar microstructure.

The typical microstructures of the alloy in the forged state and after different types of heat treatment are presented in Figs. 2.5–2.8, respectively. The forged alloy was prepared by induction melting and was ingot-cast and forged into plates in a stainless steel can at 1200 °C. The microstructures observed using electron microscopy (SEM) are shown in Figs. 2.9 and 2.10.

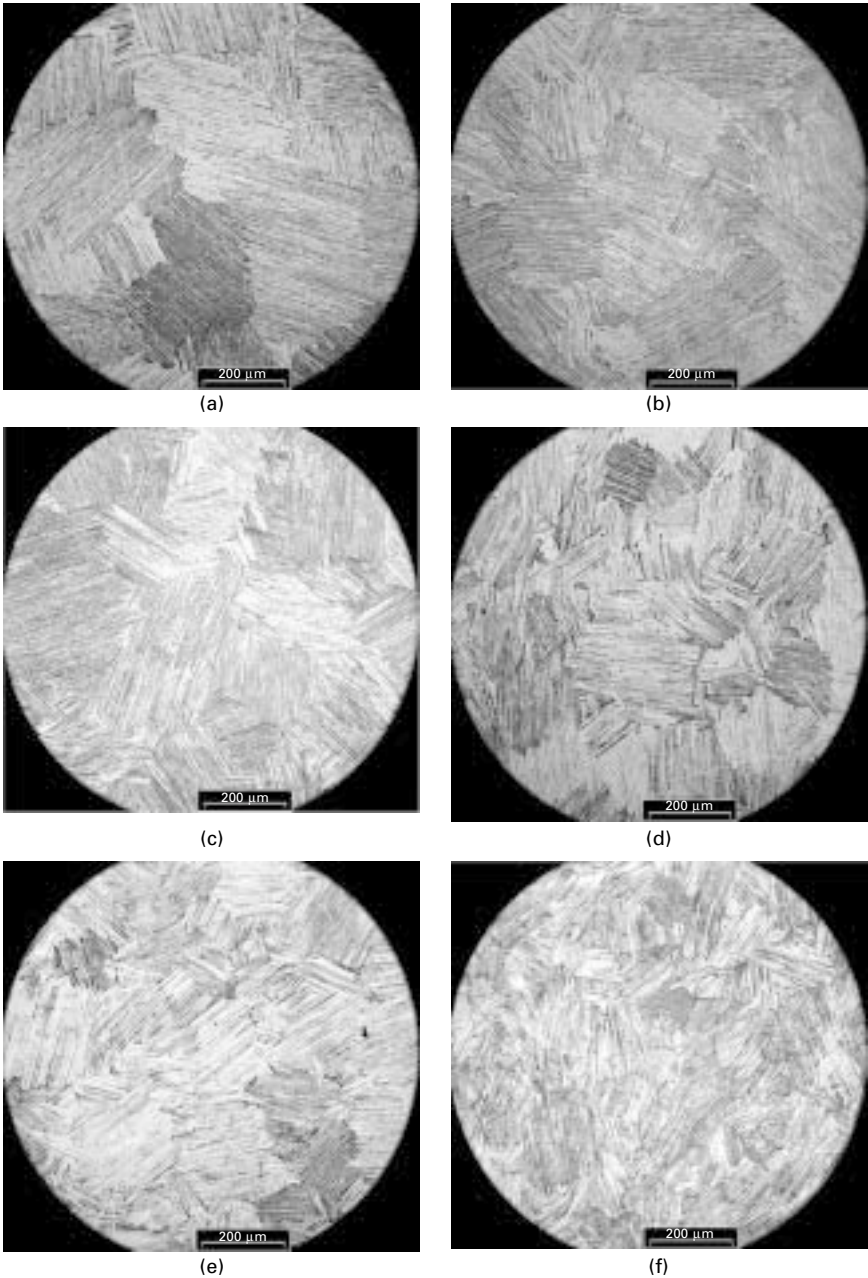
The forged state is typical of the classical duplex microstructure in gamma Ti–Al alloys consisting mainly of fine equiaxed and lamellar γ grains, with a few α_2 plates and particles dispersed in the matrix along grain boundaries mostly (Chen *et al.*, 2001; Guo *et al.*, 2001). The γ grain size varies from 5 to 15 μm (Qin *et al.*, 2000).

For all the three types of heat treatment, we have the fully lamellar microstructure.

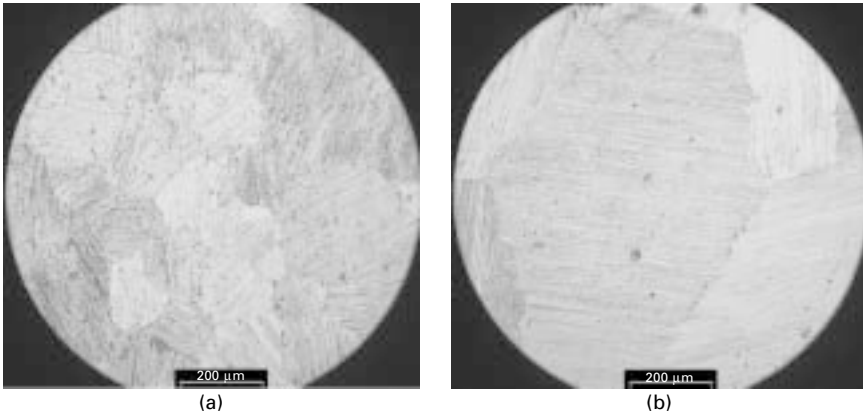
Furnace cooling from the single phase (disordered α phase) or the two-phase region (disordered α and β phases) generally results in a fully lamellar structure where the lamellae are mostly γ intermixed with α_2 lamellae. Slow cooling (with cooling rates of 5–10 °C/min) results in a two-phase lamellar structure consisting of different orientations of lamellae of γ and some α_2 lamellae, as shown in Fig. 2.6a,b. Fast cooling simply refines the lamellar structure (Fig. 2.6e,f), but the grain structure still remains relatively coarse if compared to refined fully lamellar with grain size of 30 μm and under



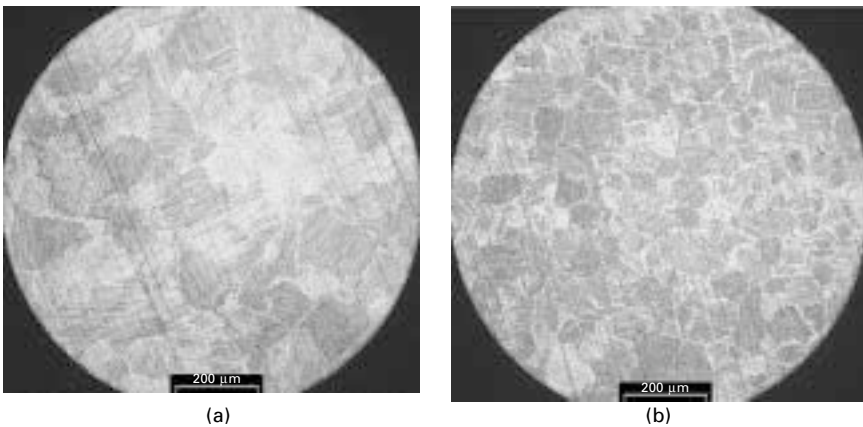
2.5 Optical micrograph showing duplex microstructure of Ti-46Al-1.9Cr-3Nb alloy in forged state.



2.6 Optical micrographs showing fully lamellar microstructure of Ti-46Al-1.9Cr-3Nb alloy after continuous cooling from 1450 °C with different cooling rates. (a) 5 °C/min, (b) 10 °C/min, (c) 20 °C/min, (d) 30 °C/min, (e) 40 °C/min, (f) 50 °C/min.



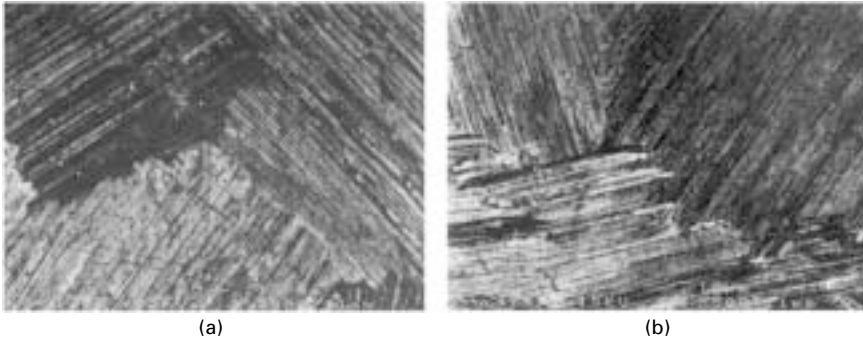
2.7 Optical micrographs showing fully lamellar microstructure of Ti-46Al-1.9Cr-3Nb alloy after holding at 1450 °C for different lengths of time: (a) 10 min, (b) 2 hours, followed by cooling at a rate of 20 °C/min.



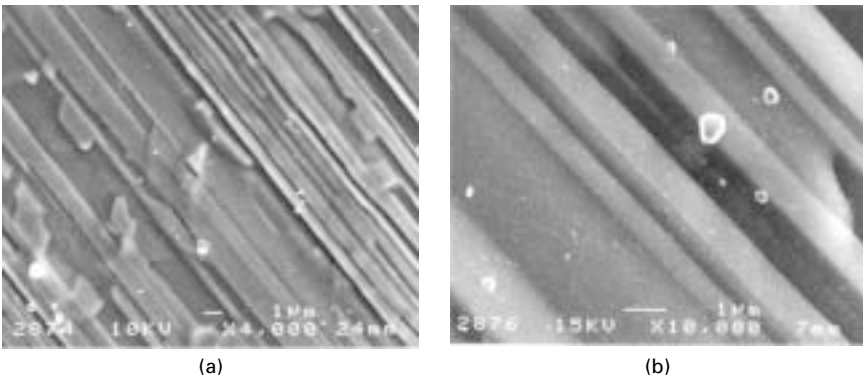
2.8 Optical micrographs showing fully lamellar microstructure of Ti-46Al-1.9Cr-3Nb alloy after furnace cooling from 1450 to 1000 °C followed by: (a) air cooling, (b) water quenching.

(Wang and Xie, 2000). The grain size here is of the order of 100 μm, which is typical for this kind of heat treatment and cooling with this range of rates in this type of alloy. Some authors received only a coarse fully lamellar structure with grain size about 1000–5000 μm (Qin *et al.*, 2000; Wen *et al.*, 2000), or 500–800 μm, which might be attributed to the different temperatures of annealing (about 1350–1380 °C), and different processing procedures, such as extrusion.

For the isothermal heat treatment (Fig. 2.7a), increasing the holding time



2.9 Scanning electron micrographs showing fully lamellar microstructure of Ti-46Al-1.9Cr-3Nb alloy after continuous cooling from 1450 °C with cooling rates of: (a) 5 °C/min, (b) 50 °C/min.



2.10 Scanning electron micrographs showing fully lamellar microstructure of Ti-46Al-1.9Cr-3Nb alloy after continuous cooling from 1450 °C with a cooling rate of 5 °C/min, at different high magnifications.

at 1450 °C results in the coarsening of the fully lamellar microstructure, reaching the grain size values of 200 μm for 2 hours holding time (Fig. 2.7b).

The next type of heat treatment is quite exotic, where we furnace cool with the same rate the samples from 1450 °C ($\alpha + \beta$ field) to the temperature of 1000 °C, which is below the α -transus for this alloy, and then cool with different rates – furnace cooling, air cooling and water quenching (Fig. 2.8). We should not expect a difference in the results for these different cooling rates, because the final lamellar formation temperatures were reported to be around 1250 °C for the similar alloys (Hu, 2001). We do observe, however, for water-quenched samples a grain size of 50 μm (Fig. 2.8b), which is the finest in our experiments.

For the heat treatment of this last type, we did not need to etch the samples after the heat treatment to reveal the microstructure, because the microstructure was visible without etching and polishing. This effect might be associated with the so-called thermal etching effect (Section 2.1). The thermal etching is based on the difference in the thermal expansions of the different phases in the alloy. As a result, the topography of the sample surface is changed and the microstructure becomes visible for the optical microscope. A small effect is possible from some kind of chemical reaction with tantalum foil as the samples were wrapped for this type of treatment at such high temperatures as 1450 °C.

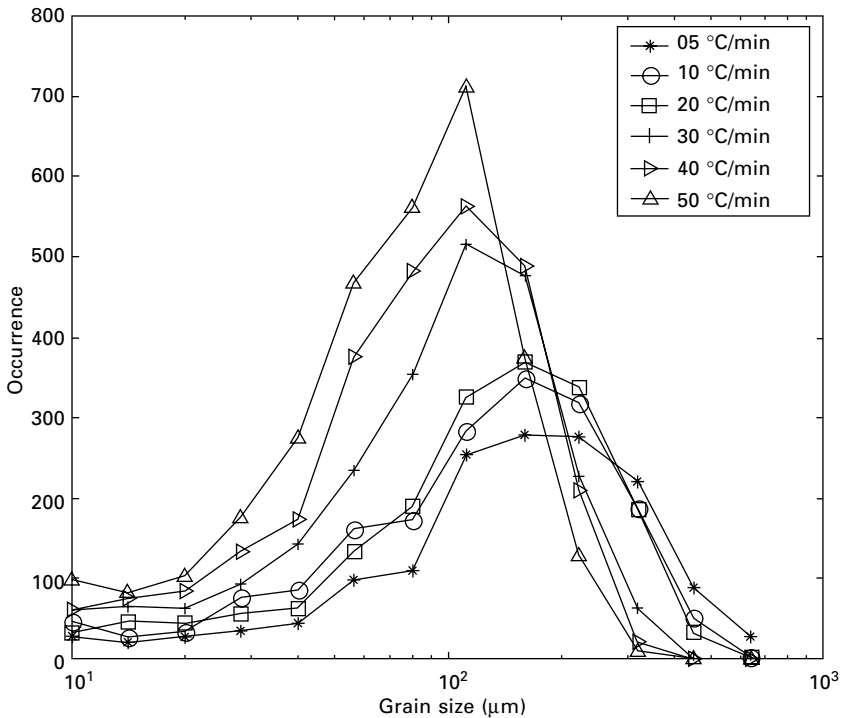
The line-intercept method is used to obtain an average grain size, as summarised in Table 2.1 and Fig. 2.11 after different cooling rates. For statistical purposes, each grain is intercepted a number of times.

Table 2.1 demonstrates that the grain size is large for slowly cooled samples, where the grains just have more time for the growth in the $\alpha + \beta$ field, and fine for fast cooling, where more defects can be produced, because of the increased chemical stress (Wang and Xie, 2000). The grain size is much larger for the samples held at 1450 °C for 2 hours than for the samples held for 10 min. In contrast to expectation, the formation of lamellae continues even below 1000 °C on cooling, resulting in coarsening of grain size with slowing down the cooling rate.

Table 2.1 Grain size distribution in Ti-46Al-1.9Cr-3Nb alloy after various types of heat treatment

Heat treatment	Cooling	Average (μm)	Standard deviation (μm)	l_{50}^* (μm)	Surface to volume ratio (1/mm)
1450 °C/10 min	5 °C/min	186	128	134	21.5
	10 °C/min	152	104	112	26.4
	20 °C/min	145	95	104	27.7
	30 °C/min	113	72	87	35.5
	40 °C/min	100	62	76	40.1
	50 °C/min	88	53	67	45.7
1450 °C/30 min	20 °C/min	133	94	97	30.0
1450 °C/120 min	20 °C/min	203	218	127	19.7
1450 °C/10 min	75 °C/min	68	45	51	58.4
	75 °C/min to 1000 °C,	72	45	52	55.6
	then air cooling				
	75 °C/min to 1000 °C, then water quenching	52	33	41	76.4

*The grain size below or above are 50% of all grains.



2.11 Grain size distribution in Ti-46Al-1.9Cr-3Nb alloy after the heat treatment of furnace cooling from 1450 °C with different cooling rates.

The grain size decreases with increasing cooling rate, although Zhang *et al.* (2000) reported that the grain size does not change dramatically with different cooling rates, for it was very fine (about 40 μm) before heat treatment. The refining of the grain size with rapid cooling is partly supported by Wang and Xie (2000), but the heat treatment suggested by Wang and Xie (2000) involves cycling rapid cooling and fine fully lamellar with a grain size of 10 μm was received.

These contradict the other claims that the grain size is similar for cooling rates from 5 to 50 °C/min, about 2000 μm (Qin *et al.*, 2000) or 500 μm (Wen *et al.*, 2000), and for rates from furnace cooling to water quenching, 370 μm (Cao *et al.*, 2000). These authors prove, however, the dramatic changes in the lamellar spacing with different cooling rates.

The lamellar thickness of 0.2–2 μm is typical of the fine fully lamellar structure (Chen *et al.*, 2001; Yamaguchi *et al.*, 2000). The lamellar thickness does not change dramatically with increasing cooling rate, the average thickness remaining within the range of 0.5–0.8 μm. A change in lamellar thickness after different cooling rates is noticeable however in Cao *et al.* (2000) and

Wen *et al.* (2000). It is generally believed that the key to high strength in fully lamellar TiAl-based alloys lies in refining the lamellar size rather than the grain size. Quenching from the α phase field and further ageing can be applied to refine lamellar thickness to less than 10 nm (Yamaguchi *et al.*, 2000). Transmission electron microscopy (TEM) of the fully lamellar structure is needed to establish fully the relationship between the grain size and the lamellar thickness in these alloys. This will be discussed in the next section.

2.2.3 Summary

Heat treatment of the Ti-Al alloy at 1450 °C followed by cooling leads to the formation of the fully lamellar microstructure which consists of γ lamellae mostly and of a small amount of α_2 lamellae. Air cooling and water quenching lead to a refinement of the grain size of the fully lamellar microstructure compared with furnace cooling. The grain size of the lamellar structure falls into the hundreds of micrometer range and is refined with increasing cooling rate. Increasing the holding time makes the grain structure coarser. The lamellar thickness varies from 0.2 to 2 micrometers.

2.3 Transmission electron microscopy of microstructural evolution

Section 2.2.2 and Chapter 3 describe the effect of different heat treatments on the grain size and α_2 and γ phases distribution, respectively. This section discusses transmission electron microscopy of the microstructure of the Ti-46Al-1.9Cr-3Nb alloy, in particular the lamellar thickness, before and after heat treatment.

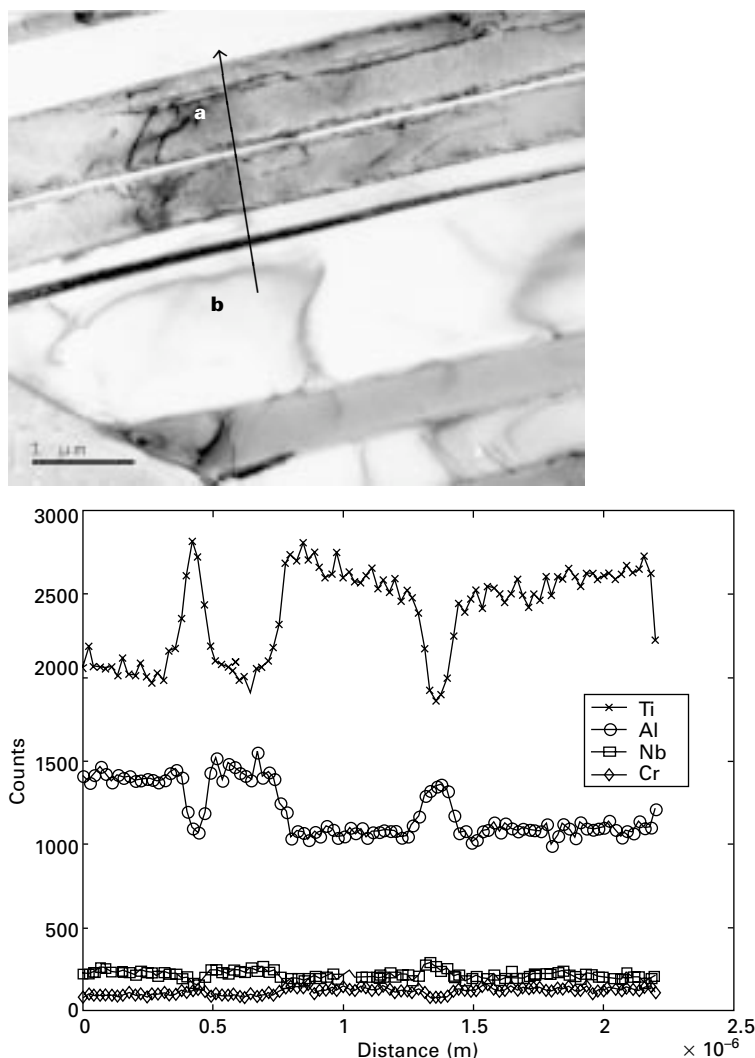
2.3.1 Chemical composition

Table 2.2 summarises and Fig. 2.12 illustrates the composition of α_2 and γ phases in the forged state and in the alloy after heat treatment. Table 2.2 does

Table 2.2 Energy dispersive X-ray mapping of the elemental composition of the α_2 and γ phases before (primary equiaxed structure) and after (lamellar structure) heat treatment

Analysed phase	Al (at.%)	Ti (at.%)	Cr (at.%)	Nb (at.%)
Primary equiaxed α_2	38.7	55.7	2.6	3.0
Primary equiaxed γ	49.1	46.9	1.2	2.9
Lamellar $\alpha_2^{(a)}$	42.1	53.2	2.1	2.6
Lamellar $\gamma^{(b)}$	53.2	42.1	1.4	3.3

^{(a)(b)}The positions in Fig. 2.12 where the analyses were made.



2.12 Transmission electron microscopy bright field micrograph showing α_2 and γ lamellar structure for the Ti-46Al-1.9Cr-3Nb alloy cooled from 1450 °C at 5 °C/min and corresponding energy dispersive X-ray profile of each element. Letters (a) and (b) indicate the positions at which the elemental composition for α_2 and γ phases is shown in Table 2.2.

not present an average composition for the two phases, but the local composition. Place-to-place variations of the composition are quite significant here.

The α_2 phase is supersaturated with aluminium in a lamellar structure in comparison with the forged state, which is fairly close to the equilibrium

concentration of about 37 at.% aluminium for the α_2 phase. The supersaturation of aluminium in the lamellar α_2 phase, as well as a high aluminium concentration in γ lamellae in comparison with the composition in the forged state, is indicative of a slow diffusion process. The heat treatment at 1450 °C before further furnace cooling, which was applied to the present alloy, lies in the $\alpha + \beta$ phase field and does not completely equilibrate the composition. The same correlation, although with slightly different values of the elemental composition, was reported by Chen *et al.* (2001) and Qin *et al.* (2000). Nearly equal values of aluminium content (and titanium balance) for both phases, received by energy-dispersive X-ray (EDX) analysis of rapidly cooled samples of Ti-45Al-2Nb-2Mn alloy (Prasad *et al.*, 2002) might be explained only by the very high cooling rates that were applied.

As opposed to earlier results (Chen *et al.*, 2001; Prasad *et al.*, 2002; Qin *et al.*, 2000) that stated that niobium is almost homogeneous in both phases, the results in Table 2.2 and Fig. 2.12 clearly show that niobium is enriched in the γ lamellar phase, while chromium has the totally opposite tendency. Only in the forged state does niobium not exhibit any preferential partitioning between the two phases.

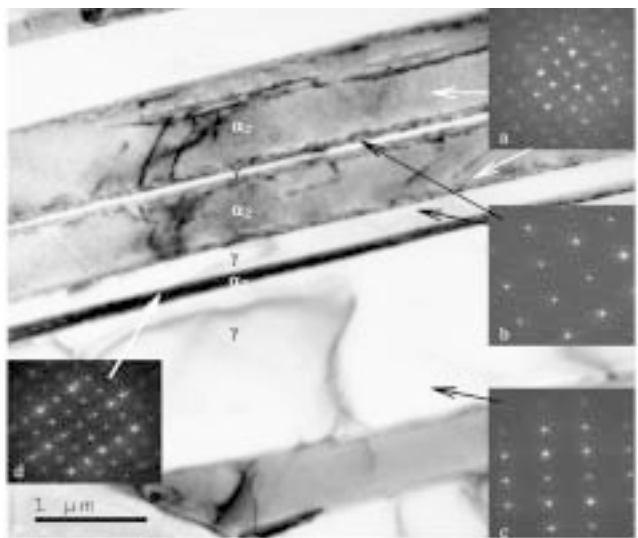
The EDX analysis undoubtedly proves that the dark and the bright lamellae in the TEM bright field image have different chemical composition, corresponding to the composition of the α_2 and γ phases, respectively.

2.3.2 Microstructural analysis

Microdiffraction of the fully lamellar structure of Ti-46Al-1.9Cr-3Nb after the heat treatment is shown in Fig. 2.13, which shows the example of a sample cooled at 5 °C/min. The electron diffraction data prove directly that the dark and the bright lamellae in the TEM bright field image belong to different crystal structures – ordered α_2 (Ti₃Al with the DO₁₉ structure based on an hcp lattice) and γ (near-cubic face-centred tetragonal L1₀ crystal structure), respectively. This is in strict correspondence with studies by Gupta and Wiezorek (2003).

The lamellar phase thickness is defined as the edge-to-edge dimension (measured perpendicular to the phase boundary) of the adjacent lamellae for a given phase. The existence of γ variant is not seen in the TEM micrographs (Figs. 2.12 and 2.13) and therefore each variant is not discriminated. The thickness of the bright regions is measured, whatever the number of variants (invisible), so the measured thickness is equivalent to inter- α_2 thickness or α_2 inter-spacing. The average lamellar thicknesses of the fully lamellar microstructure for each phase after different cooling rates are given in Table 2.3. Figure 2.14 shows log-normal distribution of the thicknesses of γ and α_2 lamellae.

A number of authors have studied the lamellar thickness of fully lamellar



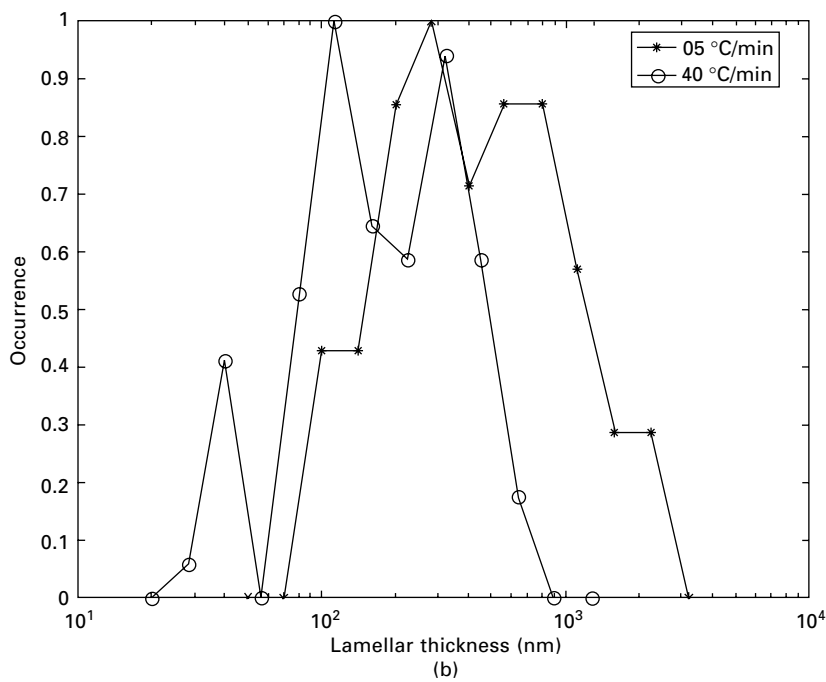
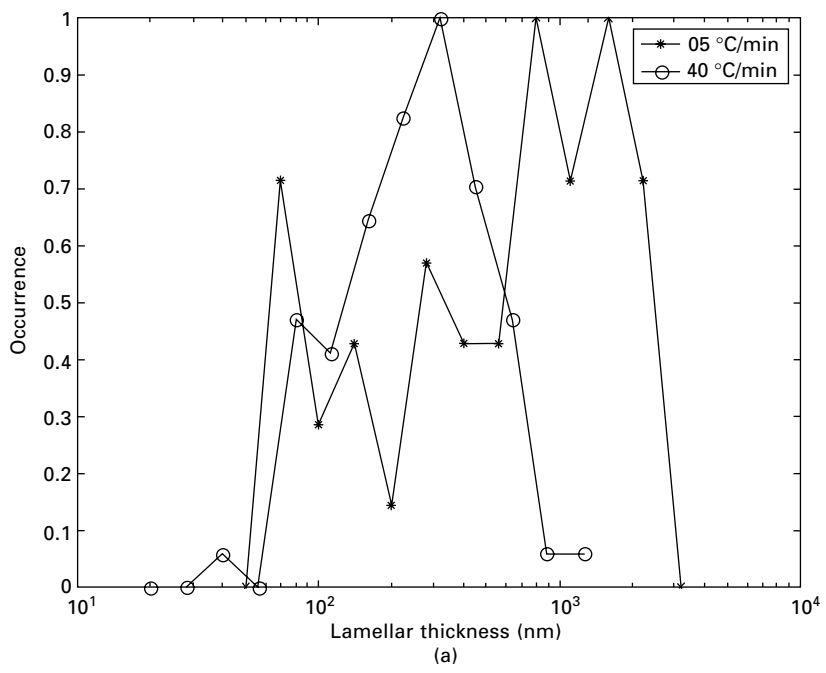
2.13 Transmission electron microscopy bright field micrograph showing α_2 and γ lamellar structure for the Ti-46Al-1.9Cr-3Nb alloy cooled from 1450 °C at 5 °C/min. The insets show selected area diffraction (SAD) patterns corresponding to (a) the [010] axis of α_2 phase, (b) the [111] axis of γ phase, (c) the [110] axis of γ phase and (d) the overlapped pattern with [111] γ and [010] α_2 axes.

Table 2.3 γ and α_2 phases' lamellar thickness distribution in Ti-46Al-1.9Cr-3Nb alloy after furnace cooling with two different cooling rates

Cooling rate (°C/min)	γ		α_2	
	Average (μm)	Standard deviation (μm)	Average (μm)	Standard deviation (μm)
5	0.88	0.73	0.61	0.55
40	0.29	0.19	0.21	0.14

structure regardless of lamellar phases at different conditions, and they have reported the lamellar thickness to be in the range of 0.1–2 μm , depending on heat-treatment, processing and alloy composition (Zhang *et al.*, 2000). Some authors distinguish γ and α_2 phases (Gupta and Wiezorek, 2003). There are data on the dependence of mean lamellar thickness on cooling rate (Beschliesser *et al.*, 2002; Cao *et al.*, 2000; Wen *et al.*, 2000). The lamellar thickness of both α_2 and γ phases is refined with increasing cooling rate.

Figure 2.15 shows typical fully lamellar microstructure, revealing an important aspect of characterising gamma alloys: the lamellae develop in a regular fashion with alternating γ and α_2 laths. This occurrence is common

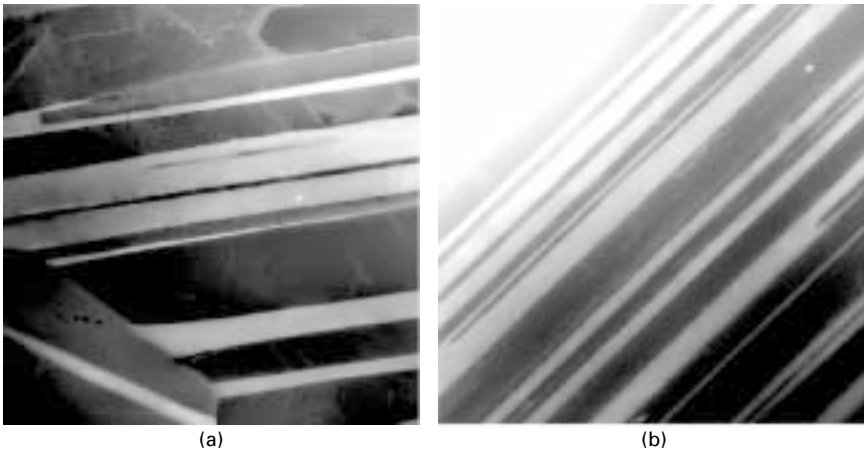


2.14 Lamellar thickness distribution for the Ti-46Al-1.9Cr-3Nb alloy furnace cooled from 1450 °C with 5 and 40 °C/min cooling rates: (a) γ lamellae, (b) α_2 lamellae.

for the quaternary alloy composition and the processing scheme illustrated in this chapter.

Each α_2 lamella (bright in Fig. 2.15) may vary significantly in thickness, or even terminate, which implies considerable interfacial curvature of the α_2/γ boundaries. The curvature and its change are largest around the end of a terminated α_2 . Fine, fragmented or terminated α_2 lamellae are frequently observed along with thicker α_2 and γ lamellae. The frequent presence of terminating γ and α_2 lamellae and of significantly curved interface segments implies that the instability mechanism of termination migration is chiefly responsible for the coarsening of the fully lamellar microstructure. Each event of boundary splitting of a lamella produces two terminations, which then can propagate relatively rapidly by diffusional processes at the curved migrating interface segments and coarsen the fully lamellar structure (Gupta and Wierzok, 2003).

The formation of γ phase within the α_2 lamellae requires a change in the crystal structure as well as a change in concentrations of titanium, aluminium and alloying elements. One of the possible mechanisms of the transformation of the α_2 structure to γ structure is a ledge migration mechanism. The process of continuous coarsening of γ is carried out then by the movement of Shockley partial dislocations. This diffusion controlled migration process is supported by the observation of the ledges along α_2 - γ interfaces (Beschliesser *et al.*, 2002). Although the decomposition process had already started during cooling with relatively slow cooling rates, as applied to the alloy here, long-term exposure should be applied in order to reveal all the details of the process.



2.15 Scanning transmission electron microscopy (STEM) dark field micrograph showing α_2 (bright) and γ (dark) lamellar structure for the Ti-46Al-1.9Cr-3Nb alloy cooled from 1450 °C at (a) 5 °C/min and (b) 20 °C/min.

Transfer of slip either via dislocations or twinning in the γ phase is apparently not always possible since fracture has been observed frequently at α_2 - γ interfaces. It is possible that specific dislocation sources are required at these interfaces in order for slip to take place in the α_2 before fracture intervenes. The relatively coherent boundaries that are characteristic of lamellar structures are not likely to contain a high density of such sources.

2.3.3 Summary

The dark and the bright lamellae in the TEM bright field image belong to the different crystal structures – ordered α_2 (Ti_3Al with the DO_{19} structure based on an hcp lattice) and γ (near-cubic face-centred tetragonal L1_0 crystal structure), respectively. The lamellar thickness of both α_2 and γ phases varies significantly, falling into the hundreds of nanometres range and is refined with increasing cooling rate.

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Abstract: This chapter concentrates on the use of high-resolution synchrotron X-ray diffraction technique for research into phase transformations in titanium alloys and aluminides. Both room and high temperature measurements are described, the former for studying the structure of the alloys after different heat treatments and the latter for *in situ* study of the transformations on the sample surface at elevated temperatures. The phase equilibria of the alloys are calculated and compared with the molar phase fractions of phases derived after the fitting procedure of the diffraction patterns at elevated temperatures.

Key words: X-ray diffraction, phase transformation, heat-treating, synchrotron radiation, crystal structure.

3.1 Introduction

In situ studies of the phase transformations are not common for titanium alloys. Most of the research on the microstructure evolution and the kinetics of the phase transformations is performed at room temperature on samples quenched after heat treatments.

Titanium alloys are appropriate for applications at elevated temperatures. Understanding the processes and transformations taking place on the alloys' surface during high temperature exposure is important for reliable exploitation.

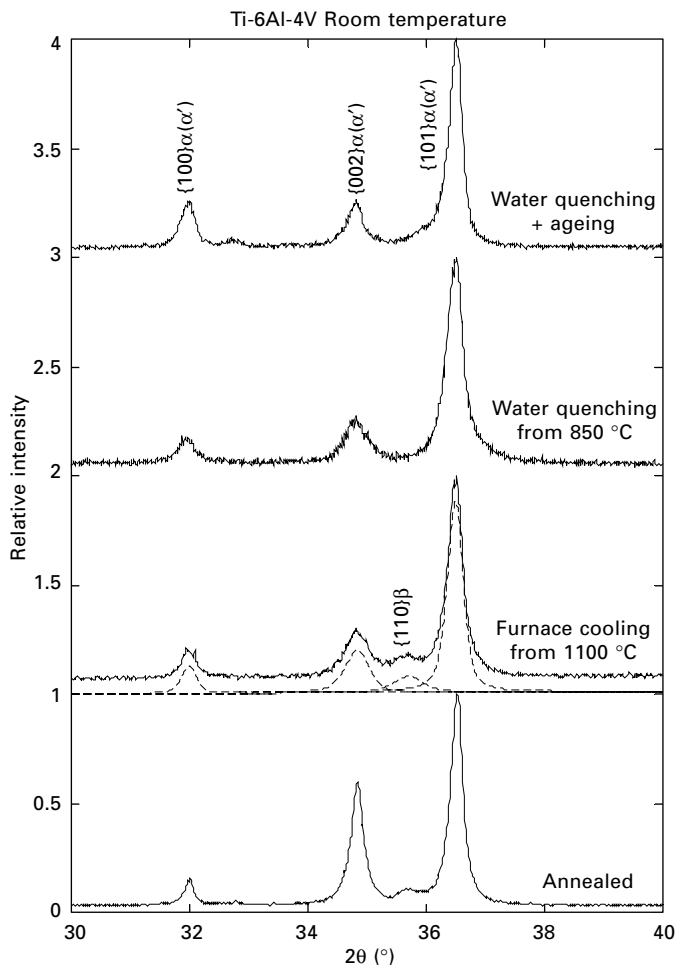
High-resolution X-ray diffraction (HR-XRD) available at a synchrotron radiation source (SRS) is currently a very powerful technique for detailed studies of structure and phase transformations in materials. The main advantages are the inherent high brightness and the tuneable monochromatic beam, which allow the development of a high-resolution powder diffraction instrument. Further developments allow a variety of experiments by users from a diverse scientific community (MacLean *et al.*, 2000). With a relatively small instrumental contribution ($\Delta 2\theta$ of the order of 0.006°), it can be used for diffraction line profile analysis of microstructures. These facilities allow *in situ* studies of materials phenomena occurring at elevated temperatures.

Berberich *et al.* (2000) has reported on the potential use of synchrotron-based methods to study various effects in titanium alloys.

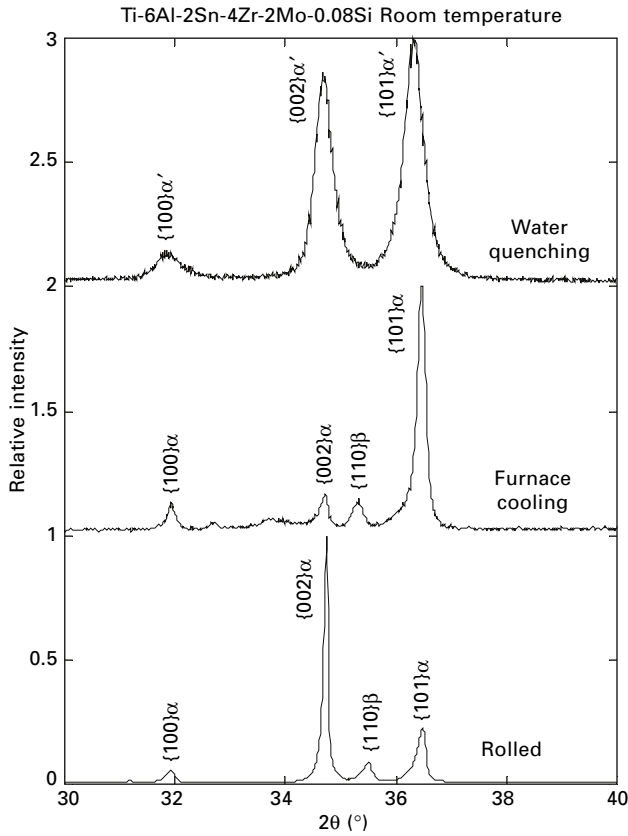
The main aim of this section is to illustrate room- and high-temperature synchrotron radiation HR-XRD measurements to study the phase transformations taking place in the most commonly used titanium alloys. This should lead to an understanding of the processes at the alloys' surfaces during high-temperature exposure.

3.2 Measurements at room temperature

The diffraction patterns obtained from the SR measurements at room temperature for Ti 6-4, Ti 6-2-4-2 and β 21s alloys with different heat treatment conditions are shown in Figs. 3.1, 3.2 and 3.3.



3.1 Diffraction patterns at room temperature and profile fits (dotted lines) in the range of 30–40° 2θ for Ti-6Al-4V under different heat treatment conditions. The intensities are given relative to the {101} α reflection. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

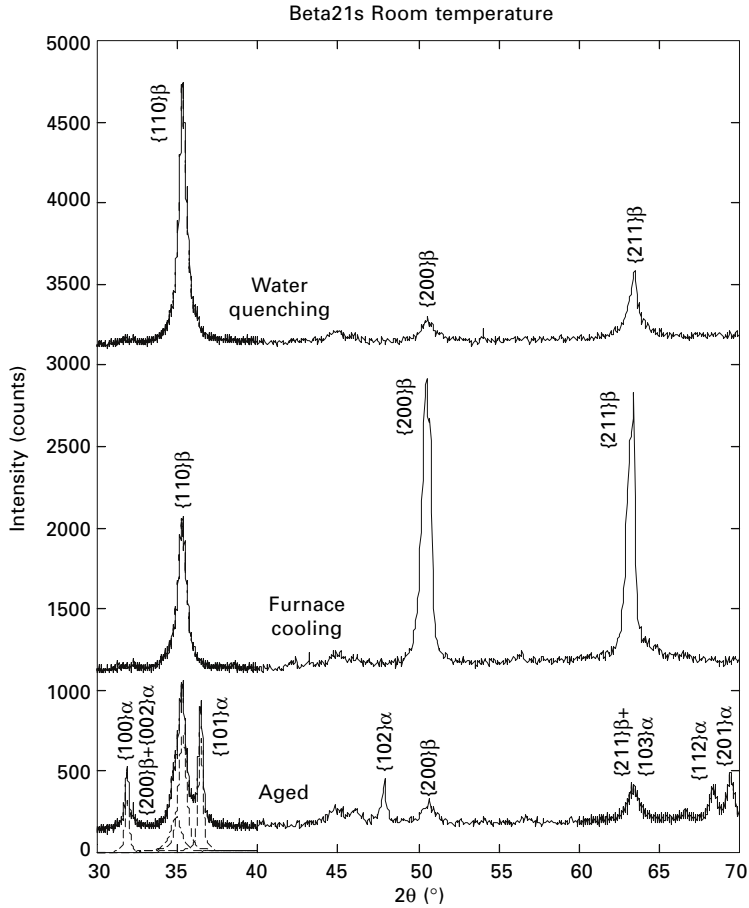


3.2 Diffraction patterns at room temperature in the range of 30–40° 2θ for Ti-6Al-2Sn-4Zr-2Mo-0.08Si under different heat treatment conditions. The intensities are given in relative values. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

3.2.1 Ti-6Al-4V

Ti 6-4 alloy in five different heat treatment conditions is examined:

- (i) annealed (this is the starting state of the alloy, which is rolled with a reduction degree not less than 60% at temperatures in the $\alpha + \beta$ field, followed by recrystallisation annealing at 800 °C for two hours);
- (ii) furnace cooling, with a cooling rate of 0.5 °C/s, after β -homogenisation at 1100 °C;
- (iii) water quenching after β -homogenisation at 1100 °C;
- (iv) water quenching after homogenisation in $\alpha + \beta$ region at 850 °C; and
- (v) water quenching after homogenisation in $\alpha + \beta$ region at 850 °C, followed by ageing at 600 °C for 20 hours.



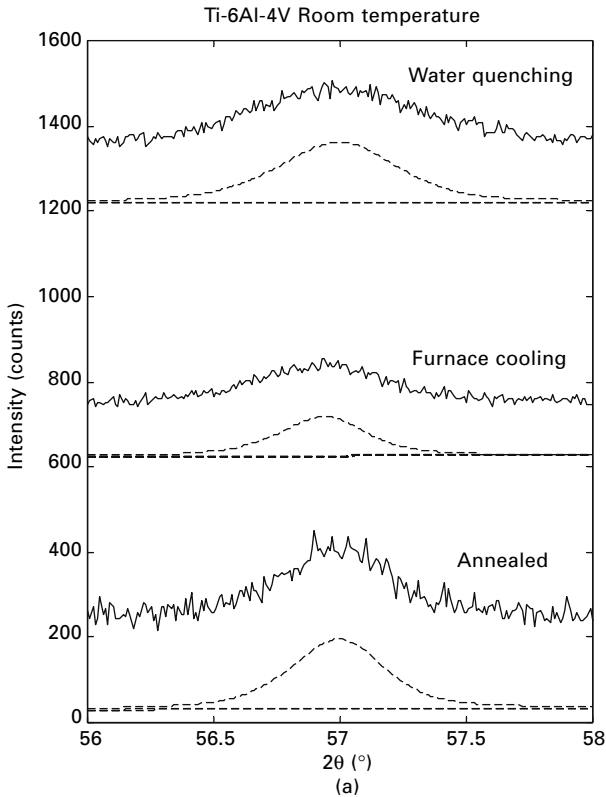
3.3 Diffraction patterns at room temperature and profile fits (dotted lines) in the range of 30–70° 2θ for β 21s under different heat treatment conditions. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

This most commonly used titanium alloy is classified as an $\alpha + \beta$ titanium alloy. The phase composition of the Ti 6-4 alloy after different heat treatments is mainly α phase (see Fig. 3.1), with a small amount of β phase in the annealed condition, 5 wt.%.

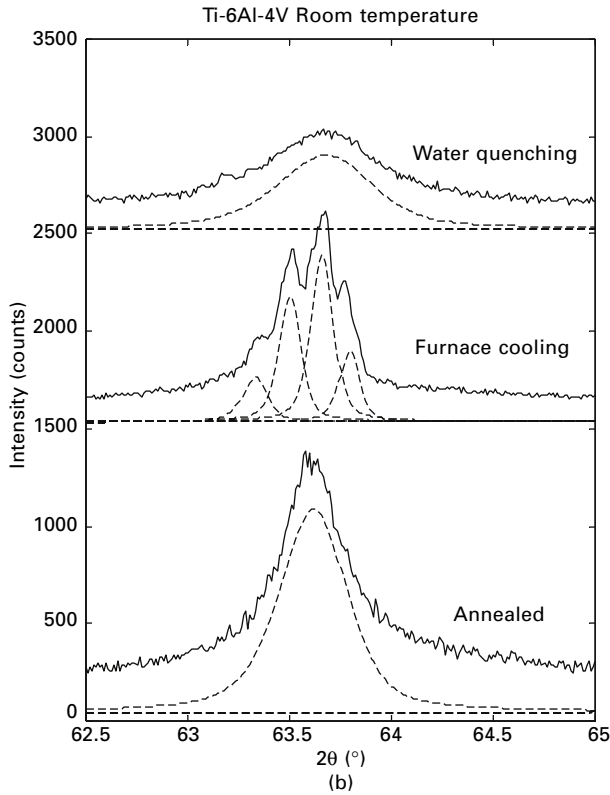
There is also a small amount of retained β phase after furnace cooling from the β -region (see the small peak at 35.6° in 2θ in Fig. 3.1). During slow cooling, the diffusional redistribution of the alloying elements leads to enrichment of the β phase with β stabiliser (vanadium in the case of Ti-6Al-4V). As a result, a small amount of β phase remains stable at room temperature. A similar observation for the alloy studied is shown in Chapter 7 for cooling

from the β -region with different cooling rates. The amount of the β phase after furnace cooling is about 7 wt.%.

An interesting observation is ascertained for the Ti 6-4 alloy regarding the reflections at high 2θ angles. After furnace cooling, the reflection $\{103\}\alpha$ consists of a number of subpeaks (see Fig. 3.4b, 'Furnace cooling'). This fact is also observed for $\{102\}\alpha$ and $\{112\}\alpha$ reflections, but not for hkl reflections having $l = 0$ (see Fig. 3.4a). After slow furnace cooling, α phase with different c and the same a lattice parameters is formed. The a lattice parameter of the α phase after furnace cooling is 0.2938 nm, while the c lattice parameter corresponding to the four subpeaks in Fig. 3.4b is 0.4701, 0.4684, 0.4668 and 0.4655 nm (see Table 3.1). The above observation can be explained by considering the nature of the β to α transformation in titanium alloys. For titanium alloys, the transformation from β to α is of monovariant type. For different temperatures, different amounts of α and β phases are in



3.4 Reflections and profile fits (dotted lines) of (a) $\{110\}\alpha$ and (b) $\{103\}\alpha$ for Ti-6Al-4V under different heat treatment conditions. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.



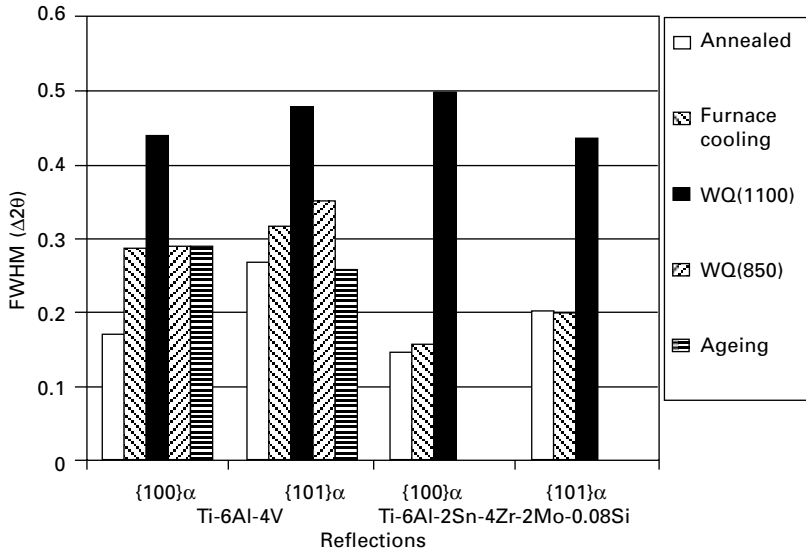
3.4 Cont'd

equilibrium and the α phase can be precipitated at different stages (temperatures) during slow continuous cooling. The α phase precipitated at different temperatures has different morphology – finer lamellae are attributed to lower temperatures of transformation (Chapter 6). This may result in different levels of the residual stresses for α phase precipitated at different temperatures. In addition, the composition in terms of alloying elements of the α phase precipitated at different temperatures is different. The above two reasons are the most plausible explanation for the α phase observed with different c lattice parameters.

After water quenching from both β -region (1100 °C) and $\alpha + \beta$ region (850 °C), the structure of the Ti 6-4 alloy consists only of hcp α phase. No amounts of β phase are present. This structure is a product of diffusional (small fraction in final structure) β to α and diffusionless (large fraction) β to α' transformations upon quenching. The diffusionless transformation occurs at temperatures below 700–750 °C and results in the formation of the martensite structure (α'). The evidence for the presence of martensite in these cases is the much wider α reflections (see Fig. 3.5). The full-width half maximum

Table 3.1 Lattice parameters in nanometers at room temperature for titanium alloys after different heat treatments

Alloy	Phase	Lattice parameter	Annealed	Furnace cooled from β	Water quenched from β	Water quenched from $\alpha + \beta$
Ti-6Al-4V	α	a	0.2935	0.2938	0.2935	0.2939
		c	0.4673	0.4701	0.4668	0.4673
				0.4684		
				0.4668		
				0.4655		
Ti-6Al-2Sn-4Zr-2Mo-0.08Si	β	a	0.3226	0.3228		
	α	a	0.2937	0.2942	0.2949	
		c	0.4687	0.4698	0.4690	
	β	a	0.3254	0.3264		
β 21s	α	a	0.2943			
		c	0.4686			
	β	a	0.3267	0.3272	0.3266	



3.5 Full-width half maximum for α reflections of Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si under different heat treatment conditions.

(FWHM) values of all α reflections are nearly twice those in the furnace cooled and annealed alloy. It is suggested that, for Ti 6–4 alloy, quenching from the 750–900 °C temperature range produces an orthorhombic martensite (α''). This is not confirmed in the diffraction patterns shown here. The diffraction patterns of Ti 6–4 quenched from 1100 and 850 °C are similar, showing the presence of hcp martensite only. Ageing at 600 °C of the alloy quenched from 850 °C leads to small changes in the diffraction pattern (Fig. 3.1, top). A shoulder appears on the left side of the $\{101\}\alpha$ reflection. In addition, a new reflection is observed at 32.75° ($d = 0.2483$ nm). There is a new phase precipitated from the α' phase. It is possible that the orthorhombic martensite (α'') is precipitated upon ageing, but the reflections are weak.

3.2.2 Ti-6Al-2Sn-4Zr-2Mo-0.08Si

Ti 6-2-4-2 in three different heat treatment conditions is examined, namely rolled (this is the starting state of the alloy, which was processed from an ingot at a temperature above the β -transition and then successively α/β rolled) and furnace cooling and water quenching after β -homogenisation at 1100 °C. The phase composition under all three conditions is mainly α phase (see Fig. 3.2). Small amounts of β phase are present in the rolled and furnace cooled alloy, 8 wt.% for both cases. The intensity of the $\{002\}\alpha$ reflection in the rolled alloy is significantly higher than the intensities of $\{100\}\alpha$ and $\{101\}\alpha$ reflections due to the presence of crystallographic texture. No retained

β phase is present after water quenching. The only phase in the alloy after water quenching is the hcp martensite (α') phase (see Figs. 3.2 and 3.5). The phase constitution of Ti 6-2-4-2 after different heat treatments is similar to that of Ti 6-4 under the same heat treatment conditions. The lattice parameters of the α phase in both alloys are similar. The lattice parameters of the β phase for Ti 6-2-4-2 alloy are appreciably larger than those for Ti 6-4 alloy (Table 3.1). This effect most probably is due to the different composition of the β phase at room temperature. In Ti-6Al-4V alloy, the β phase is stabilised at room temperature as a result of its enrichment with vanadium. More than 15 wt.% vanadium (corresponding to Mo-equivalent $[\text{Mo}]_{\text{eq}}$ of 11 wt.%) is necessary to stabilise the β phase at room temperature. In Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy, the β phase is stabilised at room temperature as a result of its enrichment with molybdenum. The β phase for this alloy has more than 20 wt.% molybdenum at room temperature (Chapter 6). Since vanadium has lower atomic radius as compared to titanium it causes a decrease in the lattice parameter of the β phase in the substitutional solution. Molybdenum, conversely, with its larger atomic radius, causes an increase in the lattice parameter.

Considering the schematic pseudo binary phase diagram of titanium alloys, the Ti 6-2-4-2 alloy is to the left-side of the Ti 6-4 alloy. This implies that the amount of the residual β phase in Ti 6-4 should be larger than in Ti 6-2-4-2 alloy. The X-ray data indicate that the amount of the residual β phase in Ti 6-4 alloy is slightly lower when compared to the Ti 6-2-4-2 alloy. The reason for this discrepancy most probably is due to the difference in the oxygen levels in the two alloys. The amount of oxygen in the Ti 6-4 alloy (0.19 wt.%) is significantly higher than in the Ti 6-2-4-2 alloy (0.065 wt.%). Oxygen stabilises the α phase. The β phase is therefore depressed in the Ti 6-4 alloy because of the high oxygen content, and promoted in the Ti 6-2-4-2 alloy because of the low oxygen content.

3.2.3 $\beta 21s$

$\beta 21s$ in three different heat treatment conditions is examined – aged (this is the starting state of the alloy, which was processed through β solution treatment followed by ageing) as well as furnace cooling and water quenching from 900 °C. In the aged alloy, a mixture of $\alpha + \beta$ crystal structures is present (see Fig. 3.3). The amount of the α phase is 58 wt.%. The presence of α phase in the aged condition is a result of the heat treatment, i.e. β solution treatment followed by ageing. This is a typical condition for a commercial $\beta 21s$ alloy because α precipitation provides strengthening.

Both water quenching and furnace cooling from 900 °C produce pure β phase microstructure. α phase is not observed after heat treatment. The martensite transus temperature in this alloy is lowered by the alloying elements

(15.75% [Mo]_{eq}) to temperatures below room temperature. This means that martensite phase (α') cannot exist in this alloy. As a result, retention of the β phase at room temperature is permitted if the β to α phase transformation is suppressed upon cooling. The α phase does not form even after slow furnace cooling at a cooling rate around 0.5 °C/s. Since a certain amount of α phase should be in equilibrium, the reasons for the suspending of the α phase are kinetic.

The lattice parameters of the β phase in the β 21s alloy are larger than those in Ti 6-4 and Ti 6-2-4-2 alloys (see Table 3.1). Again, the reason is in the alloy composition (14.1 wt.% Mo, 3 wt.% Al and 3.48 wt.% Nb). Both molybdenum and niobium have higher atomic radii than titanium, and therefore they increase the lattice parameter when substituting titanium atoms in the bcc β phase.

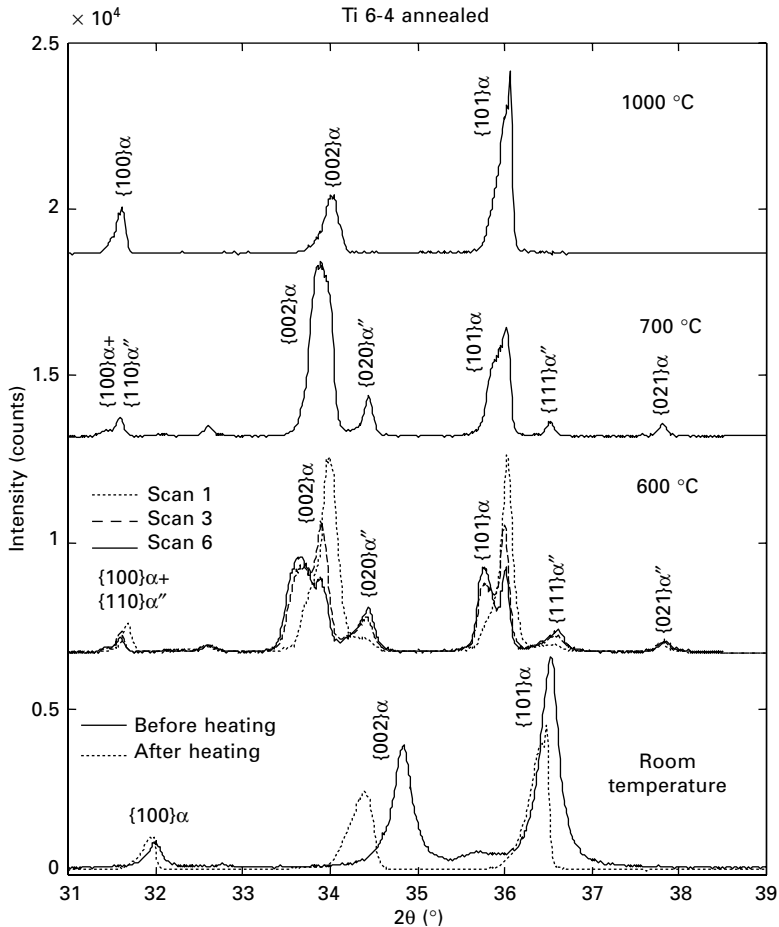
3.3 Measurements at elevated temperatures

Consecutive HR-XRD measurements at different high temperatures with a number of scans at each temperature are needed in order to reveal the kinetics of possible phase transitions, for alloys under different heat treatment conditions. Some of the diffraction patterns obtained from the high temperature measurements of Ti 6-4, Ti 6-2-4-2 and β 21s alloys are shown in Figs. 3.6, 3.7 and 3.8.

The oxygen content of the alloys after high temperature HR-XRD measurements is increased, to 0.6 wt.%, 0.5 wt.% and 0.8 wt.% for Ti 6-4 (annealed), Ti 6-2-4-2 (rolled) and β 21s (furnace cooled), respectively. These values are the average oxygen contents of the bulk samples. The vacuum level (0.3 Pa) of the furnace chamber is not sufficient to completely prevent oxidation.

An increase in the oxygen content raises the β -transus temperature. The phase equilibria of the alloys at the elevated temperatures are calculated for different oxygen contents (see Fig. 3.9), with Thermo-Calc software and using the Ti-database, for oxygen contents in the range from 0 to 1.4 wt.%. The Ti-database is validated for oxygen concentrations up to 0.3 wt.%. Therefore, large errors above this value are possible. Indeed, a very significant influence of the oxygen content on the equilibrium contents of α and β phases is demonstrated. The increased oxygen content enhances and stabilises the α phase in respect to the β phase.

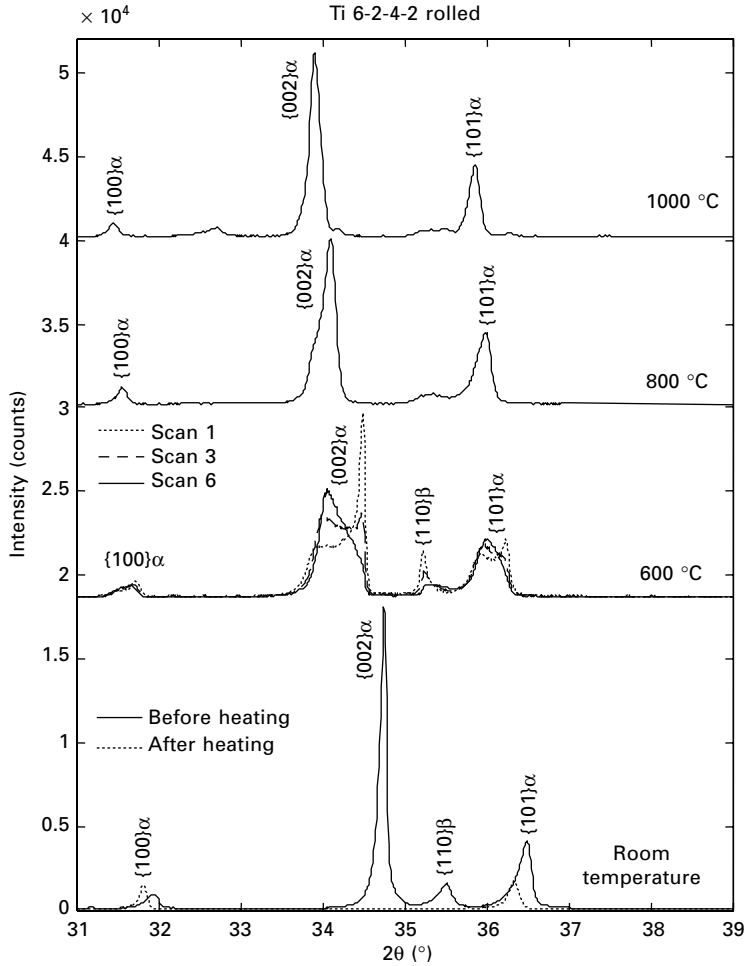
The microstructure analysis of cross-sections of Ti 6-4 and Ti 6-2-4-2 after high-temperature HR-XRD measurements using scanning electron microscopy shows the presence of a surface oxidised layer (see Fig. 3.10). The microstructure of the surface layer consists of coarse α phase lamellae. This is a well-defined layer with an obvious boundary between the layer and the matrix. In addition, some coarse α phase colonies, grown from the surface



3.6 Diffraction patterns at different temperatures for Ti-6Al-4V alloy. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

layer towards the core, are present. The microstructure of the core consists of very fine $\alpha + \beta$ plates colonies. The microhardness of the surface layer for Ti 6-4 alloy is 528 HV1 while the microhardness of the matrix is 382 HV1. The difference in the microhardness of the surface layer and that of the matrix is due mainly to the difference of the microstructure. The difference in the oxygen level may also have an influence on the microhardness difference.

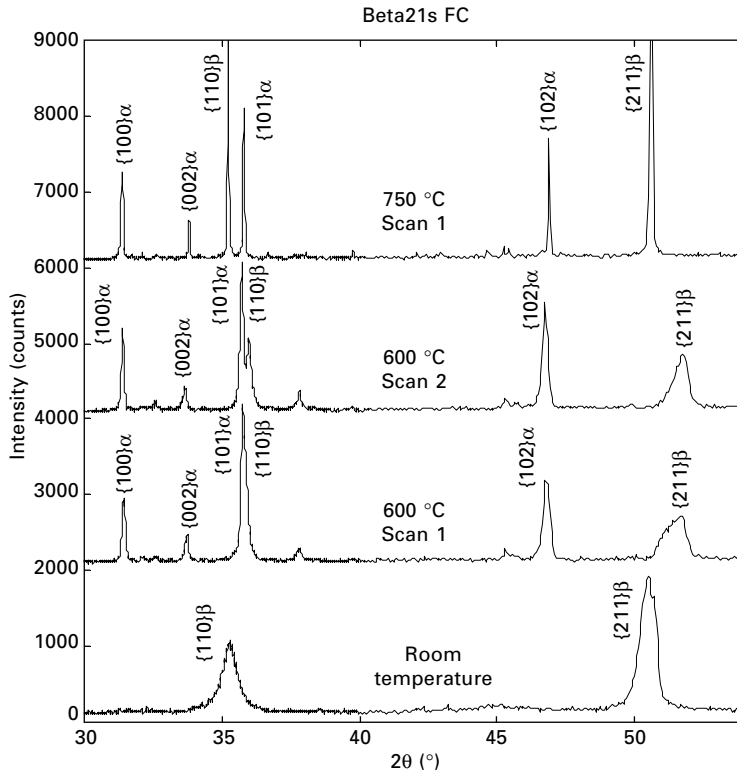
The measurements performed on the cross-sections using scanning electron microscopy with energy dispersive X-ray and wavelength dispersive X-ray with an oxygen detection capability of 0.8 wt.% did not detect any change in the oxygen counts for the surface layer and the matrix. Hence, the difference in the oxygen levels between the surface layer and the core is small.



3.7 Diffraction patterns at different temperatures for Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

The surface layers were formed during the entire cycle of high-temperature measurements. The surface layer shown in Fig. 3.10 has a thickness of 145–160 μm , and is a result of high temperature exposure as follows: 1.5 hours at 600 °C, 1 hour at 700 °C, 0.5 hour at 800 °C, 0.5 hour at 900 °C and 0.5 hour at 1000 °C. Hence, the phase transformations observed at high temperature are in conditions of concurrent oxidation.

The diffraction patterns are obtained from a surface layer the thickness of which is limited by the depth of the X-ray beam penetration. The depth of the X-ray penetration is in the range of 5–6.5 μm for a scan in the range of 30–40° in 2θ and 12 μm at 70° in 2θ . Hence, the diffraction patterns are



3.8 Diffraction patterns at different temperatures for β 21s alloy. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

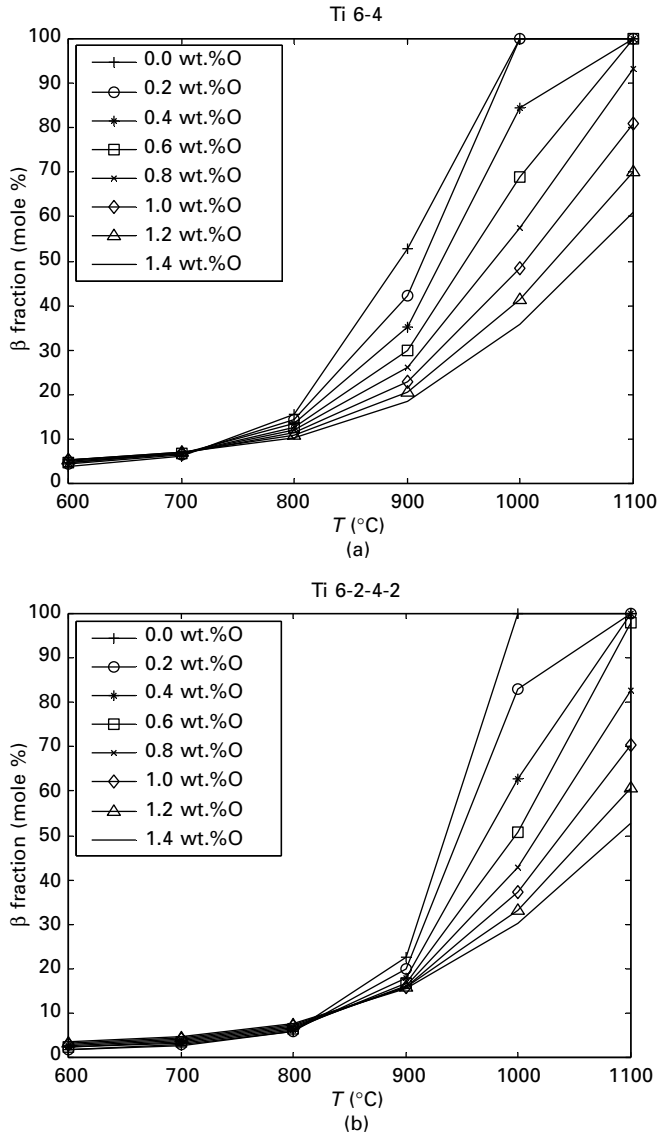
related to the phase transformations taking place within surface layers with these thickness ranges.

3.3.1 Ti-6Al-4V

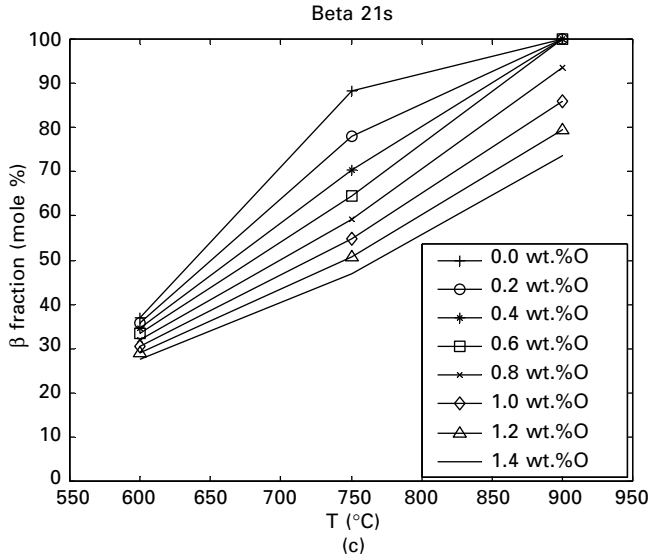
Transformations on the alloy surface during high temperature exposure

High temperature measurements of Ti 6-4 in three different heat treatment conditions give similar results. What follows will therefore concentrate on one condition, the annealed alloy. The microstructure of annealed Ti 6-4 at room temperature, as has been stated, is α phase plus a small amount, 5 wt.%, of β phase. Fig. 3.6 shows some of the data from the high temperature HR-XRD measurements. In all diffraction patterns at high temperatures, the reflections corresponding to hcp α phase are mainly observed. The β phase is not observed at high temperatures. The reason for this, most probably, is the increased oxygen content of the alloy.

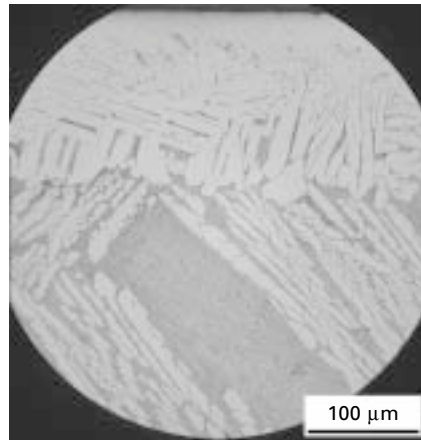
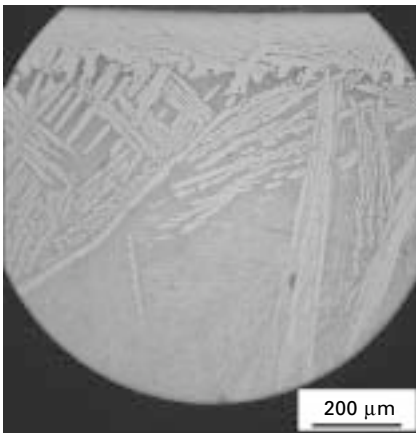
At 600 °C, complicated diffraction patterns are recorded (see Figs. 3.6 and 3.11). All reflections are shifted to lower 2θ angles as compared to the room temperature reflections due to the effect of thermal expansion. The peaks of the hcp α phase consist of two ingredients having two separate sets



3.9 Calculated equilibrium β -phase fractions versus temperature for different oxygen levels for (a) Ti-6Al-4V, (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si and (c) β 21s titanium alloys.



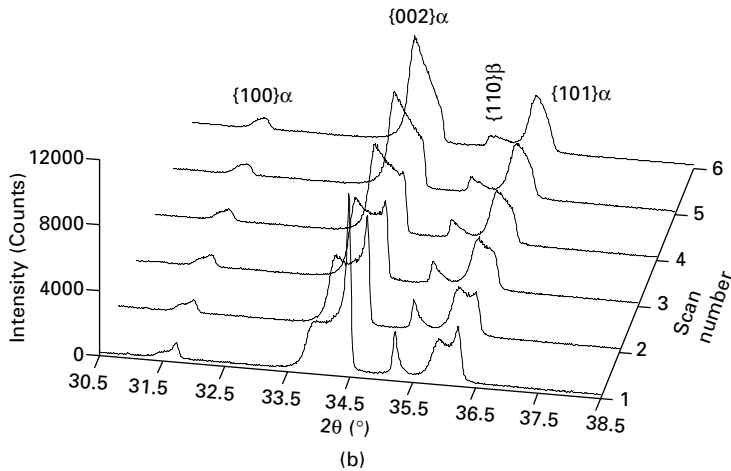
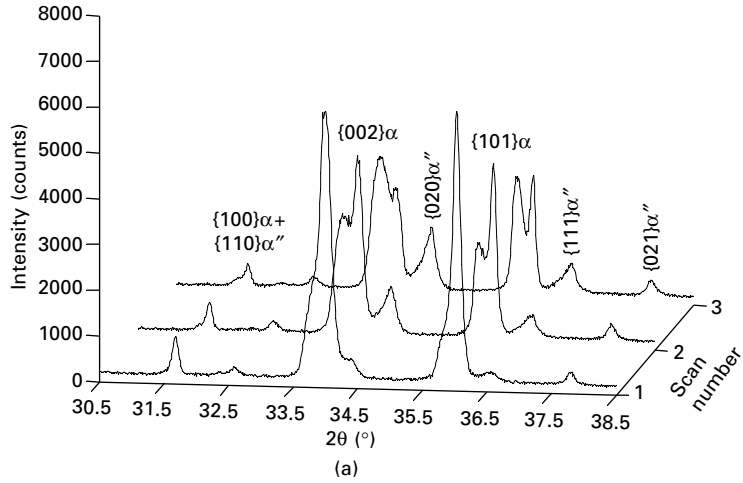
3.9 Continued



3.10 Microstructure of surface oxidised layer after high temperature HR-XRD measurements of Ti-6Al-4V alloy.

of hcp lattice parameters. Some additional small peaks also are present. These peaks are not identified as additional titanium oxides, which are different from the oxidised hcp structure.

The diffraction patterns at 600 °C can be explained with surface oxidation. The ingredients of the hcp reflections, which are shifted to lower 2θ angles, belong to the oxidised surface layer. The ingredients of the hcp reflections,



3.11 X-ray diffraction patterns in the range of $30.5\text{--}38.5^\circ$ 2θ for (a) Ti-6Al-4V and (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si, showing the kinetics of the transformation during isothermal exposure at 600°C .

which are at higher 2θ angles, belong to the unoxidised α phase layer underneath. These results imply the apparent existence of a concentration gap for the oxygen content in the hcp structure on the surface. The results are in agreement with the observed well-defined sharp boundary between the oxidised layer and the matrix. At this stage, the oxidised surface layer (Fig. 3.10) has a thickness less than the depth of the X-ray penetration. The small additional reflections are identified as belonging to orthorhombic α'' phase.

This phase is present at temperatures 600 and 700 °C (see Fig. 3.6). At higher temperatures (800–1000 °C), only the main reflections of the hcp α phase are present indicating that the α'' phase has disappeared.

With increasing time at 600 °C, there is an increase of the integral intensities of the ‘low 2θ angle’ (oxidised) with respect to the ‘high 2θ angle’ (unoxidised) hcp phase (see Figs. 3.6 and 3.11), and a simultaneous increase of the integral intensities of the α'' reflections. This observation can be explained by oxide layer growth with time, and, therefore, the increase in thickness. However, even in the third scan, there are still reflections from the underneath matrix, which means that the thickness of the surface oxidised layer is still less than the depth of X-ray penetration (6 μm). On the other hand, the increasing intensities of the α'' reflections indicate that this phase behaves as a stable phase in the temperature range of 600–700 °C.

When the temperature is increased up to 700 °C, the diffraction pattern shows single reflections of the hcp phase and reflections of the α'' phase (see Fig. 3.6). The peaks belonging to the α phase are not in pairs and are quite broad. The diffraction patterns from the first and the second scans at 700 °C are identical. The oxide layer has grown to a thickness greater than the effective penetration depth of the beam. Furthermore, the diffraction pattern is from an inhomogeneous surface oxidised layer with a continuous concentration gradient of oxygen from the surface into the depth.

A further increase of the temperature up to 800–1000 °C shows the presence of the main reflections of the hcp α phase only (Fig. 3.6). The β phase, as well as reflections of orthorhombic α'' phase, are not present. The peaks are sharp, implying homogeneity. At these stages, the surface oxidised layer is much thicker. There is still an oxygen gradient in the entire oxidised layer, but the diffraction pattern is from the first 6 μm of the layer, where the oxygen concentration can be regarded as constant.

At these temperatures, the α to β phase transformation should take place. In the inner (unoxidised) part of the alloy, this transformation has occurred. The experimental confirmation for this is the observed very fine $\alpha + \beta$ colonies microstructure in the core (see Fig. 3.10). This microstructure is a product of β to $\alpha + \beta$ phase transformation, which has taken place upon fast cooling from the final temperature of measurements (1000 °C) to room temperature. However, the increased oxygen content suppresses the α to β transformation on the surface upon heating. This results in the formation of a coarse α microstructure on the surface during heating and after cooling. Finally, it may also be assumed that, at high temperatures, some processes of homogenisation in respect to the oxygen may take place. As a result, the difference in the oxygen levels of the surface layers and the matrix becomes smaller.

Influence of the temperature and oxygen on the lattice parameters

The diffraction patterns obtained at different temperatures are displaced in respect to each other along the 2θ , due to differences in the lattice parameters. There are two main reasons, which in this case may have an influence on the lattice parameter of the α phase, namely the oxygen content and the thermal expansion. These two factors have concurrent influence, but they can be distinguished. The influence of the oxygen content can be derived from the difference between the diffraction patterns at room temperature before heating (normal oxygen content) and after heating (increased oxygen content). The influence of the temperature (the thermal expansion) can be derived from the difference between the diffraction patterns at the last high-temperature measurement, at 1000 °C, and the room-temperature measurement after cooling. Note that the cooling from 1000 °C after completing the measurement is fast, within a few seconds, accompanied by negligible oxidation.

The diffraction patterns at room temperature before and after high-temperature experiments are not identical. In both cases, the diffraction patterns show the presence of α phase. However, after heating, the reflections of the α phase are shifted to lower 2θ angle due to increased lattice parameter(s) (see Fig. 3.6, bottom). The increase of the lattice parameters of the hcp α phase is due to the increased amount of oxygen. The oxygen is an interstitial element and increases the lattice parameters of the α phase by occupying a fraction of the octahedral interstitial sites. One should note that the shift to lower 2θ angles is significantly larger for the $\{002\}\alpha$ reflection as compared to the peak shifts of the $\{100\}\alpha$ and $\{101\}\alpha$ reflections (see Fig. 3.6, bottom). The lattice parameters of the α phase are $a = 0.2935$ nm and $c = 0.4673$ nm for the annealed alloy before heating (0.19 wt.%/0.55 at.% oxygen) and $a = 0.2935$ nm and $c = 0.4719$ nm after heating. Hence, the enrichment of the α phase with oxygen results in the increase of the c lattice parameter.

The lattice parameters of the α phase at 1000 °C are $a = 0.2965$ nm and $c = 0.4786$ nm. The coefficients of thermal expansion in the temperature range of 20–1000 °C can be derived by comparing these lattice parameters with the lattice parameters at room temperature after cooling. Values of $14.48 \times 10^{-6}/^{\circ}\text{C}$ and $10.43 \times 10^{-6}/^{\circ}\text{C}$ for the c and a parameters, respectively, are the result. The value for c is larger than the value for a . This difference is characteristic of the hcp structure.

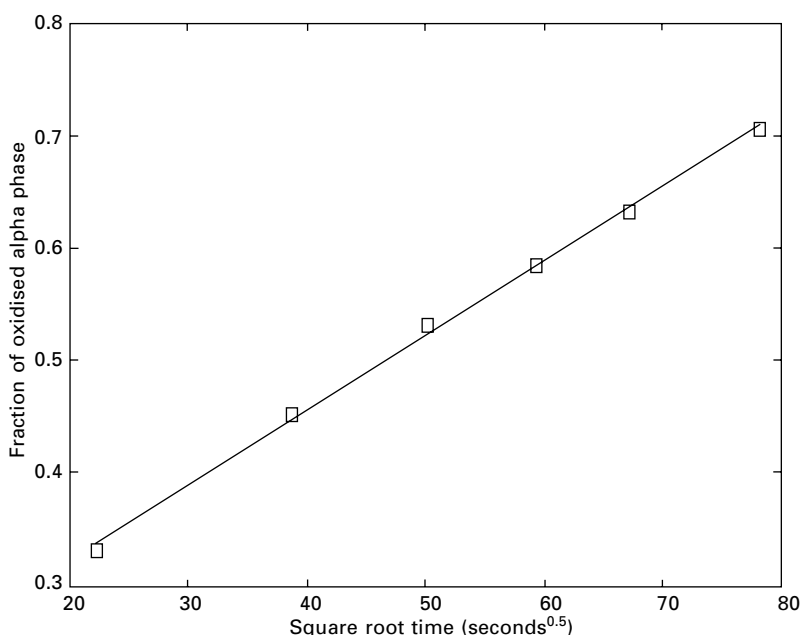
3.3.2 Ti-6Al-2Sn-4Zr-2Mo-0.08Si

Ti 6-4 and Ti 6-2-4-2 alloys have very similar behaviour in respect to the thermodynamics and kinetics of the phase transformations under different conditions (Chapter 6). Diffraction patterns from the Ti 6-2-4-2 alloy are presented in Fig. 3.7.

Transformations on the alloy surface during high temperature exposure

At 600 °C, the peaks of the hcp α phase consist of two components (see Figs. 3.7 and 3.11) similar to Ti 6-4, namely one shifted to lower 2θ angles (belonging to the oxidised surface layer) and one at higher 2θ angles (belonging to the unoxidised underneath material). The effect of peak separation is more obvious for $\{002\}\alpha$ reflection since, as stated above, the oxygen has a much stronger influence on the c lattice parameter. Additional reflections from other phases are not present for this alloy. Some amount of β phase exists.

The increase in time at 600 °C leads to increasing of the intensities of the low 2θ angles component of the hcp reflections in respect to the high 2θ angles component and a decrease in the amount of the β phase (see Figs. 3.7 and 3.11). A number of consecutive scans are shown in order to reveal the kinetics of the oxide layer growth (see Fig. 3.11b). The amounts of the oxidised α phase can be assessed from the ratio of the integrated intensity of the low 2θ angle component (after curve fitting) and the total intensity of the corresponding reflection, for scans after different periods of time at 600 °C. Figure 3.12 shows the fraction of the oxidised α phase versus the square root of the time. The data, plotted in this way, can well be approximated with a straight line which is characteristic of diffusional processes. Since all



3.12 Amount of oxidised α phase versus square root of the time plot, showing the kinetics of surface oxidation of Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy at 600 °C.

consecutive scans are at the same conditions, the increase of the amount of the oxidised phase with time traces the kinetics of growth of the surface oxidised layer.

At higher temperatures (700–1000 °C), single peaks from α phase are present. The reflections are from the oxidised surface α phase. The oxide layer has grown to a thickness greater than the X-ray beam penetration. Very small amounts of β phase still exist. The lower oxygen content in this alloy, as compared to the Ti 6-4 alloy, is the most plausible reason for the presence of small amounts of β phase. The surface oxidised α phase has different lattice parameters at different temperatures due to the thermal expansion.

Influence of the temperature and oxygen on the lattice parameters

The reflections at the room-temperature measurements are shifted, after heating, to lower 2θ angles (see Fig. 3.7, bottom) in a similar way to the Ti 6-4 alloy as a result of increased lattice parameters due to oxidation. The $\{002\}\alpha$ reflection is not shown at room temperature after the high temperature exposure. The lattice parameters after heating are $a = 0.2947$ nm and $c = 0.4727$ nm. The influence of the oxygen content on the lattice parameters can be estimated from a comparison between the lattice parameters before heating ($a = 0.2937$ nm and $c = 0.4687$ nm) and after heating. Again, a much stronger influence of the oxygen on the c lattice parameter is apparent.

The coefficients of thermal expansions in both a and c directions are derived for the temperature intervals 20–600 and 20–1000 °C. The calculations for the temperature interval 20–600 °C are based on the diffraction patterns at room temperature before heating and at 600 °C (unoxidised) ($15.8 \times 10^{-6}/^{\circ}\text{C}$ and $11.5 \times 10^{-6}/^{\circ}\text{C}$ for the c and a parameters, respectively). The calculations for the temperature interval 20–1000 °C are based on the diffraction patterns at room temperature after heating and at 1000 °C ($16.8 \times 10^{-6}/^{\circ}\text{C}$ and $12.1 \times 10^{-6}/^{\circ}\text{C}$ for the c and a parameters, respectively).

3.3.3 $\beta 21s$

$\beta 21s$ alloy after two different heat treatment conditions is examined here. The heat treatment conditions of the alloy are water quenching and furnace cooling after β -homogenisation. The initial states of both are homogeneous β phase (see Fig. 3.3). High temperature HR-XRD of both shows very similar behaviour. In the following, the furnace cooled alloy is discussed.

Consecutive scans reveal the kinetics of possible phase transformations. Diffraction patterns obtained from HR-XRD study of $\beta 21s$ alloy at high temperatures are presented in Fig. 3.8.

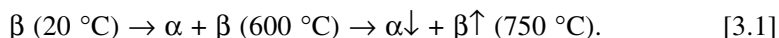
Starting with the initial 100% β phase at room temperature, at 600 °C, hcp α phase appears. The reflections of the β phase are shifted to higher 2θ

angles. The $\{110\}\beta$ and $\{101\}\alpha$ reflections are overlapped at the first scan (see Scan 1 at 600 °C in Fig. 3.8). With the increasing time at 600 °C, there is a further small shift of the β reflections to higher 2θ angles. The $\{110\}\beta$ and $\{101\}\alpha$ reflections are partially separated (see Scan 2 at 600 °C in Fig. 3.8).

The β to $\alpha + \beta$ phase transformation takes place on the sample surface when the alloy is heated from room temperature to 600 °C. Two concurrent reasons for this transformation are suggested: (i) precipitation of the α phase during the high temperature measurements (ageing); (ii) the increased oxygen content on the sample surface, which enhances and stabilises the hcp α phase in respect to the bcc β phase. In spite of the thermal expansion, the reflections of the β phase are shifted to higher 2θ angles. This shows a decreased lattice parameter of the β phase at 600 °C as compared to room temperature. There is some evidence for an increase of the lattice parameters of the α phase during the isothermal exposure at 600 °C. These changes can be associated with the diffusional redistribution of the alloying elements between the α and the β phases during β to $\alpha + \beta$ phase transformation, namely decreasing of the amounts of molybdenum and niobium in the β phase and increasing in the α phase.

Increase of the temperature up to 750 and 900 °C results in (i) increasing the amount of the β phase and decreasing of the α phase and (ii) a significant shift of the reflections of the β phase to lower 2θ angles (see Fig. 3.8 top). The diffraction patterns from the second scans at 750 and 900 °C are identical to the first scans. This shows that no phase transformations take place during isothermal holding and the phase equilibrium has been achieved. All reflections become sharp, implying phase homogenisation.

A reverse transformation α to β takes place when the temperature is raised from 600 to 750 °C, in agreement with what is expected from the phase diagram, where the β phase is the high-temperature phase. The phase transformations taking place on the sample surface during high-temperature HR-XRD can be expressed as:



The diffraction pattern at 900 °C still shows the presence of α phase. The most plausible reason for the presence of the α phase is the increased oxygen content, which increases the β -transus temperature.

The lattice parameters of both α and β phases are affected by the above transformations. However, in this case it is difficult to distinguish between the contributions from the different factors (temperature, oxygen content, alloying elements redistribution).

The experimentally observed and the calculated amounts (Fig. 3.9) of α and β phases at different temperatures are in agreement for the $\beta 21s$ alloy. However, for Ti 6-4 and Ti 6-2-4-2 alloys, the calculated amounts of β phase

are much higher than those experimentally observed. A possible reason for this discrepancy is that the oxygen level of the samples is significantly higher than the usual for titanium alloys due to the oxidation. The calculations of the phase equilibria, based on the Ti-database, are not accurate for such high oxygen contents. In spite of this, the calculation can be used to examine the trend of phase equilibrium with varying oxygen levels.

3.3.4 Summary

Room-temperature HR-XRD experiments using a SRS reveal the structure of Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-0.08Si and β 21s titanium alloys after different heat treatments. The α , α' and β phases are observed in different combinations depending on the heat treatment conditions and the alloy. The results are consistent with what is expected from the theory of the phase transformations in titanium alloys. A multicomponent α phase with different c and the same a lattice parameters exists in Ti-6Al-4V after furnace cooling.

High-temperature HR-XRD experiments are used for an *in situ* study of the transformations in the titanium alloys surface at elevated temperatures, to:

- trace the kinetics of surface oxidation and the concurrent phase transformations taking place at different conditions;
- derive the coefficients of thermal expansion in different crystallographic directions of the hcp α phase; and
- derive the influence of oxygen content on the lattice parameters of the α phase.

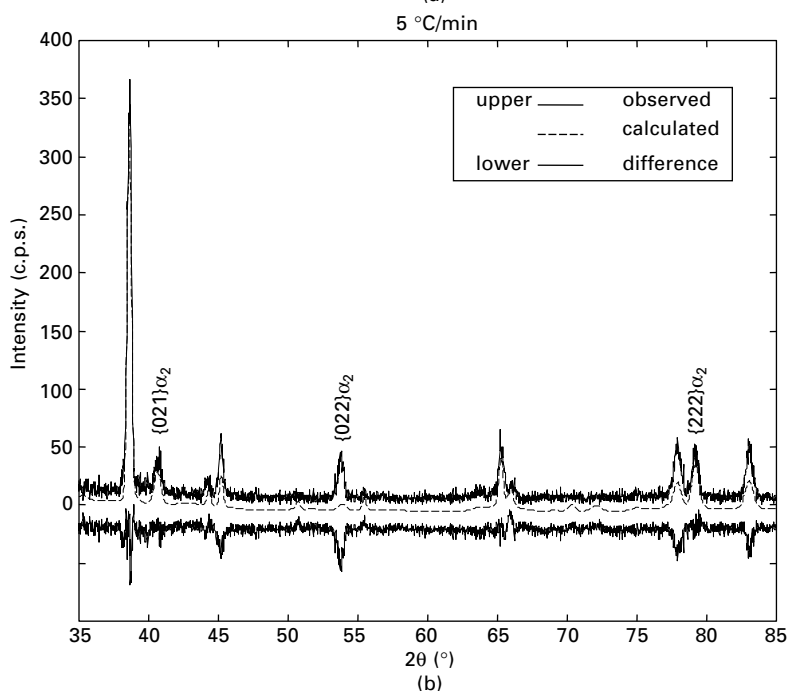
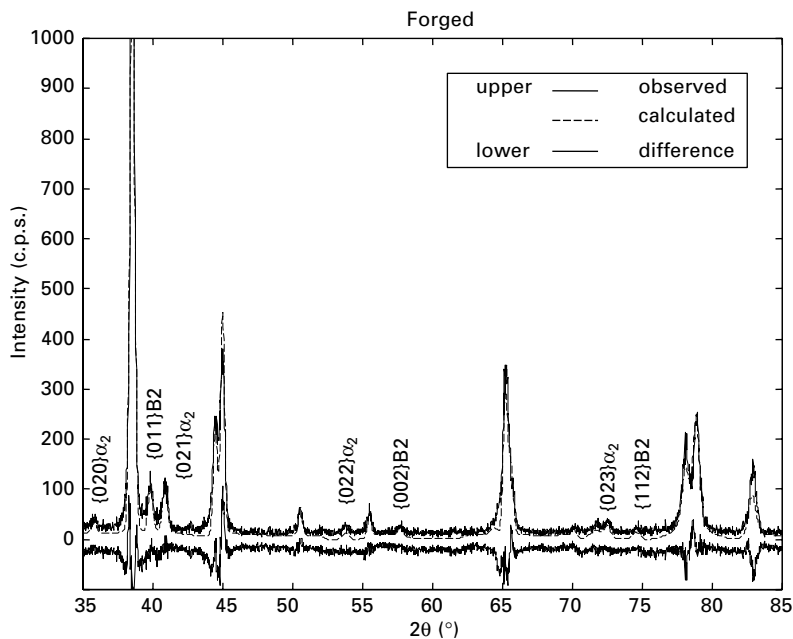
The transformations and processes on the surface of titanium alloys during high temperature exposure have a significant practical importance.

3.4 Gamma titanium aluminide

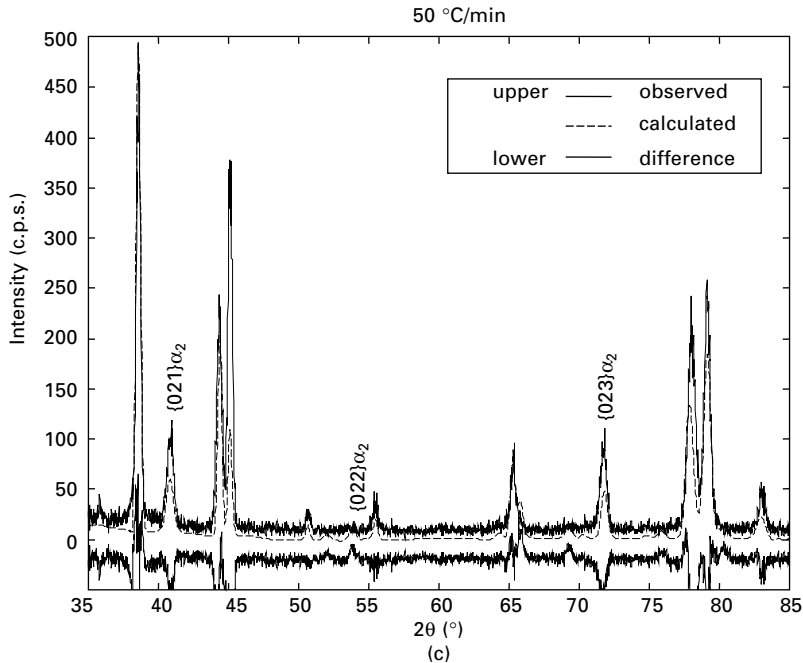
3.4.1 Effects of heat treatment

Quantitative phase analysis identifies the exact set of phases before and after the heat treatment.

The examples of result of fitting procedure for experimental X-ray diffraction patterns are shown in Fig. 3.13. The fitting program calculates the weight and molar fractions for each phase refined, on the assumption that the phases analysed account for 100% of the specimen, via Hill and Howard relation. This relation includes the refined scale factor, the weight of the unit cell in atomic weight units and the volume of the unit cell for a particular phase among all the phases present. In order to reduce error due to possible presence of preferred orientations, the quantitative analysis is based on the entire



3.13 X-ray diffraction patterns, calculated profiles (dotted lines) and the difference curves for (a) forged and (b) and (c) heat treated Ti-46Al-1.9Cr-3Nb alloy with different cooling rates from 1450 °C. The reflections of the B2 and the α_2 phases are indexed. All the other reflections belong to the γ phase.



3.13 Continued

diffraction pattern instead of using single reflections. The principle of averaging the integral intensities is applied.

All the diffraction patterns from the alloy with different cooling rates confirm that the alloy is in the two-phase state: γ phase (about 97 wt.%) and α_2 phase (about 3 wt.%), in agreement with previous literature (Guo *et al.*, 2001; Hao *et al.*, 2000). The amount of α_2 phase varies from 1.5 wt.% to 5 wt.% under different cooling rates. The highest content of α_2 phase corresponds to the fastest cooling rate (50 °C/min) and the lowest corresponds to the slowest rate (5 °C/min), the same as was reported by Qin *et al.* (2000). This proves that the α to γ transformation with lamellar formation is quite sluggish, which makes the subsequent ordering of the remaining α phase, $\alpha + \gamma$ to $\alpha_2 + \gamma$, more favourable at high cooling rates. At very high cooling rates such as those during water quenching, the mechanism of the transformation is different and the α to γ transformation takes place in a massive fashion, in which case there is no retained α_2 phase.

The low volume fraction of the α_2 phase has also been found by Qin *et al.* (2000) and Guo *et al.* (2001). With the addition of chromium, the fraction of the α_2 decreases, and the addition of niobium to the Ti-46Al binary alloy does not change much the volume fraction of the α_2 phase (Hao *et al.*, 2000). The different intensities of the peaks attributed to the α_2 phase are explained

by the presence of the different types of preferred orientations in the different samples. The Rietveld–Toraya model is used in the calculation to take into account the preferred orientation effect.

The alloy in the forged state differs significantly from the others. Its diffraction pattern shows vividly the presence of the third phase, namely the bcc ordered B2 phase, due to the presence of chromium alloying element in the composition. The content of B2 phase is just about 1 wt.%, but it manifests itself by the presence of the strongest {011} reflection. There is no evidence of the B2 phase in heat-treated samples, for above 1200 °C the B2 phase disappears by solid solution in the $\alpha_2 + \gamma$ matrix. The lattice parameter of the B2 phase is 0.3186 nm.

The results of matching of the calculated to experimental intensity profiles are satisfactory. For the forged alloy, for example, such indicators of progress of a refinement as R -factors are $R_p = 16.8\%$ with $R_{\text{expected}} = 13.43\%$. The

pattern R -factor is defined as $R_p = \frac{\sum |y_{oi} - y_{ci}|}{\sum |y_{oi}|}$, where y_{oi} is the observed intensity at the i th step, y_{ci} is the calculated intensity at the i th step, and the sum is over all data points. R_{expected} characterises the observed pattern and includes the total number of data points, the number of parameters adjusted and the number of constraints applied.

The lattice parameters of the structure of γ phase matched are presented in Table 3.2. The heat treatment affected the lattice parameter a and the tetragonality degree. The tetragonality of the γ phase unit cell is smaller in the forged state than in the state after heat treatment.

The difference in the lattice parameters of the forged and heat-treated states might reflect the difference between the chemical compositions of these states. Addition of chromium decreases tetragonality, compared with other alloying elements. In the forged state c/a is much smaller than that in typical manganese-containing alloys.

Table 3.2 Values of the lattice parameter a and tetragonality c/a for γ phase in forged Ti-46Al-1.9Cr-3Nb alloy and the alloy after heat treatment with different cooling rates

Heat treatment	Lattice parameter a (nm)	Tetragonality c/a
Forged	0.4013	1.011
5 °C/min	0.3997	1.019
10 °C/min	0.3982	1.022
20 °C/min	0.3999	1.018
30 °C/min	0.3999	1.017
40 °C/min	0.3998	1.016
50 °C/min	0.4002	1.016

3.4.2 High-temperature study of phases

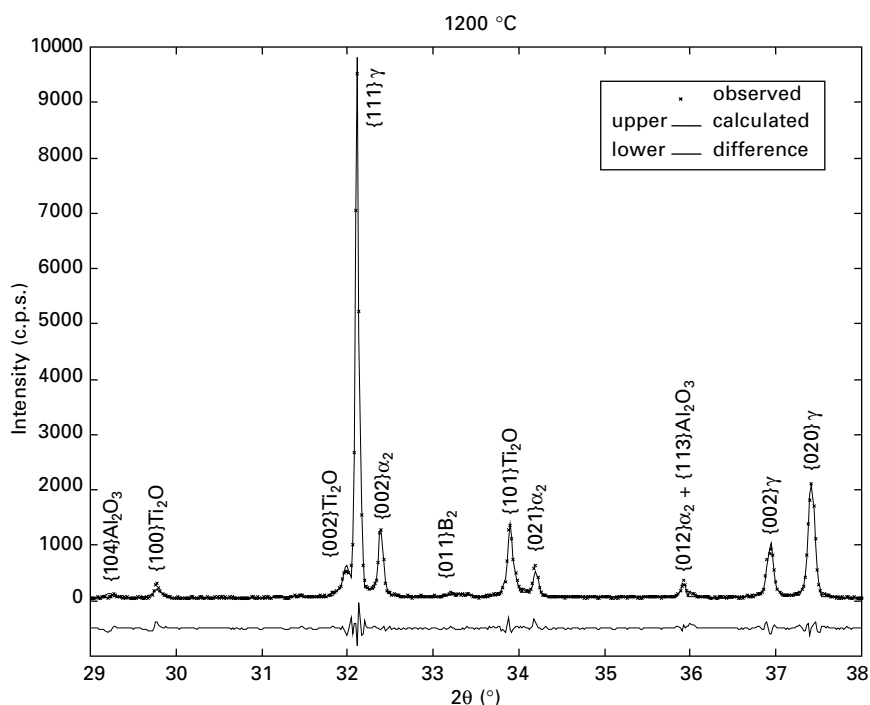
In situ studies of the phase changing are not common for TiAl-based alloys.

This section applies synchrotron radiation high-resolution XRD measurements to show *in situ* the composition of the phases in the Ti-46Al-1.9Cr-3Nb alloy over a wide temperature range, up to 1450 °C, with the objective of understanding the processes at the alloy surface during high-temperature exposure.

Diffraction

Alloy phases

The quantitative phase analysis identifies the exact set of phases in the alloy and deduces the amount of each phase at each temperature. An example of the results after using the fitting procedure for an experimental X-ray diffraction pattern is shown in Fig. 3.14.



3.14 X-ray diffraction pattern, calculated profile and the difference curve for the Ti-46Al-1.9Cr-3Nb alloy at 1200 °C. All the reflections are indexed.

The results of matching the calculated-to-experimental intensity profiles are acceptable. For the pattern in Fig. 3.14, for example, $R_p = 8.47\%$ with $R_{\text{expected}} = 4.93\%$.

The alloy under study transforms in the following sequence upon slow cooling from the liquid: $L \rightarrow \beta + L \rightarrow \beta \rightarrow \beta + \alpha \rightarrow \alpha \rightarrow \alpha + \gamma \rightarrow \alpha_2 + \gamma + B2$. The diffraction patterns in the range of 20–1450 °C indicate that the alloy is in the two-phase (γ and α/α_2 phases) state mostly and has the ordered bcc B2 phase – the third phase – at some temperatures.

Niobium substitutes mainly titanium sites, while chromium substitutes either titanium or aluminium sites depending upon the aluminium content (Ducher *et al.*, 2002), but, in our models below, we use only titanium and aluminium atoms, assuming the equatomic composition.

The structure of α -Ti is disordered A3, which belongs to the space group D_{6h}^4 . We used the setting $P6_3/mmc$ with:

$$A : 2(c) : \frac{1}{3}, \frac{2}{3}, \frac{1}{4}, \quad B : 2(c) : \frac{2}{3}, \frac{1}{3}, \frac{3}{4}. \quad [3.2]$$

The values of the lattice parameters at 1300 °C, as a result of fitting, are $a = 0.58128$ nm; $c = 0.46667$ nm.

The structure of Ti_3Al α_2 phase is ordered DO_{19} , which belongs to the space group D_{6h}^4 . We used the setting $P6_3/mmc$ with:

$$A : 2(c) : \frac{1}{3}, \frac{2}{3}, \frac{1}{4}, \quad B : 6(h) : x, 2x, \frac{1}{4}. \quad [3.3]$$

The values of the lattice parameters at room temperature and atomic coordinates, as a result of fitting, are $a = 0.5764$ nm; $c = 0.4664$ nm; $x = 0.8333$.

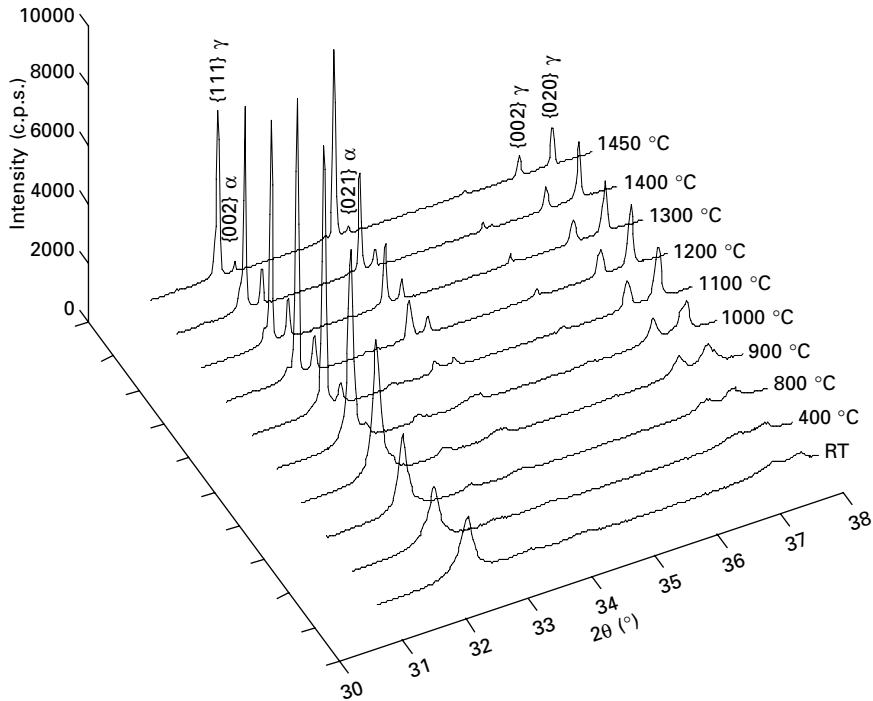
The structure of $TiAl$ γ phase is ordered $L1_0$, which belongs to the space group D_{4h}^1 . We used the setting $P4/mmm$ with:

$$\begin{aligned} A : 1(a) : 1, 0, 0, 0, \quad 1(c) : 2, \frac{1}{2}, \frac{1}{2}, 0, \\ B : 2(e) : 1, 0, \frac{1}{2}, \frac{1}{2}, \quad 2, \frac{1}{2}, 0, \frac{1}{2} \end{aligned} \quad [3.4]$$

The values of the lattice parameters at room temperature, as a result of fitting, are $a = 0.40126$ nm; $c = 0.40591$ nm.

The transformation of the phases above, disordering of the ordered γ and α_2 phases with temperature, results in appearance of α -Ti phase reflections above 1200 °C. This, its further growth and the decreasing of the integral intensities of the γ phase reflections as the temperature increases are clearly seen in Fig. 3.15, which shows the evolution of the phases. The reflections of all the phases become sharp with temperature, to δ -like theoretically, due to phase homogenization and grain growth.

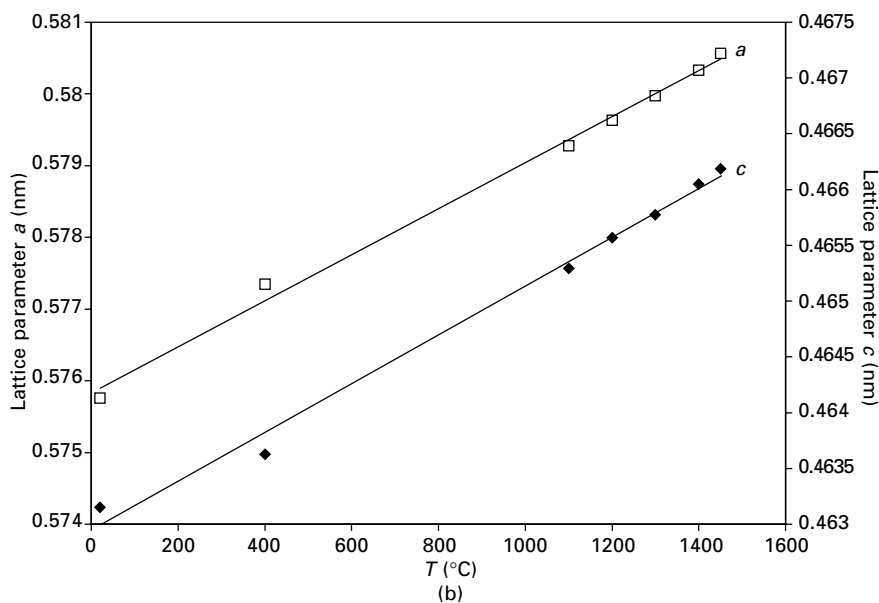
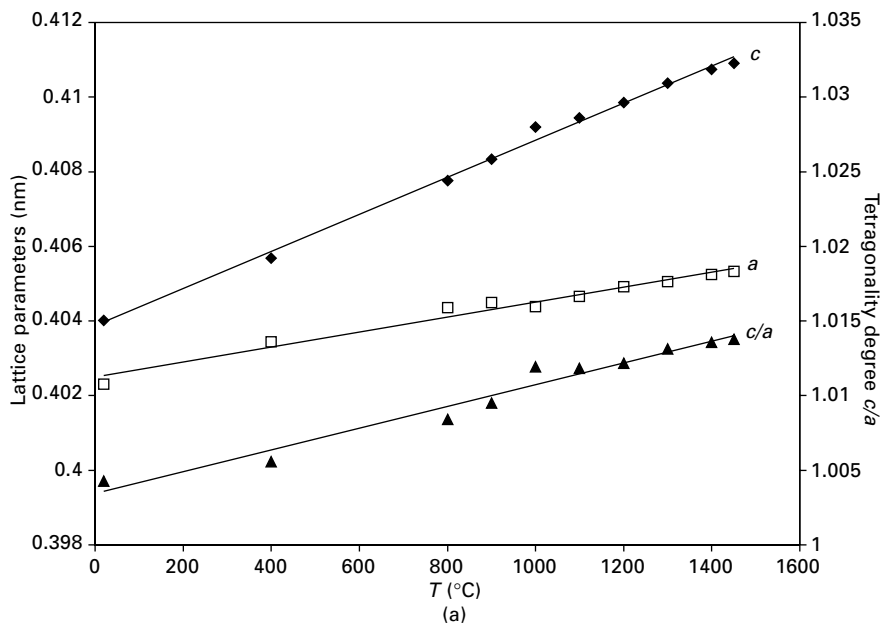
The temperature dependency of the lattice parameters for the γ and α/α_2 phases is presented in Fig. 3.16. The coefficients of thermal expansion (CTE)



3.15 X-ray diffraction patterns for Ti-46Al-1.9Cr-3Nb, showing the evolution of the transformation with temperature. The reflections of the γ and the α phases are indexed. All the other reflections belong to the titanium and aluminium oxides.

in the temperature range of 20–1450 °C can be derived by comparing the lattice parameters at high- and room-temperatures, although the CTE are known to be influenced by the quantity of thermal vacancies, not only by change in lattice parameters. A comparison of the derived values for both γ and α/α_2 phases and some previously published data are shown in Table 3.3. There is a big difference between the CTE along the a and c axes of the γ phase, but there is only a quite slight difference between the CTE along the a and c axes of the α/α_2 phase. Such different behaviour for γ and α/α_2 phases is because adjacent γ and α/α_2 phases have the crystallographic relationship $[1\bar{1}0]\gamma//[11\bar{2}0]\alpha_2$ and $\{111\}\gamma//\{0001\}\alpha_2$.

The published data refer to different alloy compositions, and more importantly, were obtained from a different technique of CTE measurement (Zhang *et al.*, 2001; Zupan and Hemker, 2001). The technique used by Zhang *et al.* (2001) and Zupan and Hemker (2001) is single crystal capacitance dilatometry, which is unable to distinguish the two phases, if present. Only the bulk linear expansion is measured (Zhang *et al.*, 2001; Zupan and Hemker,



3.16 (a) Lattice parameters and tetragonality degree for γ phase, and (b) lattice parameters for α/α_2 phase as functions of temperature of Ti-46Al-1.9Cr-3Nb alloy.

Table 3.3 Thermal coefficients of linear expansion of γ -TiAl alloys

Alloy composition	Phase	Temperature interval (°C)	Reference	Coefficient of thermal expansion, $\times 10^{-6}/^{\circ}\text{C}$	
				a direction	c direction
Ti-46Al-1.9Cr-3Nb	γ	20–450	–	5.1	12.4
Ti-55.5Al	γ	400–1000	Zupan and Hemker (2001)	14.0	13.0
Ti-46Al-1.9Cr-3Nb	α/α_2	20–1450	–	5.7	4.8
Ti-47Al-4(Nb,W,B)	Mean	20–1000	Zhang <i>et al.</i> (2001)	9.7	9.7

2001). For multiphase alloys, the CTE is a complicated function of the thermal and elastic properties of the individual components, as well as the electronic structure, so the difference between our data and the published ones (Table 3.3) is the result of the different composition of the alloys under comparison. The lower thermal expansion, as in the case of the alloy used here, offers a potential advantage in lower thermal stresses and increasing thermal shock and fatigue resistance. The CTE for this alloy is obtained independently for both γ and α/α_2 phases in both [100] and [001] directions.

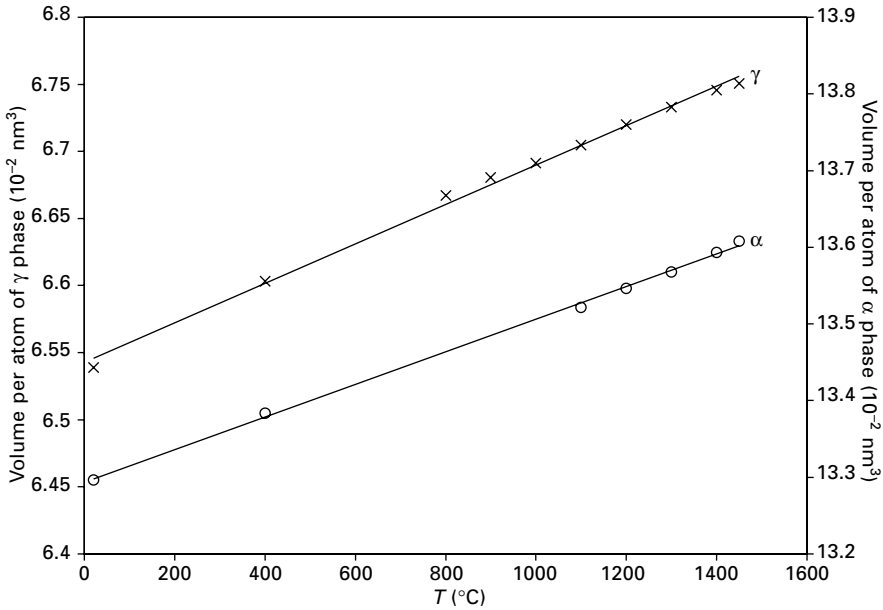
The temperature dependency of atomic volume for both γ and α/α_2 phases is given in Fig. 3.17. The relative change in the volume per atom for γ phase during ordering, i.e. between 1100 and 1300 °C, is 0.4%, and for α/α_2 phase 0.3%. The volume change of the same order is typical for the martensitic transformation of austenite, or B2 to R type in NiTi (Daróczy *et al.*, 2000).

The diffraction patterns in the range of 800–1100 °C show the presence of B2 phase. The content of B2 phase is about 1 wt.%. Figure 3.18 illustrates the evolution of the phase with temperature. Above 1200 °C, the B2 phase disappears by solid solution in the more close-packed $\alpha + \gamma$ matrix. B2 phase is a grain growth restricting agent, and thus, as soon as the B2 phase disappears, large α phase colonies having uniform orientation of the lamellae upon cooling form, resulting in a remarkable increase of the scale of microstructure.

An ordered B2 structure belongs to the space group O_h^1 . We used the setting Pm3m with:

$$A : 1(a) : 0, 0, 0, \quad B : 1(a) : \frac{1}{2}, \frac{1}{2}, \frac{1}{2}. \quad [3.5]$$

The value of the lattice parameter at elevated temperatures is 0.31893 nm, which correlates well with Zhang *et al.* (2000).



3.17 Volume per atom for γ and α/α_2 phases as a function of temperature of Ti-46Al-1.9Cr-3Nb alloy.

Oxide phases

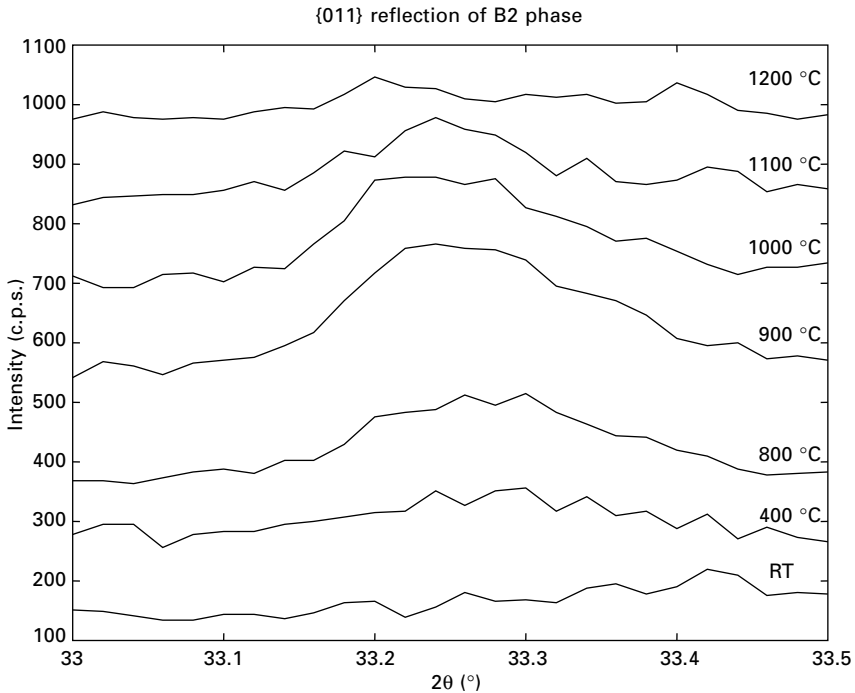
At high temperatures, starting from 1100 °C, the reflections of Ti_2O phase are present in the diffraction patterns, and of Al_2O_3 starting from 1200 °C. The vacuum level (15 mPa) of the furnace chamber was not sufficient to completely prevent oxidation. The titanium aluminides are characterized by a strong tendency to form TiO_2 (Tang *et al.*, 2002) and protective Al_2O_3 scales at 1200 °C (Palm *et al.*, 2002; Tang *et al.*, 2002). Some authors report the presence of TiO oxide in γ -TiAl-based alloys (Li X Y *et al.*, 2003; Li Z *et al.*, 2003).

The structure of α - Al_2O_3 belongs to the space group D_{3d}^6 . We used the setting $R\bar{3}cH$ with:

$$A : 12(c) : 0, 0, z, \quad B : 18(e) : x, 0, \frac{1}{4}. \quad [3.6]$$

The values of the lattice parameters at elevated temperatures and atomic coordinates, as a result of fitting, are $a = 0.47949$ nm; $c = 1.30995$ nm; $x = 0.8333$; $z = 0.35274$.

Both TiO and TiO_2 models are inadequate when applied to the diffraction patterns. The only structure that shows good R -factors during fitting procedure is the structure of Ti_2O oxide.



3.18 X-ray diffraction patterns, showing the evolution of {011} reflection of B2 phase with temperature for Ti-46Al-1.9Cr-3Nb alloy. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

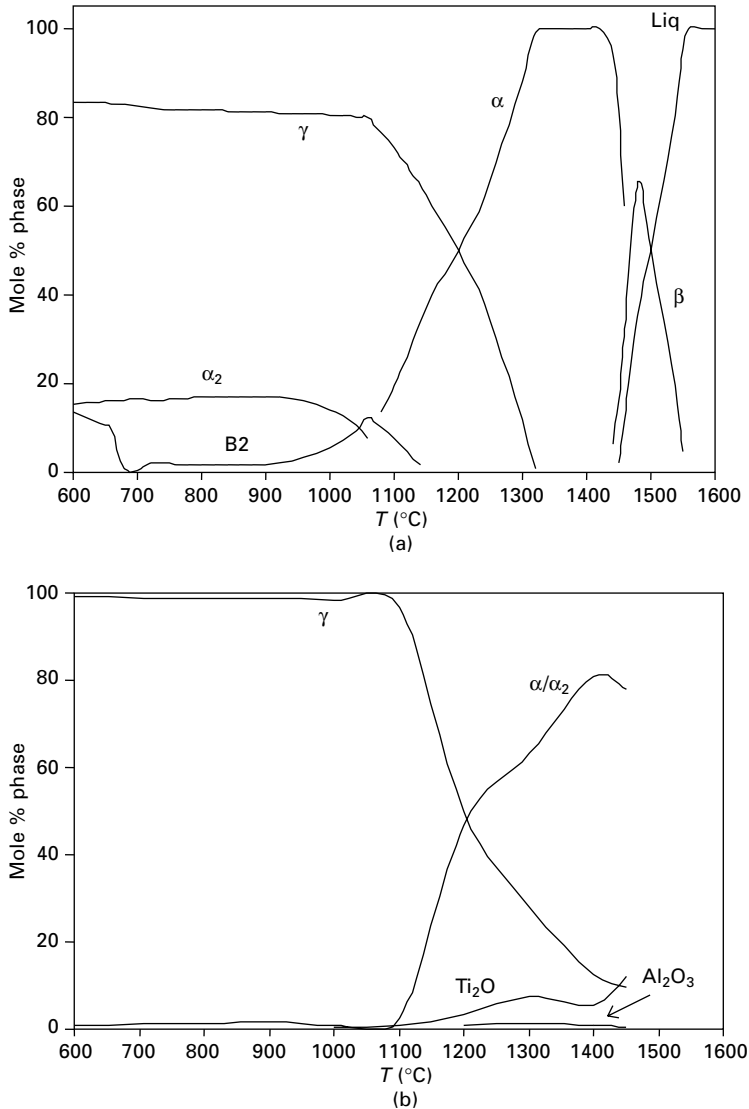
The structure of Ti_2O belongs to the space group D_{3d}^3 . We used the setting $P\bar{3}1m$ with:

$$A : 1(a) : 0, 0, 0, \quad B : 2(d) : \frac{2}{3}, \frac{1}{3}, z. \quad [3.7]$$

The values of the lattice parameters at elevated temperatures and atomic coordinates, as a result of fitting, are $a = 0.29194$ nm; $c = 0.47130$ nm; $z = 0.13937$.

Phase equilibria

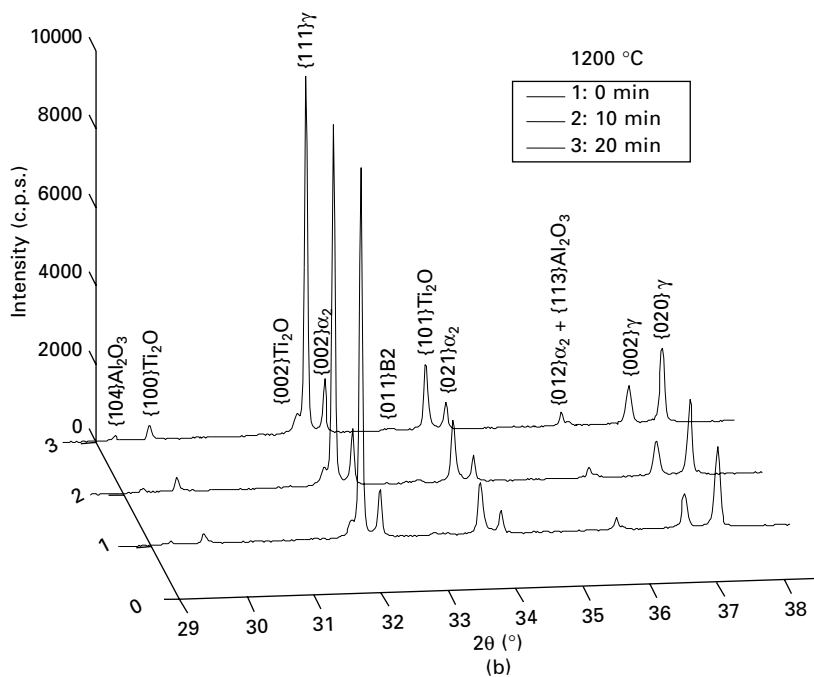
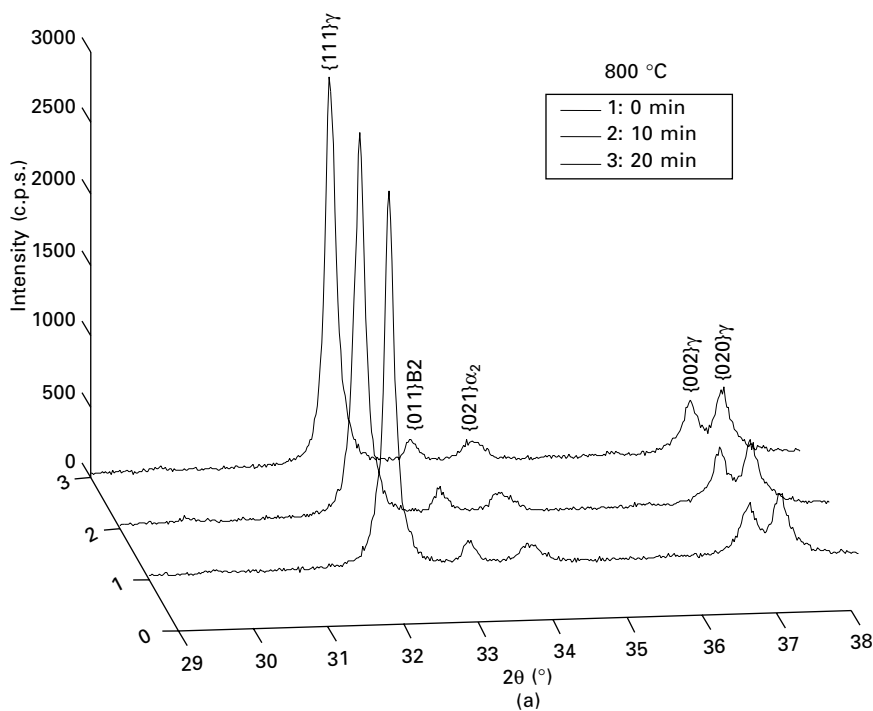
The phase equilibria for the composition of the alloy at different temperatures calculated with the Thermo-Calc software and using a TiAl-database are presented in Fig. 3.19a. From the experimental data, the molar fraction for each phase can be derived using the full-profile quantitative phase analysis (Fig. 3.19b). This phase diagram is not complete, for the content of B2 is about 1 mol% (also 1 wt.%), and the experiments are conducted only up to



3.19 Mole percent versus temperature plot, representing the entire set of the phases in the Ti-46Al-1.9Cr-3Nb alloy (a) calculated using the Thermo-Calc software, and (b) derived after the fitting procedure of the diffraction patterns.

1450 °C. At elevated temperatures, above 1100 °C, the amounts of α and γ are affected by the presence of the oxides and the oxygen in solid solution.

A number of scans at each temperature reveal the kinetics of the phase transformations. Figure 3.20 shows the scans measured in 10 min. steps each for two temperatures. The diffraction patterns of the several scans at each



3.20 X-ray diffraction patterns for Ti-46Al-1.9Cr-3Nb alloy, showing the kinetics of the transformation during isothermal exposure at (a) 800 and (b) 1200 °C.

temperature are similar. The phase transformations are very fast and thermodynamic equilibria have been achieved in minutes or shorter. No phase transformations are observed with prolonged time.

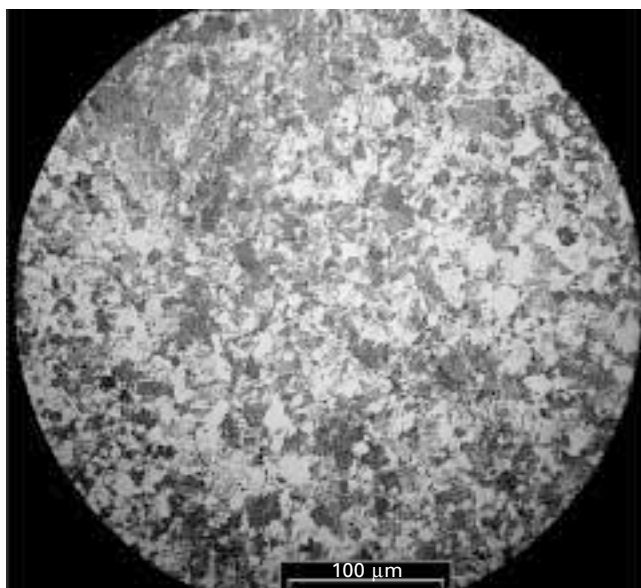
Metallography and scanning electron microscopy

The microstructure after high-temperature exposure is of a duplex nature as in the forged state (Chapter 2) (Fig. 3.21).

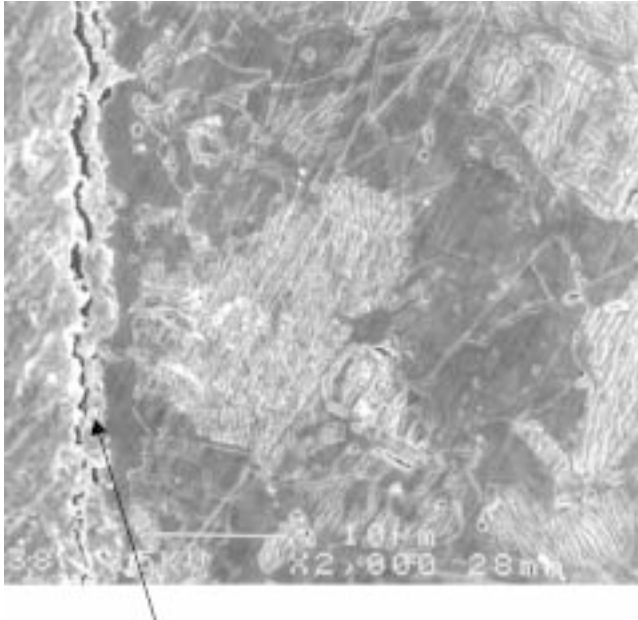
In Fig. 3.22, the oxidised layer is shown. The depth of the X-ray penetration is 5–6.5 μm for scan in the range of 30–40° in 2θ , and 12 μm at 70° in 2θ .

3.4.3 Summary

The full-profile quantitative phase analysis of the set of X-ray diffraction patterns collected at high temperatures allows measurement of the molar fraction versus temperature for every phase in the Ti-46Al-1.9Cr-3Nb alloy. A thermodynamically calculated phase diagram of the Ti-46Al-1.9Cr-3Nb alloy corresponds well to the results of the molar phase fraction derived after the fitting procedure of the X-ray diffraction patterns. The coefficients of thermal expansion in the temperature range of 20–1450 °C are derived for both γ and α/α_2 phases independently. X-ray diffraction and microscopy



3.21 Optical micrograph, showing duplex microstructure of Ti-46Al-1.9Cr-3Nb alloy after high-temperature measurements.



3.22 Scanning electron microscopy image, showing the surface oxidised layer (arrow) of Ti-46Al-1.9Cr-3Nb alloy after high-temperature measurements.

data prove the presence of a titanium and aluminium oxide layer at the alloy surface. The Ti_2O oxide forms in the surface of the gamma titanium aluminide alloy at high temperature.

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Differential scanning calorimetry and property measurements

Abstract: Differential scanning calorimetry can reveal reproducibly the thermal effects upon heating of titanium alloys and aluminides. The main part of this chapter describes the kinetics of the $\gamma + \alpha$ to α phase transformation in the Ti-46Al-1.9Cr-3Nb alloy, derived quantitatively from the calorimetry data, giving phase compositions at any point during the transformation upon continuous heating. This is followed by discussions of mechanical property testing, and hydrogen penetration measurement. For the latter purpose, alloys are cathodically charged with hydrogen in acid solutions for various times at different current densities and temperature, followed by X-ray diffraction to determine the nature of the microstructural change.

Key words: phase transformation, microstructure, intermetallics, hydrogen absorbing materials, high-temperature alloys.

4.1 Phase and structural transformations

This section explains the transformation behaviour in Ti-46Al-1.9Cr-3Nb alloy, combining differential scanning calorimetry, microscopy, X-ray diffraction, and thermodynamic calculations.

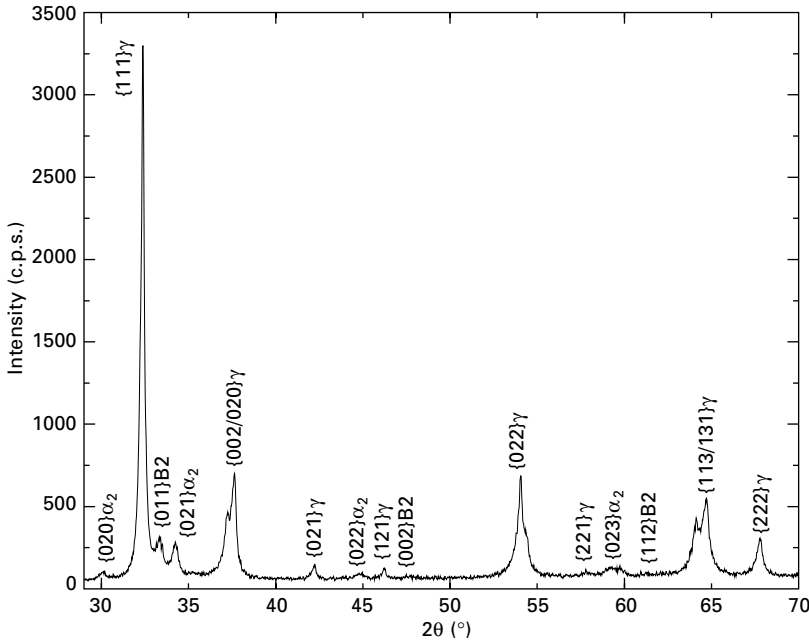
4.1.1 Forged alloy

The forged microstructure (Fig. 2.5) is as expected, considering the history of heat and thermomechanical processing of the forged alloy (Chapter 2). This duplex microstructure should result in good ductility.

The X-ray diffraction analysis of the forged alloy shows the presence of γ , α_2 and a small amount of B2 phases (Fig. 4.1). The B2 phase is clearly detectable, especially with high-resolution synchrotron radiation diffraction. More detailed interpretation of the X-ray results is given in Chapter 3.

4.1.2 Differential scanning calorimetry

There are many peaks in the differential scanning calorimetry curves for continuous heating (Fig. 4.2), with different character and appearance. We now denote the different thermal effects present as TE1, TE2, TE3, TE4, TE5, TE6 and TE7. All these thermal effects are reproducible during repeated experiments.

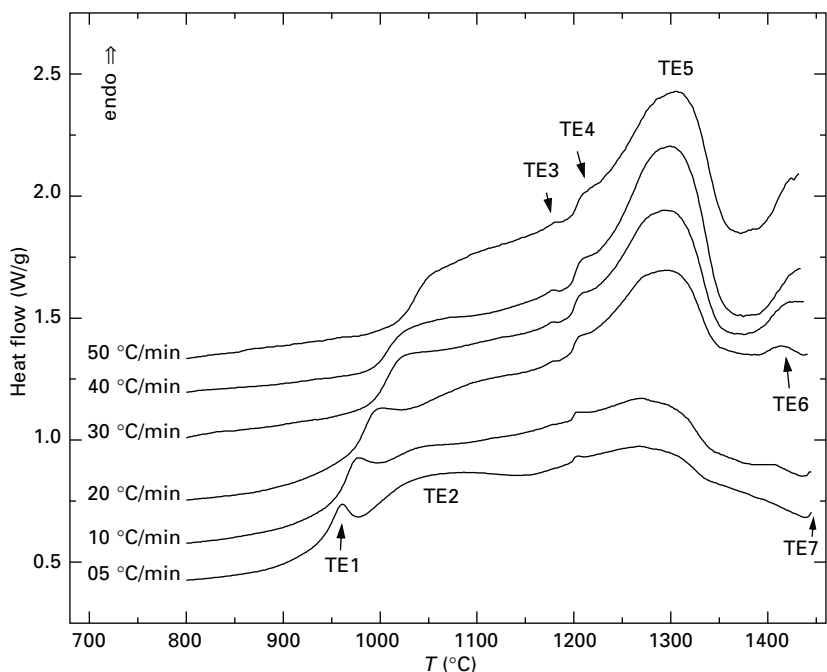


4.1 Synchrotron radiation X-ray diffraction pattern of forged Ti-46Al-1.9Cr-3Nb alloy.

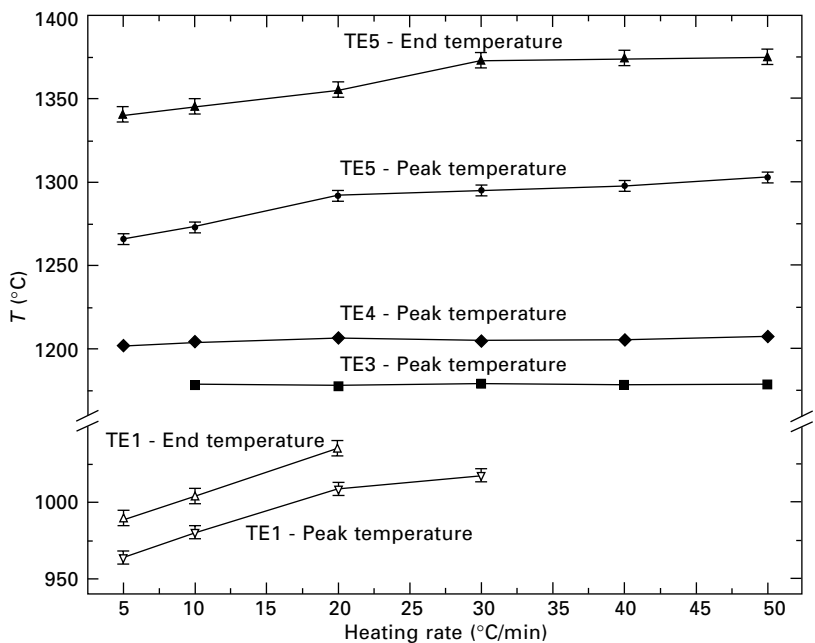
In the temperature range of 900–1150 °C, there are two thermal effects – TE1 and TE2 (Fig. 4.2). These are quite well separated when heating with slow heating rates (5, 10 and 20 °C/min). Thermal effect TE1 is sharp and well defined. Its start temperature, however, is not clearly measurable. TE2 is very broad and ranges from 980 to 1160 °C at a heating rate of 5 °C/min. TE1 is highly influenced by the heating rate and shifts significantly to higher temperatures when faster heating rates are applied (Figs. 4.2 and 4.3). At high heating rates, the two thermal effects, TE1 and TE2, are overlapped.

At a further increase of the temperature to about 1200 °C, there are two small peaks, TE3 and TE4. TE4 is clearly observed at all heating rates. TE3 is clear at the higher heating rates (20 °C/min or higher) but is hardly visible at the heating rates of 5 and 10 °C/min. There is a perfect reproducibility for both peaks at different runs with error bar within a range of ± 1.5 °C. Moreover, both peaks appear at constant temperatures and are not influenced by the heating rate (Figs. 4.2 and 4.3). The peak temperature of TE3 varies within a narrow temperature interval of 1177–1179 °C and the peak temperature of TE4 varies in the temperature interval of 1203–1207 °C, for different heating rates (Fig. 4.3).

The major thermal effect, TE5, appears in the temperature interval from 1200 to 1350 °C. Its start temperature is not well defined, while the peak and



4.2 Differential scanning calorimetry curves for Ti-46Al-1.9Cr-3Nb alloy employing different heating rates. For clarity, the calorimetry curves are shifted along the vertical axis with respect to each other.



4.3 Influence of the heating rate on the different thermal effects observed at continuous heating of Ti-46Al-1.9Cr-3Nb alloy.

end temperatures are easily measurable and are influenced by the heating rate. There is a small shift to higher temperatures when faster heating is applied (Fig. 4.3).

TE6 is pronounced at heating rates of 10 and 20 °C/min. At higher heating rates (30, 40 and 50 °C/min), this thermal effect is not completed. At a lower heating rate (5 °C/min), TE6 is not clearly seen with only some signs, given by the presence of an inflection point in the curve, at about 1340 °C. At further increase of the temperature above 1440 °C, there is some indication for the presence of another thermal effect, only at heating rates of 5 and 10 °C/min.

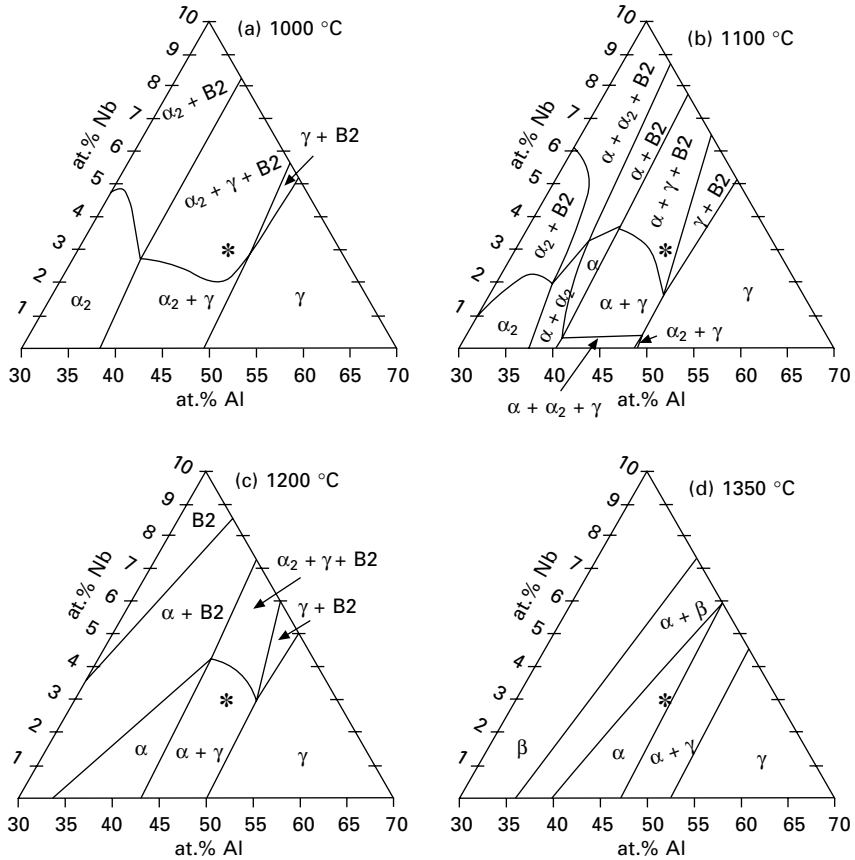
4.1.3 Interpretation of the calorimetry data

The variety of peaks and their appearances indicate several phase and structural changes during heating. Such variety of peaks has not been observed during differential thermal analysis (Ohnuma *et al.*, 2000) of other gamma titanium aluminides. Careful analysis is necessary in order to correlate the thermal effects with the corresponding phase and structural changes. In order to correctly interpret the calorimetry curves, additional theoretical and experimental study is necessary involving: (i) thermodynamic calculations of the phase equilibria in the Ti–Al–Cr–Nb system; (ii) additional experiments involving microstructure investigations of alloy heated to different temperatures; and (iii) calorimetry runs on repeat, or secondary, heating.

Thermodynamic calculations of the phase equilibria in the quaternary Ti–Al–Cr–Nb system are made with Thermo-Calc using the TiAl-database. This database can be used for the prediction of stable and metastable phase equilibria in multi-component gamma titanium aluminides. The calculations are for the actual alloy composition for both taking and not taking into account the oxygen content of 700 ppm (0.07 wt.% or 0.17 at.%). The calculation results are similar, with and without taking into account the oxygen content. The extent of similarity can be assessed by comparing the calculated equilibrium mole% of phases versus temperature plots with oxygen (this chapter) and without oxygen (Chapter 3). Though there are five elements in the alloy compositions, the term quaternary is used because the content of oxygen as an impurity in these calculations is fixed and small.

Figure 4.4 shows the phase equilibrium diagram at different temperatures, obtained by keeping the chromium concentration constant and varying the aluminium and niobium contents. The isothermal diagrams are plotted for ranges of aluminium and niobium that are of practical interest for gamma titanium aluminides. The actual alloy composition is also depicted in the diagrams. The thermodynamic calculations suggest the following conclusions:

- The B2 phase, which does not exist in the binary Ti–Al diagram, is an equilibrium phase in the quaternary Ti–Al–Cr–Nb phase diagram at certain

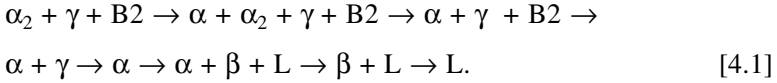


4.4 Calculated isothermal sections of the quaternary Ti–Al–Cr–Nb system with the composition of the alloy plotted on them. The calculations are for Cr = 1.9 at.%. For clarity, only the range of compositional interest for gamma titanium aluminides is plotted.

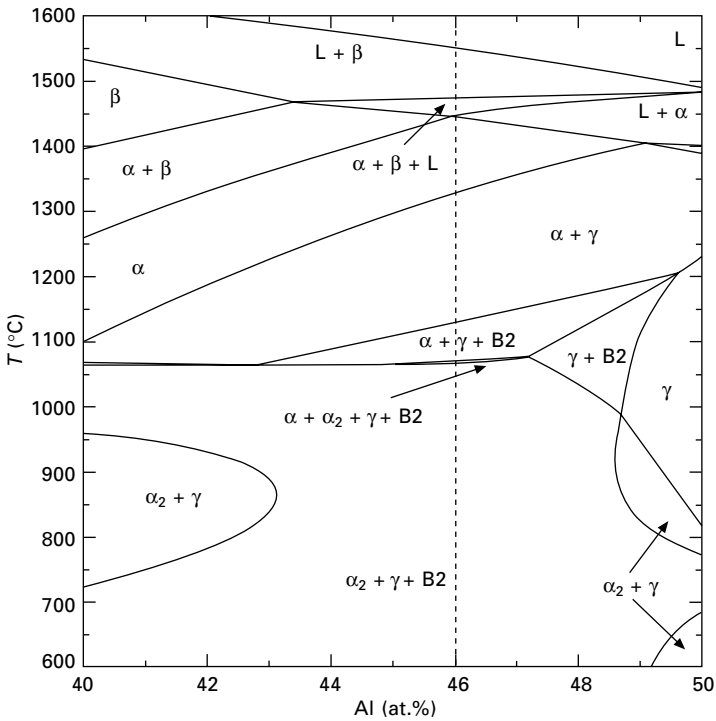
thermodynamic conditions. It exists in a wide concentration range, including the composition of the alloy here, and forms a variety of two-phase and three-phase equilibria involving the α , γ , and α_2 phases, depending on the temperature.

- The alloy composition falls into different phase equilibrium fields, depending on the temperature, that include $\alpha_2 + \gamma + \text{B2}$ at 1000 °C, $\alpha + \gamma + \text{B2}$ at 1100 °C, $\alpha + \gamma$ at 1200 °C and homogeneous α at 1350 °C (see Fig. 4.4). This suggests that at heating/cooling, the alloy phase composition would undergo a variety of phase transformations that are more complicated as compared to those in the binary Ti–Al phase diagram. $\alpha + \gamma$ to α is the major phase transformation and, on the calorimetry curve, should appear as a prominent wide peak.

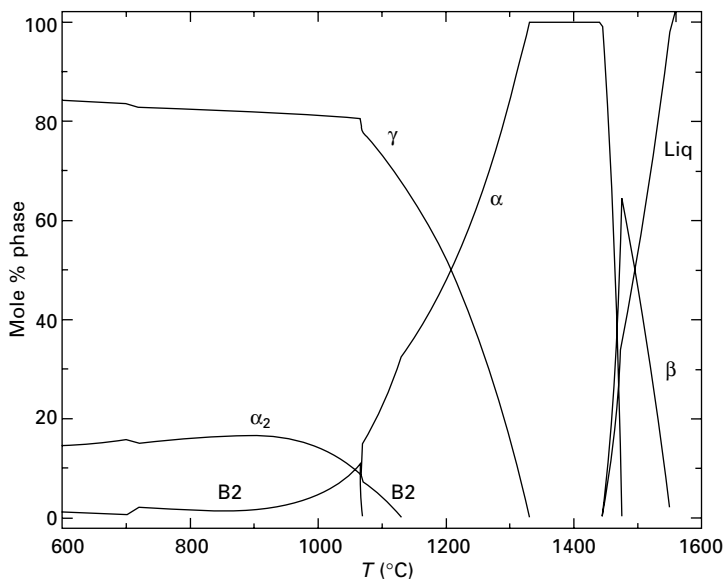
A polythermal section of the phase diagram (Fig. 4.5) traces the change of the equilibrium phase composition of the alloy with temperature. In the calculations, the chromium and niobium compositions are kept constant, and the aluminium concentration and the temperature are varied. In the same figure, we depict (see dashed line) the alloy composition. From these calculations, one can suggest that the equilibrium phase compositions change in the following sequence on increasing the temperature from room temperature to 1600 °C:



Further, the amounts of phases are shown (see Fig. 4.6). Though, usually, the kind of sharp change of the equilibrium mole percent curves of phases around 700 °C in Fig. 4.6 is caused by the change of phase equilibrium, Fig. 4.5



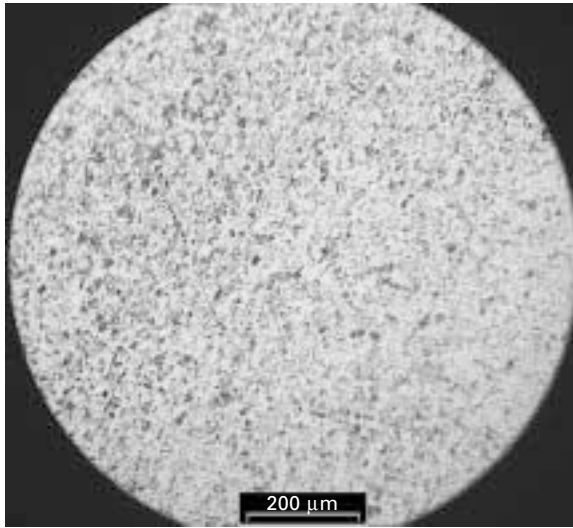
4.5 Calculated polythermal sections of the quaternary Ti–Al–Cr–Nb system with the composition of the alloy plotted on them. The calculations are for Cr = 1.9 at.% and Nb = 3 at.%. For clarity, only the range of compositional interest for gamma titanium aluminides is plotted.



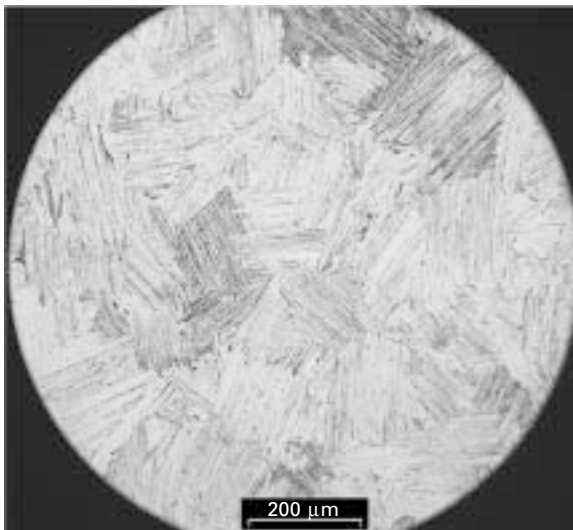
4.6 Calculated equilibrium mole percentage of phases versus temperature for Ti-46Al-1.9Cr-3Nb-0.17O alloy.

clearly shows that this is not the case in the present system. Based on the above analysis we suggest that:

- (i) The thermal effect TE5, which is the major peak in the calorimetry curves (Fig. 4.2), is due to the γ to α phase transformation at continuous heating. Microstructures of the alloy heated to different characteristic temperatures in the calorimetry curve, viz. 900, 1020, 1160, 1200, 1220 (Fig. 4.7a) and 1390 °C (Fig. 4.7b), prove this. These temperatures are purposely chosen as the temperatures of the ends of the different thermal effects. After heating to and cooling from 1220 °C, which is about the start temperature of TE5 at heating with the rate of 20 °C/min (see Fig. 4.2), the microstructure (Fig. 4.7a) remains similar to the initial microstructure (Fig. 2.5) in respect to the grain morphology. We might expect some changes, since thermal effects TE1–TE4 are passed. However, these changes are possibly at a finer microstructure level, and are not observable by optical microscopy. On the other hand, the microstructure of the alloy heated to the next temperature (1390 °C), which is about the end temperature of TE5 at heating with rate 20 °C/min (see Fig. 4.2), is totally different. The microstructure is fully lamellar, which is typical for the alloy after cooling from temperatures above α -transus. This is an experimental proof that the thermal effect TE5 is a result of the γ to α phase transformation in the alloy.



(a)



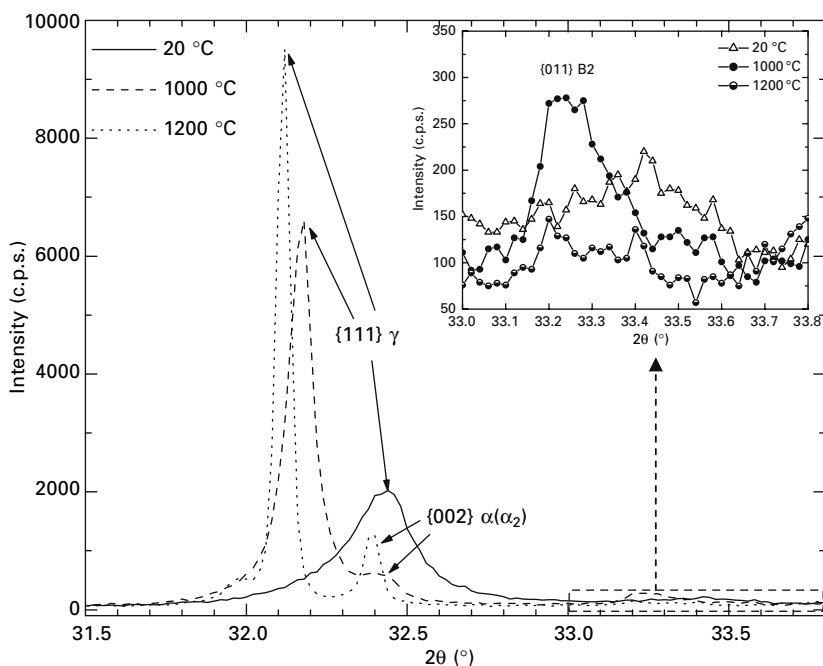
(b)

4.7 Microstructure of Ti-46Al-1.9Cr-3Nb alloy after heating with a rate of 20 °C/min to (a) 1220 and (b) 1390 °C and cooling with a rate of 20 °C/min.

- (ii) The thermal effect TE4, which is just before TE5, is due to the disappearance of the B2 phase, where the alloy moves from the $\alpha + \gamma + \text{B2}$ to $\alpha + \gamma$ phase equilibrium ranges. This effect is small because of the small amount of the B2 phase. The thermodynamic calculations

show that the equilibrium temperature for this transformation is 1130 °C, but in the calorimetry curves, this effect is observed at about 1200 °C. Probably, overheating above the equilibrium temperature is necessary for this transformation to take place. The disappearance of the B2 phase at 1200 °C is also detected by high-temperature X-ray diffraction in isothermal conditions at elevated temperatures (see Chapter 3 and Fig. 4.8).

- (iii) The thermal effect TE3 is due to the transition of $\alpha_2 + \gamma + \text{B2}$ to $\alpha + \gamma + \text{B2}$ by crossing the four phase $\alpha + \alpha_2 + \gamma + \text{B2}$ region. In the quaternary Ti–Al–Cr–Nb system, this transition is in a narrow temperature range. The effect is relatively small, because of the small amount of the α_2 phase. The thermodynamic calculations show that the equilibrium temperature range for this transformation is 1067–1070 °C. On the calorimetry curves for continuous heating, it is observed at higher temperatures – around 1170 to 1180 °C. Again, this difference can be due to kinetics reasons. Appreciable increase in the amount of α phase at temperatures higher than 1100 °C has been shown for the same alloy (Chapter 3), which is in agreement with what is suggested above. Finally, effects like TE4 and TE3 have not been observed in differential



4.8 *In situ* synchrotron radiation diffraction patterns of Ti-46Al-1.9Cr-3Nb alloy at different temperatures.

thermal analysis and differential scanning calorimetry curves of other gamma titanium aluminides where the B2 phase does not exist (Ohnuma *et al.*, 2000).

- (iv) The broad thermal effect TE2 is associated with gradual change of the ratios between the α_2 , γ and B2 phases. The ratios between these phases change upon heating to above 900 °C (Fig. 4.6), where the amount of the B2 phase increases, while the amounts of α_2 and γ phases decrease. Such an increase in the amount of B2 phase is experimentally validated for the same alloy (see Fig. 4.8 and Chapter 3). The amount of B2 phase increases when the temperature is increased from room temperature to 1000 °C (Fig. 4.8). Further increase of the temperature to 1100 and 1200 °C results in decrease and disappearance of the B2 phase. At higher heating rates, as earlier stated, TE1 and TE2 are overlapped. Even at low heating rates where these peaks are separated, the start temperature of TE2 seems to be before the end of TE1.
- (v) It is not possible to explain the appearance of TE1 on the basis of the calculated phase equilibria. We therefore suggest that TE1 is due to transformation towards equilibration of the initial thermomechanically forged alloy. Though X-ray analysis shows the presence of α_2 , γ and B2 phases in the forged state, the phase composition in terms of the amounts of phases may differ from the equilibrium one. Heating to above 900 °C would allow diffusion processes to take place that would lead to equilibration of the phase constitution. In addition, in the temperature range where TE1 and TE2 exist, homogenisation diffusion processes in the γ phase occur. These are shown by X-ray measurements (Chapter 3 and Fig. 4.8). An experiment with two heating cycles to a temperature just above the TE1 further proves this. TE1 is clearly present during the first heating, but it is not present during cooling or during repeat heating. Hence, we suggest that this peak is related to, in the main, the non-equilibrium structure after thermomechanical processing.

The thermodynamic calculations suggest that, for the composition, the homogeneous α phase (after completion of TE5) at heating would transform directly through peritectic transformation of α to $\alpha + \beta + L$ without the α to $\alpha + \beta$ phase transition before that. The α to $\alpha + \beta$ transition occurs in the binary Ti–Al phase diagram. Our calorimetry data show that the thermal effect TE6 could be assigned only to the solid state α to $\alpha + \beta$ phase transition, and TE7 involves the liquid phase. Indications for this are the appearance and shape of the TE6 peak as well as the temperature range where it appears. TE6 is not completed for heating with rates of 30, 40 and 50 °C/min, probably because of kinetic reasons. Next, TE7, which has just started at about 1440 °C for small heating rates (5 and 10 °C/min), most probably is due to

the beginning of partial melting ($\alpha + \beta$ to $\alpha + \beta + L$). In these samples, after the calorimetry experiments, there were partially melted parts around the edges. The calorimetry measurement is not an equilibrium process. It is possible for the calorimetry results to deviate from the thermodynamic calculation. The alloy composition of each phase cannot reach uniformity at any time due to the diffusion barrier. The transformations $\alpha \rightarrow \alpha + \beta \rightarrow \alpha + \beta + L$ may be interpreted according to the non-equilibrium reason.

Table 4.1 summarises these effects.

4.1.4 Kinetics of the γ to α phase transformation

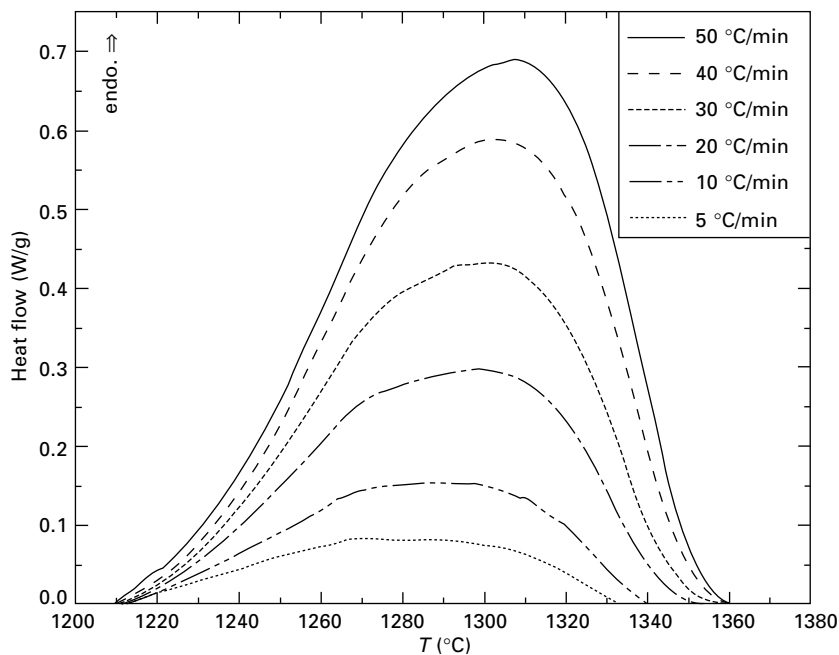
As discussed in the previous section, a variety of phase transformations take place during continuous heating. The different phase transformations appear with different thermal effects, affected differently by the heating rate.

Since the γ to α phase transformation is the major phase transformation and has practical importance in the heat treatment of the gamma titanium aluminides, here, we pay a special attention to it. The transformation involving γ at continuous heating starts at TE3, where the α_2 phase disappears. However, in some temperature range, from TE3 to TE4, it proceeds with the presence of another phase – B2. In its pure form, where only the two phases exist, the γ to α phase transformation starts after TE4, when the B2 phase also disappears. The pure γ to α phase transformation is represented by TE5. This phase transformation does not start with 100% γ phase but with a mixture of about 66% γ + 34% α phases (at the end of TE4), and completes with homogeneous 100% α at the α -transus temperature.

In order to reveal the kinetics of the γ to α phase transformation from the calorimetry signal, we extract the signal corresponding to pure γ to α phase transformation only (Fig. 4.9), without the presence of other phases. This is done by baseline connecting the end of TE4, where the B2 phase disappears

Table 4.1 Thermal effects in the differential scanning calorimetry curves at continuous heating and corresponding phase transformations of Ti-46Al-1.9Cr-3Nb alloy

Thermal effect	Phase transformation
TE1	Equilibration and homogenisation of the alloy
TE2	Change of phase ratios between α_2 , γ and B2 phases. Increase of B2 in respect to α_2 and γ
TE3	$\alpha_2 + \gamma + B2$ to $\alpha + \gamma + B2$
TE4	$\alpha + \gamma + B2$ to $\alpha + \gamma$ (disappearance of B2)
TE5	$\gamma + \alpha$ to α
TE6	α to $\alpha + \beta$
TE7	$\alpha + \beta$ to $\alpha + \beta + L$



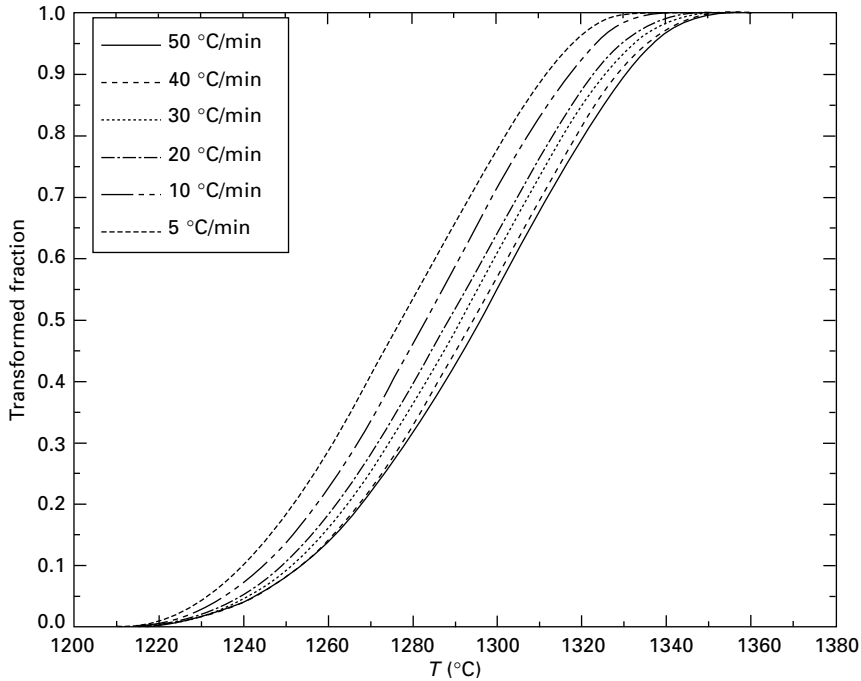
4.9 Processed calorimetry curves for the γ to α phase transformation in Ti-46Al-1.9Cr-3Nb alloy at different heating rates.

Table 4.2 Enthalpy of the $\gamma + \alpha$ to α phase transformation at continuous heating with various heating rates

Heating rate (°C/min)	Enthalpy (J/g)
50	65.9
40	69.6
30	68.1
20	70.6
10	72.0
5	78.2

and pure γ to α phase transformation starts, and the end of TE5, where this transformation completes with 100% of α phase. The calculated enthalpy values using the processed calorimetry curves are similar for the different heating rates (Table 4.2), confirming that these calorimetry signals correspond to one same phase transformation at different heating rates.

The degree of transformation is calculated (Fig. 4.10), using the method detailed in Chapter 7. The calculated curves trace the course of the γ to α phase transformation in the Ti-46Al-1.9Cr-3Nb alloy at continuous heating. Transformed fraction does not mean the amount of the α phase. At zero transformed fraction, the phase composition is 66% γ + 34% α , while at

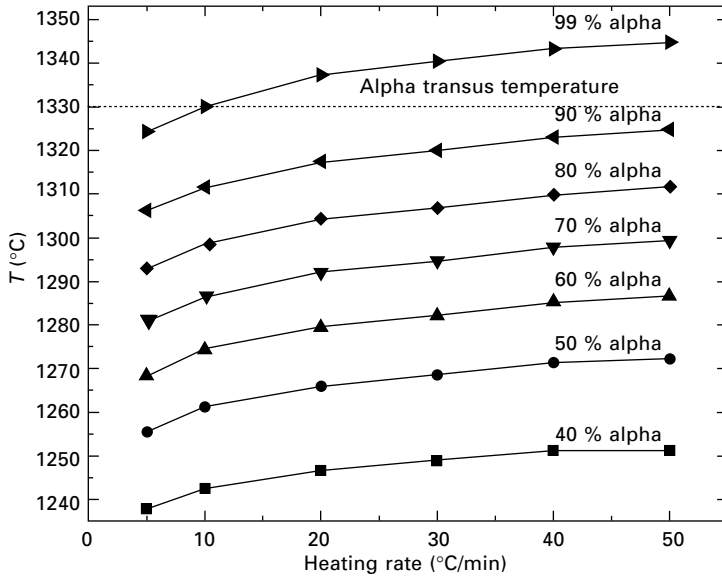


4.10 Calculated transformed fractions as a function of the temperature for the γ to α phase transformation in Ti-46Al-1.9Cr-3Nb alloy at different heating rates.

transformed fraction = 1, the phase composition is 100% α phase. Based on this, we calculate the amounts of the α phase at different temperatures and heating rates. The iso-lines in Fig. 4.11 show the dependence of the amount of the α phase on the heating rate. Such a thermo-kinetic diagram can be used to trace the course of transformation in real products, where the heating rate varies significantly from the surface to the core. This is important for titanium-based materials that have relatively low heat conduction coefficients.

4.1.5 Summary

The Ti-46Al-1.9Cr-3Nb alloy after being forged at 1200 °C without further treatment has a duplex microstructure, consisting of fine equiaxed and lamellar γ grains, with a small amount of α_2 plates and particles and about 1 wt.% B2 phase. Differential scanning calorimetry can reveal, reproducibly, several thermal effects upon heating of the as-forged alloy. These thermal effects are related to the equilibration and homogenisation of the alloy, change of phase ratios between α_2 , γ and B2 phases (in particular, the increase of B2 in respect to α_2 and γ), and the following five phase transformations: $\alpha_2 + \gamma +$



4.11 Calculated thermo-kinetics diagram plotted as temperature versus heating rate. Iso-lines show the amounts of the α phase.

$B2 \rightarrow \alpha + \gamma + B2 \rightarrow \alpha + \gamma \rightarrow \alpha \rightarrow \alpha + \beta \rightarrow \alpha + \beta + L$. The observation of these transformations by differential scanning calorimetry is largely in agreement with literature phase diagrams and thermodynamic calculations, though care is needed to consider the different alloy compositions. Kinetics of the $\gamma + \alpha$ to α phase transformation in the Ti-46Al-1.9Cr-3Nb alloy can be quantitatively derived from the calorimetry data, giving phase compositions at any point during the transformation upon continuous heating.

4.2 Mechanical properties of β 21s alloy

This section investigates and shows the effect of heat treatment parameters with respect to the microstructure and mechanical properties of β -type titanium alloys. β alloys are the most versatile class of titanium alloys. They offer very attractive combinations of strength, toughness, and fatigue resistance, at large cross-sections. The disadvantage compared to $\alpha + \beta$ alloys is an increase in density and cost.

β 21s (Ti-15Mo-3Al-2.7Nb-0.25Si) is a relatively recently developed metastable β alloy. Molybdenum, as an alloy agent to titanium, up to 15%, provides oxidation resistance and improves corrosion resistance. Aluminium is an α stabiliser, but it is added to β 21s to improve ductility and to reduce the weight. Strip is the main product form, and the material can be economically rolled to foil.

β 21s is metallurgically stable for at least 1000 hours at temperatures up to 615 °C. However, at elevated temperatures, oxygen absorption at the surface degrades the tensile ductility of the material.

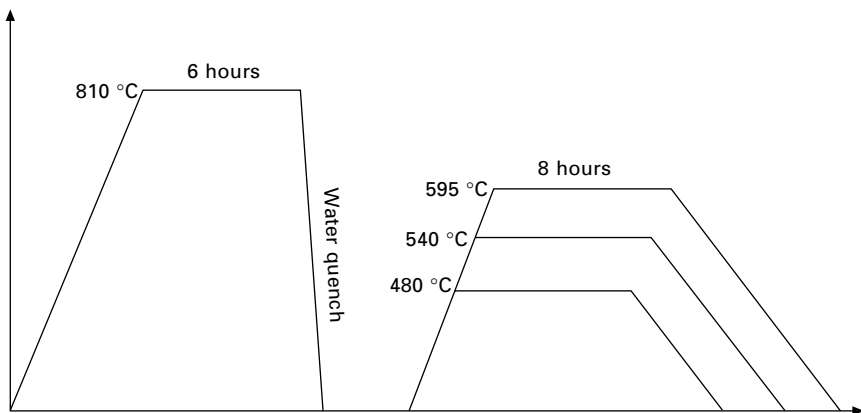
Five different thermal processing conditions are considered here (Fig. 4.12):

- (i) aged (this is the starting state of the alloy, which was processed through β solution treatment followed by ageing)
- (ii) heat treated and then water quenched,
- (iii) water quenched and ageing at 480 °C for 8 hours,
- (iv) water quenched and ageing at 540 °C for 8 hours,
- (v) water quenched and ageing at 595 °C for 8 hours.

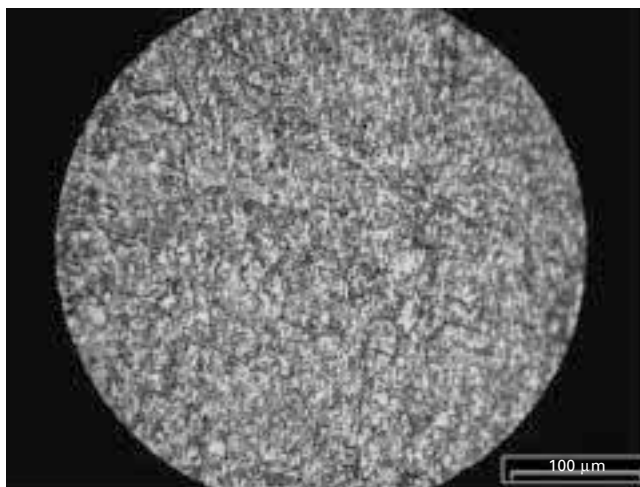
The thermal processing has produced a fully equiaxed microstructure with α phase precipitating at the grain boundaries of the β phase with varying grain sizes (Fig. 4.13).

The Vickers hardness after water quenching decreases as compared to the initial aged condition (see Fig. 4.14), due to the formation of mostly metastable β microstructure during fast cooling from the β homogenisation field. Ageing after quenching causes an increase of hardness, as compared to the quenched condition. The reason for this is the formation of fine α precipitates during ageing. There is a clear trend showing that as the ageing temperature is increased, the hardness decreases. The reason for this decrease is the formation of coarser precipitates during ageing at higher temperature, and possibly relief of the micro-stresses.

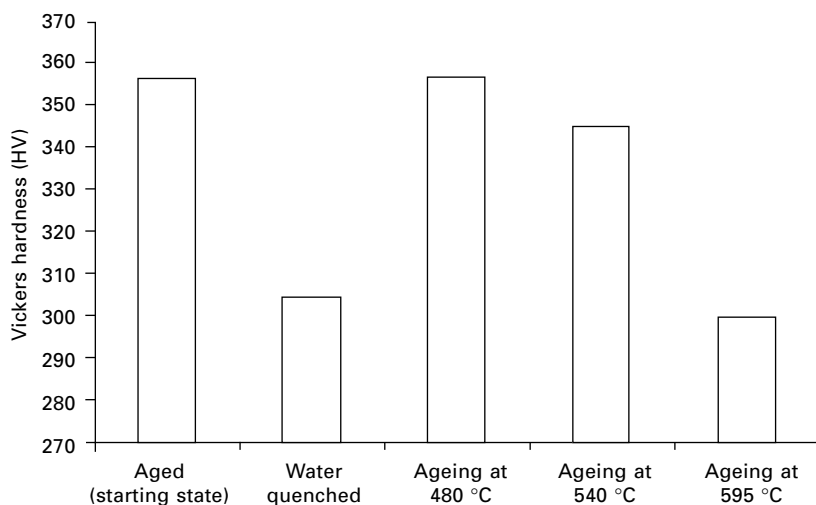
The same trend, i.e. decrease at higher temperatures of ageing, is observed with the ultimate tensile strength (Fig. 4.15), for the same reasons as for hardness changes. The trend for change of the elongation, a measure of the



4.12 Schematic presentation of heat treatments for β 21s alloy.

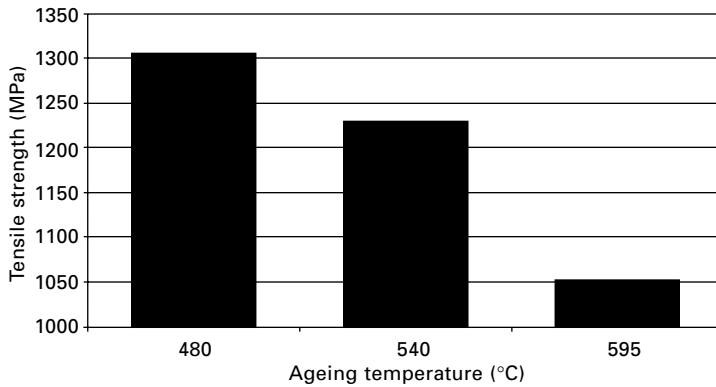


4.13 Microstructure of $\beta 21s$ alloy after water quenching and ageing at 480 °C for 8 hours.

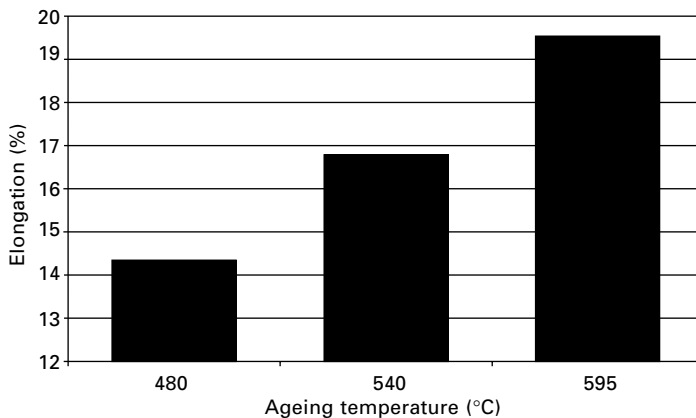


4.14 Vickers hardness of $\beta 21s$ alloy with different processing conditions.

material's ductility, is the opposite, namely the elongation increases, with higher temperature of ageing (Fig. 4.16). Obviously, the ageing temperature is a very significant parameter for control of the microstructure and properties in β -titanium alloys. By altering this temperature, the desirable combination of strength and ductility can be achieved.



4.15 Tensile strength of $\beta 21s$ alloy after ageing at different temperatures.



4.16 Elongation of $\beta 21s$ alloy after ageing at different temperatures.

4.3 Effects of hydrogen penetration

Titanium alloys are susceptible to hydrogen, which causes embrittlement, leading to the deterioration of the properties of the alloys. For a Ti-42Al-11Nb (at.%) alloy, the yield strength increases with increasing amount of hydride, but the ultimate tensile strength, ductility and fracture toughness decrease. Therefore, the amount of hydrogen that a titanium alloy can absorb during service is a major measure of the ability of the alloy to retain good properties. Much effort has been made to quantify the hydrogen susceptibility of titanium alloys. This section describes the effect of hydrogen.

Confusion exists concerning the form of hydrogen after entering titanium alloys. It was suggested that a hydride with the structure $(TiAl)H_x$ might form. Samples of Ti-49.9Al (at.%) were ground, polished and cathodically

charged in a 1 mol/l NaOH and 250 mg/l As_2O_3 solution at room temperature with a current density of 300 A/m^2 . X-ray diffraction showed that for a sample with a single γ phase before charging, a hydride phase was formed after 4 hours of charging. The hydride phase was determined to be $(\text{TiAl})\text{H}_{0.5}$, with tetragonal lattice parameters $a = 0.450 \text{ nm}$ and $c = 0.327 \text{ nm}$ ($c/a = 0.727$).

The surface of a γ and α_2 two-phase titanium aluminide sample was covered with a black layer after prolonged cathodic hydrogen charging. Analytical transmission electron microscopy showed that the surface layer was a hydride based on $(\text{TiAl})\text{H}_x$. It was determined that the hydride had a tetragonal crystal structure with lattice parameters $a = 0.452 \text{ nm}$ and $c = 0.326 \text{ nm}$ ($c/a = 0.721$), and it was present up to $25 \mu\text{m}$ in depth from the surface of the sample after charging for 2 hours. The charging condition was a 5% H_2SO_4 solution, and current density equal to 5000 A/m^2 . The weight change of the sample with increasing charging time was also measured. The weight decreased with increasing charging time after 1 hour.

Hydrogen charging of Ti-42Al, Ti-45Al and Ti-50Al induced crack formation after a short charging time, while additional charging produced pits within the γ phase in the γ and α_2 two-phase coexisting grains. However, no damage was seen in the α_2 phase or equiaxed single α grains.

Cast Ti-48Al-2Cr and wrought Ti-46.5Al-4(Cr,Nb,Ta,B) gamma titanium aluminides were cathodically charged with hydrogen for various times to study possible hydrogen trap sites and the nature of the hydride being formed (Sundaram *et al.*, 2000). The charging solution was 1 N H_2SO_4 solution with 1 g/l thiourea. The charging time varied between 1 and 24 hours and the current density was 1 A/m^2 . No visible change was noted on the charged surface after 8 hours as compared with the uncharged surface. However, after 16 hours, small black particles, presumably hydrides, were observed on the surface. After 24 hours, a black hydride layer covered the surface. After X-ray diffraction patterns were obtained, Sundaram *et al.* (2000) stated that the result proved to be similar to the previous findings.

Sundaram *et al.* (2000) determined that a hydride was formed when hydrogen entered their samples. However, this does not discount the possibility that some hydrogen may occupy the interstitial sites in the alloys. Both could take place simultaneously.

The following summarises the further investigation into the hydrogen susceptibility of $\beta 21$ s and Ti-46Al-1.9Cr-3Nb alloys, by measuring the amount of hydrogen penetrating into the sample within a specific charging time. Establishing a rate of penetration can give an indication of the ability of the alloy to resist hydrogen.

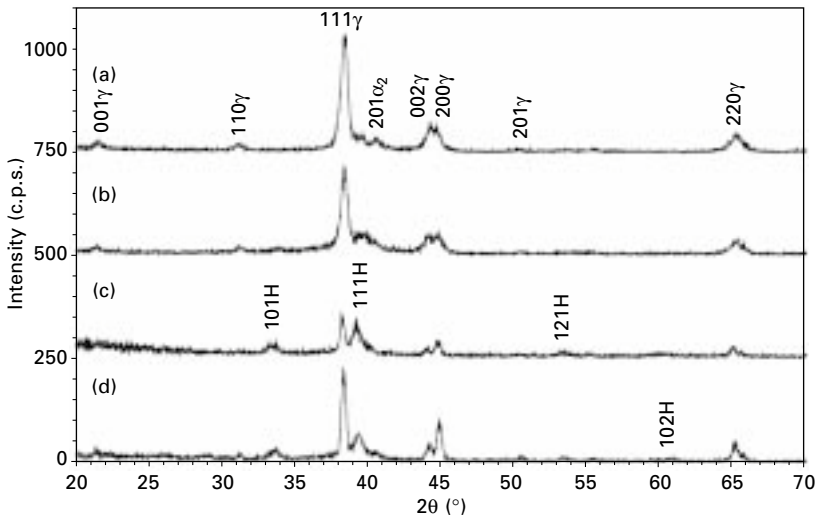
Immediately after charging, some of the samples were placed in a solution of glycerine for 48 hours at room temperature. This technique had been used before, and the quantity of hydrogen released during 48 hours at room

temperature was used as a measure for the quantity of hydrogen absorbed during permeation. After such experiments, no hydrogen was released and collected after 48 hours. The hydrogen remained within the samples.

The average Rockwell hardness numbers before and after charging were exactly the same. Some of the samples cracked, however, on using the Rockwell hardness indentation after charging.

The effects of hydrogen on the samples could be clearly seen after the experiment, especially after severe charging, such as 4 hours at 85 °C in 2.8% H_2SO_4 at 250 A/m^2 . The samples had suffered extensive corrosion while the remainder was covered with a black layer. Sundaram *et al.* (2000) reported similar damage.

The additional peaks present in the X-ray diffraction patterns for charged samples indicate the presence of a hydride (Fig. 4.17). The plane index values corresponding to the peaks in the diffraction patterns were determined by comparison with data by Sundaram *et al.* (2000), as the hydride peaks established here are similar to XRD data of hydrides available from these authors. The intensity of the peaks is summarised in Table 4.3. The fluctuation in the total integrated intensities of the peaks in the XRD patterns is, most likely, due to the inevitable positional variation in the experimental set-up for different samples.



4.17 X-ray diffraction patterns for Ti-46Al-1.9Cr-3Nb alloy. (a) Uncharged; (b) charged for 1 hour at room temperature, 250 A/m^2 , 5% H_2SO_4 solution; (c) charged for 4 hours at 85 °C, 250 A/m^2 , 2.8% H_2SO_4 solution; (d) charged for 2 hours at room temperature, 5000 A/m^2 , 5% H_2SO_4 solution.

Table 4.3 X-ray diffraction peak relative height of titanium aluminide after hydrogen charging

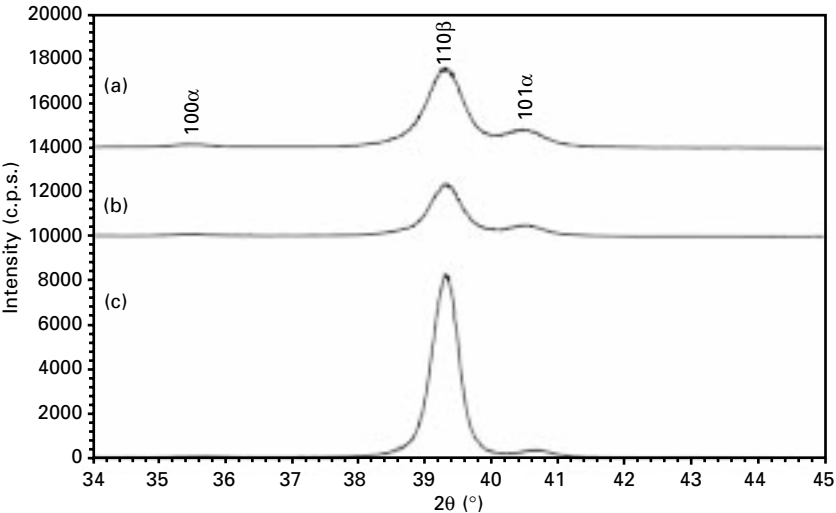
Phase	<i>hkl</i>	Uncharged	5% H ₂ SO ₄ , 0.2 g/l As ₂ O ₃ , 250 A/m ² , 1 h, room temperature	2.8% H ₂ SO ₄ , 1 g/l thiourea, 250 A/m ² , 4 h, 85 °C	5% H ₂ SO ₄ , 0.2 g/l As ₂ O ₃ , 5000 A/m ² , 2 h, room temperature
γ	001	11	12	–	17
	110	8	12	22	11
	111	100	100	100	100
	002	26	26	25	21
	200	25	26	35	46
	201	4	5	13	8
	220	18	20	25	24
α_2	201	13	–	–	–
(TiAl)H _x	101	–	–	40	16
	111	–	26	85	30
	121	–	–	18	8
	102	–	–	11	4

There is a small amount of α_2 phase present in the uncharged Ti-46Al-1.9Cr-3Nb alloy. However, the small amount of α_2 phase disappears with charging (see Fig. 4.17).

Ti-46Al-1.9Cr-3Nb alloy subject to cathodic charging has shown cracking.

The XRD pattern for the β 21s alloy charged in the solution of H₂SO₄ with 0.2 g/l As₂O₃ produces no additional peak in the 2θ range between 20 and 70°, when compared with the XRD pattern for the uncharged alloy (Fig. 4.18). No hydride has formed. Comparison of the XRD patterns for uncharged alloy shows the possible heterogeneity of the material, concerning the shift of peaks, although there might be a contribution from experimental factors. Both intensity and 2θ can be altered, depending on the level at which the sample is placed within the XRD apparatus. Therefore, if all peaks move in the one direction, or if all peaks drop in intensity, it is possible that this is due to samples being placed at different levels during the XRD experiments. However, if the intensity of one peak increases while that of another peak decreases in relation to the uncharged XRD pattern of the sample in question, this is not because of an experimental factor. There is an increase in the amount of β phase while the amount of α phase decreases.

In spite of the absence of hydride, the surface of β 21s still displays damage caused by hydrogen charging, and this could be seen even with the naked eye. Charging for 2 hours at room temperature, 5000 A/m² in 5% H₂SO₄ solution produced extensive cracking, while the surfaces of the samples charged for 2 hours at 85 °C and 250 or 5000 A/m² were blackened when compared to their original appearance.



4.18 X-ray diffraction patterns for $\beta 21s$ alloy. (a) Uncharged; (b) charged for 2 hours at room temperature, 5000 A/m², 5% H₂SO₄ solution; (c) charged for 2 hours at 85 °C, 5000 A/m², 5% H₂SO₄ solution.

Table 4.4 Rates of hydrogen penetration

Material	Current density (A/m ²)	Temperature (°C)	Time (h)	Hydrogen (ppm)	Hydrogen entered (ppm)	Rate of penetration (ppm/h)
Ti-46Al-1.9Cr-3Nb	Uncharged	–	–	24	–	–
	250	room	1	99	75	75
	250 ^(a)	85	4	638 ^(b)	614	154
	5000	room	2	643	619	310
$\beta 21s$	Uncharged	–	–	963	–	–
	250	85	2	1132	169	85
	5000	85	2	1293	330	165

^(a)The charging solution was 2.8% H₂SO₄. A 5% H₂SO₄ solution was used for all other samples.

^(b)This corresponds to 2.5 at.% of hydrogen.

Table 4.4 shows the hydrogen analysis results. It has already been established that a hydride phase based on (TiAl)H_x forms in Ti-46Al-1.9Cr-3Nb alloy during cathodic charging, but no hydride forms in $\beta 21s$ during cathodic charging. Table 4.4 shows that hydrogen does enter $\beta 21s$, and this leads to the conclusion that the hydrogen occupies the interstitial sites in $\beta 21s$.

From Table 4.4, the amount of hydrogen present before charging is approximately 40 times greater in $\beta 21s$ than Ti-46Al-1.9Cr-3Nb alloy. However,

calculating the rates of hydrogen penetration for each of the samples has demonstrated that $\beta 21s$ is less susceptible to hydrogen penetration. Both an increase in the current density and an increase in the temperature of the solution cause an increase in the rate of hydrogen penetration.

In summary, the small amount of α_2 phase in the Ti-46Al-1.9Cr-3Nb alloy becomes undetectable after hydrogen charging. A hydride based on $(TiAl)H_x$, which has tetragonal lattice parameters of $a = 0.452$ nm and $c = 0.326$ nm ($c/a = 0.721$), forms in Ti-46Al-1.9Cr-3Nb alloy after cathodic charging. Hydrogen charging induces crack formation on both Ti-46Al-1.9Cr-3Nb alloy and $\beta 21s$. No hydride is formed in $\beta 21s$ by cathodic charging. The hydrogen enters the alloy and occupies the interstitial sites between the atoms. During charging, there is an increase in the amount of the β phase and a decrease in the amount of the α phase on the $\beta 21s$ surface. $\beta 21s$ is less susceptible to hydrogen penetration than Ti-46Al-1.9Cr-3Nb alloy. The ability of $\beta 21s$ to resist hydrogen penetration, when compared with the ability of Ti-46Al-1.9Cr-3Nb alloy, is approximately greater by a factor of two.

4.4 References

- Ohnuma I, Fujita Y, Mitsui H, Ishikawa K, Kainuma R and Ishida K (2000), 'Phase equilibria in the Ti-Al binary system', *Acta Mater*, 48 (12), 3113–23.
- Sundaram P A, Quadackers W J and Singheiser L (2000), 'Hydrogen effusion in cathodically charged gamma titanium aluminides', *J Alloys Compd*, 298 (1–2), 274–78.

Abstract: Thermodynamic calculations using Thermo-Calc are used to quantify the phase fraction and element partition in a number of conventional titanium alloys and γ -TiAl based alloys, chosen from all of the titanium alloy groups and including both well investigated alloys and those that are relatively new. Calculations of the phase constitution and element distribution in these alloys show a good agreement with the experimental measurement. In addition, Thermo-Calc calculation can help identify the existence of some phases that are not readily observed experimentally. It can be used as a guide in alloy design.

Key words: titanium aluminides based on TiAl, phase transformation, precipitates, phase stability, thermodynamics.

5.1 Introduction

The thermodynamics modelling is usually based on the Gibbs energy calculation. Two most commonly used calculation packages are Thermo-Calc (Andersson *et al.*, 2002) and MTDATA (Davies *et al.*, 2002). These packages have been successfully applied for thermodynamic calculations of different materials systems (Dore *et al.*, 2000; Ekroth *et al.*, 2000; Eskin, 2002; Gorsse and Shiflet, 2002; Guo and Sha, 2000; Jarvis *et al.*, 2000; Sha, 2000; Zackrisson *et al.*, 2000) (Chapters 3 and 6).

Thermodynamic calculation can supplement experimental characterisation, and allows the prediction of phase type, and fraction and element distribution in different phases. Thermo-Calc is a computer package developed particularly for thermodynamic calculations of multi-component equilibrium as a function of pressure, temperature and the combined effect of alloying elements, using a databank of assessed thermodynamic data and models for the phases in the system that are as good an approximation of the nature as possible. It employs rigorous thermodynamic expressions and numerical methods of minimising the chemical energy of the system, so that interpolation between the available experimental data can be made. Good agreement has been obtained in the past between the calculated phase compositions and experimental measurements.

In this chapter, thermodynamic calculations of the phase equilibria in different titanium alloys will be shown, including Ti-6Al-4V (Ti 6-4), Ti-6Al-2Sn-4Zr-2Mo (Ti 6-2-4-2), Ti-6Al-2Sn-4Zr-6Mo (Ti 6-2-4-6), Ti-8Al-1Mo-1V (Ti 8-1-1), Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si (IMI 834), Ti-6Al-7Nb (IMI 367), Ti-10V-2Fe-3Al (Ti 10-2-3) and TIMETAL β 21s. These alloys are chosen from all of the titanium alloy groups and include both well-

investigated alloys and those which are relatively new. The calculations are performed for the actual alloy composition taking into account all major alloying elements. Further thermodynamic calculation procedures are given in Chapters 3 and 6. The results from the thermodynamic calculations and their coupling with the models for simulation of the microstructure evolution in titanium alloys are discussed in several chapters in this part of the book.

5.2 Conventional titanium alloys

In conventional titanium alloys, there are different equilibrium amounts of α and β phases as well as equilibrium compositions of both phases at different temperatures. We shall calculate the phase equilibria for different titanium alloys in wide temperature ranges. The calculated data are compared with experimentally obtained data (Chapter 6).

5.2.1 Ti-6Al-4V (Ti 6-4)

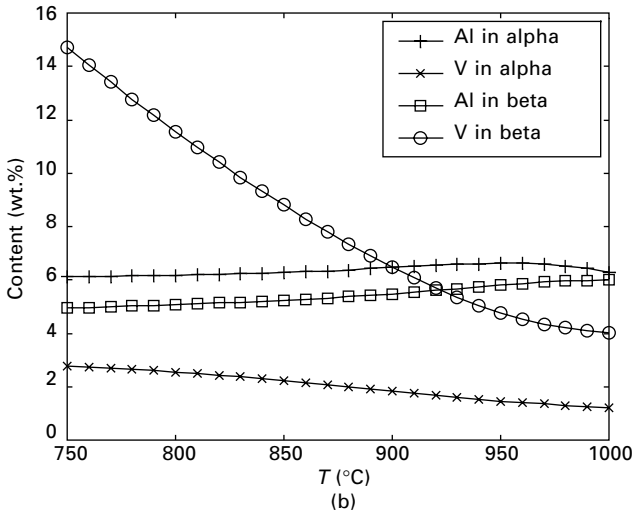
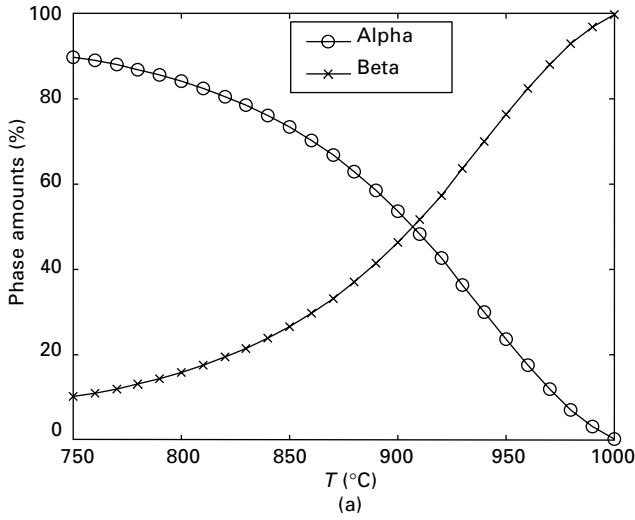
The calculated amounts of the α and the β phases for the Ti-6Al-4V alloy are given in Fig. 5.1a, showing increased equilibrium amount of the α phase when the temperature decreases. The tendency is in agreement with the behaviour of the $\alpha \rightarrow \beta$ phase transformation in titanium alloys.

Further, we calculate the equilibrium chemical compositions of both α and β phases as functions of the temperature (Fig. 5.1b). Such calculation is important for further modelling work because it gives information for the diffusion redistributions between the two phases during the course of β to α transformation.

5.2.2 Ti-6Al-2Sn-4Zr-2Mo (Ti 6-2-4-2)

The calculation for the Ti-6Al-2Sn-4Zr-2Mo alloy also shows increased amounts of the α phase and decreased amounts of the β phase with temperature decrease (Fig. 5.2a). Compared to the Ti-6Al-4V alloy, the α phase in the Ti-6Al-2Sn-4Zr-2Mo alloy is more stable in the entire temperature range. The amount of the α phase at lower temperature for this alloy approaches 100%, while in the Ti-6Al-4V alloy, there is some amount of the β phase remaining. On the other hand, for the Ti-6Al-4V alloy, the phase composition of 50% α + 50% β is at about 905 °C, while in the Ti-6Al-2Sn-4Zr-2Mo alloy, the 50% α + 50% β phase composition is at around 955 °C. This is why the Ti-6Al-2Sn-4Zr-2Mo alloy is considered as a high-temperature titanium alloy, and can work at higher temperatures as compared to the Ti-6Al-4V alloy.

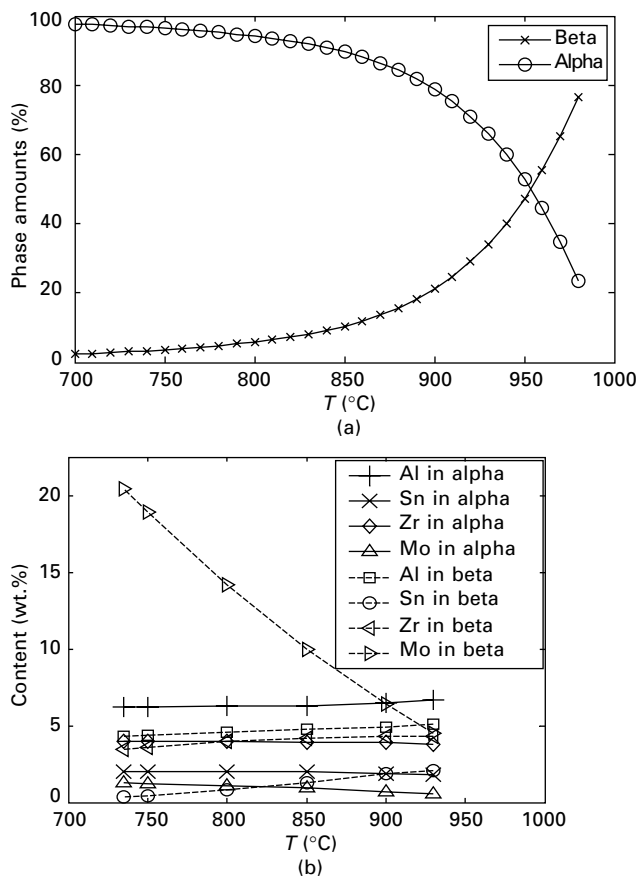
The calculations of the equilibrium concentrations of the alloying elements in the α and the β phases for this alloy suggest that the β to α transformation



5.7 Calculated equilibria versus temperature in the Ti-6Al-4V alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of aluminium and vanadium in the α and the β phases. The calculations are for composition of Al = 6 wt.%; V = 4 wt.%; Fe = 0.2 wt.%; O = 0.15 wt.%; N = 0.03 wt.%; and C = 0.01 wt.%.

at cooling is in conditions of diffusional redistribution and enrichment of molybdenum in the β phase (Fig. 5.2b).

The Ti-6Al-2Sn-4Zr-6Mo alloy is similar to the Ti-6Al-2Sn-4Zr-2Mo alloy but with a higher amount of molybdenum, and is classified as an $\alpha + \beta$ alloy. The thermodynamics of the two alloys is similar.

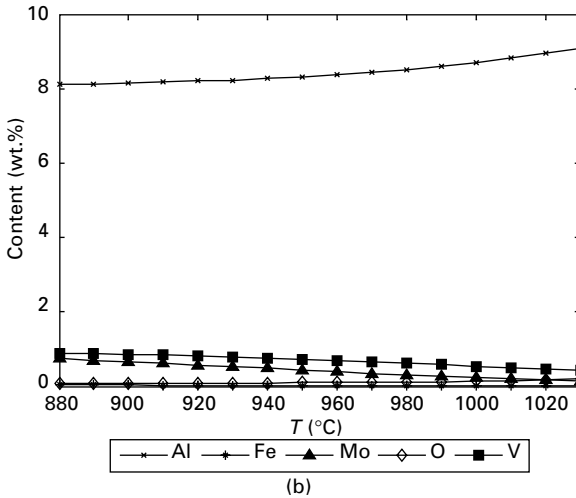
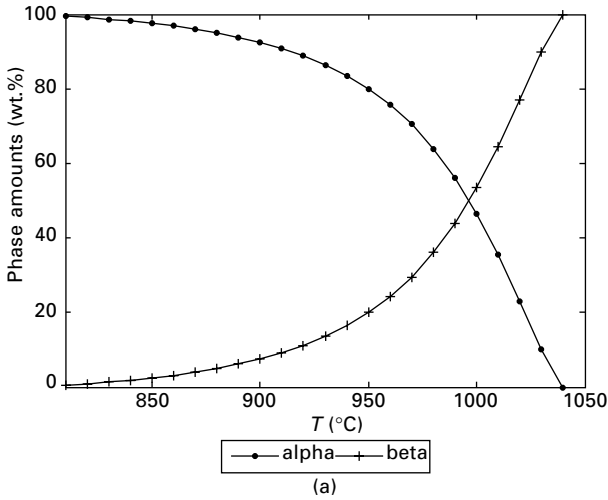


5.2 Calculated equilibria versus temperature in the Ti-6Al-2Sn-4Zr-2Mo alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of the alloying elements in the α and the β phases.

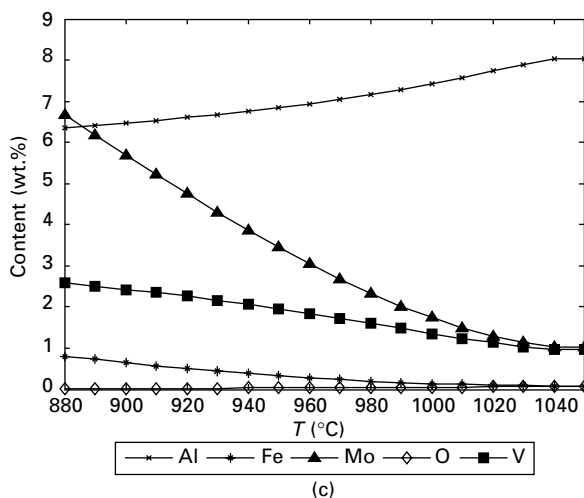
5.2.3 Ti-8Al-1Mo-1V (Ti 8-1-1)

The Ti-8Al-1Mo-1V alloy, similarly to Ti-6Al-2Sn-4Zr-2Mo, is classified as a near- α alloy and should have similar phase compositions as functions of the temperature. For this alloy, again, the tendency is that the amount of the α phase at lower temperature approaches 100% (Fig. 5.3a). The α phase is stable to higher temperatures as compared to both Ti 6-4 and Ti 6-2-4-2 alloys. The phase composition of 50% α + 50% β is at 995 °C and the β -transus temperature is 1040 °C, which is in good agreement with the experimentally measured one. Note should be taken that the β -transus temperature depends significantly on the oxygen content. The influence of the oxygen content on the phase equilibria is described in Section 5.2.9.

The equilibrium chemical compositions of the α and the β phases as functions of the temperature for this alloy, shown in Fig. 5.3b and c respectively, suggest that the β phase becomes enriched with molybdenum at lower temperatures (Fig. 5.3c), as the α phase forms. A similar tendency for enrichment but to a lesser extent can be seen for the vanadium content. This result is not surprising as both molybdenum and vanadium are β -stabilising



5.3 Calculated equilibria versus temperature in the Ti-8Al-1Mo-1V alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of the alloying elements in the α phase; (c) equilibrium concentrations of the alloying elements in the β phase.



5.3 Continued

elements. In this alloy, on slow cooling, the β to α phase transformation will be controlled by the kinetics of diffusional redistribution of molybdenum and vanadium between the α and the β phases.

The above four alloys, Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-2Sn-4Zr-6Mo, and Ti-8Al-1Mo-1V, are among the most widely used near- α and $\alpha + \beta$ titanium alloys. In what follows, we shall show thermodynamic calculations for other alloys from the same classes, as well as for some metastable β alloys.

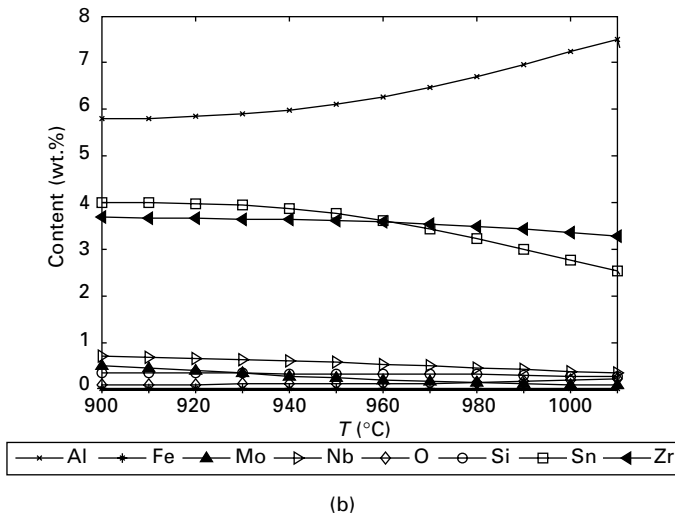
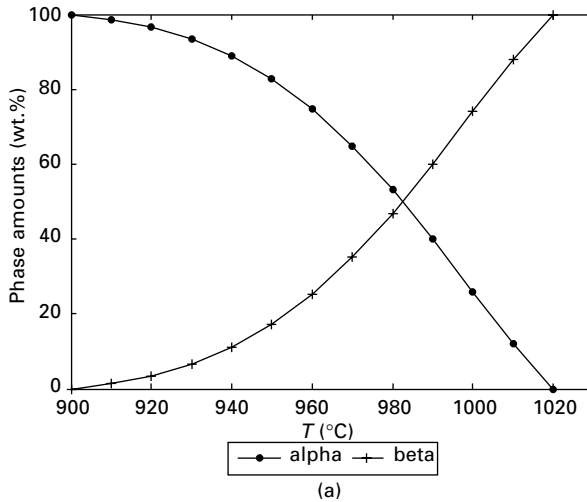
5.2.4 Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si (IMI 834)

IMI 834 is a newer near- α titanium alloy, designed to work at high temperature with high strength and good fatigue resistance. The thermodynamic equilibria show that this alloy lies between the Ti-6Al-2Sn-4Zr-2Mo and the Ti-8Al-1Mo-1V alloys in terms of α/β ratios at different temperatures. The amount of the α phase at lower temperature approaches 100%, the phase composition of 50% α + 50% β is at about 985 °C and the β -transus temperature is 1020 °C (Fig. 5.4a).

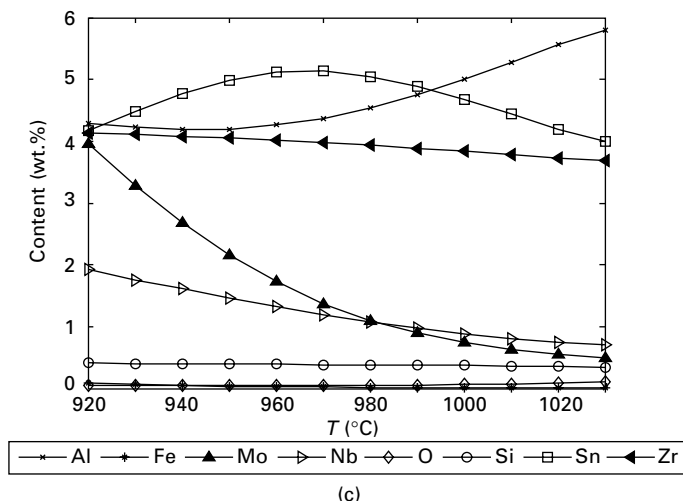
The equilibrium concentrations of the alloying elements, shown in Fig. 5.4b and c for the α and the β phases, respectively, suggest that the diffusional β to α phase transformation at cooling in IMI 834 alloy is controlled by redistribution of molybdenum and niobium between α and β phases toward enrichment of the β phase with these two β -stabilising elements at low temperature.

5.2.5 Ti-6Al-7Nb (IMI 367)

This alloy, classified as $\alpha + \beta$, is also relatively new, and not well studied yet. It was initially designed as a high-strength titanium alloy with biocompatibility for surgical implants. In terms of the phase composition, i.e. α/β ratio, as a function of the temperature, this alloy is similar to Ti-6Al-



5.4 Calculated equilibria versus temperature in the Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si (IMI 834) alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of the alloying elements in the α phase; (c) equilibrium concentrations of the alloying elements in the β phase.



5.4 Continued

4V (Fig. 5.5). At room temperature, there is a small equilibrium amount of the β phase remaining. The 50% α + 50% β phase composition is at 915 °C and the β -transus temperature is 1010 °C.

The equilibrium concentrations of the alloying elements in the α and the β phases for this alloy suggest that the β to α transformation on cooling is in conditions of diffusional redistribution and enrichment of niobium in the β phase (Fig. 5.5c).

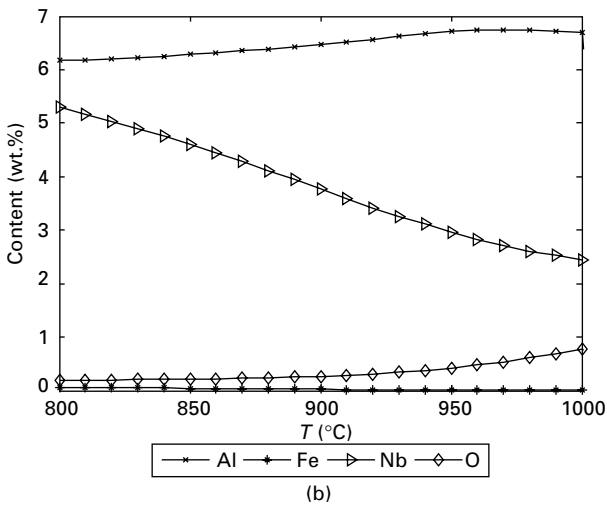
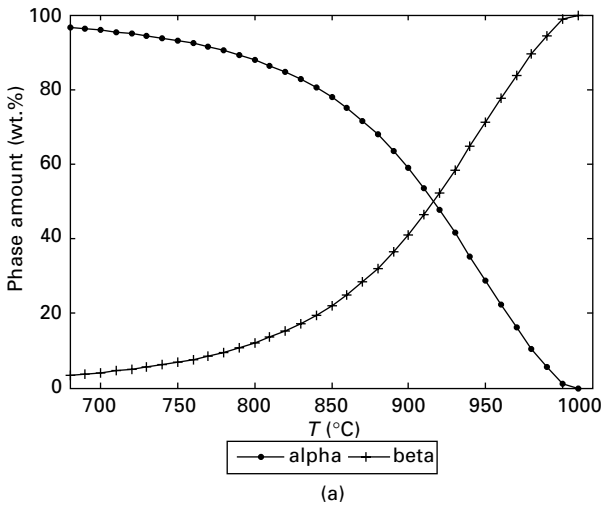
5.2.6 Ti-10V-2Fe-3Al (Ti 10-2-3)

Ti-10V-2Fe-3Al is one of the most popular near- β (or metastable β) titanium alloys. This alloy is capable of attaining a wide variety of strength levels depending on the heat treatment. There is still 15–20% of β phase remaining at low temperatures, below 400 °C, according to the thermodynamic equilibria for this alloy as functions of the temperature, presented in Fig. 5.6. The β -transus temperature is 790 °C, identical to the experimentally measured value. The equilibrium phase compositions for this alloy also show that the β to α transformation at cooling should be controlled by diffusional redistribution and enrichment of the β phase mainly with vanadium and to a lower degree with iron, both β -stabilising elements (Fig. 5.6c).

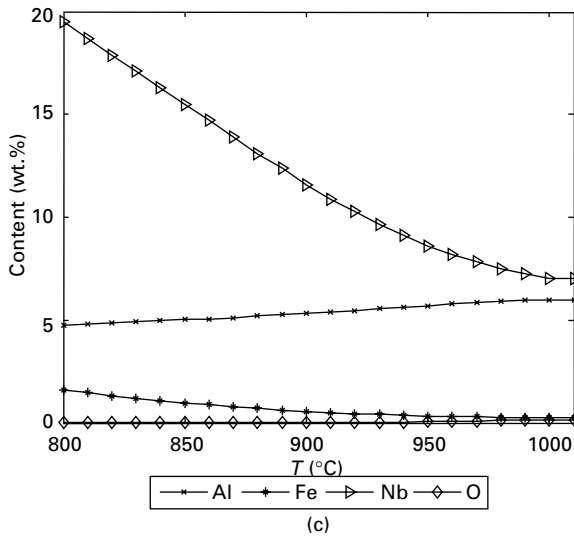
5.2.7 TIMETAL β 21s

This alloy is a metastable β alloy with high-strength. The phase equilibria for the β 21s alloy, shown in Fig. 5.7, are typical for near- β alloys, with

remaining amount of the β phase at room temperature, and a relatively low β -transus temperature. The temperature at which the phase composition is 50% α + 50% β is in the range of 650–660 °C, similar to that of the Ti 10-2-3 alloy.



5.5 Calculated equilibria versus temperature in the Ti-6Al-7Nb (IMI 367) alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of the alloying elements in the α phase; (c) equilibrium concentrations of the alloying elements in the β phase.



5.5 Continued

5.2.8 Summary of equilibrium calculations

The equilibrium amount of β phase at room temperature is different for the different alloys. For the Ti-6Al-2Sn-4Zr-2Mo, the Ti-8Al-1Mo-1V and IMI 834 alloys, the phase composition at room temperature approaches 100% α phase. For the Ti-6Al-4V and IMI 367, there is a small amount of remaining β phase at room temperature, and for the Ti-10V-2Fe-3Al and the β 21s alloys, there are higher amounts of remaining β phase. The β -transus temperature for the different alloys decreases in the order of Ti 8-1-1, IMI 834, Ti 6-2-4-2, IMI 367, Ti 6-4, β 21s, Ti 10-2-3.

These modelling data are consistent with the positions of these alloys in the schematic pseudo binary phase diagram of titanium alloys and their molybdenum and aluminium equivalents (Table 5.1).

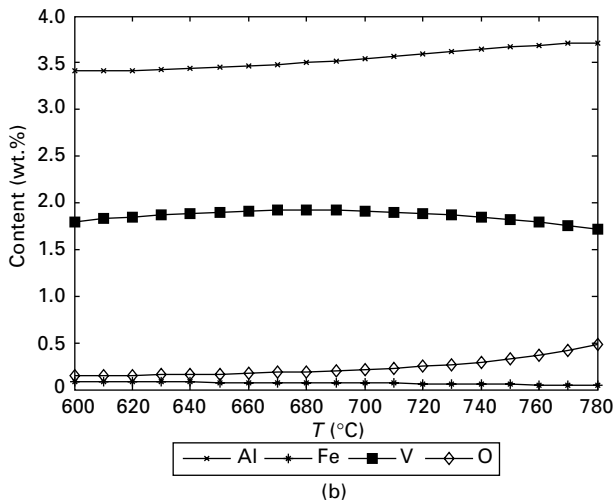
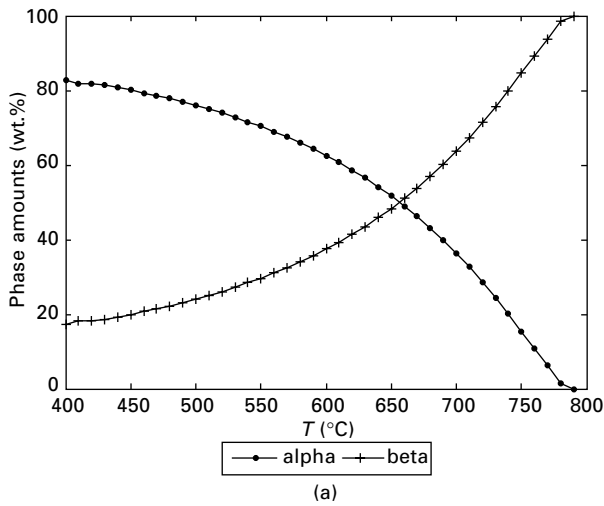
The equilibrium amounts of α and β phases in different titanium alloys as functions of the temperature can be used to derive unknown parameters for a simulation model of the microstructure evolution during the course of the β to α phase transformation, particularly diffusional growth of the α phase Widmanstätten plates. This will be illustrated in the next few chapters.

5.2.9 Influence of oxygen

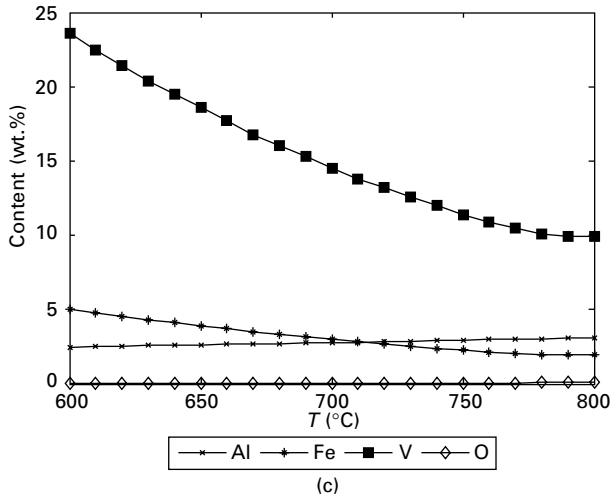
In this section, we will analyse the effect of oxygen on the phase equilibria in titanium alloys. Thermodynamic calculations are performed for oxygen contents of 0, 0.2, 0.4, ..., 1.4 wt.%. The variation of β phase amounts with

oxygen content in the alloys is shown in Fig. 5.8. Figure 5.9 plots the variation of transformation temperatures with oxygen content.

Although the calculations from the database may not be accurate at high oxygen levels, as the database has not been validated above 0.3%, they are useful to determine the trend of increasing oxygen levels on the phase transformation. The general result is that increasing the oxygen content stabilises



5.6 Calculated equilibria versus temperature in the Ti-10V-2Fe-3Al alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of the alloying elements in the α phase; (c) equilibrium concentrations of the alloying elements in the β phase.



5.6 Continued

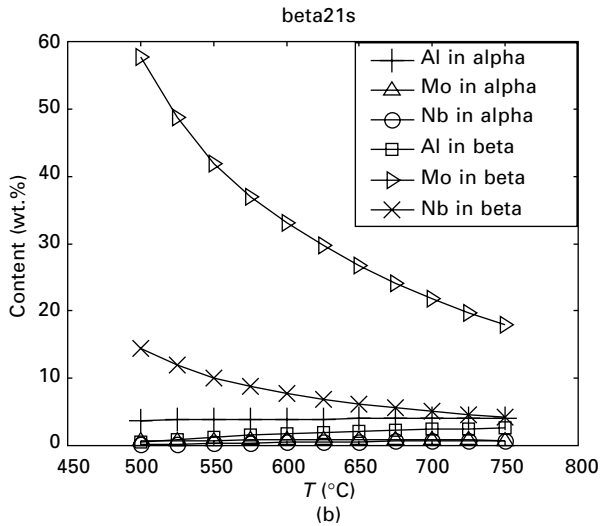
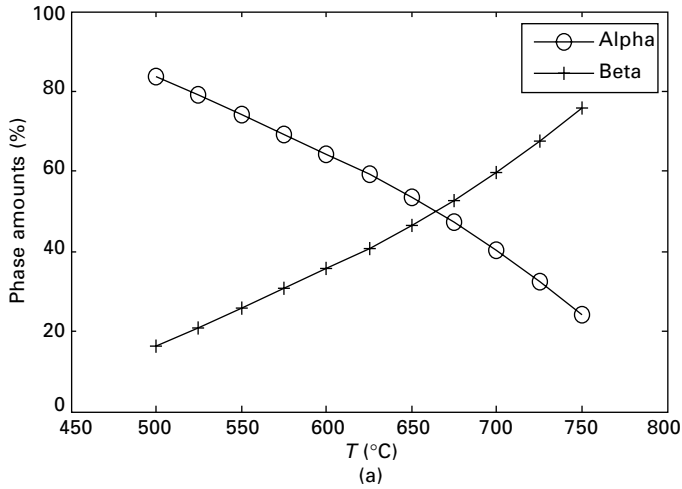
the α phase, increases the β -transus temperature and so reduces the amount of β phase present in the alloy at a given temperature. Also, the transformation temperature range is widened with increasing oxygen content.

5.2.10 Calculation of the driving force

Next, we use the thermodynamic modelling package to calculate the driving force for formation of α phase for different alloy compositions as a function of the temperature, reflecting the degree of undercooling below the β -transus temperature (Fig. 5.10). This is done by fixing the α phase as ‘dormant’ and calculating the driving force for its formation. The driving force at different thermodynamic conditions is further used to calculate the activation barrier for nucleation of α phase. This is necessary for computer simulations of the phase nucleation process in the model for the morphology of the β to α phase transformation in titanium alloys (see Chapter 8).

5.3 Titanium aluminides

A reasonable experimental work literature has now been built up on Ti–Al–x ternary phase diagrams. However, although these basic systems give insight to phase equilibrium in certain commonly used γ -TiAl based alloys, it is difficult to interpret phase relationships in multi-component alloys using just this information. Thermodynamic calculation offers a means by which phase equilibrium in multi-component alloys can be predicted. With the development of TiAl-DATA, a database for the calculation of stable and metastable phase



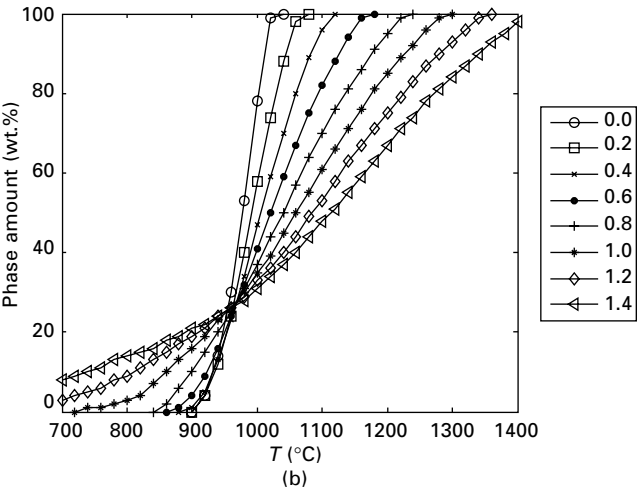
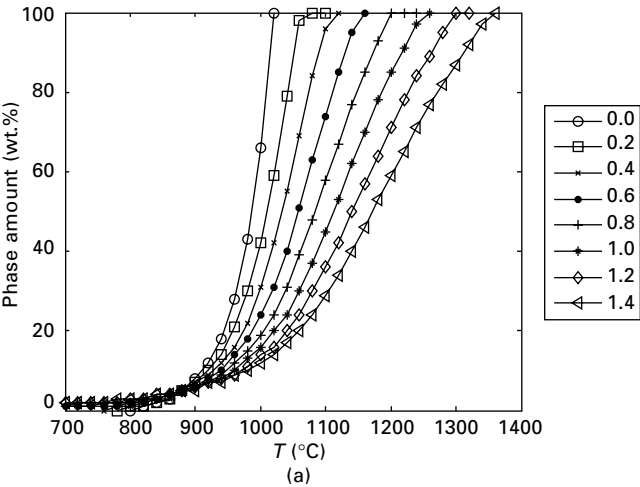
5.7 Calculated equilibria versus temperature in the $\beta 21s$ alloy: (a) equilibrium amounts of the α and the β phases; (b) equilibrium concentrations of the alloying elements in the α and the β phases. The calculations are performed for composition Al = 3.00, Mo = 14.12, Nb = 3.48, Si = 0.14, Fe = 0.32, C = 0.016, N = 0.024, and O = 0.15, all in wt.%.

equilibria in multi-component γ -TiAl based alloys (Section 5.3.1), it becomes possible to quantify the phase type and composition in multi-component γ -TiAl alloys.

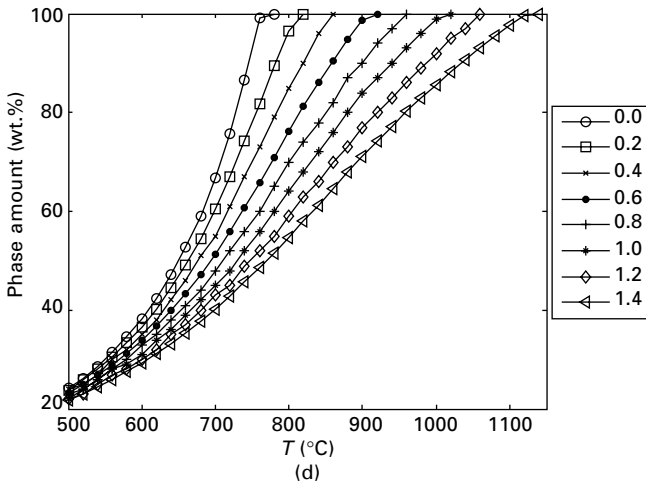
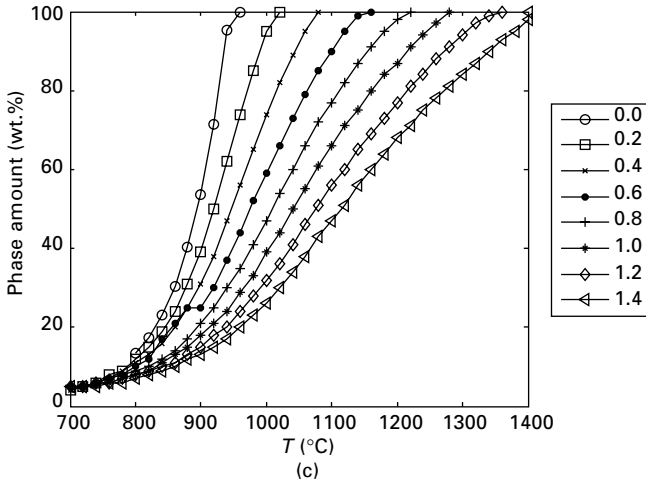
In this section, Thermo-Calc (TC) is used to quantify the phase constitution and element distribution in some γ -TiAl intermetallics with various additions

Table 5.1 Aluminium and molybdenum equivalent values of some titanium alloys

Alloy	Aluminium equivalent (wt.%)	Molybdenum equivalent (wt.%)
Ti 8-1-1	8	1.7
IMI 834	7.5	0.6
Ti 6-2-4-2	7.4	2
Ti 6-4	6	2.7
IMI 367	5.5	1.8
Ti 10-2-3	3	11.7
β21s	3	15



5.8 Calculated equilibrium β phase fractions versus temperature for different oxygen levels for (a) Ti 8-1-1, (b) IMI 834, (c) IMI 367, and (d) Ti 10-2-3 alloys.



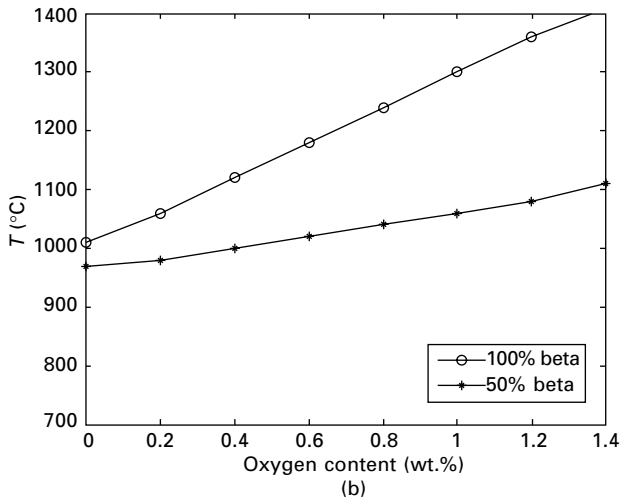
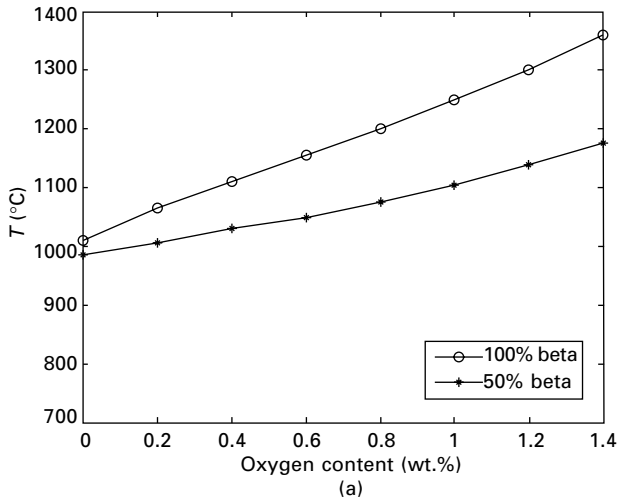
5.8 Continued

of alloying elements. Some calculated data are compared with experimental measurements by atom probe microanalysis.

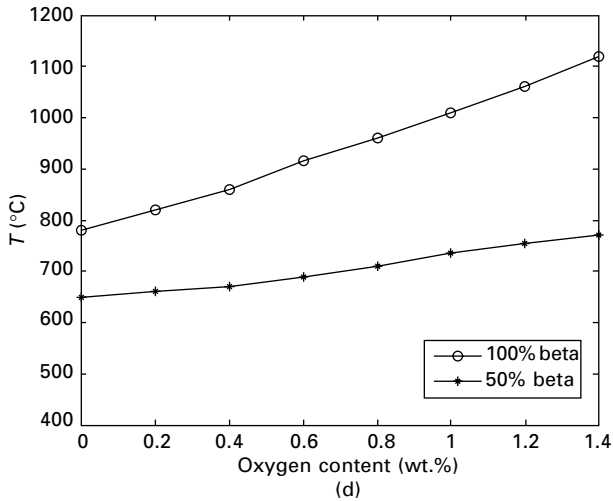
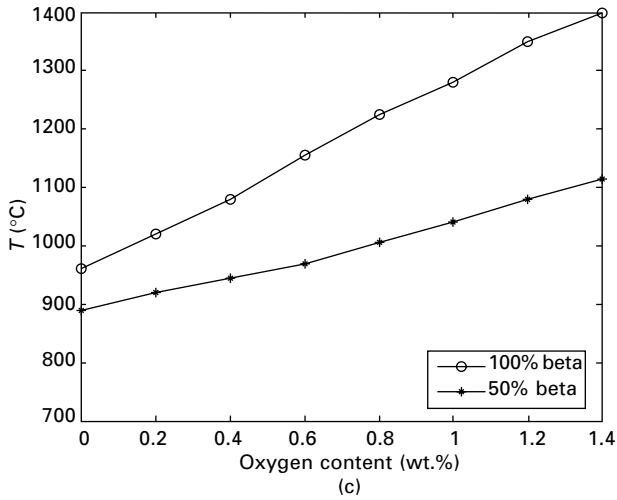
Previous attempts to study TiAl systems include the α -transus temperatures of various γ -TiAl based alloys, which are in good agreement with experimental data. Phase diagrams of the multi-component systems were also calculated. The following features calculations in binary and multi-component TiAl based systems. The concentration in this section is in at.%.

5.3.1 TiAl-DATA

TiAl-DATA has the following elements included: Ti, Al, Cr, Mn, Mo, Nb, Si, Ta, V, W, Zr, B, and O, with data for the following phases: liquid, γ -TiAl, α_2 -Ti₃Al, B2, bcc (β), hcp (α), Al₃(Ti,Mo,Nb,V...), Laves C14, Laves C15, σ -(Nb,Ta)₂Al, Ti₅Si₃, TiZrSi, TiB, TiB₂, and Al₂O₃. This database includes features which allow, uniquely, the inclusion of oxygen in the α_2 -Ti₃Al and γ -TiAl phases and the incorporation of new models to allow for the important



5.9 Variation of characteristic transformation temperatures with oxygen content for (a) Ti 8-1-1, (b) IMI 834, (c) IMI 367, and (d) Ti 10-2-3 alloys.

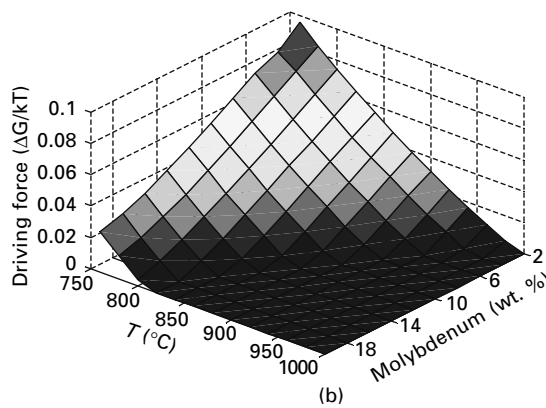
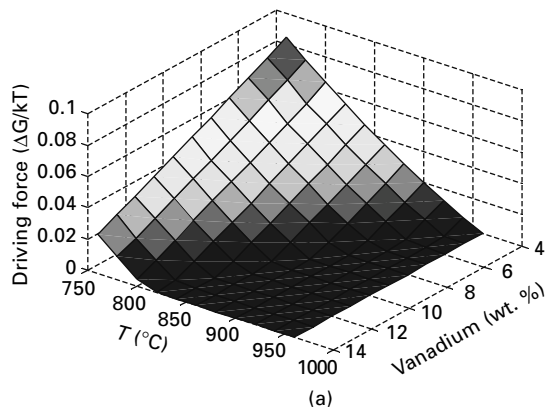


5.9 Continued

bcc to B2 transformation to be reproduced in multi-component alloys. The database has been constructed using a combination of published information, unique proprietary data and newly developed extrapolation methods. It was designed for use with γ -TiAl alloys but can, to a certain degree, also be used with super α_2 -Ti₃Al based alloys.

5.3.2 Ti-46Al

Since industrial multi-component alloys are based on the Ti–Al binary system, it is important to have a good understanding of phase transformations in



5.10 Calculated driving force for formation of α phase in (a) Ti 6-4 alloy at different temperatures and vanadium concentrations, and (b) Ti 6-2-4-2 alloy at different temperatures and molybdenum concentrations.

Table 5.2 Calculated phase constitution and element distribution in a Ti-46Al alloy at 1000 $^{\circ}C$

Phase	Ti	Al	%
γ	51.3	48.7	73.2
α_2	61.4	38.6	26.8

binary alloys. Table 5.2 gives the calculated values, from Thermo-Calc, of both the phase fraction and element partition.

5.3.3 Ti-48Al-2Cr-2Nb

The phase constitution and element distribution in this alloy are shown in Table 5.3. α_2 contains more chromium. TC calculation also shows that the

Table 5.3 Calculated phase constitution and element distribution in a Ti-48Al-2Cr-2Nb alloy at 1000°C

Phase	Ti	Al	Cr	Nb	Mol.%
γ	47.8	48.2	2.0	2.0	98.0
α_2	57.8	37.8	2.9	1.5	2.0

Table 5.4 Calculated phase constitution and element distribution in a Ti-48Al-2Cr-0.175O alloy at 1000°C

Phase	Ti	Al	Cr	O	Mol.%
γ	48.9	49.1	2.0	0.06	91.7
α_2	60.2	36.1	2.2	1.5	8.3

Table 5.5 Calculated phase constitution and element distribution in a Ti-47Al-2Cr-1Nb-1V alloy at 1000°C (with data after 216 hours at 800 °C from atom probe measurement in parentheses)

Phase	Ti	Al	Cr	Nb	V	Mol.%
γ	47.3 (49.8)	48.7 (45.3)	0.9 (1.0)	2.1 (3.0)	1.0 (0.8)	86.5
α_2	60.0	35.9	1.5	1.4	1.2	13.5

B2 phase seems to be more stable than the α_2 phase, which implies that long-time ageing will eventually result in a mixture of γ and B2 phases.

5.3.4 Ti-48Al-2Cr-0.175O

The influence of oxygen on phase fraction and element distribution is studied. The composition of the studied alloy is Ti-48Al-2Cr-0.175O-0.055C. Carbon is neglected in the calculation, since it is not included in the TiAl database. The phase constitution and element distribution in this alloy are shown in Table 5.4.

5.3.5 Ti-47Al-2Cr-1Nb-1V

Precipitation and partition of alloying elements in a Ti-47Al-2Cr-1Nb-1V alloy were investigated using a position sensitive atom probe (Qin *et al.*, 2000). The alloy was held at 800 °C for 216 hours. The phase identity, fraction and element distribution in different phases are listed in Table 5.5, where experimental data are also given. Only the composition of the γ phase was measured.

5.3.6 Ti-47Al-2Cr-1.8Nb-0.2W-0.15B

The TC calculated data at 900 °C are shown in Table 5.6. The majority of boron is in a variety of borides such as TiB₂, TiB, and Ti₂B. Due to a limitation of the database, the partition of boron in α_2 and γ phases is not predicted. The boride from the TC calculation is of the form of TiB₂. TiB and Ti₂B may be phases formed before the equilibrium is reached. TC calculation also indicates the existence of the B2 phase at this temperature, which is enriched in chromium, niobium and tungsten. One may argue that these elements may segregate at interface boundaries. However, only tungsten was found to segregate to inter-phase boundaries. Experimental measurement implies the existence of a chromium-rich phase.

The phase identity, fraction and element partition of the alloy after ageing at 800 °C are listed in Table 5.6. Apart from the experimentally observed α_2 and γ phases and the boride, TC calculation predicts the existence of a Laves phase. This phase is enriched in chromium and tungsten. Its existence can explain why the amounts of chromium in both α_2 and γ phases are lower than the nominal concentration. Indeed, a Ti(Cr,Al)₂ Laves phase is observed in a similar alloy system (see next section).

5.3.7 Ti-47Al-2Cr-1Nb-0.8Ta-0.2W-0.15B

TC calculation gives B2 at 900 °C, and Laves phase at 800 °C (Table 5.7). The former was not observed through atom probe. However, the latter phase was found and identified as Ti(Cr,Al)₂. Calculation shows that Ta partitions to the α_2 phase.

Table 5.6 Calculated phase constitution and element distribution in a Ti-47Al-2Cr-1.8Nb-0.2W-0.15B alloy

Temperature (°C)	Phase	Ti	Al	Cr	Nb	W	B	Mol.%
900	γ	48.1	48.4	1.6	1.8	0.14	0	88.9
	α_2	59.1	37.0	2.5	1.3	0.19	0	7.4
	B2	48.0	36.2	11.5	2.5	1.84	0	3.5
	TiB ₂	33.3	0	0	0	0	66.7	0.2
800	γ	48.4	48.6	1.0	1.9	0.19	0	89.5
	α_2	60.7	36.1	1.6	1.3	0.28	0	7.6
	Laves (Ti(Cr, Al) ₂)	32.0	29.0	37.4	1.2	0.4	0	2.7
	TiB ₂	33.3	0	0	0	0	66.7	0.23

Table 5.7 Calculated phase constitution and element distribution in a Ti-47Al-2Cr-1Nb-0.8Ta-0.2W-0.15B alloy

Temperature (°C)	Phase	Ti	Al	Cr	Nb	W	Ta	B	Mol.%
900	γ	47.8	48.7	1.6	1.0	0.13	0.7	0	86.2
	α_2	58.4	37.1	2.4	0.7	0.19	1.3	0	10.1
	B2	47.6	36.5	11.0	1.4	1.8	1.7	0	3.5
	TiB ₂	33.3	0	0	0	0	0	66.7	0.22
800	γ	48.1	48.9	1.0	1.0	0.19	0.75	0	87.1
	α_2	59.8	36.2	1.6	0.69	0.28	1.5	0	10.1
	Laves (Ti(Cr, Al) ₂)	32.4	29.2	37.3	0.68	0.41	0	0	2.6
	TiB ₂	33.3	0	0	0	0	0	66.7	0.23

5.3.8 Summary

Thermo-Calc calculation can help identify the existence of some phases which are not readily observed experimentally, such as B2 or Ti(Cr,Al)₂ in some titanium aluminides. It can be used as a guide in alloy design of the γ -TiAl based alloys.

5.4 References

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The Johnson–Mehl–Avrami method: isothermal transformation kinetics

Abstract: This chapter is concerned with the thermodynamics and kinetics of metastable β phase decomposition under conditions of isothermal exposure in a wide temperature range in different types of titanium alloys. Experimental data are from *in situ* resistivity techniques, optical microscopy, and X-ray diffraction analysis. Two predominant mechanisms of α precipitation are discussed: heterogeneous nucleation and growth on β grain boundaries at $\alpha + \beta$ temperatures close to the β -transus, and homogeneous transformation within β grains at lower temperatures. The kinetics of β to α transformation are modelled in the framework of the Johnson–Mehl–Avrami theory.

Key words: kinetics, resistivity, metallography, high temperature alloys, X-ray diffraction.

6.1 Introduction

The mechanical properties of titanium alloys are very sensitive to the microstructure and depend on the characteristics of it (Boyer *et al.*, 1994). It is important to know the thermodynamics and kinetics of the phase transformation, which would allow the optimisation of the processing parameters (temperature, time, cooling rate) to achieve the desired microstructure.

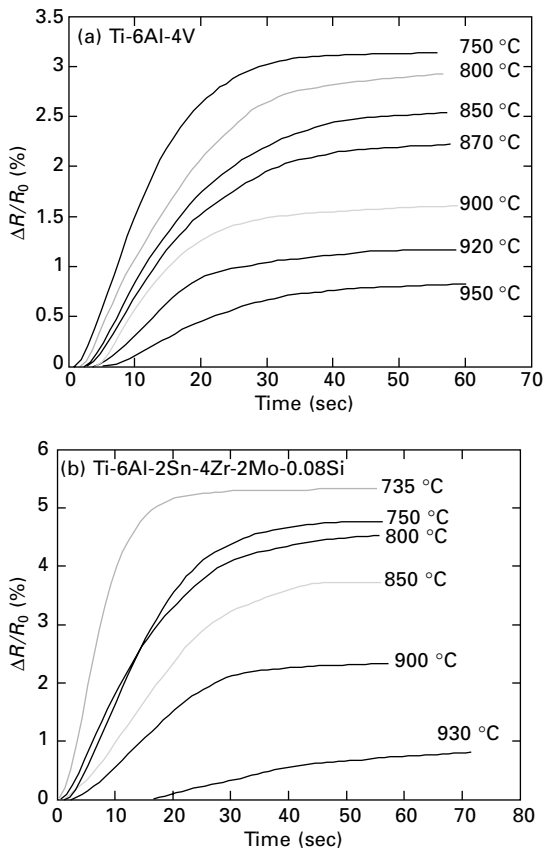
The thermodynamics of the phase equilibria in titanium alloys is generally well-studied and known. Most of the binary and ternary titanium phase equilibrium diagrams are available (Boyer *et al.*, 1994). However, in the past there was no comprehensive knowledge on the kinetics of the phase transformations in the variety of the titanium alloys under different time–temperature regimes. Despite large numbers of papers dedicated to this problem, the data available were incomplete. There was limited work on the kinetics and physical modelling of time–temperature–transformation (TTT) diagrams for titanium alloys based on the Johnson–Mehl–Avrami (JMA) theory. Outside titanium, models for the kinetics of phase transformations taking place in different alloys at different time–temperature conditions (Filip and Mazanec, 2001; Janlewing and Koster, 2001; Kempen *et al.*, 2002; Mittemeijer and Sommer, 2002; Starink, 2001; Suñol *et al.*, 2002) are largely related with the JMA theory.

In this chapter, we present models for the kinetics of the β to $\alpha + \beta$ phase transformation, i.e. β phase decomposition, in the commercial $\alpha + \beta$ titanium alloy Ti-6Al-4V, near- α (also called pseudo α) titanium alloys Ti-6Al-2Sn-4Zr-2Mo-0.08Si and Ti-8Al-1Mo-1V, and β 21s metastable β titanium alloy

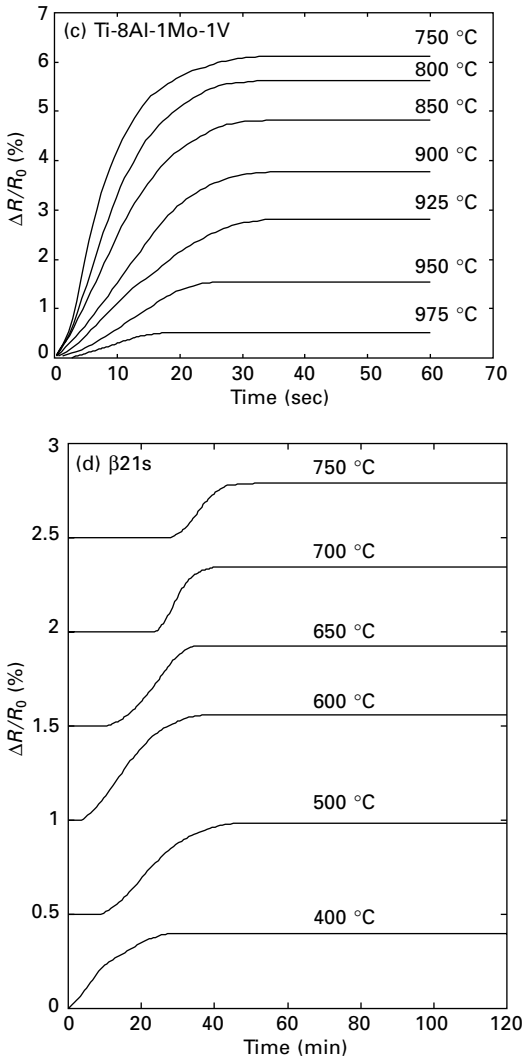
under isothermal conditions. An *in-situ* electrical resistivity technique is introduced to experimentally study the course of the transformation. Experimental procedures are described in original research papers (Malinov *et al.*, 2001, 2002, 2003; Markovsky *et al.*, 2004). The kinetics are traced within the theoretical frame of the JMA theory.

6.2 Resistivity experiments

Following experiments, sets of curves showing the relative increase of the resistivity during isothermal exposure ($\Delta R/R_0$) versus time for different temperatures can be recorded. Typical resistivity curves are shown in Fig. 6.1. Generally, for all these alloys, there is increase of resistometric signal



6.1 Resistivity data at different temperatures of isothermal exposure (a) Ti-6Al-4V; (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si; (c) Ti-8Al-1Mo-1V; (d) β 21s. For clarity, the resistivity curves are shifted with respect to each other along the vertical axis.



6.1 Continued

with lowering of temperature. Two factors may have influence on the resistivity: (i) different amounts of the α and the β fractions, e.g. the increase of the α fraction, and (ii) change of the compositions of the α and the β phases, e.g. the enrichment of the β phase with vanadium in the case of Ti-6Al-4V. In order to separate the above two effects, calibration curves are needed. The results from the optical microscopy quantitative study of samples quenched after heating to different temperatures for different times can be used to build the calibration curves of the relative resistance ($\Delta R/R_0$) versus the

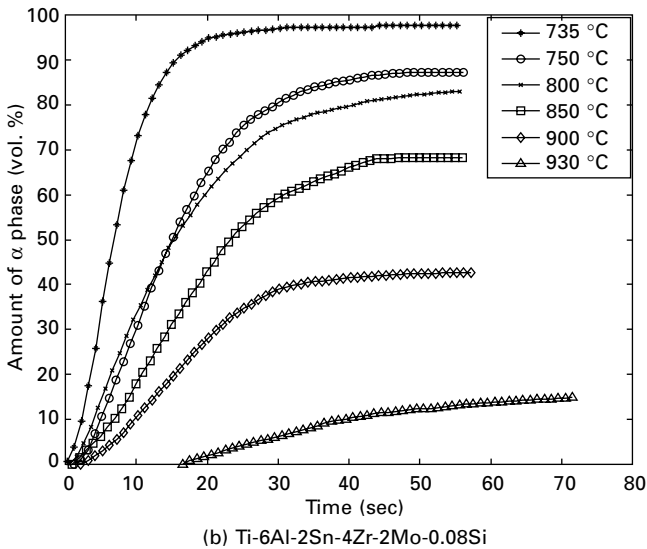
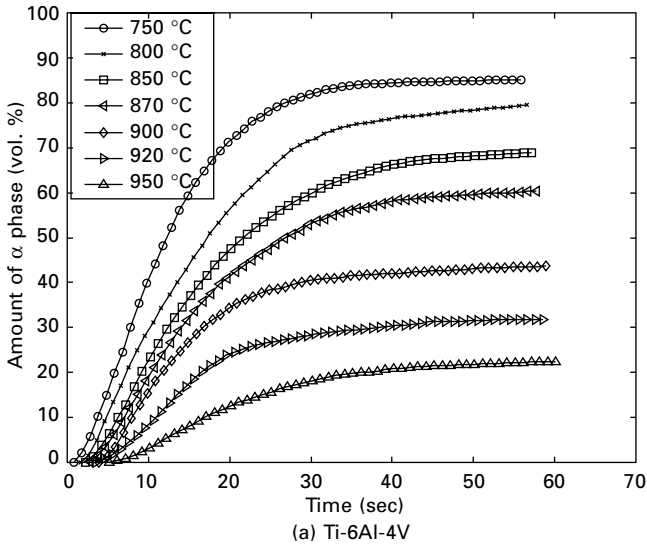
amount of precipitated α phase (%) for each alloy. Such calibration curves are necessary for converting resistivity data into α phase fraction. For Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-0.08Si, and Ti-8Al-1Mo-1V alloys, linear relations between $\Delta R/R_0$ and the amount of α are found. The linear relation is well proved and very clear when the degree of transformation varies between about 10 and 90%. The relative error of the calibration curve within this range is about 5%. For the very early stages (<10% degree of transformation) as well as for the final stages (>90% degree of transformation), there are some deviations from the linear relation and larger errors are possible.

The following remarks on the resistivity effect are also significant:

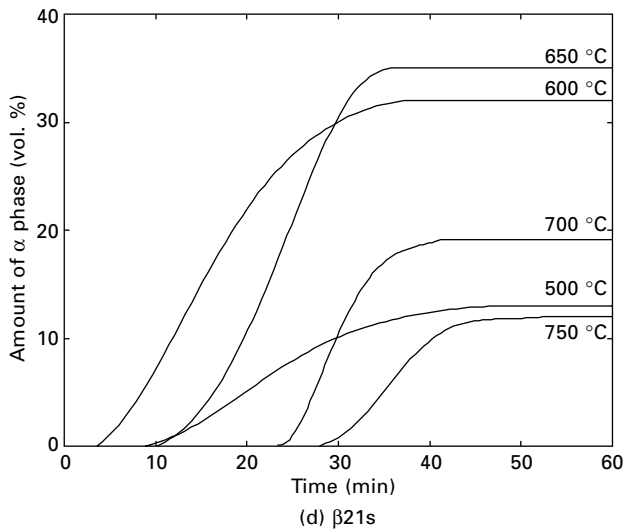
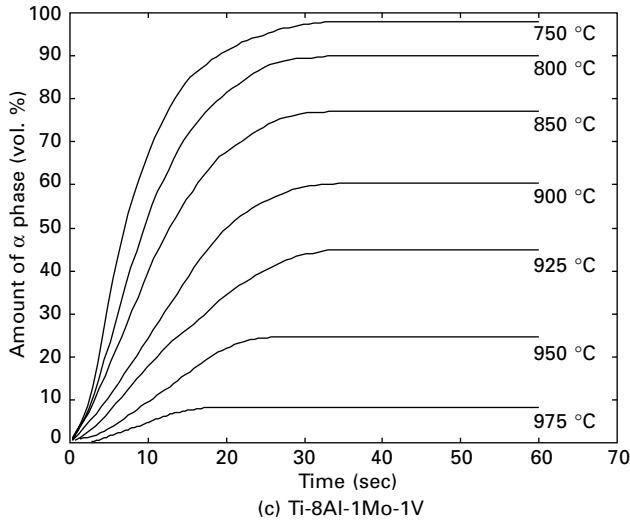
- Only primary α phase has influence on the resistivity effect, because just this phase is formed during the isothermal exposure. Secondary α phases, i.e. α' or α'' martensite, are formed as a result of residual β phase decomposition on subsequent quenching or further cooling, which allows one to evidently recognise and numerically evaluate the quantity of phases formed at different stages of β decomposition. Their influence on resistivity is not considered when studying the β phase decomposition under isothermal conditions only.
- The effects of α , α' and α'' phases on the resistivity differ mainly in the kinetics and the temperature ranges when these transformations take place on cooling. In the present case, resistivity is used for studying stable α phase formation under isothermal conditions.
- The different morphology of the α phase in the initial state, before heating to the single β -phase field, can influence the initial value of the specimen resistivity (R_0). However, there is no difference in the material's behaviour after solid solutioning at temperatures above β -transus, because alloys with any starting microstructure become the same, consisting of coarse grains of β phase.

Using the aforementioned calibration relations, the experimental resistivity curves can be recalculated or converted to give the amounts of α phase versus time, for different holding temperatures (Fig. 6.2a–c), which trace the kinetics of the β to $\alpha + \beta$ transformation for the Ti 6-4, the Ti 6-2-4-2 and the Ti 8-1-1 alloys. These data can be further used for modelling and simulations. At different temperatures of isothermal exposure, different final amounts of the α phase are obtained. For titanium alloys, the transformation of β to $\alpha + \beta$ is of monovariant type. At different temperatures, different amounts of α and β phases are in equilibrium. There are different equilibrium compositions of both phases at different temperatures. This observation will be discussed in more detail in Section 6.6.

The composition of the alloy β 21s corresponds to an aluminium equivalent, $[Al]_{eq}$, of 3 wt.%, and molybdenum equivalent, $[Mo]_{eq}$, of 15.8 wt.%. This composition determines the alloy as a metastable β titanium alloy (Boyer



6.2 Kinetics of the β to $\alpha + \beta$ transformation at different temperatures of isothermal exposure (a) Ti-6Al-4V; (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si; (c) Ti-8Al-1Mo-1V; (d) β 21s.



6.2 Continued

et al., 1994). Hence, initial homogeneous β structure tends to precipitate α phase upon isothermal exposure at temperatures in the $\alpha + \beta$ equilibrium range. The alloy has $\alpha + \beta$ phase composition in the condition normally supplied for commercial use. Before resistivity measurement, the samples should be heated up to the β homogenisation field, e.g. 1000 °C, and held for 30 minutes. In order to check the completeness of the β homogenisation, one can cool samples from this stage to room temperature. The results from synchrotron X-ray study have shown that the phase composition in both air

cooled and water quenched samples is homogeneous β phase, confirming that at this stage the initial $\alpha + \beta$ structure has transformed to β . After the β homogenisation, samples can be cooled rapidly to the chosen holding temperature and then isothermally held at this temperature when the resistometric signal is recorded. A set of curves of $\Delta R/R_0$ versus time for different temperatures of isothermal exposure can be recorded (Fig. 6.1d). These curves trace the course of the α phase precipitation from the metastable β phase at the temperatures studied. Some observations from the recorded resistivity signals are discussed below.

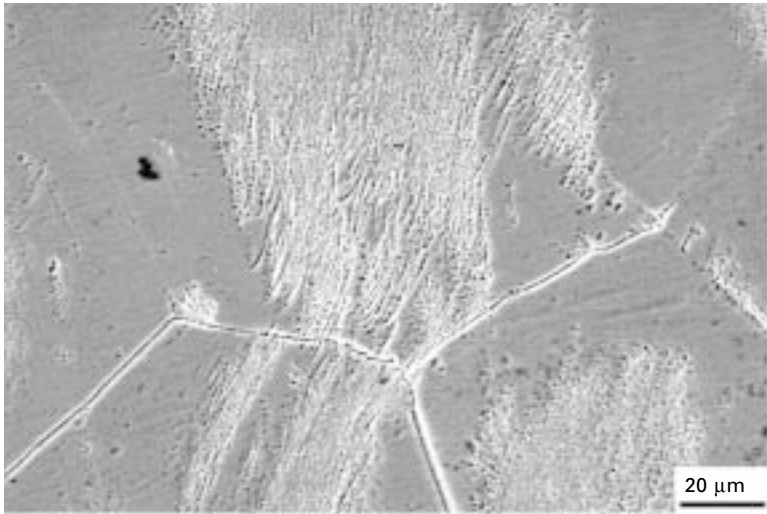
The resistivity curve at 400 °C is inconsistent with the results for the other temperatures. The signal shows immediate change of the resistivity from the very beginning of the isothermal exposure. The difference between the initial and the final values in $\Delta R/R_0$ is smaller as compared to the other temperatures. In addition, the curve shape is different. A possible reason for this difference is that, at this temperature, the transformation is not purely diffusional β to α transformation, but some precipitation of metastable phases, such as ω phase, may be involved. This temperature is not included in the further analysis.

Decomposition of the metastable β phase in the $\beta 21s$ alloy due to its higher content of β stabilising elements is considerably slower, including a pronounced incubation period (Fig. 6.1d). The longest incubation period (about 28 min) is at 750 °C. This decreases when the temperature is lower. The minimum value, i.e. the shortest, is for isothermal exposure at 600 °C. Further decrease of the temperature to 500 °C results in increase of the incubation time. These results indicate that the ‘nose’ point of the TTT diagram for this alloy should be around 600 °C. The resistivity curves at all temperatures tend to become horizontal after one hour isothermal exposure. This means that the transformation is either completed or the rate of the transformation is very slow and practically undetectable with the resistivity method used.

In order to recalculate and transform the resistivity curves to curves showing the amount of α phase versus time, we need to create calibration curves between the resistivity signal and the amount of the α phase. Samples quenched from different temperatures and after different times are studied by light microscopy (Fig. 6.3). Large deviations in the estimated amounts of the α phase are detected and the results from the metallography study are found to be too statistically unreliable to be used for the calibration purpose. The reason for this is the small amount and the fine microstructure of the α phase.

6.3 Metallography

The typical microstructures of Ti-6Al-2Sn-4Zr-2Mo-0.08Si and Ti-6Al-4V, and Ti-8Al-1Mo-1V alloys after isothermal exposure at different temperatures

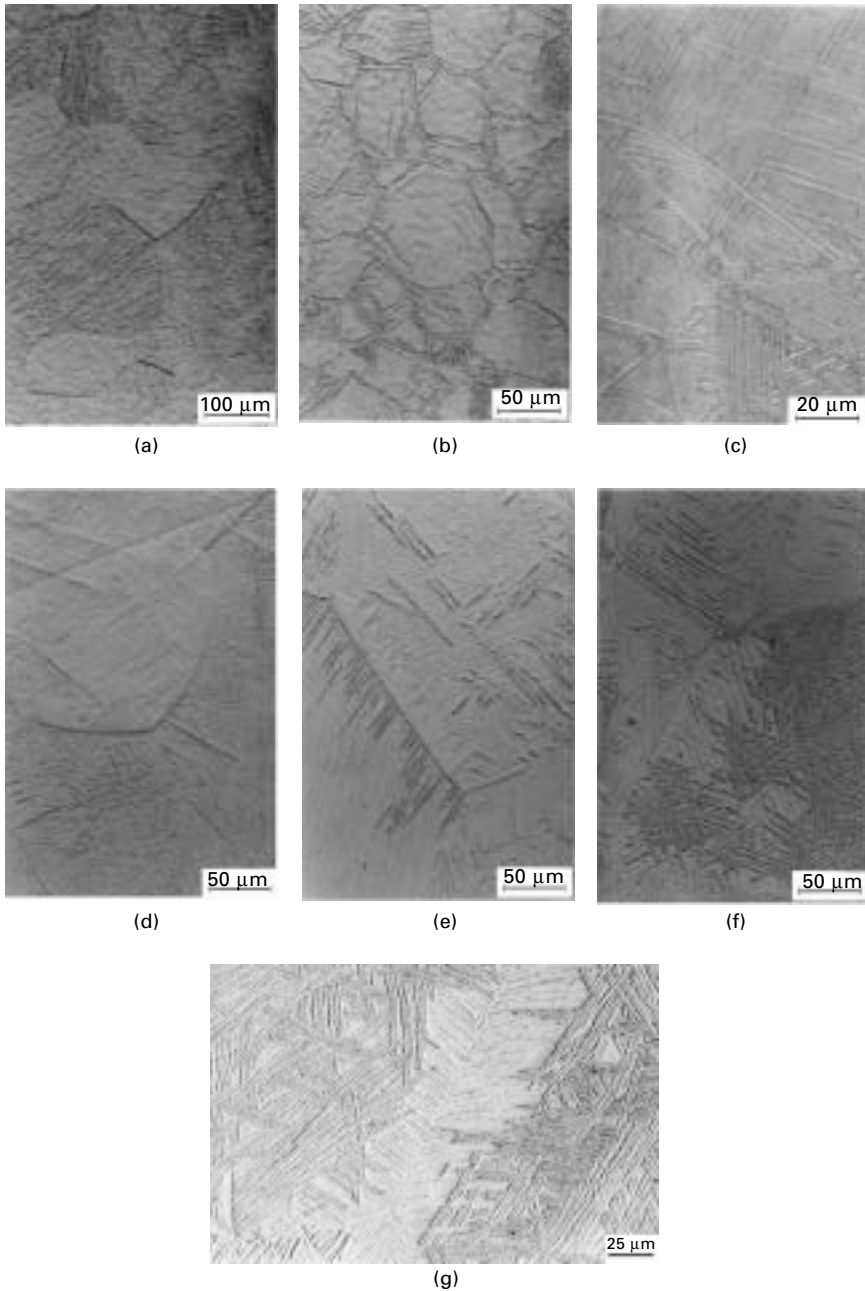


6.3 Microstructure of $\beta 21s$ alloy after isothermal exposure at 650 °C (dark field optical image).

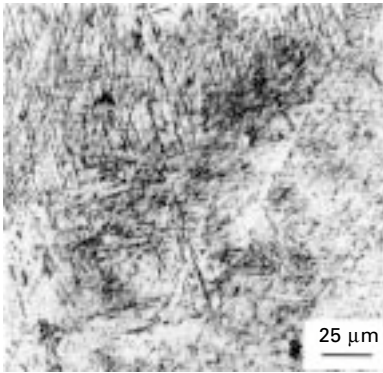
and subsequent quenching are presented in Figs. 6.4 and 6.5, respectively, illustrating distinct difference in morphology observed between primary and secondary α phases. First, it is necessary to point out that the α phase covering the β grain boundary is observed in all cases of isothermal exposure for both Ti-6Al-2Sn-4Zr-2Mo-0.08Si and Ti-6Al-4V alloys. This may be explained by the comparatively low (300 °C/s) cooling rate after β solution treatment. For the Ti 6-4 alloy, the critical cooling rate that depresses completely all diffusion processes of alloying element redistribution should be about 400 °C/s or higher. For the more diluted Ti 6-2-4-2 alloy, the critical cooling rate is even higher (≥ 500 °C/s). Hence, some diffusion processes may take place during the cooling at an insufficient rate from the β field to the temperature of isothermal exposure. These processes cause grain boundary α formation.

6.3.1 Ti 6-2-4-2 alloy

The as-quenched microstructure after isothermal exposure at 950 °C is characterised by the presence of a fine grain boundary α phase (Fig. 6.4a). The total amount of diffusionally grown α phase is about 8%. The remaining volume fraction is occupied by a martensitic phase, which is formed from the β phase on subsequent cooling. The matrix, martensite, microstructure is not homogeneous. This is due to the complex mechanism of the transformation, including partial diffusional redistribution of β alloying elements and diffusionless martensitic transformation. (Note that the cooling rate after



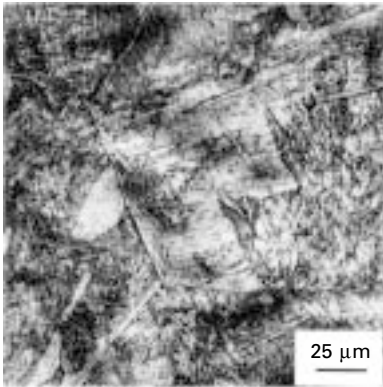
6.4 Microstructures of (a–c) Ti-6Al-2Sn-4Zr-2Mo-0.08Si and (d–g) Ti-6Al-4V alloys after different temperatures of isothermal exposure and subsequent quenching. (a) 950 °C; (b) 900 °C; (c) 850 °C; (d) 920 °C; (e) 870 °C; (f) and (g) 850 °C.



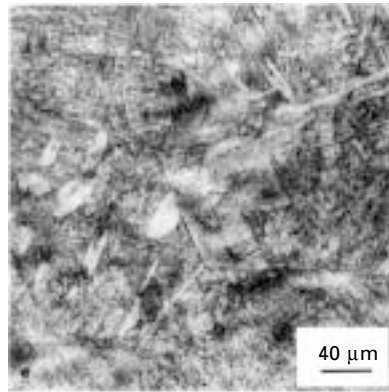
(a)



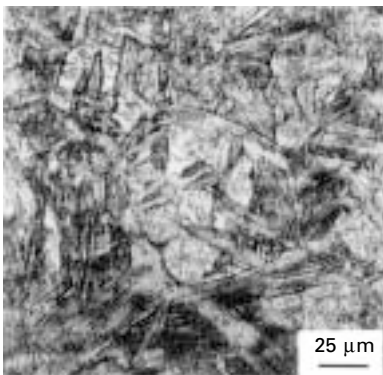
(b)



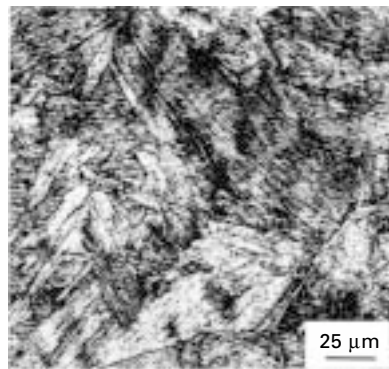
(c)



(d)



(e)



(f)

6.5 Microstructures of Ti-8Al-1Mo-1V alloy after different temperatures of isothermal exposure and subsequent quenching. (a) 925 °C; (b) 900 °C; (c) and (d) 850 °C; (e) 800 °C; (f) 750 °C.

isothermal exposure, 300 °C/s, is not high enough for pure martensitic transformation).

A decrease of the temperature of isothermal exposure down to 900 °C causes formation of a coarse α phase covering β grain boundaries. In addition, some amount of α phase has diffusionally nucleated and grown from the boundaries (Fig. 6.4b). The amount of the α phase is higher in small β grains as compared to in big ones. This observation may be associated with the influence of the grain boundary energy, which is proportional to the grain boundary curvature. The total amount of diffusionally formed α phase at 900 °C is 38%.

Lower temperatures of isothermal exposure lead to a complete change of the mechanism of α phase formation. In addition to the grain boundary α phase, formed on cooling from the β field to the temperature of isothermal exposure, an α phase nucleated and grown homogeneously inside the former β grains is observed (Fig. 6.4c). The total amounts of α phase are 69 and 80% for 850 and 800 °C, respectively. The main difference between specimens exposed at 850 and 800 °C is the different dispersion of the α lamellae – finer lamellae are attributed to lower temperatures. This may be explained by the higher contribution from the nucleation process in comparison to the growth when the temperature of isothermal exposure is lower. Nevertheless, in both cases, the morphology of the α phase allows one to suppose that it is formed with partial participation of diffusionless (shifting) processes.

6.3.2 Ti 6-4 alloy

In the specimen exposed at 950 °C and then quenched, a diffusionally formed α phase is found on some β grain boundaries, as a thin layer covering the boundaries. The volume fraction of the α phase is about 16%. After exposure at 920 °C (Fig. 6.4d), the morphology of the α phase, formed as a result of diffusional decomposition of the β phase, remains the same. Its volume fraction is slightly increased, to 20%. At 900 °C, a small portion of grain boundary α phase, as well as α plates diffusionally grown from them, are observed. The volume fraction of the α phase is about 38%.

At a lower temperature of 870 °C, the microstructure is changed principally. Some portions of the α phase nucleated and grown within the β grains appear, in addition to the grain boundary α phase (Fig. 6.4e). The volume fraction of the diffusional α phase is about 60%. A further decrease of the temperature down to 850 °C leads to an increase in the amount of homogeneously nucleated α phase within the former β grains (Fig. 6.4f and g). Some martensite is found in the regions close to the β grain boundaries. A decrease of the temperature down to 800 °C and, especially, to 750 °C causes further increase of the amount of diffusionally formed α phase, to 72 and 82%, respectively.

6.3.3 Ti 8-1-1 alloy

First, a very small amount, about 9%, of separate α phase crystals is found in the alloy exposed at 950 °C and then quenched. At 925 °C, the amount of the α phase increases to about 29%. In both cases, the α phase is observed as thin layers, covering β grain boundaries (Fig. 6.5a). Decreasing the temperature of isothermal holding, down to 900 °C, causes formation of coarser grain-boundary α phase and appearance of the first small portions of α crystals growing from this grain-boundary phase using it as a nucleating site (Fig. 6.5b). The total amount of the α phase at 900 °C is about 46%.

Further decrease of the holding temperature down to 850 °C leads to a change of the mechanism of the α phase formation. An α phase nucleated and grown homogeneously inside the former β grains is observed (Fig. 6.5c and d). A substantial increase in the total amount of the α phase (up to 70%) is detected. The grain-boundary α phase at 850 °C (Fig. 6.5c) is thinner as compared to the grain-boundary α phase at 900 °C (Fig. 6.5b). It is possible that the thin α layer covering the β grain boundary at 850 °C is formed on cooling from the β solution temperature to the temperature of isothermal exposure (note that the cooling rate was not high enough to depress completely the β phase decomposition).

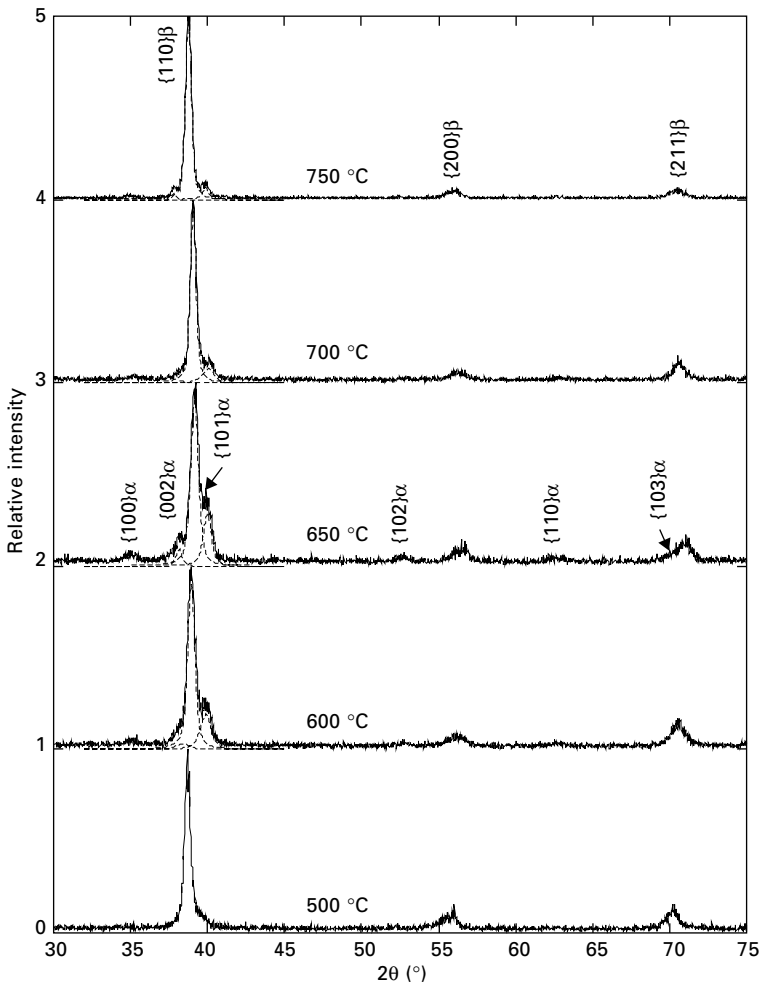
A decrease of the temperature down to 800 and 750 °C (Figs. 6.5e and f, respectively) causes further increase of the amount of α phase up to 88 and 98%, respectively. The mechanism of the α phase formation remains the same. The main part of the α phase is homogeneously formed within the former β grains as packets of lamellar α phase. Additionally, a small amount of α phase covering β grain boundary is observed which is probably precipitated on cooling from solid solutioning to the holding temperatures.

In summary, at temperatures of exposure above 900 °C, the predominant place for α precipitation is the β grain boundary, whereas at lower temperatures, most α lamellae precipitate rather homogeneously inside the β grains. Optical microscopy quantitative data are in good agreement with the contents of α phase calculated from resistivity work.

6.4 X-ray diffraction

X-ray diffraction is not usually used for quantitative study of α and $\alpha + \beta$ titanium alloys. The reason for this is that in these alloys a martensite transformation may take place and it is difficult to distinguish between the α and the α' (martensite) phases. In the $\beta 21s$ alloy, the martensite start temperature is below room temperature. Hence, mainly α and β phases in different ratios, depending on the processing and heat treatment conditions, exist. These two phases are easily detectable and distinguishable by X-ray diffraction. The equilibrium amount of the α phase should increase when the temperature is lower (see also Section 6.6).

After the resistivity experiments, $\beta 21$ s samples can be cooled to room temperature and studied by X-ray diffraction. The results from the samples after isothermal exposure for two hours at different temperatures are given in Fig. 6.6. The amount of the α phase can be calculated from the fitted diffraction patterns using the direct comparison method. In order to avoid error due to preferred orientation (crystallographic texture that usually is present in



6.6 X-ray diffraction patterns and profile fits (dotted lines) in the range of 30 to 75° 2θ ($\text{Cu K}\alpha$ radiation) of $\beta 21$ s after isothermal exposure at different temperatures for two hours. The intensities are given relative to the maximum, {110}β reflection. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

thermomechanically processed titanium alloys), the quantitative analysis should be based on the entire diffraction pattern instead of using single reflections. The principle of ‘averaging the integral intensities’ should be applied. All α and β reflections observed should be used.

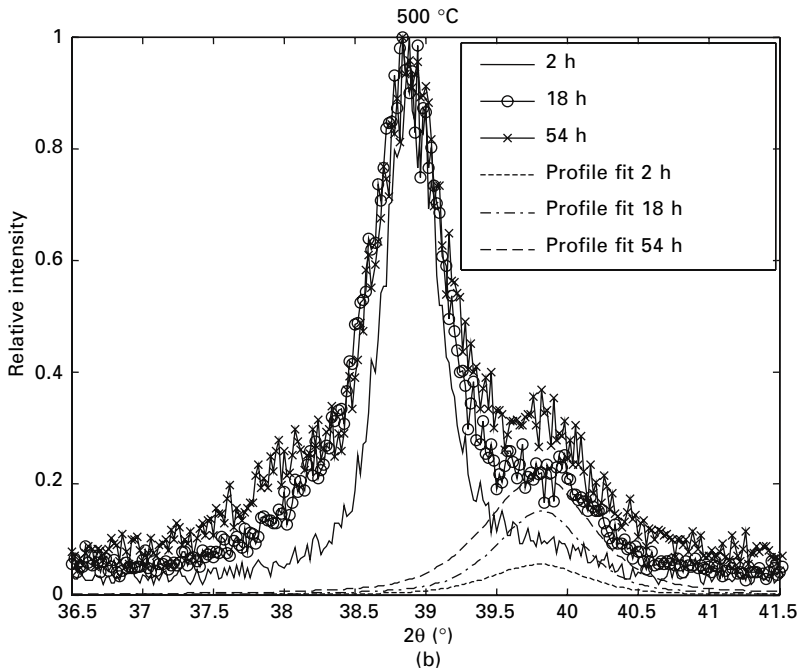
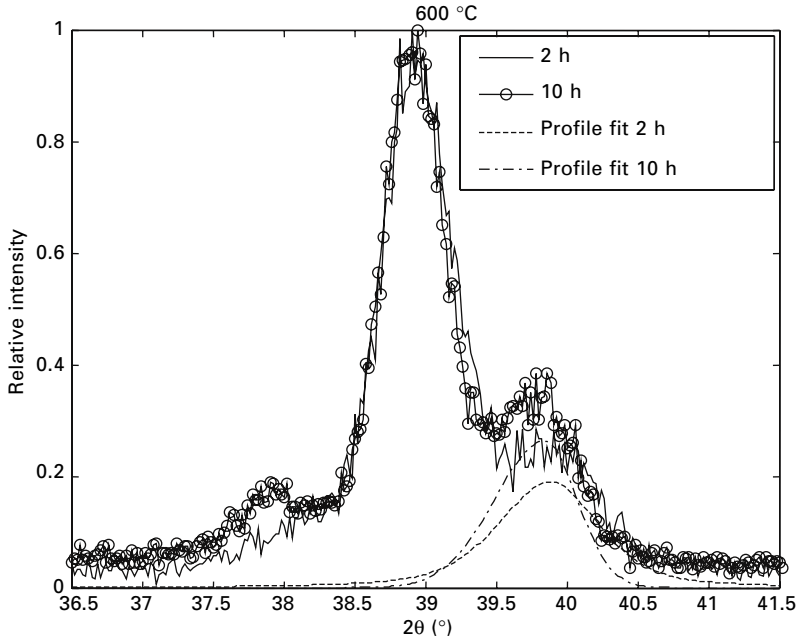
X-ray analysis of the alloy after different temperatures of isothermal exposure shows different quantities of the α phase. The total amount of the α phase precipitated after isothermal exposure at 750 °C is estimated at about 12%. Decreasing of the temperature of isothermal holding down to 700 and 650 °C results in an increase of the α phase fraction (see Fig. 6.6). The amounts of the α phase at 700 and 650 °C are 19 and 35%, respectively. Further decrease of the temperature of isothermal exposure down to 600 and 500 °C leads to decrease of the total amount of the α phase to 32 and 13%, respectively.

The increased total amount of the α phase when the temperature is decreased from 750 to 650 °C is in agreement with what is expected from the thermodynamics of this phase transformation. However, the lower amounts of the α phase after isothermal exposure at lower temperatures contradict the thermodynamic equilibria for titanium alloys. It is likely that, at lower temperatures (600 and 500 °C), the β to $\alpha + \beta$ transformation has slow kinetics, and phase equilibria are not reached during the two-hour exposure. In order to check this assumption, experiments involving additional prolonged ageing are necessary.

6.5 Additional ageing

In order to check the completeness of the phase transformation after the resistivity experiments at 650, 600 and 500 °C, the β 21s samples were reheated and held at the same temperatures for longer times. Additional ageing for two hours was applied to the sample after resistivity experiments at 650 °C. The diffraction patterns after resistivity and after the additional ageing were identical. The identical amounts of α and β phases before and after this additional ageing mean that the phase transformation was completed before the additional ageing and a phase equilibrium had been reached.

Additional ageing of 8 and 14 hours was applied for the sample at 600 °C (note that the total time of isothermal exposure was 10 and 16 hours, respectively). The diffraction pattern after additional ageing for 8 hours (10 hours in total) showed an increased amount of α phase (see Fig. 6.7a). The amount of the α phase was increased from 32% after the resistivity experiment to 36% after the additional ageing. The phase transformation at this temperature was incomplete after the resistivity experiments. A slow transformation process was still in progress upon additional ageing, but it was undetectable with the resistivity technique used. Further increase of the ageing time to 16 hours did not show any change in the diffraction pattern. So, the β to $\alpha + \beta$



6.7 X-ray diffraction patterns in the range of 36.5 to 41.5° 2θ and profile fits of the {101}α reflection for β₂₁s after isothermal exposure at (a) 600 and (b) 500 °C for different periods of time. The intensities are given relative to the maximum, {110}β reflection.

transformation at this temperature has completed at or before 10 hours of isothermal exposure.

After the resistivity experiments at 500 °C, the sample was re-heated and aged for additional times of 16, 40 and 52 hours (note that these correspond to total times of isothermal exposure of 18, 42 and 54 hours). The additional ageing at this temperature also resulted in increase of the amount of α phase (see Fig. 6.7b). The amount of α phase increased from 13% after the resistivity experiments for two hours to 25% after additional ageing for 16 hours (18 hours in total). The ageing time prolongation resulted in further increase of the amount of α phase to 33 and 40% after additional ageing for 40 and 52 hours (42 and 54 hours in total), respectively. At this temperature, the β to α + β phase transformation may still not have completed even after 52 hours additional ageing.

In addition, the X-ray diffraction patterns after exposure at different temperatures and times showed a tendency in the full width half maximum (FWHM) values of the α reflections. The FWHM values were higher when the temperature was lower, implying that the precipitated α phase at lower isothermal temperatures possesses a larger degree of inhomogeneity. On the other hand, the time prolongation resulted in decrease of the FWHM values, indicating α phase homogenisation. The change in FWHM could also be related to α grain or precipitate size, with large values indicating small sizes.

In summary, for the β alloy β 21s, more dependable data can be obtained using quantitative X-ray analysis, giving linear dependency between resistivity signal and α volume fraction. This can then be employed to convert resistivity data into curves for α phase amount versus time of isothermal exposure (Fig. 6.2d). At the same time, it is established that samples exposed at 500 and 600 °C do not reach equilibrium α + β condition after two hours resistivity experiments. Equilibrium is not reached at 500 °C even after 52 hours additional ageing.

6.6 Thermodynamic equilibria

From the fundamental theory of the phase transformations, when an alloy is held at a certain temperature for a long time it tends towards and possibly reaches a thermodynamic equilibrium. If this principle is applied here, it can be assumed that in the final stage, when the transformation has been completed, phase equilibria at the corresponding temperatures have been achieved. This means equilibrium amounts of α and β phases as well as equilibrium composition of both phases.

A Ti database which allows phase equilibria calculations to be performed for multi-component, conventional titanium alloys is available. The phase equilibria can be calculated for the compositions and the temperature range used. The calculations are carried out with Thermo-Calc software and using

the above-mentioned Ti database, for the actual alloy compositions, taking into account the Al, V, Mo, Nb, Si, Fe and O contents. The C, N and H contents are not taken into account in the calculations, except in the case of $\beta 21s$ when C and N are taken into account. The experimental (from the resistivity study) and calculated results are compared in Table 6.1 for Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si and Table 6.2 for Ti-8Al-1Mo-1V, respectively.

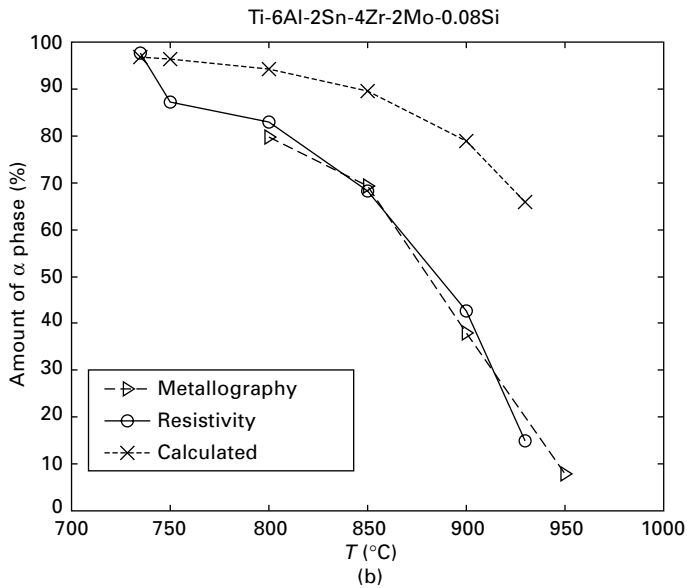
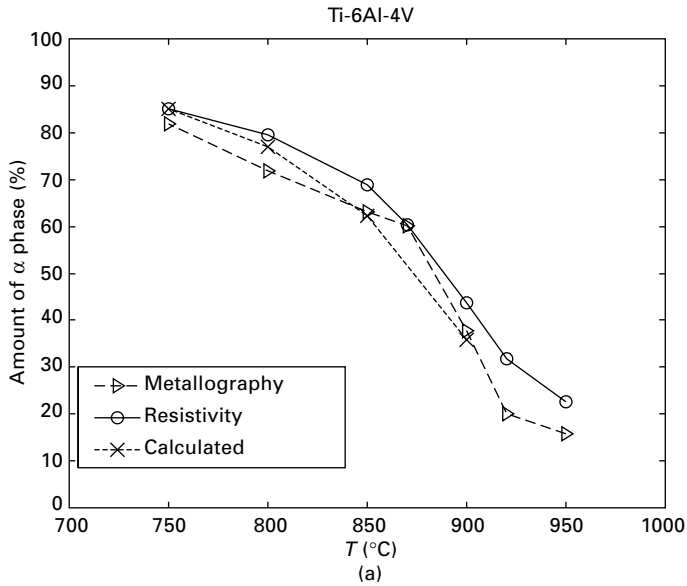
6.6.1 Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si

A good agreement between the experimental and calculated phase compositions is found for the Ti 6-4 alloy (Table 6.1). The correspondence is better at lower temperatures (750–800 °C). At higher temperatures (850–900 °C) the calculated equilibrium α amount is slightly lower than that experimentally observed. The differences between the experimental and calculated phase compositions for Ti 6-4 are within the acceptable error range.

The differences between the calculated amount of equilibrium α phase and the amount experimentally detected by the resistivity experiments are significant for the Ti 6-2-4-2 alloy, which has a more complicated composition than Ti 6-4 (Table 6.1). No reasonable explanation for this observation could be found. In order to clarify this discrepancy, additional experiments were carried out. Samples from both alloys were treated according to the same heat treatment process. Thereafter, the samples were studied by means of quantitative metallography (Fig. 6.8). Again, acceptable correspondence for the Ti 6-4 alloy was observed (Fig. 6.8a). For the Ti 6-2-4-2 alloy the experimental results from the metallography were in agreement with the experimental results of the resistivity and in disagreement with the calculated phase equilibria (Fig. 6.8b). Thus, it is reasonable to believe that the experimentally observed α -amounts were the correct ones and the calculated values for Ti 6-2-4-2 were unrealistically high. It should be noted that the curve tracing the kinetics at a high temperature (see curve corresponding to 930 °C in Fig. 6.2b) has a tendency to increase with the time prolongation. This may indicate that the transformation at this temperature is still incomplete. Possibly, a very slow transformation process is still in progress, but it is undetectable with the experimental technique used. Nevertheless, it is very unlikely that even when the time is significantly prolonged, the experimental amount of α phase (current data value 15%) will reach the amount calculated (65%). One may conclude that for both Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys, there is a better correspondence between the calculated and experimentally observed α amounts at lower temperatures.

Table 6.1 Experimental and calculated phase compositions for Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys at various temperatures

Alloy	T (°C)	Experimental		Calculated											
		α	β	α	β	Al in α	Al in β	V in α	V in β	Sn in α	Sn in β	Zr in α	Zr in β	Mo in α	Mo in β
		(vol.%)	(vol.%)	(mol.%)	(mol.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
Ti-6Al-4V	950	22.5	77.5	–	–	–	–	–	–	–	–	–	–	–	–
	900	43.7	56.3	35.9	64.1	6.9	5.8	2.0	6.7	–	–	–	–	–	–
	850	68.9	31.1	62.2	37.8	6.6	5.5	2.4	9.2	–	–	–	–	–	–
	800	79.5	20.5	76.9	23.1	6.5	5.3	2.8	12.2	–	–	–	–	–	–
	750	85.1	14.9	85.0	15.0	6.4	5.1	3.1	15.8	–	–	–	–	–	–
Ti-6Al-2Sn-4Zr-2Mo-0.08Si	930	14.9	85.1	65.8	34.2	6.7	5.1	–	–	1.8	2.1	3.8	4.3	0.56	4.5
	900	42.7	57.3	78.9	21.1	6.5	4.9	–	–	1.9	1.9	3.9	4.3	0.71	6.4
	850	68.2	31.8	89.5	10.5	6.3	4.8	–	–	2.0	1.3	3.9	4.2	0.95	10.0
	800	82.9	17.1	94.2	5.8	6.3	4.6	–	–	2.0	0.81	4.0	4.0	1.1	14.2
	750	87.3	12.7	96.4	3.6	6.2	4.4	–	–	2.0	0.45	4.0	3.6	1.2	18.9
	735	97.7	2.3	96.8	3.2	6.2	4.3	–	–	2.0	0.37	4.0	3.44	1.3	20.4



6.8 Experimental and calculated α phase amounts for (a) Ti-6Al-4V and (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys versus temperature.

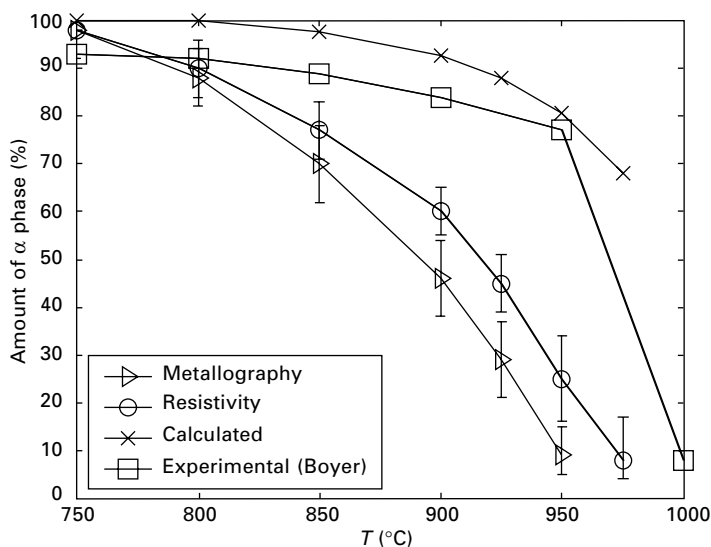
6.6.2 Ti-8Al-1Mo-1V

Significant and unacceptable discrepancy between the experimental and calculated phase compositions is found, especially at high temperatures. The agreement is better at lower temperatures (750–800 °C). At higher temperatures,

the calculated equilibrium α amount is significantly higher than that experimentally observed. In order to clarify this discrepancy, samples quenched from different temperatures were studied by means of quantitative metallography. The data obtained from the different ways are plotted in Fig. 6.9, together with the data published by Boyer *et al.* (1994).

The β -transus temperature for Ti 8-1-1 alloy with normal element contents is approximately 1040 °C (Boyer *et al.*, 1994). Using Thermo-Calc and the Ti database, a β -transus temperature of 1039 °C for the composition of the alloy used is obtained. The results from the calculation show that, at 975 °C, nearly 70% of the β phase should transform to α phase (see Table 6.2), so the major part of the transformation is between 1039 and 975 °C. Such an amount of equilibrium α phase at a temperature so close to the β -transus is probably unrealistically high. The β to α transformation in titanium alloys is in a much wider temperature range. Thus, there is reason to believe that the experimental amounts of the α phase at higher temperatures are the correct ones.

There is also a difference between the amounts of the α phase in Boyer *et al.* (1994) and in the resistivity and metallographic data here. The difference can be due to different composition of the alloys used. For example, oxygen level has a dramatic influence on the thermodynamics and kinetics of the phase transformations in titanium alloy (Chapter 14). The oxygen level of the Ti-8Al-1Mo-1V alloy used in this chapter was 0.085 wt.%, which is



6.9 Experimental and calculated α phase amounts for Ti-8Al-1Mo-1V alloy versus temperature.

Table 6.2 Experimental and calculated phase compositions for Ti-8Al-1Mo-1V alloy at various temperatures

T (°C)	Experimental		Calculated											
	α (vol.%)	β (vol.%)	α (mol.%)	β (mol.%)	Al in α (wt.%)	Al in β (wt.%)	V in α (wt.%)	V in β (wt.%)	Mo in α (wt.%)	Mo in β (wt.%)	Fe in α (wt.%)	Fe in β (wt.%)	O in α (wt.%)	O in β (wt.%)
975	8	92	67.9	32.1	8.47	7.09	0.65	1.67	0.33	2.51	0.012	0.220	0.109	0.036
950	25	75	80.5	19.5	8.31	6.84	0.74	1.96	0.44	3.46	0.018	0.331	0.098	0.031
925	45	55	88.1	11.9	8.21	6.64	0.81	2.21	0.55	4.53	0.025	0.473	0.093	0.028
900	60	40	92.8	7.2	8.14	6.47	0.86	2.43	0.66	5.70	0.034	0.648	0.090	0.025
850	77	23	97.7	2.3	8.07	6.16	0.93	2.80	0.86	8.16	0.055	1.079	0.086	0.021
800	90	10	99.9	0.1	8.02	5.86	0.98	3.13	1.03	10.80	0.078	1.560	0.085	0.016
750	98	2	100	–	8.02	–	0.98	–	1.04	–	0.080	–	0.085	–

relatively low for commercial titanium alloys dictating that the β to α transformation takes place at lower temperatures (Chapter 14). It should also be mentioned that the heat treatment conditions of the samples used by Boyer *et al.* (1994) were different. In Boyer *et al.* (1994) the samples were studied after heating at different temperatures. In this chapter, the alloys were after β homogenisation and subsequent isothermal holding at different temperatures. The different heat treatment may also have an influence on the amount of α phase.

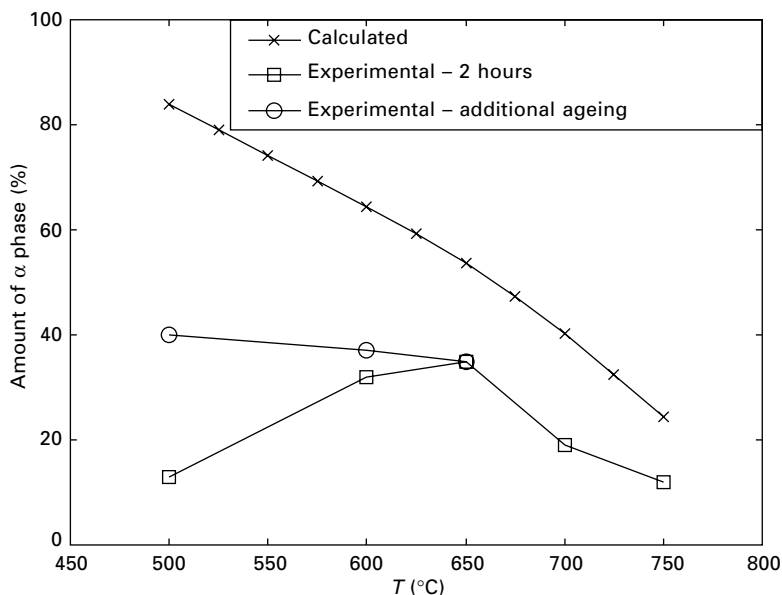
A comparison of the α phase amounts obtained from resistivity studies at different temperatures for Ti-8Al-1Mo-1V, Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys is given in Table 6.3. It is obvious that the amounts of the α phase are higher in Ti-8Al-1Mo-1V alloy as compared to the α phase amounts at the same temperatures in Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys, in agreement with the pseudo binary phase diagram of titanium alloys. In this diagram, the Ti-8Al-1Mo-1V alloy is to the left-side of the Ti-6Al-4V and the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys, implying that the amount of α phase in the Ti-8Al-1Mo-1V alloy should be higher.

6.6.3 $\beta 21s$

The calculated equilibrium amount of the α phase increases when the temperature decreases (Fig. 6.10). This tendency is in agreement with the behaviour of the phase transformation in titanium alloys. However, the large difference between the calculated and the experimentally observed values, especially at low temperatures, is apparent. The amounts of the α phase after resistivity experiments at low temperatures, as discussed earlier in this chapter, are not the actual equilibrium amounts. Nevertheless, even the amounts of the α phase after additional ageing, where in the case of 600 °C a phase equilibrium is believed to be reached, are much lower than the calculated equilibrium amounts of the α phase. The experimental amounts of the α phase are believed to be the correct ones and the calculated, especially at low

Table 6.3 Volume fractions of the α phase for Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V alloys at various temperatures from resistivity data

T (°C)	Ti-8Al-1Mo-1V	Ti-6Al-2Sn-4Zr-2Mo	Ti-6Al-4V
950	25	–	22
920–930	45	15	32
900	60	43	44
850	77	68	69
800	90	83	79
750	98	87	85



6.10 Calculated equilibrium amounts of the α phase versus temperature in the β 21s alloy compared with experimentally observed. The calculations are performed for composition Al = 3.00, Mo = 14.12, Nb = 3.48, Si = 0.14, Fe = 0.32, C = 0.016, N = 0.024, and O = 0.15, all in wt.%.

temperatures are unrealistically high. The calculated amount of the α phase at 500 °C, for example, is larger than 80% and the tendency is for further increase of the amount of the α phase as the temperature decreases. Such high equilibrium amount of α phase in β 21s alloy is in contradiction with its position in the pseudo binary β -isomorphous phase diagram (Boyer *et al.*, 1994) and the practical knowledge of this alloy. The deviations in the calculated equilibrium α amount are most probably because this alloy was not used in the Ti database validation. There is similar discrepancy between calculated and experimental amounts of the α phase for other titanium alloys (Sections 6.6.1 and 6.6.2).

The major difference in the compositions at different temperatures is the molybdenum and the niobium contents in the β phase (Fig. 5.7). There is a tendency for diffusional enrichment of the β phase with both elements when the temperature decreases. According to the phase diagram, such enrichment of β phase by β alloying elements is necessary for α phase to be formed. These calculations show the general characteristics of the phase transformation in titanium alloys. It is the enrichment with molybdenum and niobium that stabilises the β phase at room temperature. It should be noted that since the calculated equilibrium amount of the α phase is deemed too high (Fig. 6.10),

considering the materials balance, the curves tracing the equilibrium concentrations of alloying elements in the phases (Fig. 5.7b) should also be shifted. However, the tendency should remain the same. One can conclude that the β to $\alpha + \beta$ phase transformation in β 21s alloy is connected with diffusional redistribution of molybdenum and niobium between the α and the β phases.

6.7 Kinetics of the transformation

In this section, we trace the kinetics of the diffusional β to $\alpha + \beta$ transformation. The martensitic (β to α') transformation is not involved. It was suggested before on the phase relationship of Ti 8-1-1 that the β phase transforms to martensite at temperatures in the $\alpha + \beta$ field from the transus down to about 900 °C. This is not observed in the Ti 8-1-1 alloy as described above. For all the temperatures ranging from 750 to 975 °C, diffusional β to α transformation is observed. The martensitic transformation has different kinetics and a distinctly different resistivity response.

The analysis of the resistivity experimental data can be made within the framework of the Avrami theory by means of the Johnson–Mehl–Avrami (JMA) equation. The theory and equation trace the kinetics of the transformation, giving a relation between the volume fraction of transformed material and the time. For isothermal transformations, this equation has the following popular and basic form:

$$f = 1 - \exp(-kt^n) \quad [6.1]$$

where f is the product volume fraction which varies with time t , k is the reaction rate constant and n is the Avrami index that describes the nucleation and growth mechanisms.

In its general form, Eq. [6.1] applies to many real transformations. Under isothermal conditions, it describes a variety of phase transformations including polymorphic changes, discontinuous precipitation, eutectoid reactions, interface controlled growth, and diffusion controlled growth. The kinetics of the β to $\alpha + \beta$ phase transformation can be modelled by adapting the classic JMA theory. The above equation can be written in the form:

$$\frac{f_\alpha(t)}{f_\alpha^{\max}} = y = 1 - \exp(-kt^n) \quad [6.2]$$

where $f_\alpha(t)$ is the amount of α phase after a time t , $f_\alpha^{\max}$ is the maximum (equilibrium) volume fraction of the α phase at the temperature of the transformation, and y is the degree of the transformation.

It must be pointed out that the JMA equation describes the transformation from its start and does not consider the pre-processing stages and the incubation time. Hence, the time should be treated not as an absolute time but as relative

to the start of the transformation. This can be taken into account by simple subtraction of the incubation time.

Equation [6.2] can be used to analyse the experimental data by means of logarithmic plots, where $\ln(\ln(1/(1 - y)))$ is plotted versus $\ln(t)$. The slope of the linear regression line is the Avrami exponent n , while from the intercept the k value can be calculated. Such plots are presented in Figs. 6.11 and 6.12 for some of the temperatures applied in the resistivity work.

Using the above plots, n and k values for all applied temperatures can be derived (Tables 6.4 and 6.5).

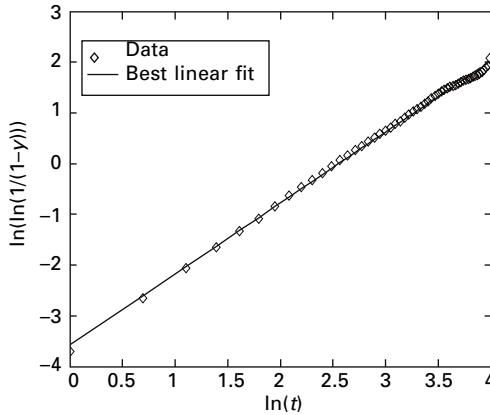
The Avrami index n obtained from these plots for all temperatures is within the narrow range of 1.15–1.60 for Ti 6-4 and Ti 6-2-4-2 alloys and 1.26–1.49 for Ti 8-1-1. This corresponds to the mechanism of the β to $\alpha + \beta$ transformation in titanium alloys, namely that β -grain boundaries are the nucleation sites and the α phase has a plate-like morphology.

6.7.1 Ti 6-4 and Ti 6-2-4-2

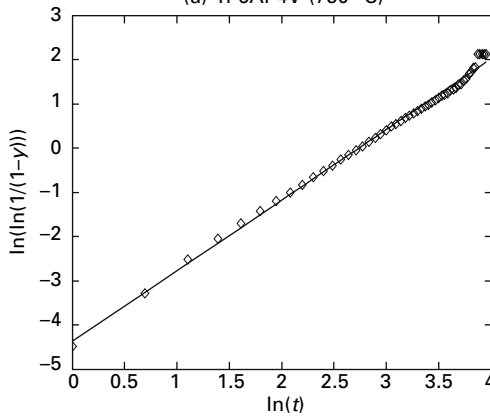
For all the temperatures, the experimental measurements are described very well by single straight lines when the plots are in the above coordinate system. This confirms that the JMA theory can be applied to describe the kinetics of the β to $\alpha + \beta$ phase transformation in the titanium alloys under isothermal conditions. Moreover, the mechanism of the transformation does not change during the course of the transformation. In near- β titanium alloys (Ti 10-2-3 and β -CEZ), the mechanism of the transformation changes during the course of the transformation when the transformation takes place at low temperatures (350 °C), indicated by obvious changes of the line slope. Such effects are not observed here.

Note, however, that although the above plots are the most usual means of deriving the JMA kinetics parameters, such a free approach may be misleading. The reader will find that acceptable good fittings between the experimental and the calculated fractions are possible for any n value ranging within 1.2–1.5 and for all curves in Fig. 6.2a and b. Since n is correlated with the nucleation and growth mechanisms (the geometry of the transformation), the next conclusion is that the mechanism of the transformation does not change in the temperature ranges concerned. This conclusion is valid for most transformations over appreciable temperature ranges. Thereby, the next step is to fit the experimental data in Fig. 6.2a and b to the JMA equation, Eq. [6.2], by setting the n value free but constant for all the temperatures used. This can be performed by an optimisation computer program, trying to minimise the sum square error between the experimental and calculated fractions for all temperatures. From such calculations, the values of $n = 1.31$ for Ti 6-4 and $n = 1.44$ for Ti 6-2-4-2 are obtained.

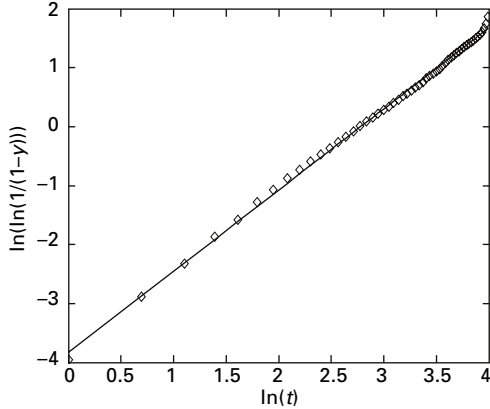
The temperature dependence of the rate constant is not monotonic in the



(a) Ti-6Al-4V (750 °C)

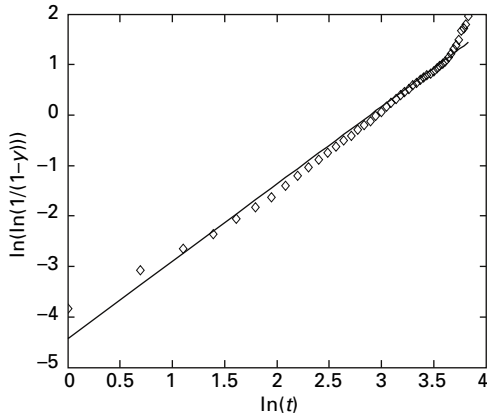


(b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si (750 °C)

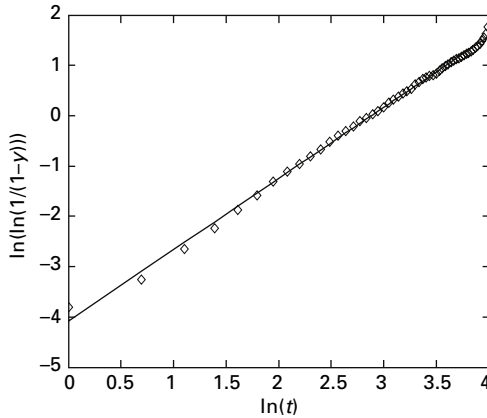


(c) Ti-6Al-4V (850 °C)

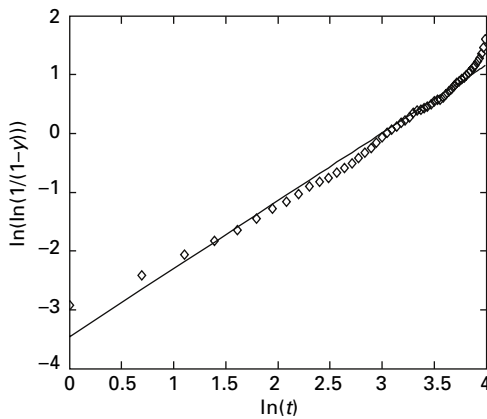
6.11 Plots of $\ln(\ln(1/(1-y)))$ against $\ln(t)$ for deriving the Johnson-Mehl-Avrami parameters for (a,c,e) Ti-6Al-4V and (b,d,f) Ti-6Al-2Sn-4Zr-2Mo-0.08Si at different temperatures. (a) Ti-6Al-4V (750 °C); (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si (750 °C); (c) Ti-6Al-4V (850 °C); (d) Ti-6Al-2Sn-4Zr-2Mo-0.08Si (850 °C); (e) Ti-6Al-4V (950 °C); (f) Ti-6Al-2Sn-4Zr-2Mo-0.08Si (930 °C).



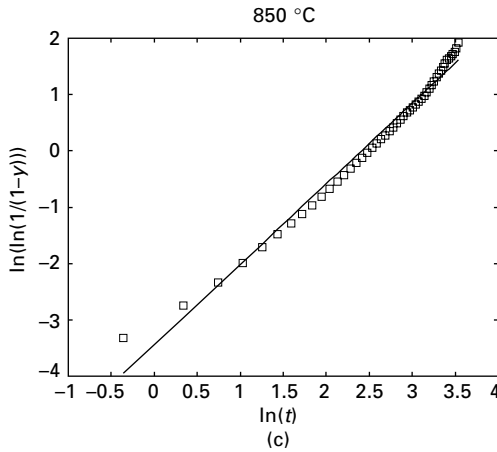
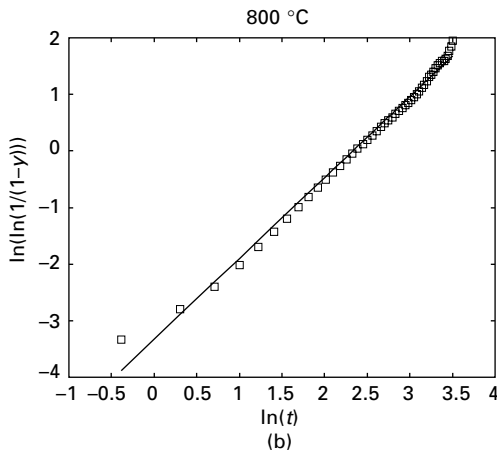
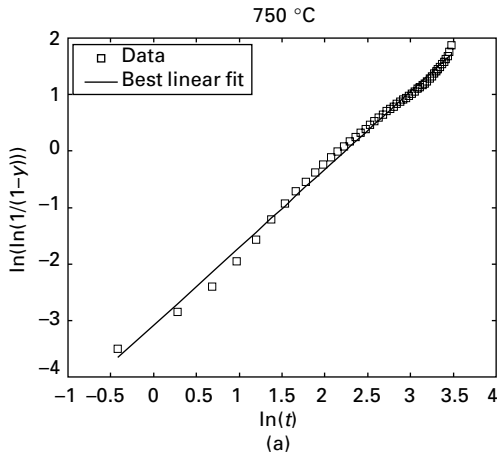
(d) Ti-6Al-2Sn-4Zr-2Mo-0.08Si (850 °C)



(e) Ti-6Al-4V (950 °C)



(f) Ti-6Al-2Sn-4Zr-2Mo-0.08Si (930 °C)



6.12 Plots of $\ln(\ln(1/(1-y)))$ against $\ln(t)$ for deriving the Johnson–Mehl–Avrami parameters for Ti-8Al-1Mo-1V alloy at different temperatures. (a) 750 °C; (b) 800 °C; (c) 850 °C; (d) 900 °C; (e) 950 °C; (f) 975 °C.

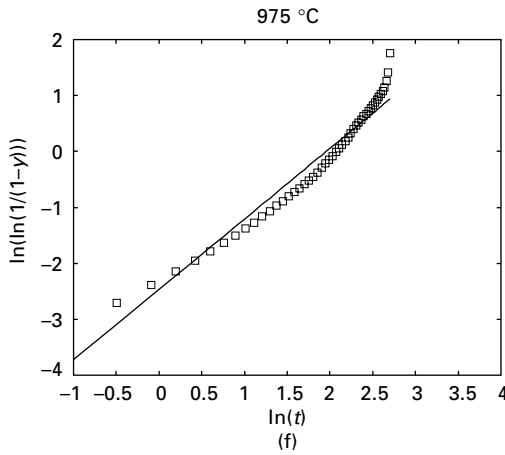
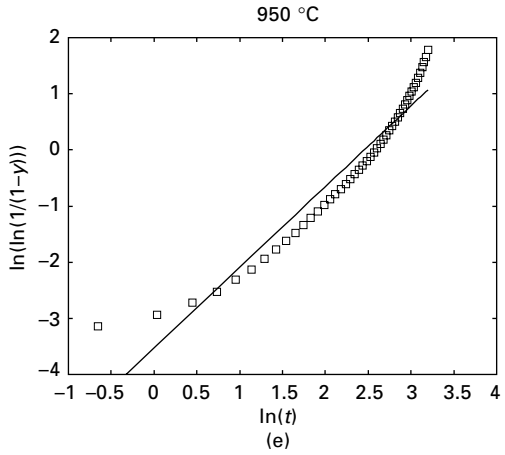
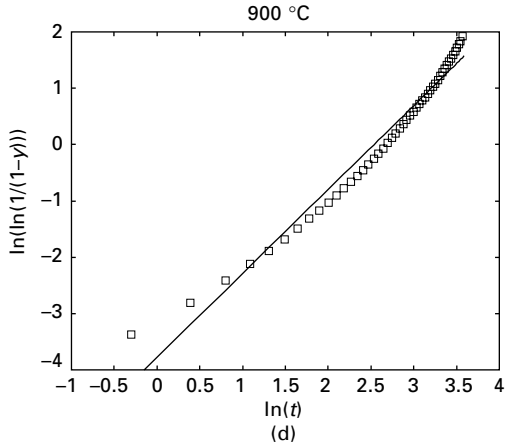


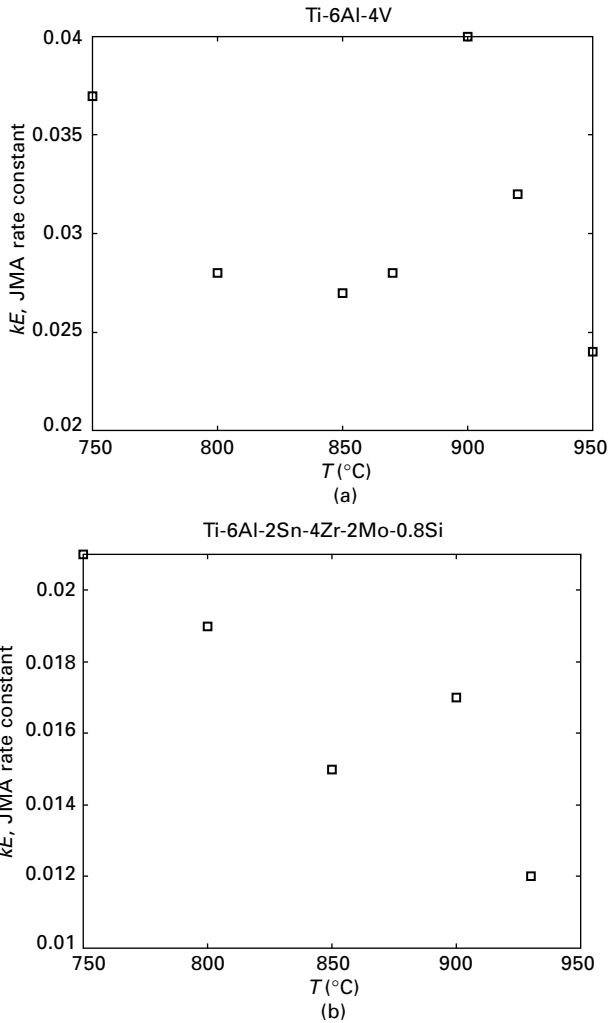
Table 6.4 Johnson–Mehl–Avrami kinetic parameters for Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys obtained by $\ln(\ln(1/(1-\gamma)))$ versus $\ln(t)$ plots

Alloy	T (°C)	n	k
Ti-6Al-4V	950	1.41	0.017
	920	1.39	0.024
	900	1.21	0.046
	870	1.34	0.025
	850	1.38	0.022
	800	1.34	0.026
	750	1.40	0.028
Ti-6Al-2Sn-4Zr-2Mo-0.08Si	930	1.15	0.032
	900	1.53	0.014
	850	1.53	0.012
	800	1.36	0.024
	750	1.60	0.013
	735	1.30	0.059

Table 6.5 Johnson–Mehl–Avrami kinetic parameters for Ti-8Al-1Mo-1V alloy obtained by $\ln(\ln(1/(1-\gamma)))$ versus $\ln(t)$ plots

T (°C)	n	k
750	1.38	0.046
800	1.43	0.036
850	1.43	0.032
900	1.49	0.023
925	1.40	0.025
950	1.44	0.029
975	1.26	0.085

above cases (Fig. 6.13). For both alloys, there is an abnormality at about 900 °C. Apparently, the transformation can be considered as having two somewhat different kinetics above and below 900 °C. Within both temperature intervals and in both alloys, the rate constant increases with decreasing temperature, i.e. increasing undercooling. Such a characteristic is usual for phase transformations taking place on cooling. These results are in agreement with the results from the metallography study of samples after isothermal exposure at different temperatures (see Sections 6.3.1 and 6.3.2). The microstructures of the α phase produced above and below 900 °C are different. For the temperatures above 900 °C, the α phase is mainly grain boundary nucleated and grown (Fig. 6.4a,b and d). For a high degree of undercooling (temperatures below 900 °C) ('Undercooling' refers to the interval between the temperature of isothermal exposure and the β transus), mixed mechanisms of the transformation are observed. The main part is homogeneously nucleated



6.13 Calculated Johnson–Mehl–Avrami rate constants for β to $\alpha + \beta$ transformation in (a) Ti-6Al-4V and (b) Ti-6Al-2Sn-4Zr-2Mo-0.8Si alloys assuming constant Avrami index (n).

(within the former β grains) and plate-like grown α phase (Fig. 6.4c,e,f and g). Small amounts of the grain boundary α are observed as well.

These observations imply that the Avrami index (n values) is different for the kinetics of the β to $\alpha + \beta$ transformations above and below 900 $^{\circ}\text{C}$. As examples, for grain boundary nucleation after saturation, $n = 1$, and for diffusion-controlled growth of plates under the assumption that all particles are present at $t = 0$ and have negligible initial dimensions, $n = 1.5$.

Following the above reasoning and fitting the resistivity data to the JMA equation assuming different n values for β to $\alpha + \beta$ transformation for temperatures above and below 900 °C, the derived kinetics parameters as well as the different mechanisms of the α phase nucleation and growth for both alloys are summarised in Table 6.6.

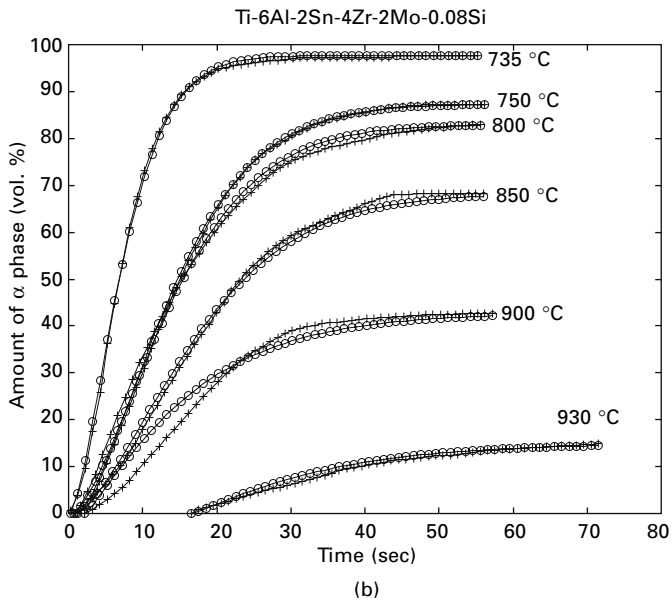
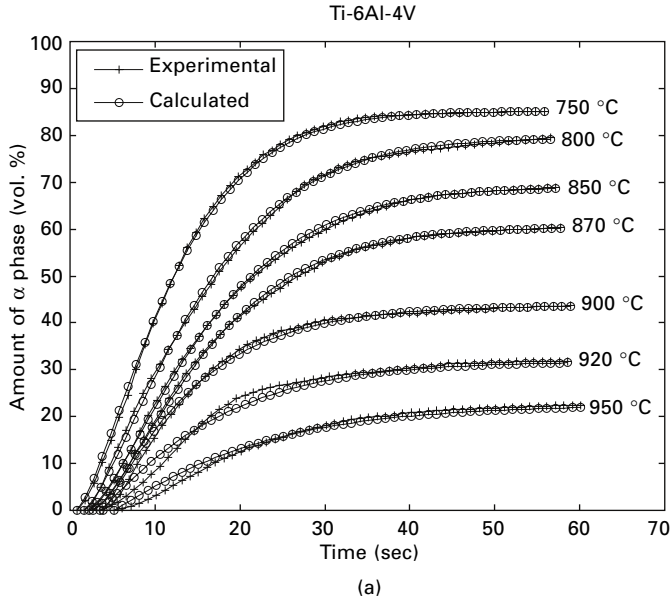
In Fig. 6.14, the calculated (from the JMA theory) and the experimental (from the resistivity measurements) transformation kinetics are compared for different constant temperatures. Calculated fractions are based on Eq. [6.2], using the n and k values given in Table 6.6. A very good agreement between the calculated and the experimental curves is evident. This agreement supports the validity of the obtained JMA kinetic parameters, which can be used in the heat treatment practice of the titanium alloys to trace and predict the course of β to $\alpha + \beta$ transformation under different isothermal conditions.

The approach described above using two different mechanisms and, respectively, two different n values of the β to $\alpha + \beta$ transformation is different from the approach used in Chapter 7: in that chapter the kinetics of the same transformation are modelled during continuous cooling based on differential scanning calorimetry data. A single n value for the entire temperature interval of the transformation is attributed to continuous cooling conditions. In the following, some explanation of the different approaches is given.

The mechanisms of the transformations are different for continuous cooling and isothermal conditions with respect to the nucleation and growth conditions. This difference is significant for phase transformations taking place on cooling

Table 6.6 Johnson–Mehl–Avrami kinetic parameters for two different mechanisms of the β to $\alpha + \beta$ transformations in Ti 6-4 and Ti 6-2-4-2 alloys at various temperatures of isothermal transformations

Alloy	T (°C)	α phase morphology	JMA parameters	
			n	k
Ti-6Al-4V	950	Grain boundary α phase, and some amounts of α plates nucleated and grown from the grain boundaries	1.1	0.045
	920			0.055
	900			0.068
	870	Mixed: Homogeneously nucleated and plate-like grown α structure, and grain boundaries nucleated and grown α phase (Fig. 6.4c)	1.35	0.025
	850			0.024
	800			0.025
	750			0.033
Ti-6Al-2Sn-4Zr-2Mo-0.08Si	930	Grain boundary α phase, and some amounts of α plates nucleated and grown from the grain boundaries	1.15	0.035
	900			0.043
	850	Mixed: Homogeneously nucleated and plate-like grown α structure, and grain boundaries nucleated and grown α phase (Fig. 6.4f)	1.48	0.013
	800			0.017
	750			0.018
	735			0.044



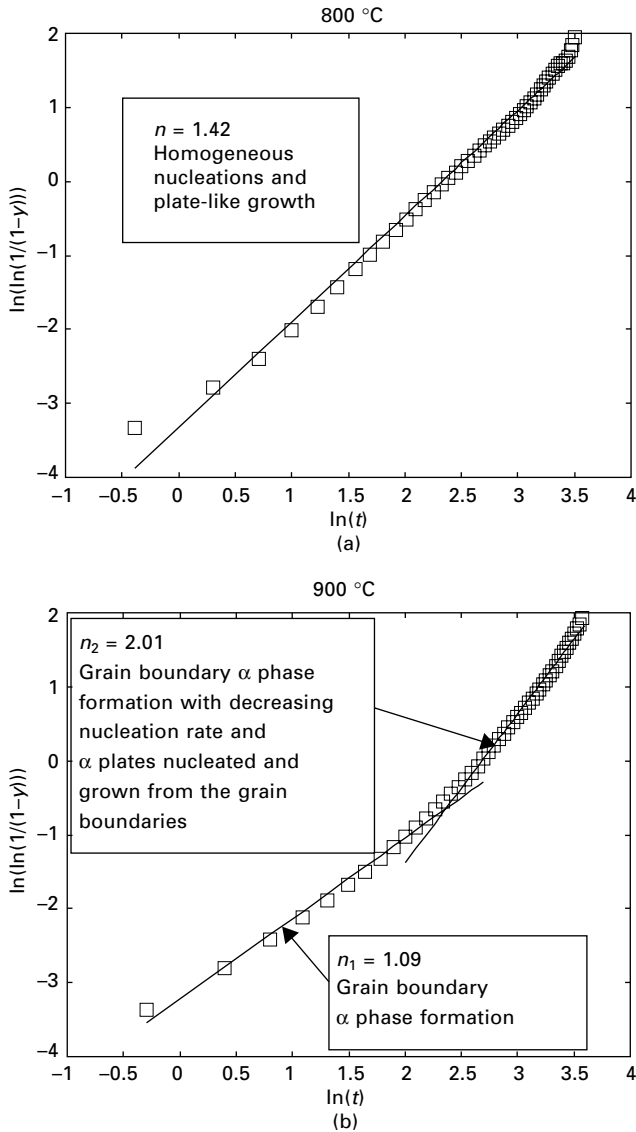
6.14 Experimental and calculated kinetics of the β to $\alpha + \beta$ transformation at different temperatures for (a) Ti-6Al-4V and (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys.

in titanium alloys. In the case of continuous cooling, at each temperature, the transformation starts and proceeds in conditions of microstructure that has been formed at previous stage(s). For example, at 850 °C, the transformation on continuous cooling is in conditions of nucleation sites that already exist (grain boundary α formed on cooling from β -transition to the current temperatures), which are preferable sites for further growth. In the case of isothermal exposure, the sample is cooled rapidly from the β -field to the temperature of isothermal exposure (e.g. 850 °C). At this temperature, spontaneous nucleation (mainly homogeneous) and growth take place. In other words, in the cases of isothermal exposure, when the undercooling is high, the amount of the α phase formed and grown within the former β grains will be higher as compared to the grain boundary α (see Fig. 6.4f and g). These two different mechanisms result in a somewhat different morphology of the α phase formed and imply a difference in the Avrami index derived from continuous cooling and isothermal experiments. Nevertheless, both approaches and models have their own importance and area of application.

6.7.2 Ti 8-1-1

For lower temperatures (750, 800 and 850 °C), the experimental measurements are described well by single straight lines (see Figs. 6.12 and 6.15). However, at higher temperatures (900 °C and above), there is an obvious tendency for change of the line slope (see Fig. 6.12d–f). The data apparently consist of two parts which can be fitted with two separate lines (see Fig. 6.15b). This observation implies that the mechanism of the transformation alters during the course of the transformation.

The above data are in agreement with metallography of the alloy quenched from different temperatures (see Section 6.3.3). There are different mechanisms for the β to $\alpha + \beta$ phase transformation in Ti 8-1-1 alloy, depending on the temperature of the isothermal transformation. At lower temperatures (<900 °C), the main part transforms by homogeneous nucleation (within the former β grains) and grows into plate-like or lamellar-like α phase. At higher temperatures (≥ 900 °C), firstly, grain boundary α phase is formed. Subsequently, the α phase fraction increases in conditions of decreasing nucleation rate (exhausting of the grain boundaries of the former β phase). Concurrently or subsequently, there is some amount (depending on the temperature) of α plates nucleating and growing from the grain boundaries. These different stages of the transformations correspond to the two separate lines in Fig. 6.15b. The first stage takes place within the first 8–15 s, depending on the temperature of isothermal transformation. Finally, it should be remembered that the mechanism of the transformation alters gradually in the time.



6.15 Plots of $\ln(\ln(1/(1-y)))$ against $\ln(t)$ showing the different mechanisms of the β to $\alpha + \beta$ transformation for Ti-8Al-1Mo-1V alloy at different temperatures. (a) 800 °C; (b) 900 °C

Acceptable good fittings are possible for any n value ranging within 1.25–1.5 and for all curves in Fig. 6.2c. Different mechanisms of the transformation give different Avrami index (n values) for the kinetics of the β to $\alpha + \beta$ transformation.

Considering all of the above, the experimental data in Fig. 6.2c can be

fitted to the JMA equation, Eq. [6.2], by setting the n value free but constant for the different mechanisms observed and discussed above. The derived parameters, as well as the different mechanisms of the α phase nucleation and growth, are summarised in Table 6.7. These are in agreement with the general theory of phase transformations. At lower temperatures, an n value of 1.42 is derived, corresponding to the transformation mechanism of homogeneous nucleation and plate-like growth. Similar n values have been derived for the β to $\alpha + \beta$ transformation at the same temperatures for Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys (Section 6.7.1). The rate constant k increases with decreasing temperature (see Table 6.7), implying that the transformation is controlled by the rate of nucleation. Lower temperature of the transformation corresponds to higher degree of undercooling, therefore higher driving force of the transformation. Under these conditions, the rate of nucleation (mainly homogeneous) controls the overall transformation rate. The Ti-6Al-4V and the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys have similar tendencies in the k values (Section 6.7.1).

At higher temperatures, as stated above, the mechanism of the transformation alters during the course of the transformation. Firstly, grain boundary α phase is formed. This corresponds to an n value of 1.01 (see Table 6.7). At this stage, clear temperature dependence of the rate constant k is not apparent. Subsequently, the mechanisms of the transformation smoothly alter to grain boundary α phase formation in conditions of exhausting grain boundaries and α -plates nucleated and grown from the grain boundaries, corresponding to an n value of 1.96. The rate constant k at this stage increases with increasing temperature (see Table 6.7). This implies that the overall transformation rate at this stage is controlled by diffusion.

The change of the mechanism of the β to $\alpha + \beta$ transformation for the Ti-8Al-1Mo-1V alloy at high temperatures is not observed in Section 6.7.1 for Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys. The reasons for this difference are mainly the difference in the composition and the microstructure of the alloys. The Ti-8Al-1Mo-1V alloy has a lower molybdenum equivalent compared to the Ti-6Al-4V and the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys, so, at the same temperature of isothermal exposure, a larger amount of the α phase is in equilibrium and needs to be transformed. The transformation continues until the equilibrium amount of α is reached, even if all grain boundaries of the former β phase are exhausted. Moreover, the Ti-6Al-4V and the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys in general (Boyer *et al.*, 1994), and in these particular cases, have finer microstructure of both the low temperature α and the high temperature β phases than the Ti-8Al-1Mo-1V alloy, implying larger amount of phase boundaries. Finally, the difference in the β -transus temperature (1000 °C for Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys and 1040 °C for Ti-8Al-1Mo-1V alloy) may also have an influence on the change of the kinetics during the course of the transformation.

Table 6.7 Johnson–Mehl–Avrami kinetic parameters and different mechanisms of the β to $\alpha + \beta$ transformation in Ti-8Al-1Mo-1V alloy at various temperatures of isothermal transformations

T (°C)	First stage		Second stage	
	Mechanism of transformation	JMA parameters		JMA parameters
		n	k	
975	Grain boundary α phase formation	1.01	0.043	Grain boundary α phase formation in conditions of exhausting grain boundaries and α plates nucleated and grown from the grain boundaries
950			0.043	
925			0.043	
900			0.043	
850	Homogeneously nucleated and plate-like grown α structure	1.42	0.029	
800			0.035	
750			0.044	

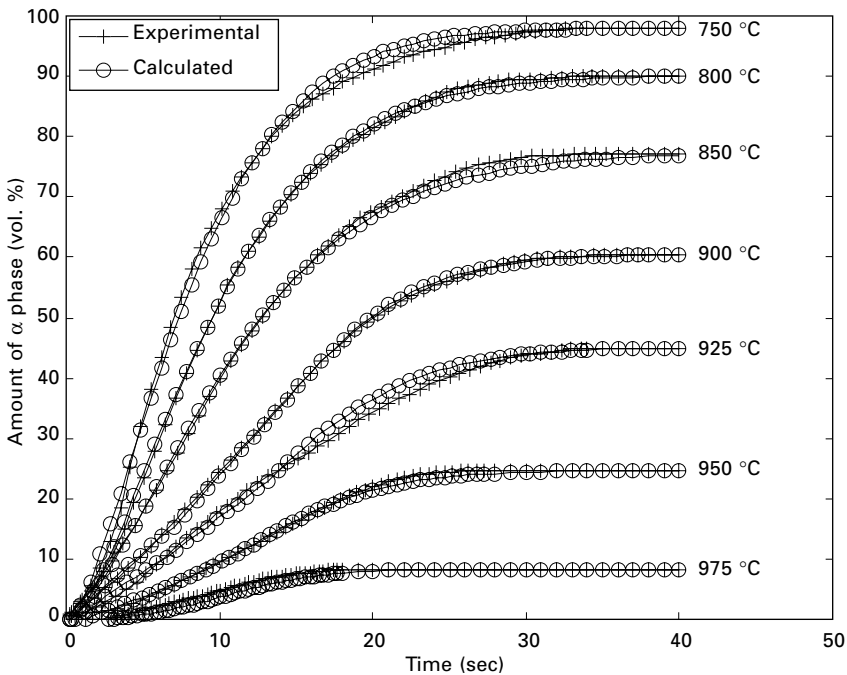
In Section 6.7.1, there is also weak evidence for altering of the mechanism of the transformation at high temperature.

It should be pointed out that the mechanisms of the β to $\alpha + \beta$ transformation in Ti 8-1-1 alloy depend on the temperature but they do not change abruptly with the temperature. The change is gradual (around 900 °C) from one mechanism to another. So, the different mechanisms suggested (Table 6.7) mean ‘the main mechanism of the transformation at the corresponding temperature’.

In Fig. 6.16, the calculated and the experimental transformation kinetics are compared.

6.7.3 β 21s

The experimental resistivity curves can be recalculated to give the amount of α phase versus time (Fig. 6.2d). The recalculation is based on the quantitative X-ray analysis after the resistivity experiments and assuming, not verified strictly for this alloy, a linear relation between the resistivity signal and the amount of the α phase at constant temperature. Remember that the curves



6.16 Experimental and calculated kinetics of the β to $\alpha + \beta$ transformation at different temperatures for Ti-8Al-1Mo-1V alloy.

for 600 and 500 °C trace only the first stages of the transformation and do not present the entire transformation until phase equilibria are achieved.

The diffusion mobility of molybdenum and niobium in the β phase, especially at low temperatures, should have influence on the control of the overall transformation rate. In β titanium, the diffusion coefficient of molybdenum is slightly lower than the diffusion coefficient of niobium. Since larger redistribution of molybdenum is required (see Fig. 5.7b) and because of the lower diffusion coefficient of molybdenum in the β phase, one may suggest that the molybdenum diffusion in the β phase controls the transformation. The diffusion distances of molybdenum in the β phase are calculated for the different ageing treatments (see Table 6.8). The calculated diffusion distances can be used only for approximate estimations of the degree of transformation, because the amount of molybdenum that needs to diffuse increases as the temperature decreases. The diffusion distance over two hours at 650 °C is 1.22 μm . The experiments show that the β to $\alpha + \beta$ phase transformation is completed after two hours at 650 °C. However, two hours are not enough for the completion of the phase transformation at 600 and 500 °C. This may well be explained with the much shorter diffusion distances after two hours at these temperatures (see Table 6.8). In simple terms, the diffusional mobility is low, and therefore longer times are required. The diffusion distance over 54 hours at 500 °C (1.07 μm) is similar to the diffusion distance over two hours at 650 °C. Hence, these two ageing regimes are equivalent in terms of the diffusion distance for the alloy. However, at the lower temperature of 500 °C, a higher amount of molybdenum needs to diffuse. It is therefore not surprising that, while at 650 °C the transformation is completed after two hours, at 500 °C at least 54 hours are necessary. Ten hours at 600 °C give a diffusion distance of 1.61 μm and so the experimental results show that the phase transformation is completed. The correlation of the calculated diffusion distances with the experimental results obtained indicates that, at temperatures below 650 °C, the β to $\alpha + \beta$ phase transformation is controlled mainly by the diffusion of molybdenum in the β phase.

For 750, 700 and 650 °C, the experimental measurements are described very well by single straight lines (see the example $\ln(\ln(1/(1 - y)))$ plot in

Table 6.8 Calculated values of the diffusion distance of molybdenum in $\beta 21\text{s}$

Ageing temperature (°C)	Ageing time (hours)	Diffusion coefficient, D ($\text{m}^2 \cdot \text{s}^{-1}$)	$\sqrt{Dt}$ (μm)
650	2	2.07×10^{-16}	1.22
600	2	7.20×10^{-17}	0.72
600	10	7.20×10^{-17}	1.61
500	2	5.86×10^{-18}	0.21
500	18	5.86×10^{-18}	0.62
500	54	5.86×10^{-18}	1.07

Fig. 6.17a). The Avrami index, n , for the temperatures of 750, 700 and 650 °C, is 1.78, 1.86 and 1.86, respectively. These characterise the mechanism of the transformation when β grain boundaries are preferable nucleation sites for α phase, which has a lamellar morphology.

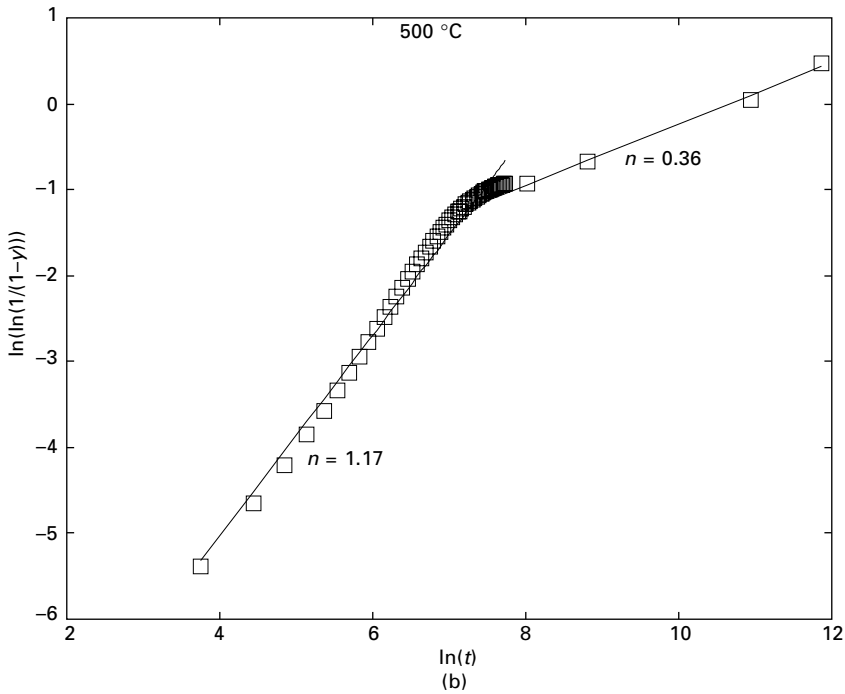
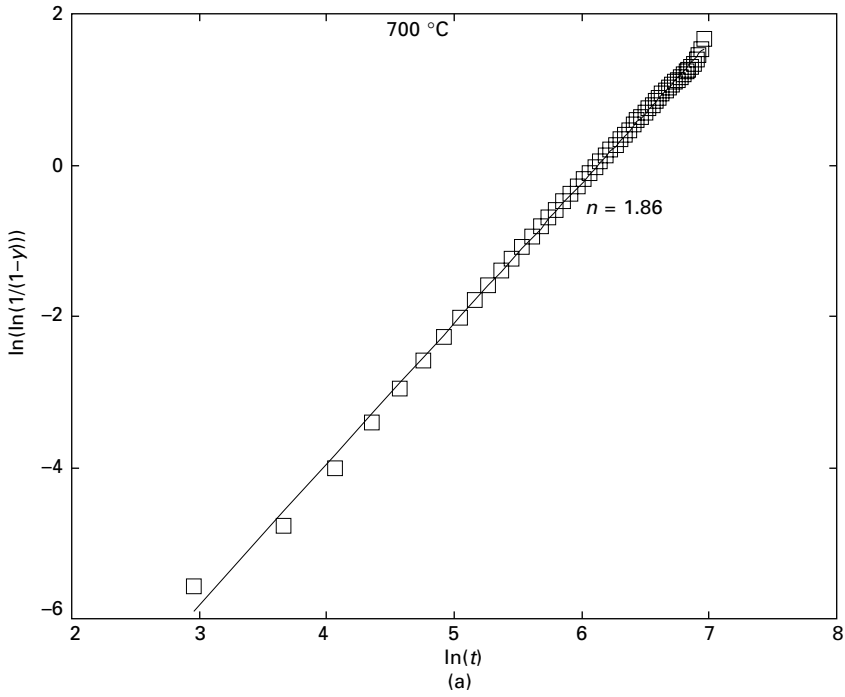
For lower temperatures (600 and 500 °C), data from both resistivity and additional ageing are traced within the framework of JMA theory. The data for these temperatures apparently consist of two parts, which can be fitted with two separate lines (see Fig. 6.17b). In the first stage of the transformation, the data fit corresponds to straight lines with slopes 1.20 and 1.17 for 600 and 500 °C, respectively. However, with time increase, there is an obvious tendency for change of the line slope (see Fig. 6.17b) to lower values of about 0.4 and 0.36 for 600 and 500 °C, respectively. Other near- β titanium alloys (Ti 10-2-3 and β -CEZ) have similar changes. At these low temperatures, the β to $\alpha + \beta$ transformation is in conditions of (i) nucleation including homogeneous nucleation (mainly at the first stages), and further (ii) slow diffusion controlled growth of very fine α plates. The change of the transformation mechanisms is gradual, at around 650 °C.

The derived JMA parameters allow the transformation kinetics to be calculated (Fig. 6.18).

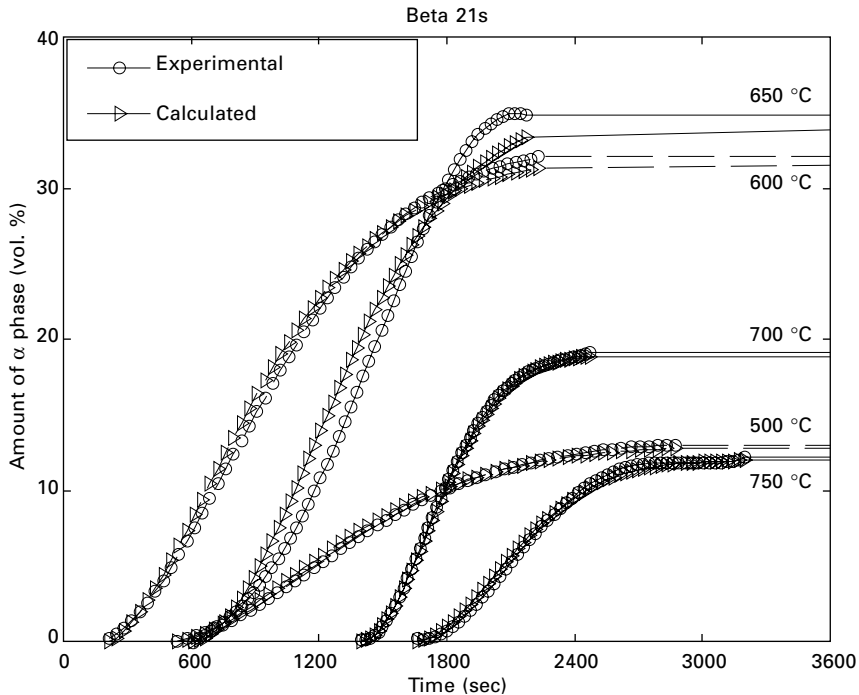
6.8 Time–temperature–transformation diagrams

6.8.1 Ti 6-4 and Ti 6-2-4-2

Using the resistivity data on the kinetics of β to $\alpha + \beta$ transformation at different constant temperatures, complete isothermal transformation diagrams can be designed. These diagrams, also known as time–temperature–transformation (TTT) diagrams, give the relationship between the temperature (plotted linearly) and the time (plotted logarithmically) for a fixed fractional amount of transformation to be attained. Such diagrams are usually used in alloy heat-treatment practice. In literature, usually, only the ‘start’ and the ‘end’ of the transformation are plotted in these diagrams. However, times corresponding to the very start and the very end of the transformation are difficult to be measured experimentally. For this reason, in calculations, we can use transformed fractions of 5 and 95% for the start and the end of the transformation, respectively (Fig. 6.19). For these titanium alloys, the ‘end of transformation’ does not correspond to when the initial phase (β phase) completely transforms to the new phase (α phase). At each temperature, a different phase composition ($\alpha + \beta$ mixture) is the final product (see Section 6.6). Hence, the start and the end of the transformation should not be read as 5 and 95% of the α phase but as 5 and 95% degree of transformation. Iso-lines are calculated and plotted on the same diagrams (Fig. 6.19), showing the real amounts of the α phase.



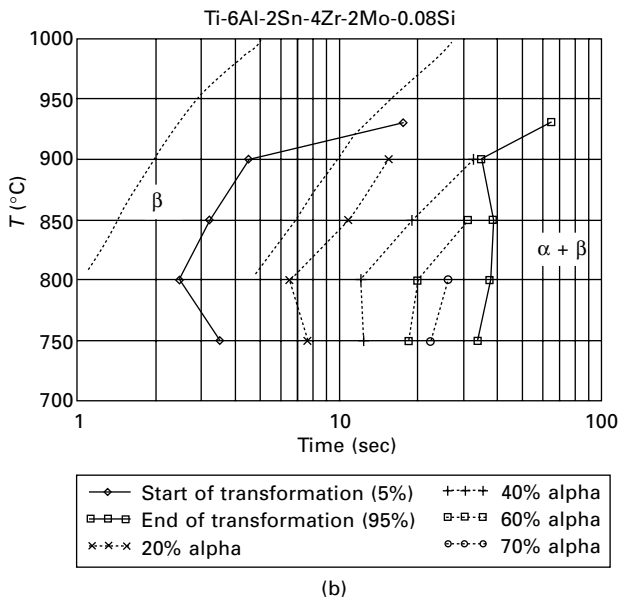
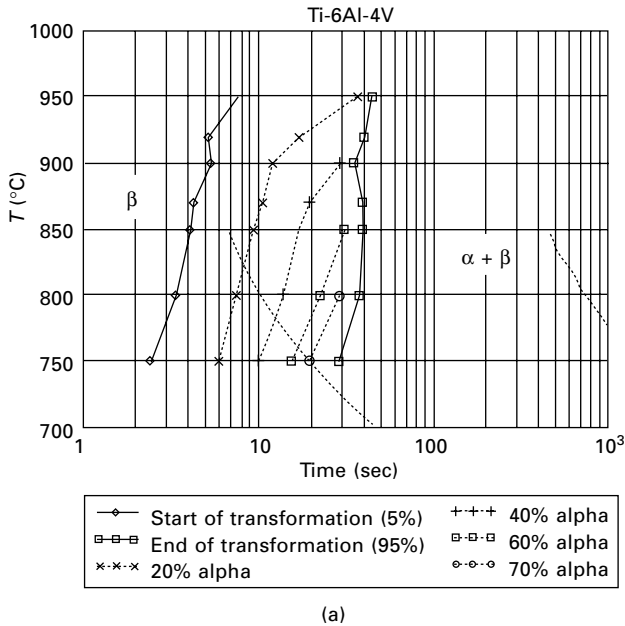
6.17 Plots of $\ln(\ln(1/(1-y)))$ against $\ln(t)$ for deriving the Johnson–Mehl–Avrami parameters for $\beta 21s$ alloy at (a) 700 and (b) 500 °C.



6.18 Experimental and calculated kinetics of the β to $\alpha + \beta$ transformation at different temperatures for β 21s alloy.

In addition, TTT diagrams available in previous literature are plotted in the same figures. From the resistivity data, we find that the kinetics of the β to $\alpha + \beta$ transformation at isothermal conditions in Ti 6-4 and Ti 6-2-4-2 alloys are very similar in the temperature range of 800–900 °C (Fig. 6.19a and b). However, the previously published TTT diagrams by VanderVoort (1991) for these alloys are very different, especially in regard to the end of the transformation. For the Ti 6-2-4-2 alloy, the end of the transformation in the above temperature range is at 5–10 s (see dot line in Fig. 6.19b), while for the Ti 6-4 alloy, it is at longer than 500 s (see dot line in Fig. 6.19a). Such a large difference in the kinetics of the β to $\alpha + \beta$ transformation in these two alloys under isothermal conditions can hardly be justified. In this respect, it is worth mentioning that the Ti 6-2-4-2 and the Ti 6-4 alloys have very similar kinetics of the β to $\alpha + \beta$ transformation under continuous cooling (Chapter 7).

The curves presenting the end of the β to $\alpha + \beta$ transformation show a small deviation from the usual ‘C-shape’ of such diagrams for both alloys. This may be due to incomplete transformations at high temperatures (>900 °C). Probably, a very slow process of transformation would still occur if the time were prolonged. However, this process is beyond the accuracy of the

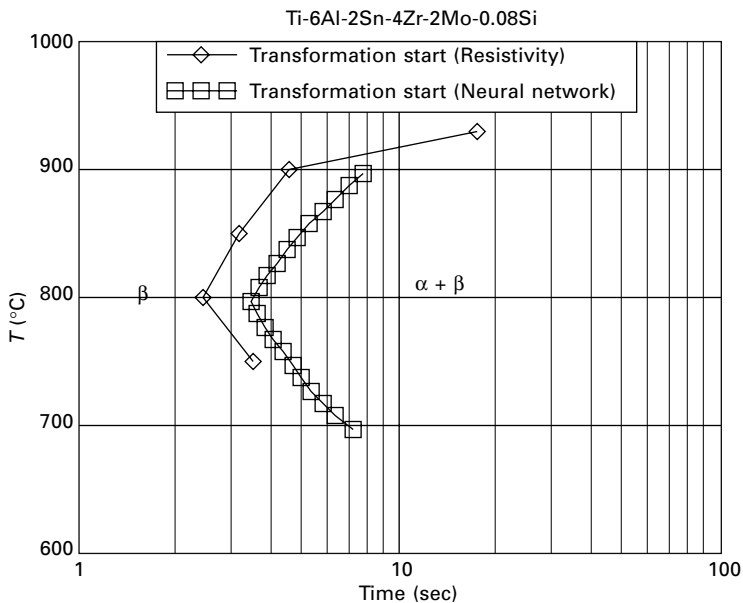


6.19 Calculated time–temperature–transformation diagrams for (a) Ti-6Al-4V and (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys plotted together with TTT diagrams published in previous literature (dot lines) (VanderVoort, 1991).

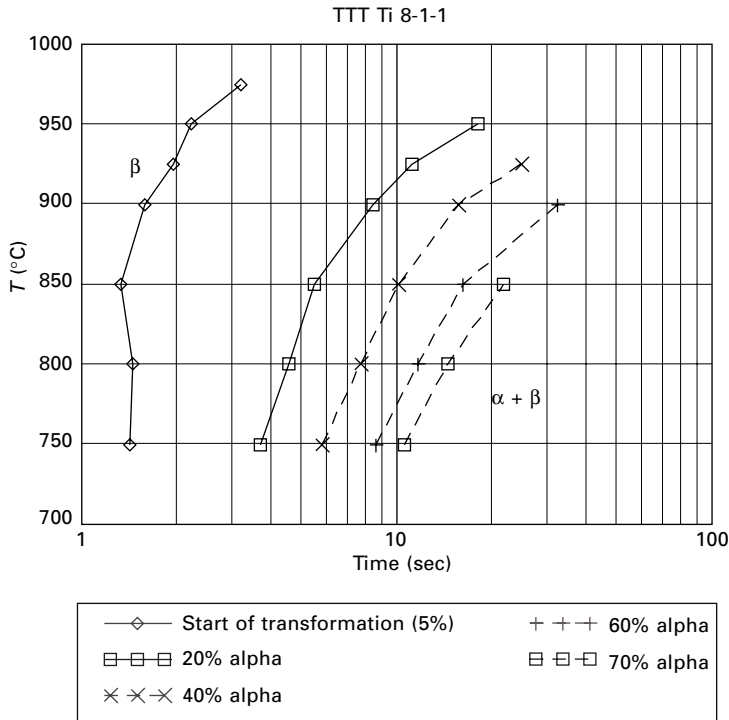
experimental technique used. For the Ti 6-4 alloy, no ‘nose’ point for the start of the transformation is found. Two possible reasons are suggested:

- (i) The vanadium content of the alloy studied is higher than the norm for the Ti 6-4 alloy. Vanadium causes a decrease of the β -transition temperature, which itself will cause a shifting-down of the TTT diagrams (Chapter 14). Hence, before the nose point appears, the mechanism of the transformation is altered from pure diffusional (above 800–850 °C) to diffusional with partial participation of diffusionless (shifting) processes. In titanium alloys, there is not a sharp boundary between diffusional and diffusionless (martensitic) transformations.
- (ii) Pre-processing and even early stages of the transformation may take place on cooling from the β -region to the temperature of the isothermal exposure. This is more likely to happen at lower holding temperatures. Since the incubation period for the transformation is very short (a few seconds), this effect may contribute to the experimental absence of the nose point.

For the Ti 6-2-4-2 alloy, a TTT diagram is calculated on the basis of an artificial neural network model (Chapter 14). Good agreement between the data obtained in different ways is found (Fig. 6.20).



6.20 Calculated start of the β to $\alpha + \beta$ transformation in Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy (TTT diagram) from resistivity experiments and from artificial neural network predictions.



6.21 Calculated time–temperature–transformation diagrams for Ti-8Al-1Mo-1V alloy.

6.8.2 Ti 8-1-1

An isothermal transformation diagram is designed (Fig. 6.21). The end of the transformation is difficult to be determined reliably, because the sensitivity of the resistivity technique at very final stages of the transformation is not high enough.

The cooling rate used ($300\text{ }^{\circ}\text{C s}^{-1}$) corresponds to a time of 1.5 s for cooling from the β homogenisation temperature ($1200\text{ }^{\circ}\text{C}$) to a temperature of $750\text{ }^{\circ}\text{C}$. This time is of the same magnitude as the incubation period for the transformation in this alloy. Nevertheless, we believe that the constructed TTT diagram can be used in the heat treatment practice for Ti 8-1-1 alloy. No previously published TTT diagram is available for comparison.

6.8.3 $\beta 21\text{s}$

A time–temperature–transformation (TTT) diagram is designed based on the data from the resistivity, additional ageing and the quantitative X-ray analyses

(Fig. 6.22). The nose point of the TTT curves is around 600 °C (for the start curve), and it gradually shifts to higher temperatures for higher amounts of α phase and the end curve.

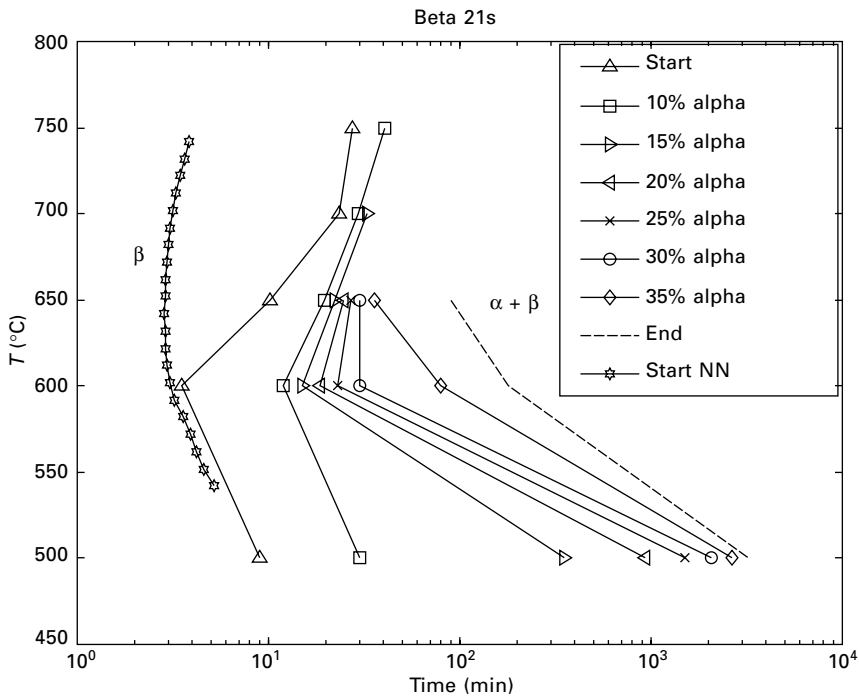
No previously published TTT diagram for the β 21s alloy is available in the literature for comparison. A TTT diagram is calculated for the composition of the alloy on the basis of an artificial neural network model (Chapter 14).

The temperature interval studied is commonly used for ageing in the heat treatment practice of metastable β titanium alloys and particularly of β 21s alloy.

6.9 Summary

Study of the thermodynamics of β to $\alpha + \beta$ transformation shows good agreement between the experimental and the calculated phase equilibria for the Ti-6Al-4V and disagreement for the Ti-6Al-2Sn-4Zr-2Mo-0.08Si, the Ti-8Al-1Mo-1V and the β 21s alloys.

The kinetics of β to $\alpha + \beta$ transformation in titanium alloys of different kinds can be quantified under isothermal conditions using resistivity, optical



6.22 Calculated time-temperature-transformation diagrams for β 21s alloy. The percentage numbers mean the amount of α phase.

microscopy and X-ray techniques. Based on data from these techniques, the kinetics of the β to $\alpha + \beta$ transformation can be modelled in the theoretical frame of the Johnson–Mehl–Avrami (JMA) theory. The JMA kinetic parameters are derived for the different alloys, temperatures and mechanisms of the transformation. A good agreement between the calculated and the experimentally measured transformed fractions is established.

Two different mechanisms of the β to $\alpha + \beta$ transformation under isothermal conditions are observed and suggested in four different alloys, depending on the temperature. In the near- α and $\alpha + \beta$ Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-0.08Si, and Ti-8Al-1Mo-1V alloys, at temperatures below 900 °C, the main part of the α phase microstructure is formed via homogeneously nucleated and grown plate-like lamellae. For temperatures above 900 °C, the mechanism of transformation is dominated with α phase nucleating on β grain boundaries and growing in lamellae form from these boundaries in the Ti-6Al-4V and the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys, while the mechanism of the transformation alters during the course of the transformation in the case of the Ti-8Al-1Mo-1V alloy. Grain boundary α phase is formed firstly, followed by α phase amount increase in conditions of decreasing nucleation rate and α plates nucleating and growing from the grain boundaries.

In the β 21s alloy, for temperatures above about 650 °C, mainly grain boundary α phase is nucleated and grown. For temperatures below about 650 °C, the mechanism of the transformation alters during the course of the transformation. The initial stage of transformation mainly consists of α phase nucleation, followed by diffusional growth of fine lamellae, which is mainly controlled by a diffusional redistribution of molybdenum between the α and the β phases.

Time–temperature–transformation diagrams are designed for the β to $\alpha + \beta$ transformation in titanium alloys, with iso-lines tracing the amounts of the α phase.

6.10 References

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The Johnson–Mehl–Avrami method adapted to continuous cooling

Abstract: This chapter describes in detail how differential scanning calorimetry measurements can be used for quantitative analysis of the phase transformation in titanium alloys and how continuous-cooling-transformation diagrams can be constructed. It shows how the Johnson–Mehl–Avrami theory can be adapted to model diffusion controlled phase transformation in two-phase titanium alloys during continuous cooling. The size of area from the start to the peak temperatures in a DSC curve is identified and explained. The low start transformation temperature is clarified for Ti-6Al-2Sn-4Zr-2Mo (Ti-6242). Experimental aspects of calorimetry and X-ray diffraction are discussed.

Key words: kinetics, phase transformation, Johnson–Mehl–Avrami, continuous-cooling-transformation diagrams, calorimetry.

7.1 Introduction

Microstructures are formed through phase transformations during heat treatment and thermo-mechanical processing. In contrast to the large volume of experimental work on phase transformations in titanium alloys, including aluminides (Butler, 1995), calculation and modelling of the kinetics of the phase transformations have not yet been extensively conducted.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are widely used experimental techniques for studying phase transformations. There is much work on calculation and modelling of the kinetics of phase transformations for various types of material systems based on calorimetric data.

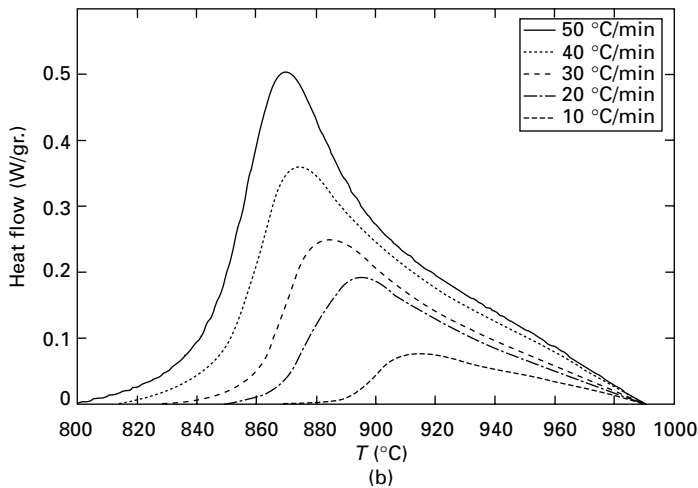
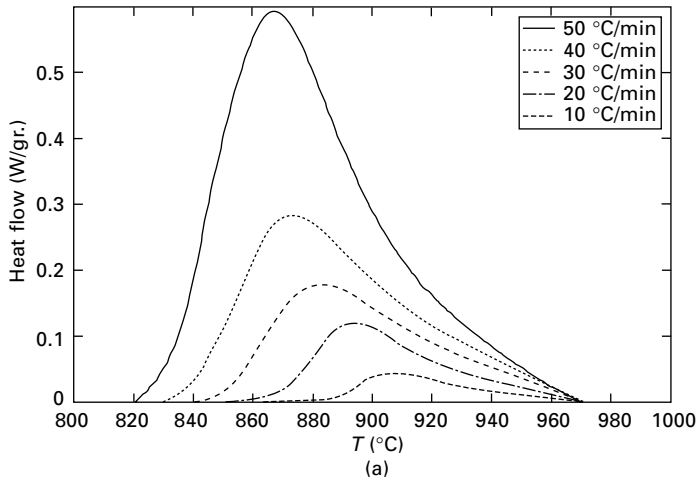
In this chapter, DSC and DTA experimental data are used to model the kinetics of β to α phase transformation in titanium alloys and γ phase formation in titanium aluminide, under continuous cooling conditions. The modelling is based on the application of the Johnson–Mehl–Avrami theory and aims at deriving and understanding fundamental kinetic and thermodynamic parameters. Experimental procedures are described in original research papers (Malinov and Sha, 2001; Malinov *et al.*, 2001a,b).

7.2 Interpretation of calorimetry data

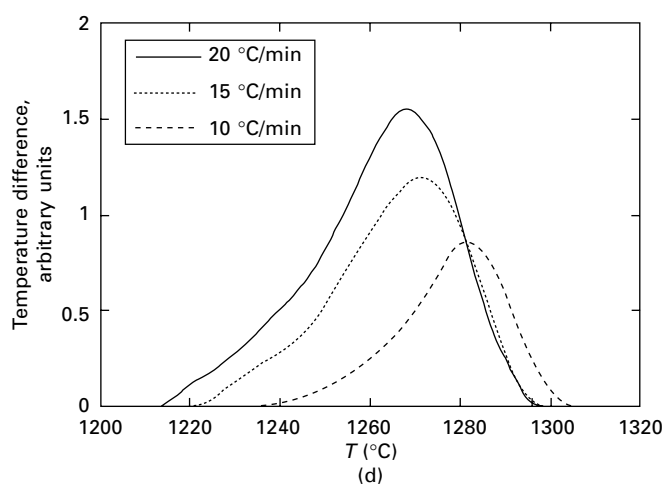
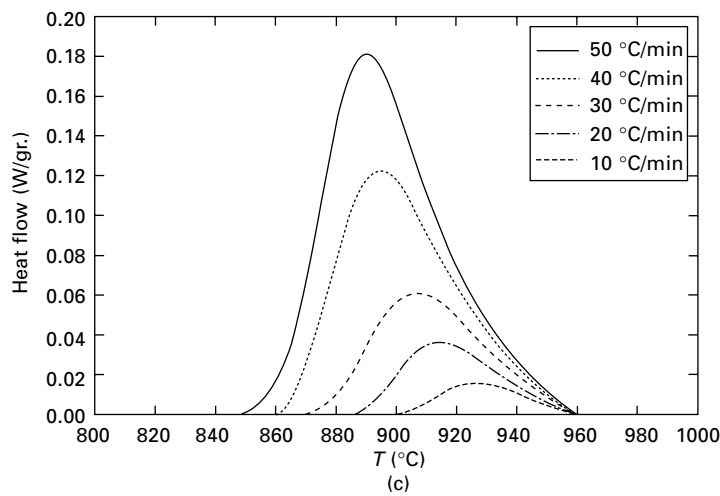
Figure 7.1 shows some processed experimental DSC or DTA curves. Each curve represents the average of several different runs using the same cooling rate and condition.

7.2.1 Ti-6Al-4V

While the temperatures corresponding to the peak and the end of the transformation are clear and accurately measurable, the temperatures corresponding to the exact start of the transformation are difficult to determine. For modelling, a best-fit start temperature of 970 °C is used for all cooling curves. This assumption agrees with the published continuous-cooling-transformation (CCT) diagrams for Ti-6Al-4V alloy (Sieniawski *et al.*, 1996).



7.1 Calorimetry curves for (a) Ti-6Al-4V, (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si, (c) Ti-6Al-7Nb and (d) Ti-46Al-2Mn-2Nb alloys employing different cooling rates. Exothermic peaks are shown.



7.1 Continued

According to the diagrams by Sieniawski *et al.* (1996), the start temperature of the β to $\alpha + \beta$ transformation in continuous cooling is about the same for quite a large range of cooling rates, up to 200 °C/min, and it is 970 °C. A similar result is obtained from the calculation of the incubation times for the cooling rates used, based on the isothermal incubation times and applying Scheil's sum.

The DSC curves for all the cooling rates have a similar asymmetry, with a tail at high temperatures, at the start of the transformation. The area under the curve from the start to the peak temperatures ranges from 61 to 64% of the entire area from the start to the end temperatures. The peak temperature

corresponds to the maximum rate of transformation. The area under the curve from the start to the peak temperatures being more than 50% means that the transformation rate increases with decreasing temperature.

The DSC results disagree with the published CCT diagram for Ti-6Al-4V (Sieniawski *et al.*, 1996), for the end of the β to $\alpha + \beta$ transformation. The end of transformation from the DSC is in the range from 820 to 865 °C, depending on the cooling rate (see Table 7.1), while for the same cooling rates, according to the CCT diagrams by Sieniawski *et al.* (1996), the end of transformation is 670 to 690 °C. The following microscopy data clarify this discrepancy. The microstructure of the samples quenched from 970, 940, 890 and 860 °C is a mixture of α and α' (martensite). Figure 7.2a is for a sample quenched from 860 °C, but the microstructure is the same in nature for samples quenched from 970, 940, 890 and 860 °C, so the micrographs for samples quenched from the other three temperatures (970, 940 and 890 °C) are not shown to avoid repetition. The amount of α' decreases, naturally, with lower quenching temperature. α' means that the β phase transformation is incomplete. The microstructure of the samples quenched from 800 and 750 °C (Fig. 7.2b) consists of only acicular α phase, implying that the transformation is completed above 800 °C. It can be concluded that the end of the β to $\alpha + \beta$ transformation at the cooling rate of 20 °C/min is between 800 and 860 °C. This conclusion supports the DSC data rather than the published CCT diagrams (Sieniawski *et al.*, 1996). The difference between the DSC data and those by Sieniawski *et al.* (1996) may be due to the difference in the composition of the alloys. For example, impurity and oxygen levels have a dramatic influence on the transformation kinetics (Chapter 14).

7.2.2 Ti-6Al-2Sn-4Zr-2Mo-0.08Si

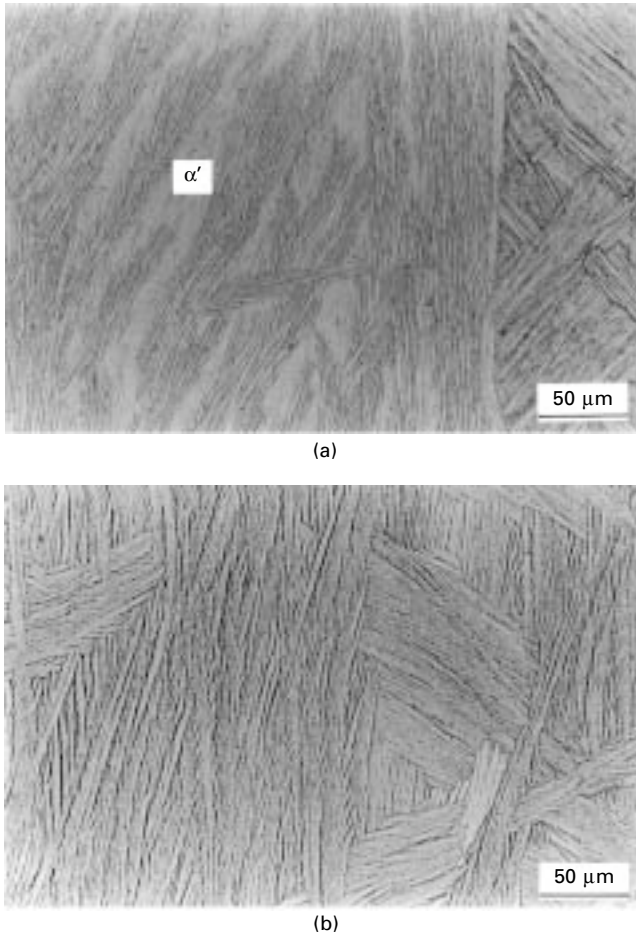
A start temperature of 990 °C is appropriate for all cooling curves, slightly higher than the start temperature for the Ti-6Al-4V alloy. The reasons for this difference could be both thermodynamic and kinetic in nature. The β -transus temperature for both alloys for commercial use is 1000 ± 15 °C, but can vary depending on the exact chemical compositions. The β -transus temperatures based of their real compositions are 1000 °C for Ti-6Al-2Sn-4Zr-2Mo-0.08Si and 995 °C for Ti-6Al-4V alloys, calculated using the ThermoCalc software and the titanium database. This difference may influence the start of the β to α phase transformation in continuous cooling.

The area under the DSC curve from the start to the peak temperatures ranges from 74 to 80% of the entire area from the start to the end temperatures (Table 7.1). The peak temperatures are very similar to the corresponding peak temperatures for the Ti-6Al-4V alloy. So, the temperature of the maximum speed of the β to α transformation in both alloys is about the same, and the

Table 7.1 Calorimetry peak parameters for Ti-6Al-4V (first number), Ti-6Al-2Sn-4Zr-2Mo-0.08Si (second number), Ti-6Al-7Nb (third number) and Ti-46Al-2Mn-2Nb (fourth number except for 15 °C/min)

Cooling rate (°C/min)	Start (°C)	Peak (°C)	End (°C)	Area from start to peak (%)	Enthalpy (J/g)
10	970/990/960/1303	908/908/926/1280	865/870/901/1236	61.4/79.7/58.4/48.0	24/28.4
15 (Ti-46Al-2Mn-2Nb)	1296	1269	1221	46.8	
20	970/990/960/1298	894/894/914/1267	850/850/887/1214	62.2/74.0/53.5/43.2	25/29.6
30	970/990/960	883/883/907	841/830/871	63.6/74.9/60.7	26/33.2
40	970/990/960	873/873/895	830/815/862	63.7/75.0/68.4	27/32.9
50	970/990/960	867/867/890	820/800/850	62.4/74.5/65.1	*/42.3*

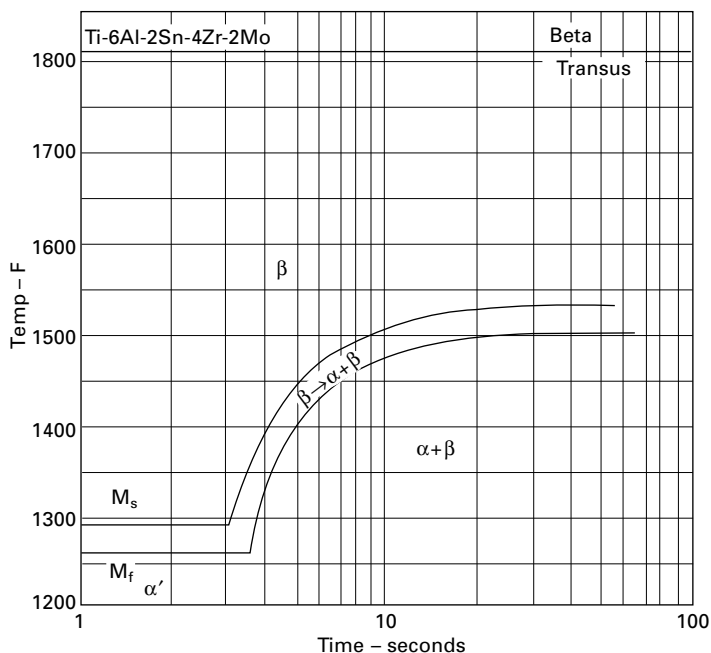
*The cooling rate of 50 °C/min is too fast to allow accurate determination of the enthalpy.



7.2 Microstructure of Ti-6Al-4V after continuous cooling at 20 °C/min and quenching from (a) 860 and (b) 750 °C.

kinetics of the transformation on continuous cooling with cooling rates ranging from 5 to 50 °C/min in the alloys are similar.

A comparison of the DSC results with published CCT diagrams for Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy reveals some discrepancies. Mitchell (1991) proposed a set of CCT diagrams where the start of the β to α transformation was 820–840 °C (Fig. 7.3), and the end of the transformation was 790–810 °C. Cias (1991) proposed similar CCT diagrams where the start of the transformation was 950–980 °C and the end was 600–650 °C. Both were for cooling rates of 5–50 °C/min. However, the temperatures and shape of the curve depend heavily on the exact chemistry of the alloy, the heat treatment history and the experimental technique used.



7.3 Continuous-cooling-transformation diagram for Ti-6Al-2Sn-4Zr-2Mo by Mitchell (1991).

7.2.3 Ti-6Al-7Nb

The start temperature of the β to α phase transformation in continuous cooling for this alloy is estimated at around 960 °C (Fig. 7.1c and Table 7.1), slightly lower as compared to both Ti-6Al-2Sn-4Zr-2Mo-0.08Si and Ti-6Al-4V alloys. The reason for the lower temperature is most likely in the kinetics of the α phase nucleation, because the β -transus temperature for Ti-6Al-7Nb is in fact slightly higher as compared to the other two alloys (see Chapter 5). On the other hand, the peak and the end temperatures for Ti-6Al-7Nb are slightly higher as compared to the above two alloys. This means a narrower temperature range for the transformation. The area under the DSC curve from the start to the peak temperatures ranges from 53 to 68% of the entire area from the start to the end temperatures, with a tendency for higher values at higher cooling rates (Table 7.1).

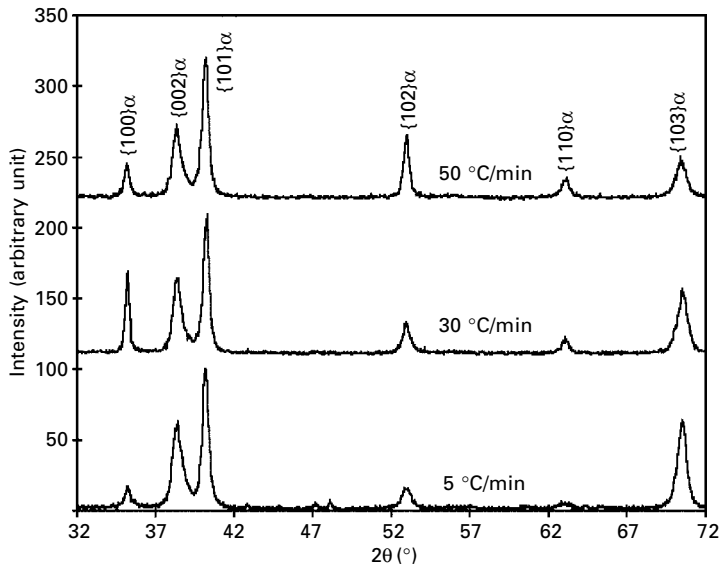
The Ti-Nb alloy exhibits a far less exothermic reaction during phase transformation than the other two titanium alloys. A possible reason is problems with the equipment. We had difficulties at the time of the experiment with the equipment calibration. Therefore, quantitatively, the DSC curves may not be quite correct in terms of enthalpy, but the shape of the curves should still trace the kinetics of the phase transformation, and this in fact is what we need and use.

7.2.4 Ti-46Al-2Mn-2Nb

The model to be discussed later in this chapter is based on published experimental results by Butler (1995) of a DTA study of the phase transformations in the Ti-46Al-2Mn-2Nb alloy. Data for the formation of the γ phase upon cooling are used (Fig. 7.1d). The DTA curves for all the cooling rates have a similar asymmetry, with a tail at low temperatures, corresponding to the end of the transformation. The area under the curve from the start to the peak temperatures ranges from 43 to 48% of the entire area.

7.3 X-ray diffraction

X-ray diffraction of Ti-6Al-2Sn-4Zr-2Mo-0.08Si cooled with different cooling rates shows the presence of α phase only, with no residual β phase (Fig. 7.4). This means that the transformation can be regarded as 100% β to 100% α . Small amounts (up to, say, 4%) of β phase are possible which are not detectable with a conventional X-ray facility. Using X-ray diffraction for determining the β volume fraction is problematic, especially when using laboratory X-ray diffraction. Laboratory X-ray diffraction is not a good method for determining β volume fraction accurately. On the other hand, there are many publications that clearly demonstrate that Ti-6242 always contains a small

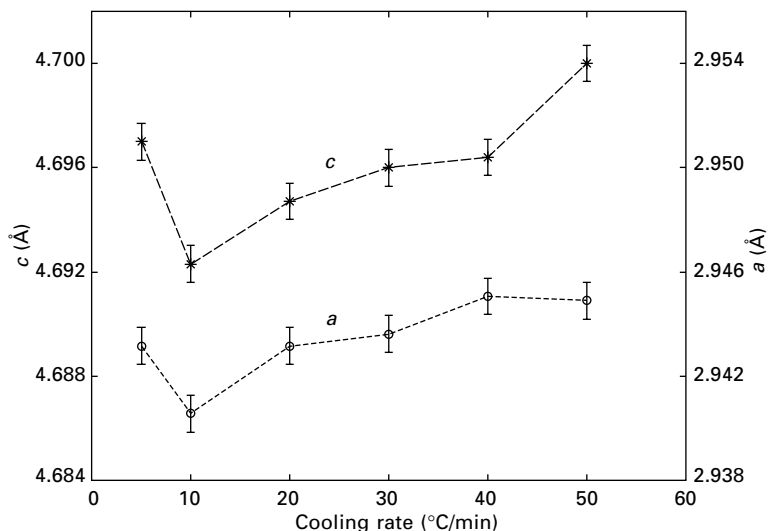


7.4 X-ray diffraction patterns of Ti-6Al-2Sn-4Zr-2Mo-0.08Si after cooling with different rates. For clarity, the diffraction patterns are shifted along the vertical axis with respect to each other.

amount of β phase unless it is very rapidly quenched (Lütjering and Williams, 2003).

Examination of the patterns can reveal increase in the relative intensities of the $\{hk0\}$ planes and decrease in the relative intensities of the $\{00l\}$ planes with increased cooling rate. This effect may be associated with preferable crystallographic orientation of the α phase growth when different cooling rates are applied. Such an effect should also depend strongly on the original alloy processing.

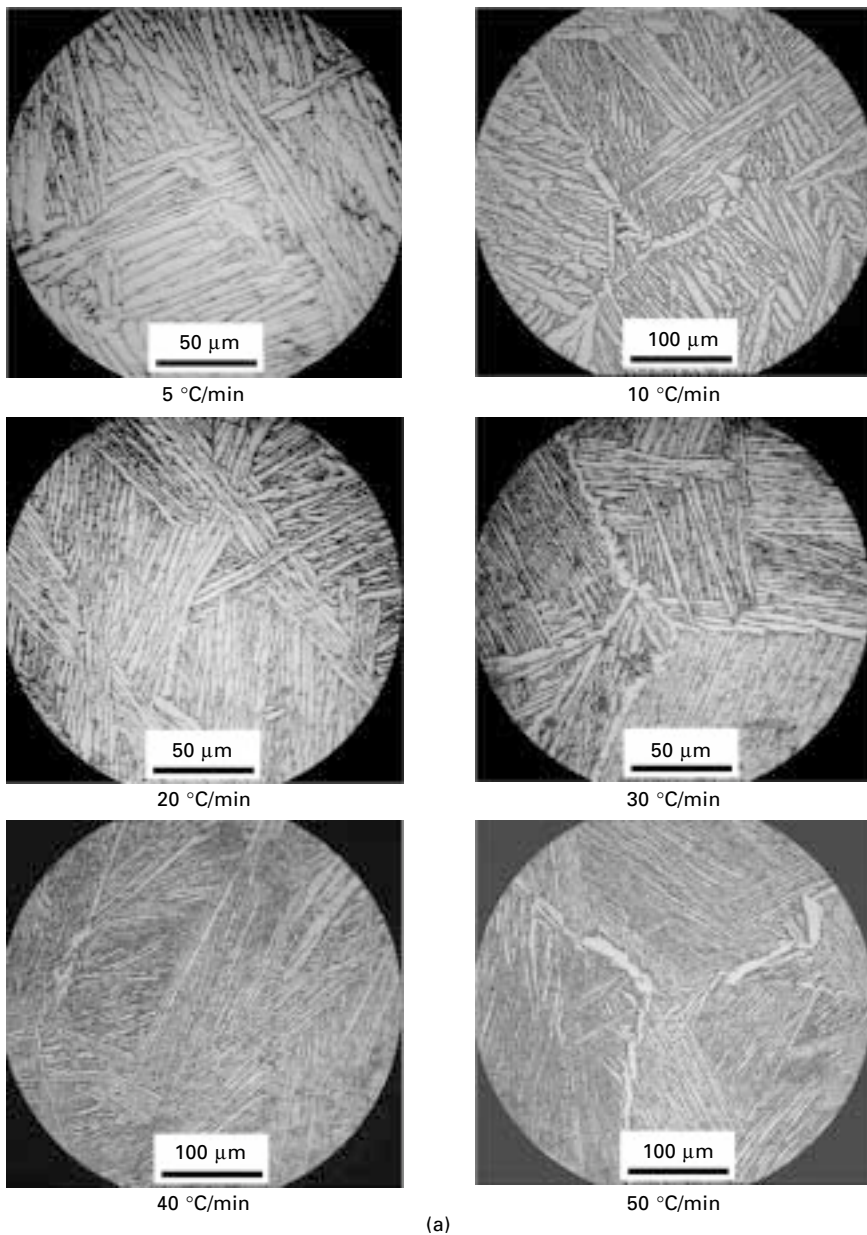
The a and c lattice parameters of the hexagonal structure are calculated from the intercept and the slope of plots of $1/d_{hkl}^2$ versus l^2 , using the reflections $\{100\}$, $\{101\}$, $\{102\}$ and $\{103\}$. An influence of cooling rate is shown in Fig. 7.5. When the cooling rate increases from 10 to 50 °C/min, both lattice parameters increase. A higher level of residual stress is a plausible explanation for the increase in lattice parameters. The formation of a lamellar structure generates high levels of residual stresses, due to lattice mismatches between the α and the β phases. The coefficient of thermal expansion of the different orientations of the hcp α phase and those between the α and the β phases are different, leading to a higher level of residual stresses at a higher cooling rate. Moreover, at a relatively slow cooling rate, redistribution of solute elements during β to α transformation may ease the level of residual stresses. In addition to residual stresses, it is also likely that chemical changes will affect the lattice spacing, since high cooling rates will avoid any partitioning of the α and β stabilisers.



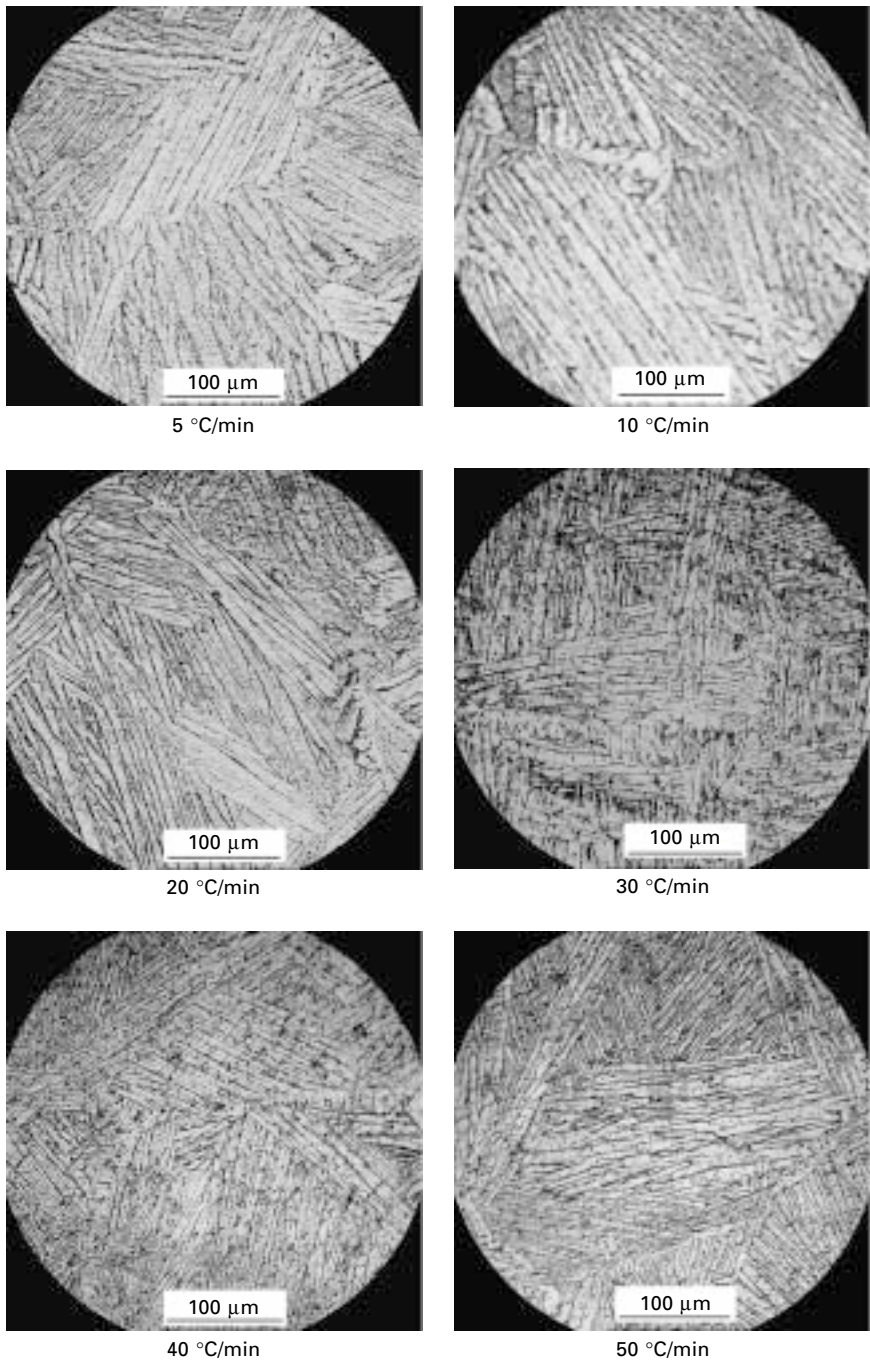
7.5 Lattice parameters of the α phase of Ti-6Al-2Sn-4Zr-2Mo-0.08Si after cooling with different cooling rates.

7.4 Microstructure and hardness

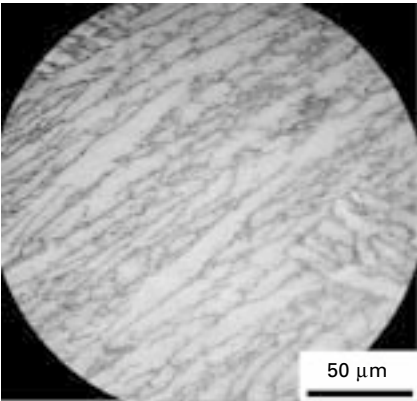
The microstructures consist of grain boundary α phase and α plate colonies, and are fully lamellar (Figs. 7.6 and 8.1). The Widmanstätten microstructure



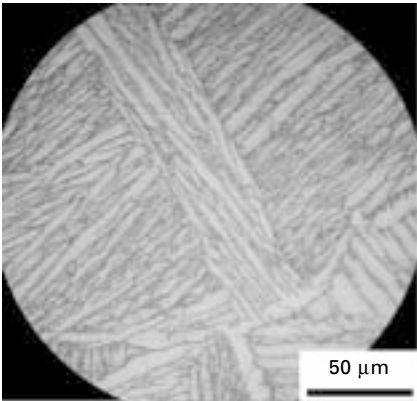
7.6 Microstructure of (a) Ti-8Al-1Mo-1V, (b) IMI 834 and (c) IMI 367 after cooling at different cooling rates.



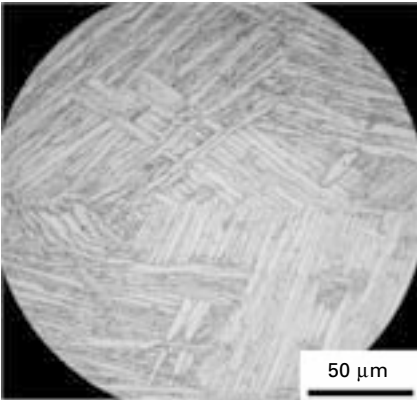
(b)



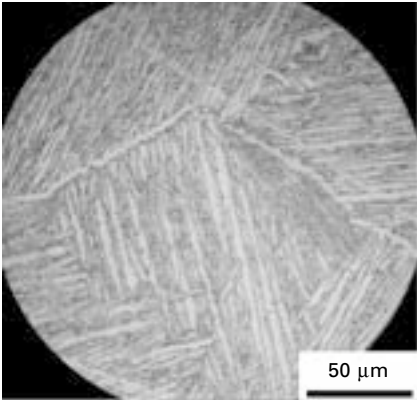
5 °C/min



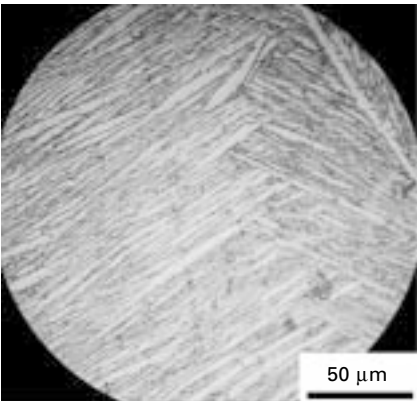
10 °C/min



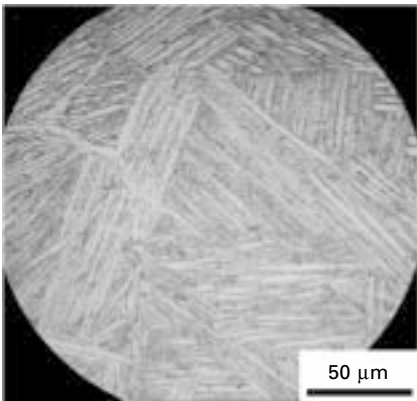
20 °C/min



30 °C/min



40 °C/min



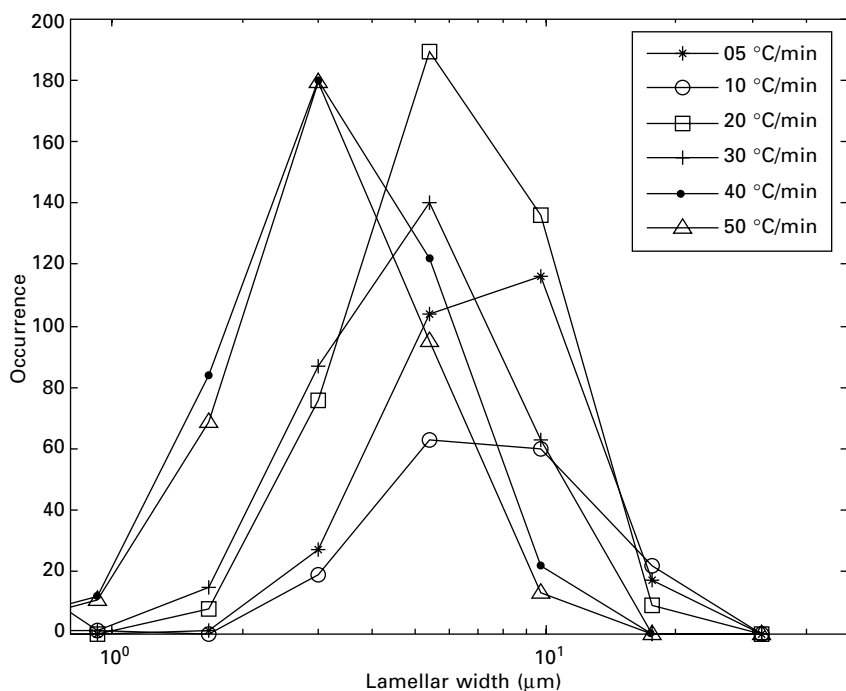
50 °C/min

(c) IMI 367

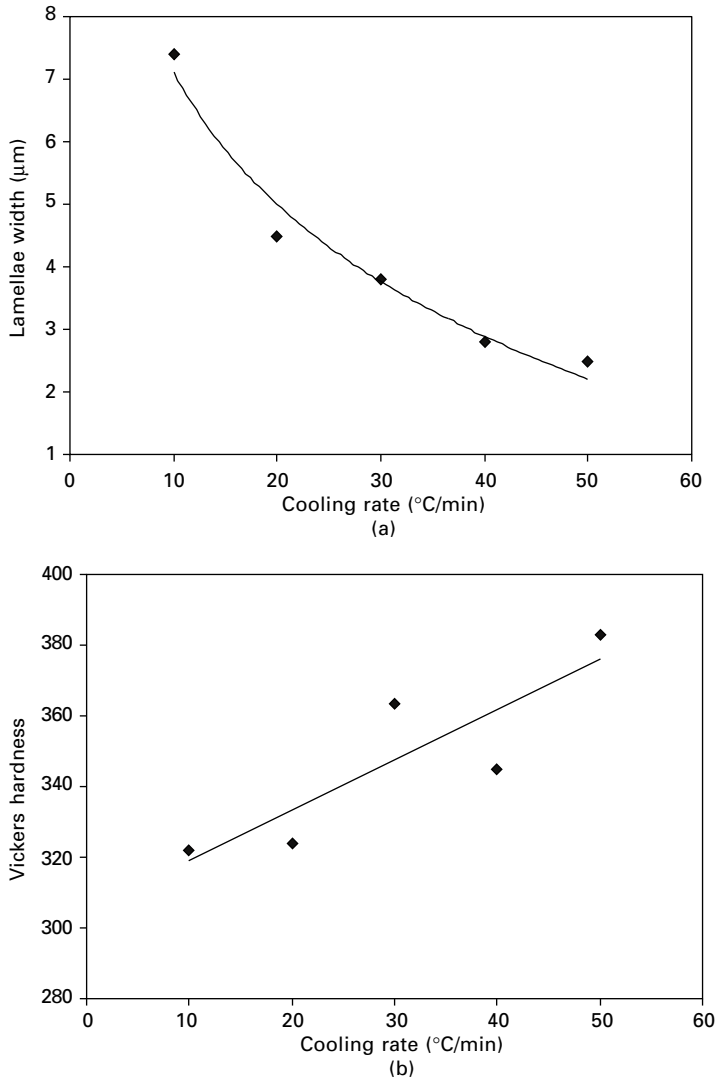
nucleates from β grain boundary (Mythili *et al.*, 2005), but this happens only if cooling rates are sufficiently small. The difference from cooling with various rates is in the α plate thickness. Thinner α plates are produced as the cooling rate increases (see Figs. 7.6, 7.7, 7.8a and 8.1). This naturally results in increase of the hardness at higher cooling rates, where the microstructure is finer (Figs. 7.8b and 7.9).

The percentage of α -stabilising element aluminium is higher in the α regions (Fig. 7.10 and Table 7.2). Conversely, the percentages of β -stabilising elements molybdenum and vanadium are higher in the β regions. This demonstrates that the mode of transformation in the Ti-8Al-1Mo-1V alloy, and by inference other titanium alloys, when continuously cooled from the β phase field, is that of diffusion. At the slow cooling rate, all of the β -stabilising elements have diffused out of the α portion.

These findings support the theory describing the transformation from β to α on cooling from the β single phase field. Under equilibrium conditions, the composition of the phases changes with the temperature (see Chapter 5). As the temperature is reduced to below β_{tr} , the β -stabilising elements diffuse out of the growing α lamellae, into the retained β portion of the microstructure.



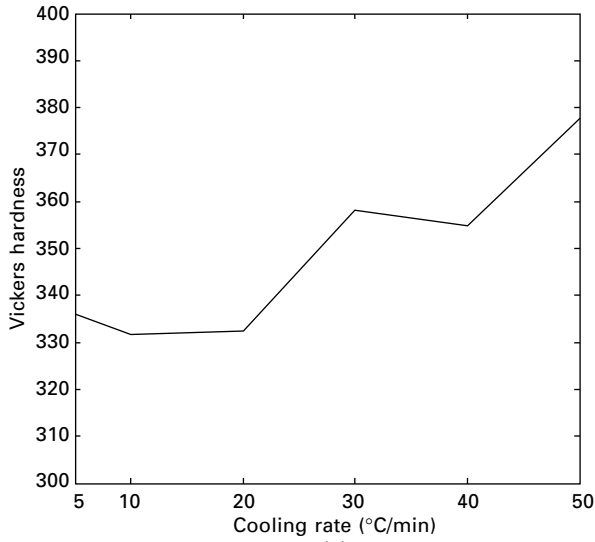
7.7 Variation of lamellar thickness with cooling rate for IMI 834.



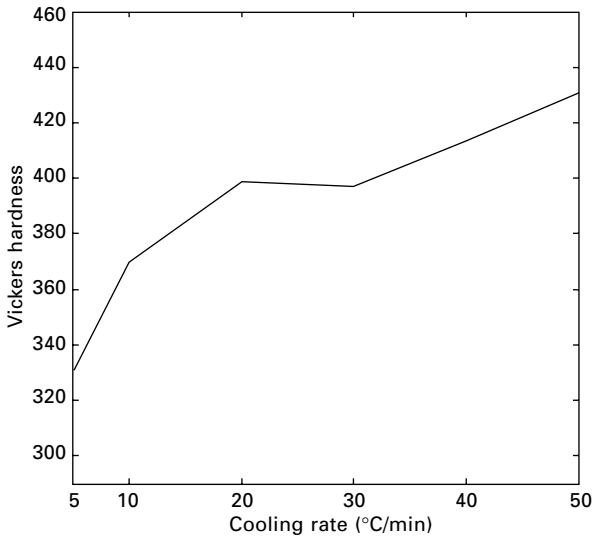
7.8 Influence of the cooling rate on (a) lamellar thickness and (b) hardness of IMI 367.

7.5 Calculation of continuous-cooling-transformation diagrams

Usually, the degree of transformation is equal to the fraction of heat absorbed or released:



(a)

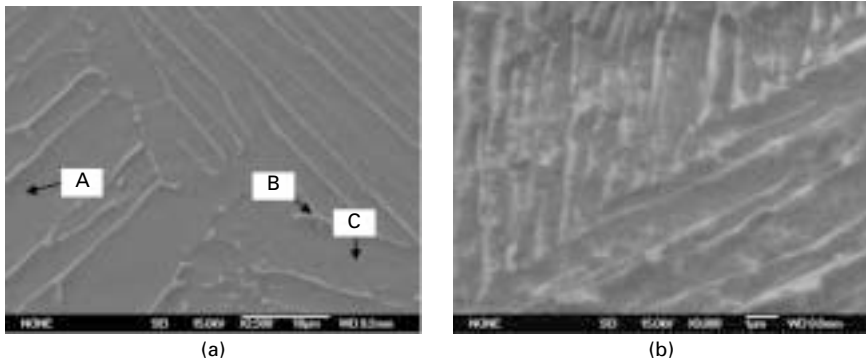


(b)

7.9 Vickers microhardness of (a) Ti-8Al-1Mo-1V and (b) IMI 834 after cooling at different cooling rates.

$$f(t) = \frac{\int_{t_S}^t \frac{\partial h}{\partial t} dt}{\int_{t_S}^{t_E} \frac{\partial h}{\partial t} dt} = \frac{\int_{T_S}^t H dt}{\int_{T_S}^{T_E} H dt} \quad [7.1]$$

where $\partial h/\partial t$ (H) is the temperature difference in the case of DTA or the heat



7.10 Scanning electron micrographs of fully lamellar microstructure in Ti-8Al-1Mo-1V after continuous cooling from 1100 °C at (a) 5 and (b) 50 °C/min.

Table 7.2 The local chemical composition of the points A–C shown in Fig. 7.10a for the cooling rate of 5 °C/min

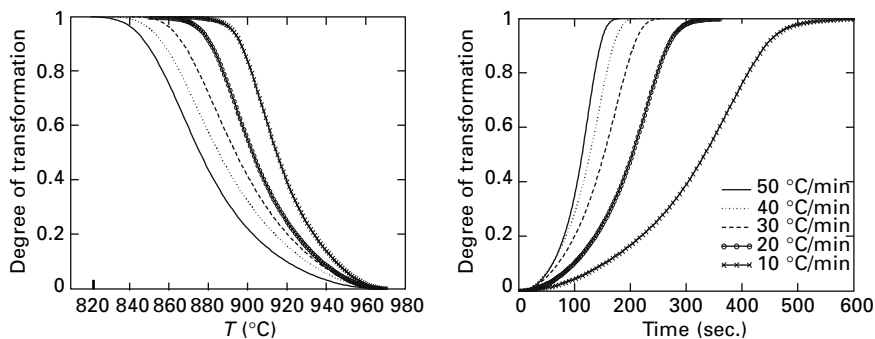
Location	Ti		Al		V		Mo	
	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%
A (α)	91.6	85.9	8.4	14.1	–	–	–	–
B (β)	85.9	83.3	6.5	11.3	4.4	4.0	3.2	1.6
C (α)	91.6	86.0	8.4	14.0	–	–	–	–

flow in the case of DSC, $f(t)$ is the degree of transformation at any given time t , and t_S and t_E are the transformation start and end temperatures corresponding, respectively to the transformation start and end temperatures T_S and T_E .

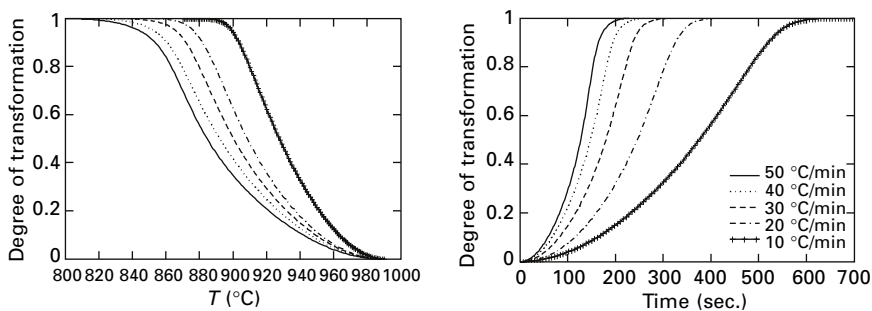
Hence, from the DSC signal (Fig. 7.1) and using Eq. [7.1], the degree of transformation as a function of the time or the temperature can be calculated and plotted (Fig. 7.11), which traces the course of the β to α transformation in the Ti-6Al-4V, the Ti-6Al-2Sn-4Zr-2Mo-0.08Si, the Ti-8Al-1Mo-1V, IMI 834 and IMI 367 alloys and the formation of the γ phase in the Ti-46Al-2Mn-2Nb alloy.

For all cooling rates, a small amount of residual (or retained) β phase, about 9 wt.% independent of the cooling rate, remains after complete transformation in Ti-6Al-4V (see Fig. 7.12). Therefore, for all cooling rates, the same phase transformation is traced (100% β to 91% α + 9% β). The only difference between X-ray diffraction patterns after different cooling rates is in the relative intensities of the different $\{hkl\}$ planes of the α phase (Fig. 7.12). This is probably due to preferred orientations of the α phase under different cooling rates, as mentioned in Section 7.3 for Ti-6Al-2Sn-4Zr-2Mo-0.08Si.

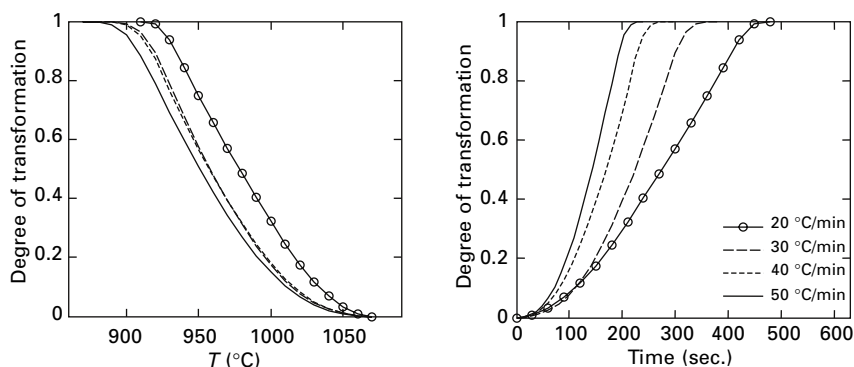
Hence, in Ti-6Al-4V, hereafter in the calculations, 100% completed transformation corresponds to an actual phase composition of 91% α + 9% β . All calculations can very easily be converted from degree of transformation (from 0 to 100%) to amount of α phase (from 0 to 91%).



(a)

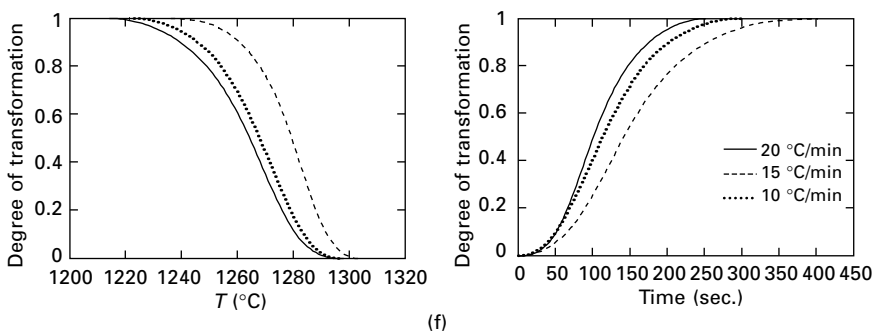
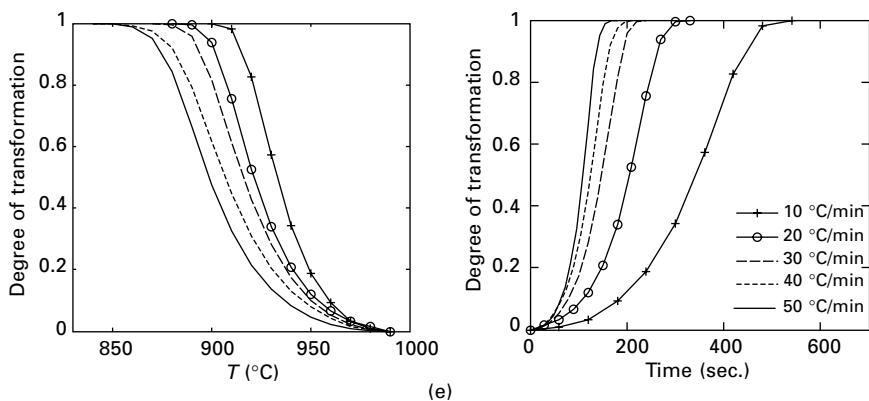
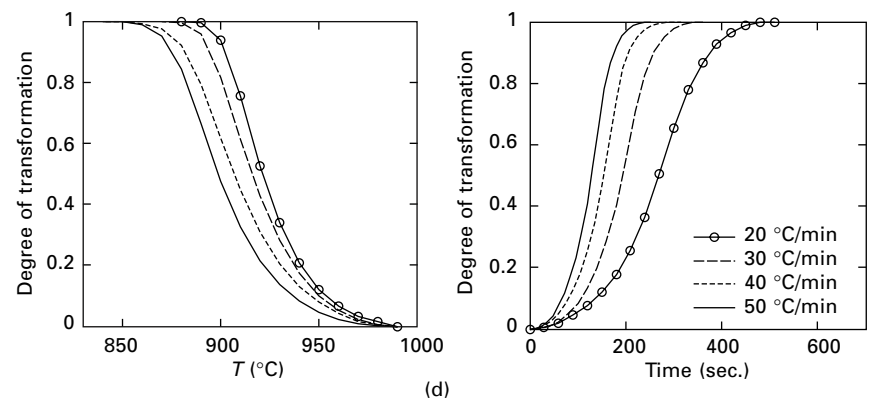


(b)



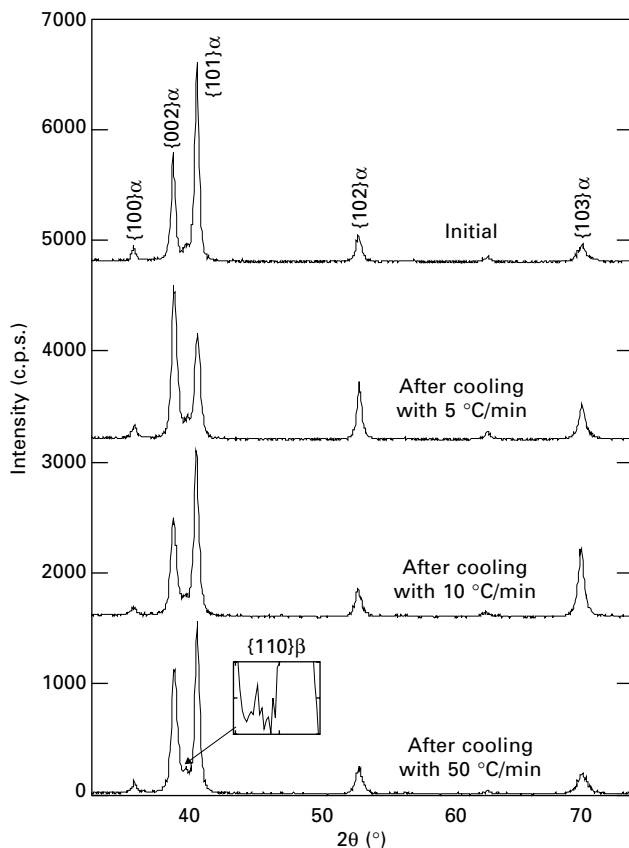
(c)

7.11 Calculated degree of transformation as a function of the temperature (left hand side) and the time (right hand side), for different cooling rates for (a) Ti-6Al-4V, (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si, (c) Ti-8Al-1Mo-1V, (d) IMI 834, (e) IMI 367, and (f) Ti-46Al-2Mn-2Nb.



7.11 Continued

Applying Eq. [7.1] again for all the cooling rates used, iso-transformation contour plots are produced (Fig. 7.13). Such diagrams are a useful tool, since they can be used to trace the course of transformation in real product, where the cooling rates in a (usually quite large) piece vary significantly from the surface to the core.

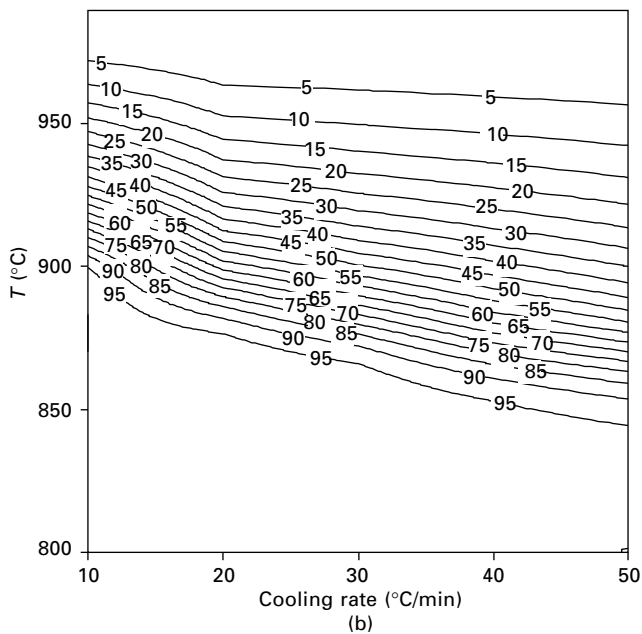
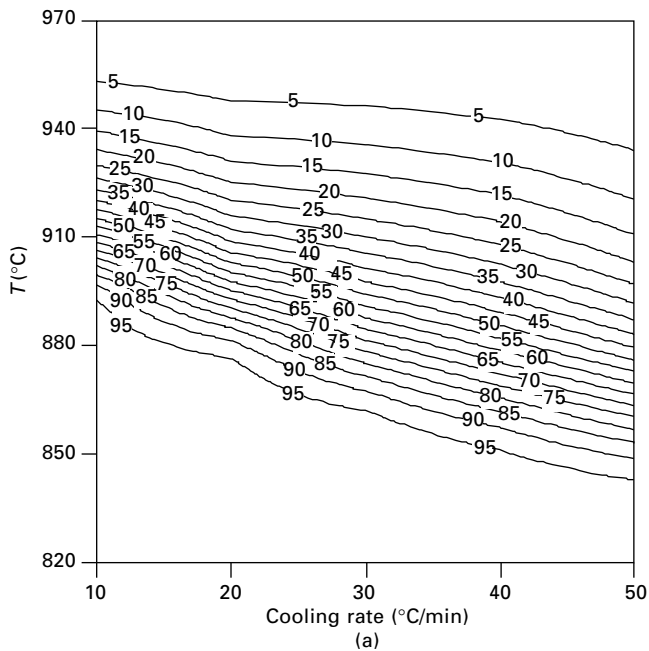


7.12 X-ray diffraction patterns of Ti-6Al-4V after cooling at different rates. For clarity, the diffraction patterns are shifted along the vertical axis with respect to each other.

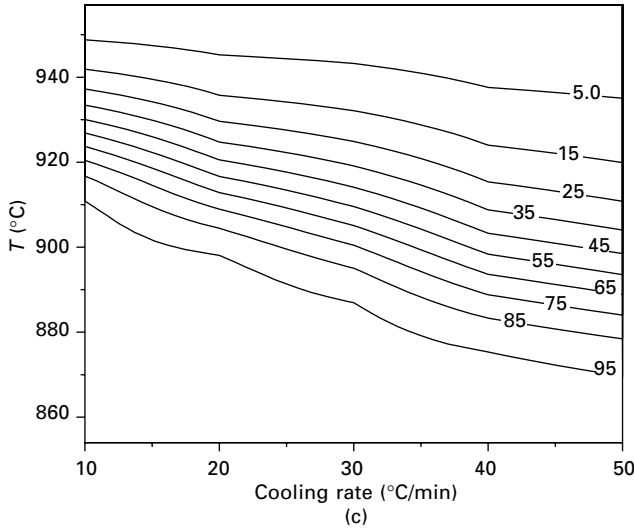
Finally, the transformation kinetics can be presented in the form of classical CCT diagrams (Fig. 7.14). In these diagrams, iso-lines of equal degree of transformation for the different cooling rates are included. The CCT diagrams are shown for two cases: (i) cooling from 1100 °C, and (ii) cooling from the β -transus of the alloys.

7.6 Calculation of transformation kinetics

The kinetics of isothermal transformations is usually expressed by the theory developed by Johnson, Mehl and Avrami (JMA), Eq. [6.1]. However, it must be emphasised that Eq. [6.1] expresses the JMA theory under the following assumptions:



7.13 Calculated thermo-kinetics diagram – temperature of transformation versus cooling rate of (a) Ti-6Al-4V, (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si and (c) IMI 367. Iso-lines show the iso-degree of transformation.



7.13 Continued

- isothermal transformation;
- nucleation frequency is either constant, or else is a maximum at the beginning of transformation and decreases during the course of transformation;
- spatially random nucleation.

In the past, this theory has been adapted for non-isothermal transformations and used as the theoretical basis for interpretation of DTA and DSC data. Different methods based on the JMA theory have been developed and used for calculating kinetic parameters. Among them, the most frequently used are the following:

- (i) Direct integration of the generalised form of the JMA equation,

$$f = 1 - \exp \left[-g \int_0^t I_V \left(\int_0^{t'} u d\tau \right)^m dt' \right] \quad [7.2]$$

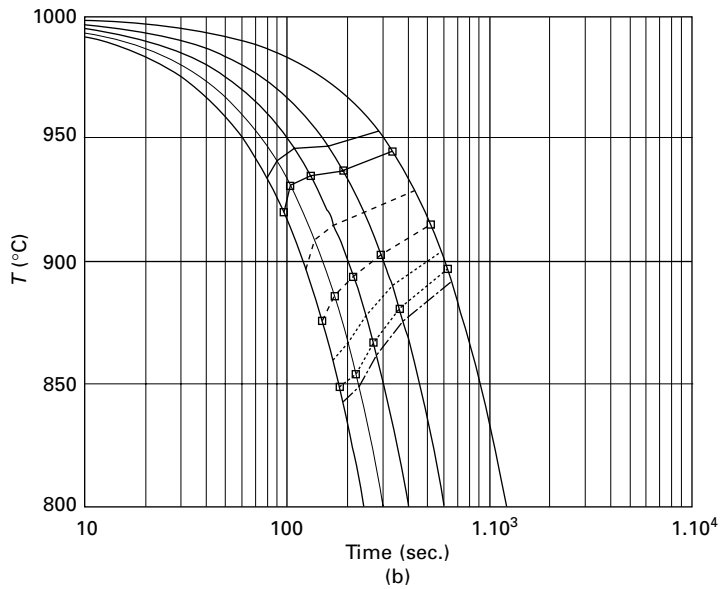
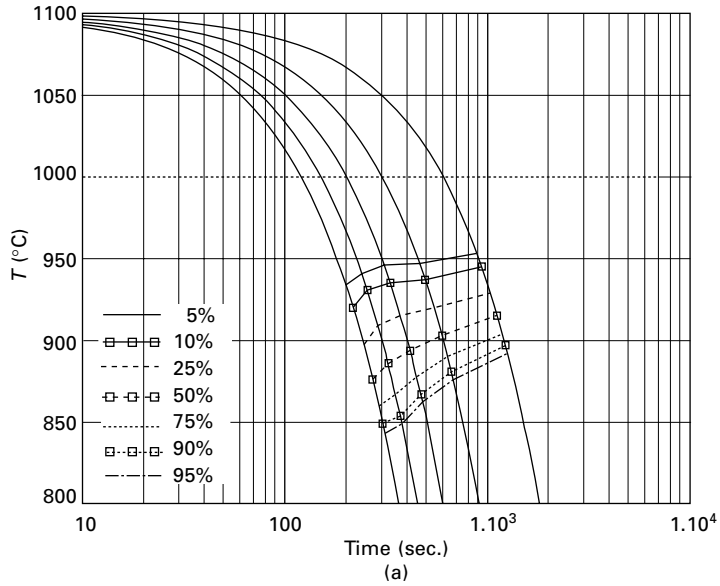
where f is transformed volume fraction at time t , I_V is the nucleation frequency, u is the growth rate, g is a geometrical factor, τ is integrated variable and $m = n - 1$.

- (ii) Introduction of new state variable,

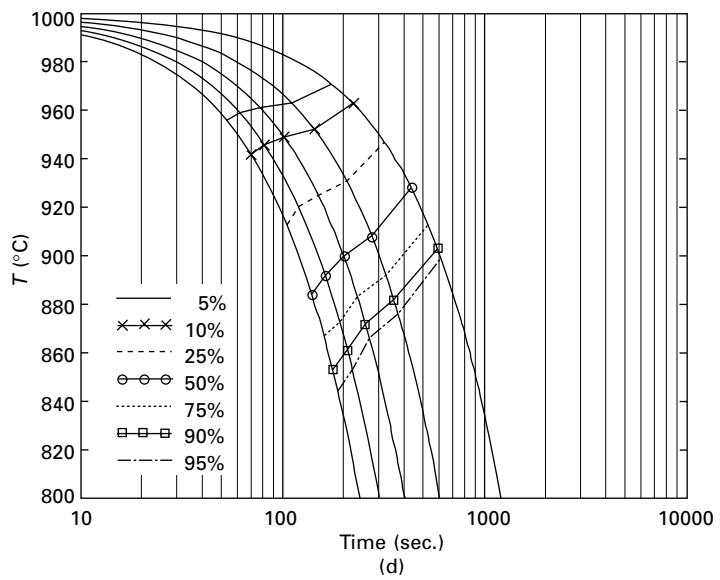
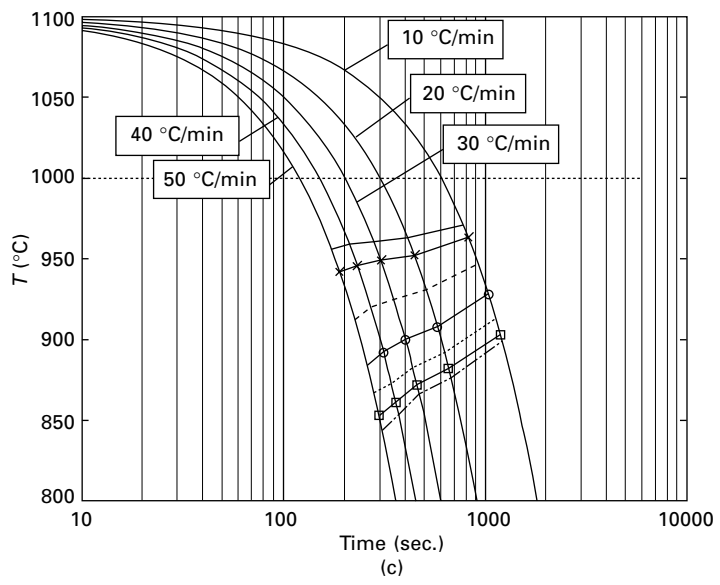
$$f = 1 - \exp(-\theta^n) \quad [7.3a]$$

where f is transformed volume fraction, n is Avrami exponent, and

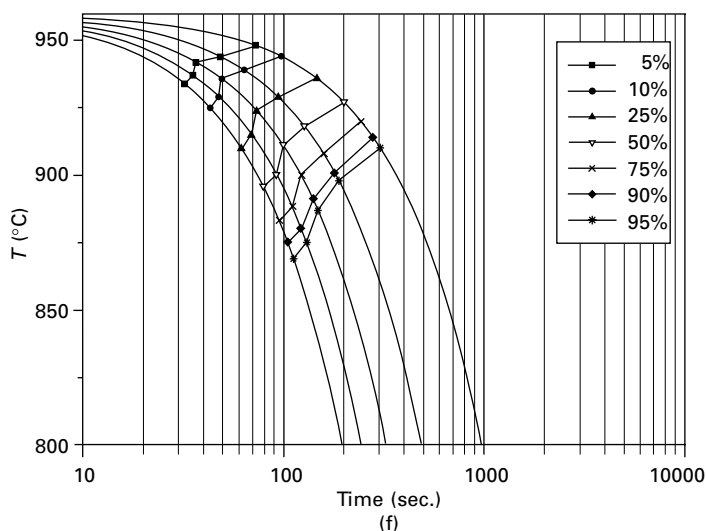
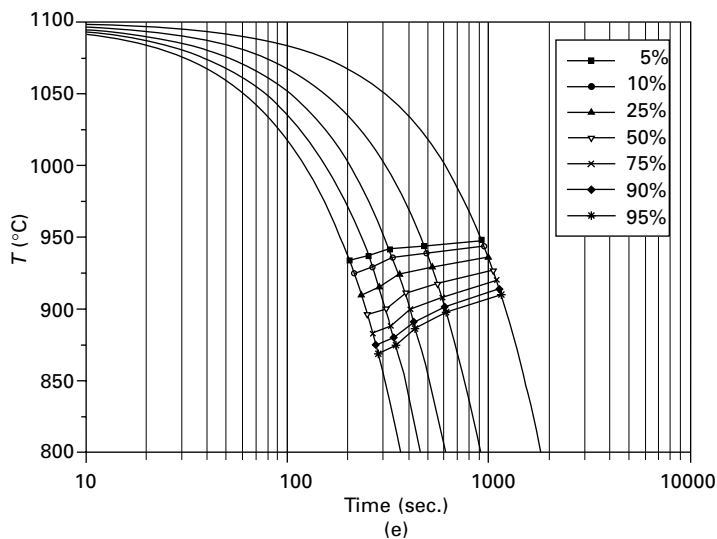
$$\theta = \int_0^t k(T) dT; \quad k(T) = k_0 \exp \left(\frac{-Q}{RT} \right) \quad [7.3b]$$



7.14 Calculated continuous-cooling-transformation (CCT) diagrams of the β to α (or β to $\alpha + \beta$) transformation in (a) and (b) Ti-6Al-4V; (c) and (d) Ti-6Al-2Sn-4Zr-2Mo-0.08Si; (e) and (f) IMI 367, for cooling from (a,c,e) 1100 °C and (b,d,f) β -transus.



7.14 Continued



7.14 Continued

where k_0 is the pre-exponential factor, Q is the activation energy and R is the gas constant.

In general, all the adaptations of JMA have been successfully applied to describe the kinetics of phase transformations during continuous heating, and mostly for the processes of crystallisation of amorphous materials. This is a relatively simple case compared with phase transformation taking place during continuous cooling, because during heating, both nucleation and growth rates increase with temperature.

On cooling, the nucleation rate is determined by a Boltzmann type equation, having an activation energy which decreases more than linearly with temperature. This gives a rapidly increasing nucleation rate as the undercooling increases (i.e. as temperature decreases). The growth rate, in contrast, is controlled by an activation energy which is considered to be temperature independent, and hence the growth rate decreases as the undercooling increases (i.e. as temperature decreases). These opposing factors give an overall transformation rate.

Taking these into account, it can be concluded that the methods described for tracing the course of phase transformation during heating cannot be directly applied to the cases of phase transformations during continuous cooling. As an alternative approach, we replace continuous cooling T - t path with the sum of small, consecutive isothermal steps. This concept has been used before, to study the kinetics of different phase transformation from DSC data. We will follow this approach to describe the kinetics of the phase transformations during continuous cooling in titanium alloys.

The T - t path of continuous cooling is replaced by the sum of consecutive isothermal steps (see Fig. 7.15), at temperatures T_1 , T_2 , T_i (note that cooling rate is a constant). For each isothermal step, JMA theory for isothermal phase transformations, Eq. [6.1], is applied. Hence, for cooling from point 0 to point 1, the following can be written:

$$f_1 = 1 - \exp(-k_1 \Delta t^{n_1}) \quad [7.4a]$$

where f_1 is degree of transformation from 0 to 1 (see Fig. 7.15), k_1 and n_1 are JMA kinetics parameters at temperature T_1 and Δt is isothermal time.

For tracing the transformation from 0–2, the principle of additivity must be adhered to. Thereby, the first fictitious time for point 1 is calculated using

$$t_2^* = n_2 \sqrt[n_2]{\frac{\ln(1 - f_1)}{-k_2}} \quad [7.4b]$$

where t_2^* refers to the time after which the amount f_1 would have been transformed if the whole transformation were at an isothermal temperature T_2 with kinetics parameters k_2 and n_2 . Thereafter, the time is increased by the increment of Δt and for interval 0–2, one may write:

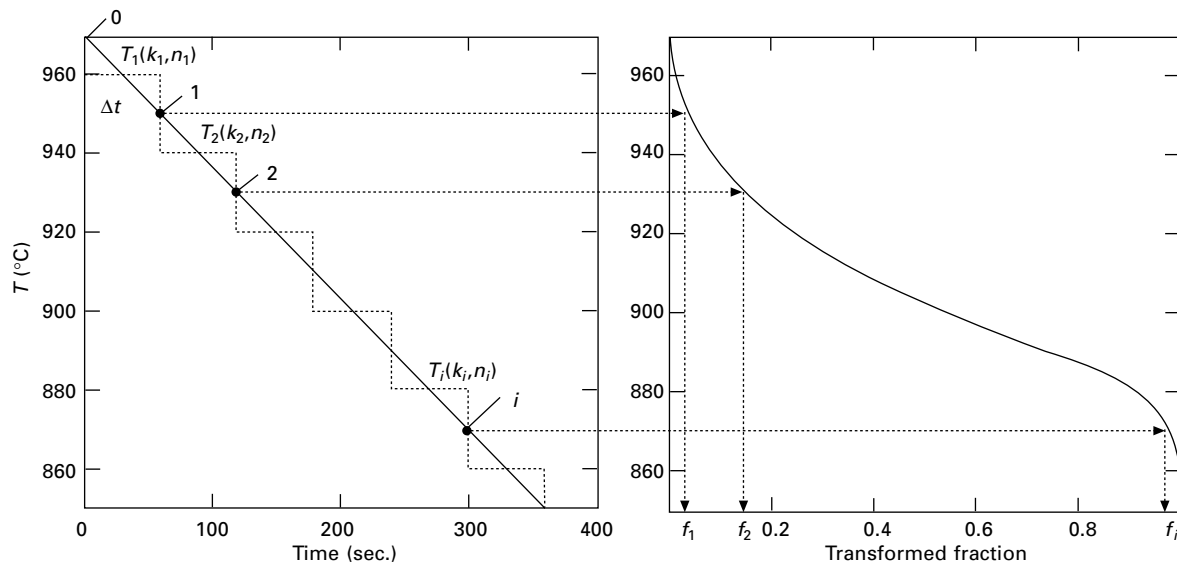
$$f_2 = 1 - \exp(-k_2 \cdot (t_2^* + \Delta t)^{n_2}) \quad [7.4c]$$

From the above reasoning, the general case for interval 0– i is as follows:

$$f_i = 1 - \exp(-k_i \cdot (t_i^* + \Delta t)^{n_i}) \quad [7.4d]$$

where

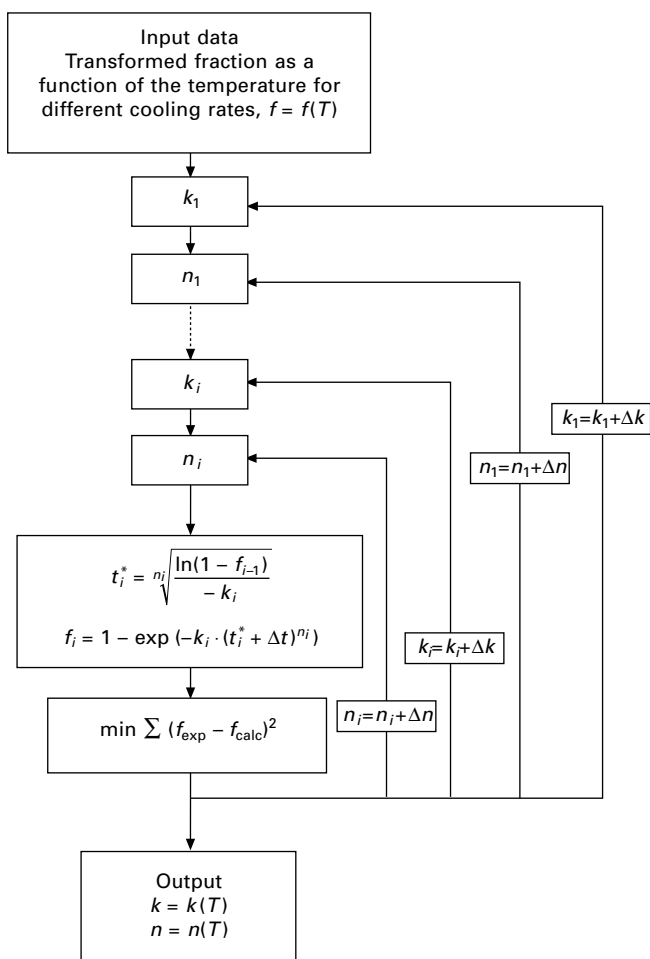
$$t_i^* = n_i \sqrt[n_i]{\frac{\ln(1 - f_{i-1})}{-k_i}} \quad [7.4e]$$



7.15 Schematic diagram for the approximation of continuous cooling as the sum of short time isothermal holding.

These calculations present a numerical solution of the general expression of the concept of additivity.

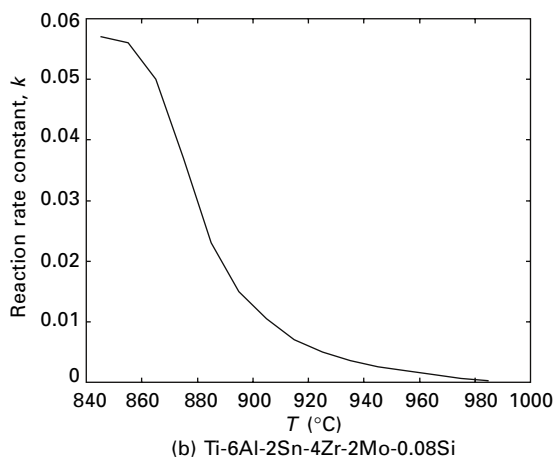
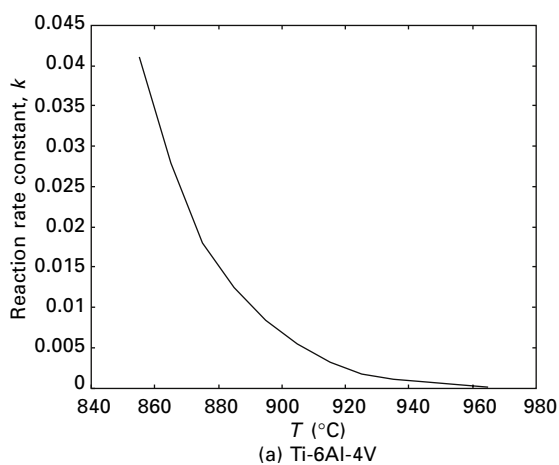
On the basis of the above description, a computer program can be created to derive the optimised JMA kinetic parameters at different temperatures from the DSC experimental data (see Fig. 7.16). The input data are the degree of transformation as a function of the temperature for cooling rates of 10, 20, 30 and 40 °C/min, etc. The program contains loops for the kinetic parameters at the different temperature stages ($k_1, k_2, \dots, k_i$ and $n_1, n_2, \dots, n_i$). The experimental degree of transformation is compared with the calculated degree of transformation and errors are minimised using a sum-squared error technique.



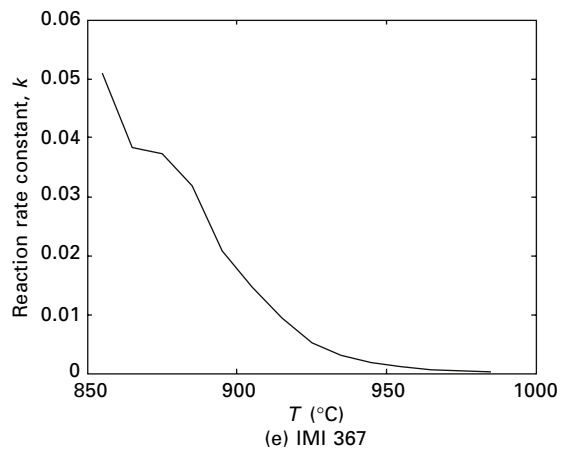
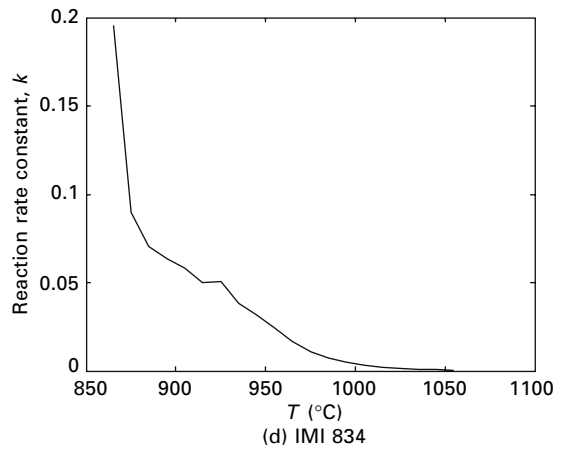
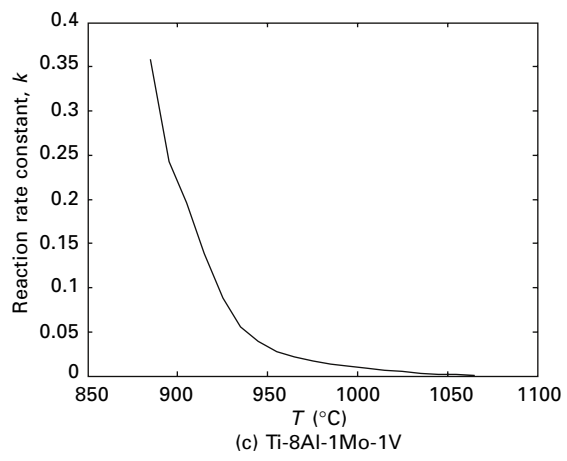
7.16 Flow diagram of program for calculation of JMA kinetic parameters.

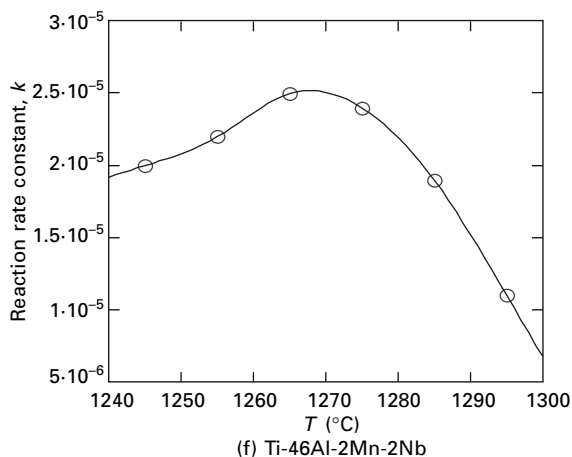
For the calculations, in these particular cases, (the β to $\alpha + \beta$ transformation in Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-0.08Si, Ti-8Al-1Mo-1V, IMI 834 and IMI 367 and the γ phase formation in Ti-46Al-2Mn-2Nb), it is accepted that n does not vary with the temperature ($n_1 = n_2 = n_i$). The value of n depends largely on the growth geometry, and therefore it should change only when this geometry varies. The output of the program to derive JMA kinetic parameters is $n = 1.13$ for Ti-6Al-4V, $n = 1.01$ for Ti-6Al-2Sn-4Zr-2Mo-0.08Si, $n = 0.82$ for Ti-8Al-1Mo-1V, $n = 0.95$ for IMI 834, $n = 1.15$ for IMI 367 and $n = 2.2$ for Ti-46Al-2Mn-2Nb, and $k = k(T)$ (see Fig. 7.17).

These n values imply that the preferable nucleation sites are β grain boundaries in the cases of β to $\alpha + \beta$ transformation in Ti-6Al-4V, Ti-6Al-



7.17 Calculated rate constant (k) as a function of the temperature. (a) to (e) β to $\alpha + \beta$ or β to α phase transformation; (f) γ phase formation in Ti-46Al-2Mn-2Nb.





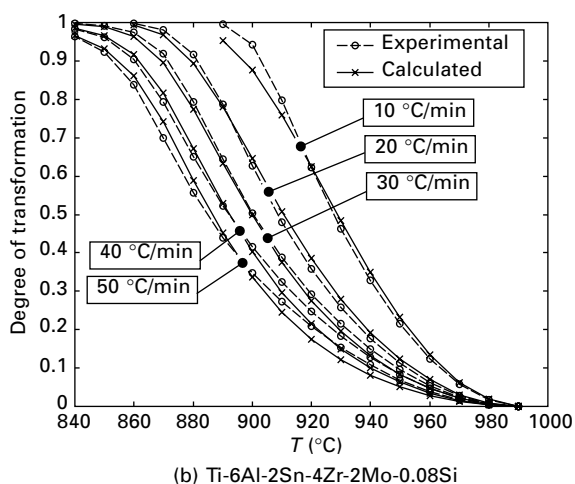
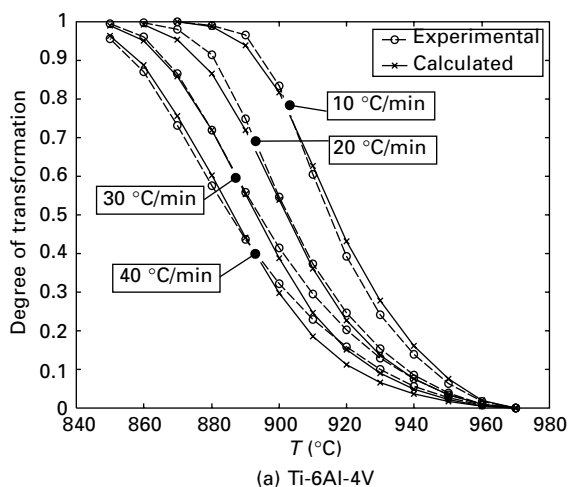
7.17 Continued

2Sn-4Zr-2Mo-0.08Si, Ti-8Al-1Mo-1V, IMI 834 and IMI 367. This is characteristic of the phase transformation during cooling in titanium alloys, and is confirmed by metallographic examinations in Section 7.4, as well as metallographic examinations at different stages of the β to $\alpha + \beta$ transformation. Similar n values have been reported for titanium alloys 6-2-4-6, β -CEZ and 10-2-3 (Bein and Bechet, 1996). Bein and Bechet (1996) found that for 6-2-4-6, $n = 1$ for the temperature range from β -transus (940 °C) to 240 °C below β -transus, and for β -CEZ, n was in the range of 1–1.2 for temperature range from β -transus (890 °C) to 290 °C below β -transus.

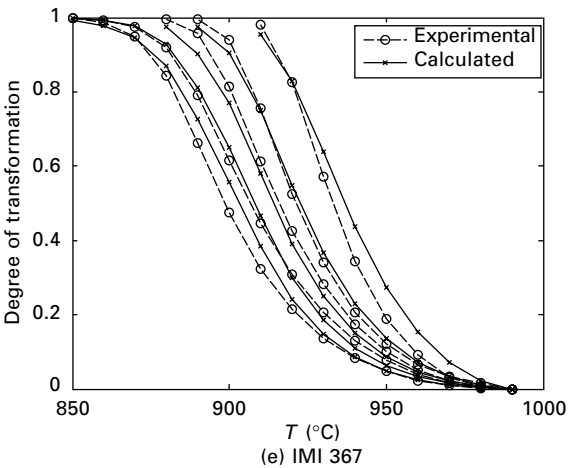
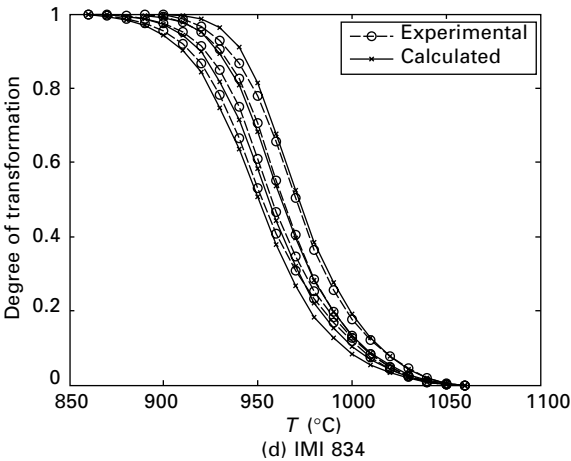
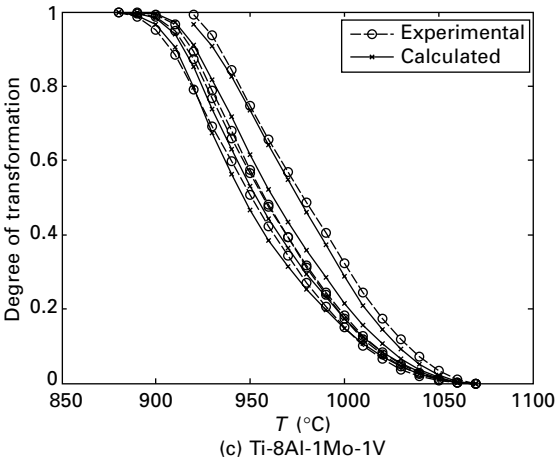
The value of k for the transformations in the alloys varies vastly with temperature (see Fig. 7.17). In the case of β to $\alpha + \beta$ transformation in Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-0.08Si, Ti-8Al-1Mo-1V, IMI 834 and IMI 367, it increases significantly when the temperature decreases from β -transus to 850 °C. In the case of γ phase formation in Ti-46Al-2Mn-2Nb, it increases significantly when the temperature decreases from 1300 to 1270 °C, and then decreases when the temperature is below 1270 °C. A similar tendency of $k(T)$ was reported for austenite to pearlite phase transformation in steels (Homberg, 1996). The way of variation of k means that, in the above temperature range, the nucleation rate controls the overall transformation rate. From the DSC data using a high cooling rate (50 °C/min), there is some evidence of a decrease of k when the temperature decreases to below 850 °C. These observations are in good agreement with C-curves of the experimental TTT diagrams for Ti-6Al-4V (Chapter 14) and Ti-6Al-2Sn-4Zr-2Mo-0.08Si (Rosenberg *et al.*, 1991), and the TTT diagram predicted from an artificial neural network model for the Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloy (Chapter 14).

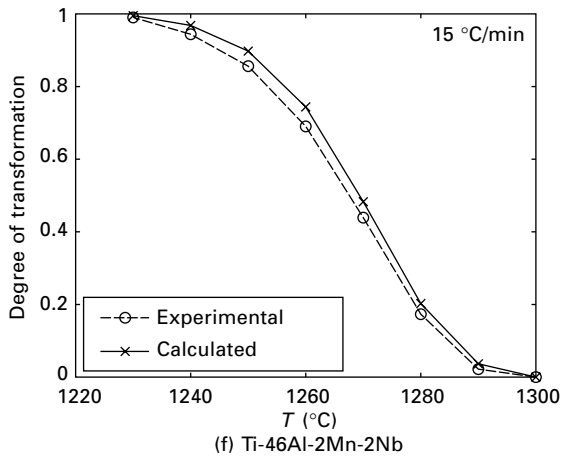
As the next step, we calculate the degree of transformation for different cooling rates, using the derived values of n and k . Good agreement between

calculated and experimental degree of transformation is shown (Figs. 7.18 and 7.19). In the case of Ti-6Al-4V, there is some deviation, at approximately 0.05 level, for temperatures above 900 °C and cooling rates above 20 °C/min. The main reason for the deviation at high temperatures is because, as stated before, the transformation start is not clearly defined in the DSC curves and a start temperature of 970 °C is attributed, for all cooling rates. Also, the experimental error is larger at higher cooling rates. Nevertheless, agreement between experimental and model results is more than acceptable.



7.18 Experimental and calculated degree of transformations for different cooling rates. (a) to (e) β to $\alpha + \beta$ or β to α phase transformation; (f) γ phase formation in Ti-46Al-2Mn-2Nb.



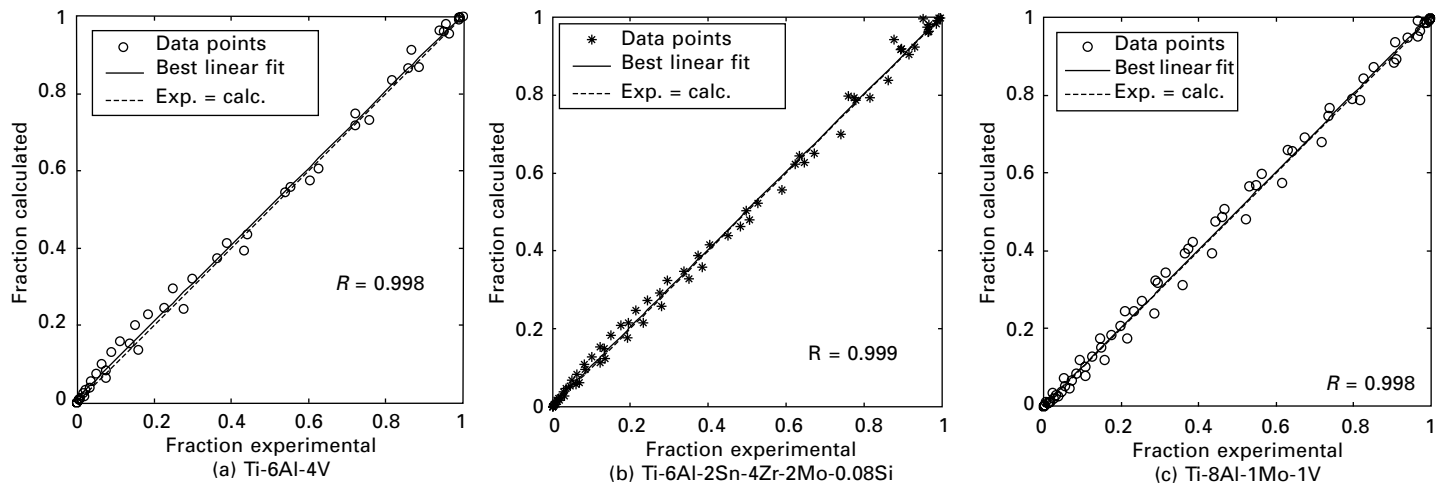


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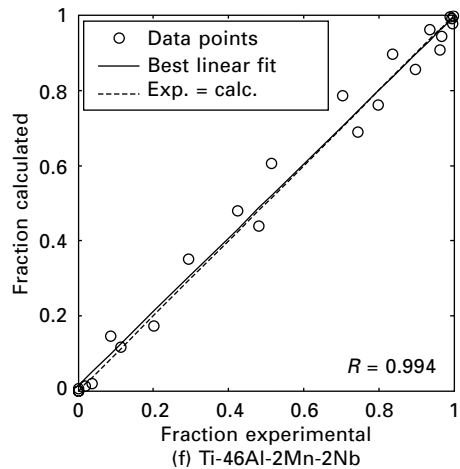
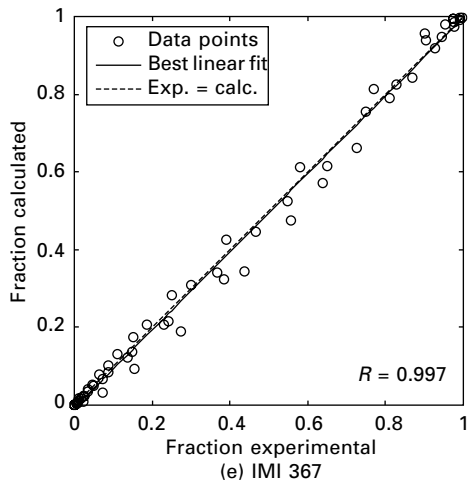
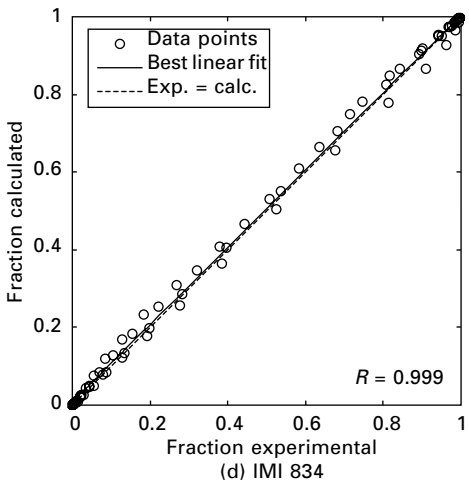
These parameters can be used to trace the course of the phase transformations in titanium alloys in real practice for any, not necessarily constant, cooling path.

7.7 Simulation and monitoring of transformations on continuous cooling

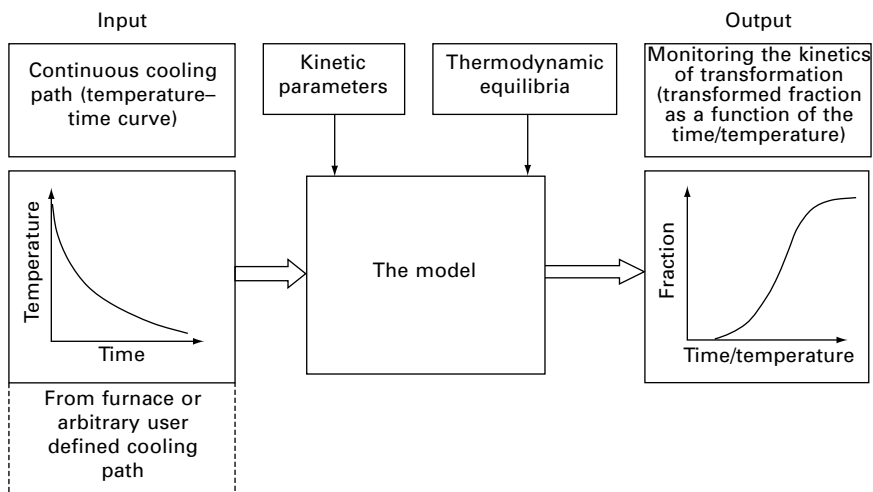
The JMA kinetic parameters are derived from DSC or DTA data with constant cooling rates. However, once obtained, these parameters can be used to trace the course of β to α transformation and γ phase formation in real practice for a non-uniform cooling rate. Based on the derived kinetic parameters, we have developed models for monitoring the β to α transformation and the γ phase formation during continuous cooling with an arbitrary cooling path (Fig. 7.20). The input for the model is the cooling path, which can be user-defined or input from a real furnace. The kinetic parameters as well as the data on the thermodynamic equilibria are incorporated in the model. Utilising the cooling laws, kinetic parameters and thermodynamic equilibria, the transformation process is calculated and displayed. The calculation procedure is similar to the calculations previously described. The arbitrary cooling path is digitised and presented as a sum of consecutive isothermal steps (note that since the cooling rate is not constant the intervals are not equal with respect to time). The calculations are then performed using the JMA models, taking into account the principle of additivity and the phase equilibrium conditions. In this way, the transformation process can be traced for any cooling path. One example generated from the model is demonstrated in Fig. 7.21. The model may not work with sufficient accuracy for high cooling rates (>100 °C/min), where martensitic transformation may be involved.



7.19 Regression analysis of calculated and measured degree of transformation during continuous cooling in different titanium alloys. The data are for all cooling rates used.



7.19 Continued



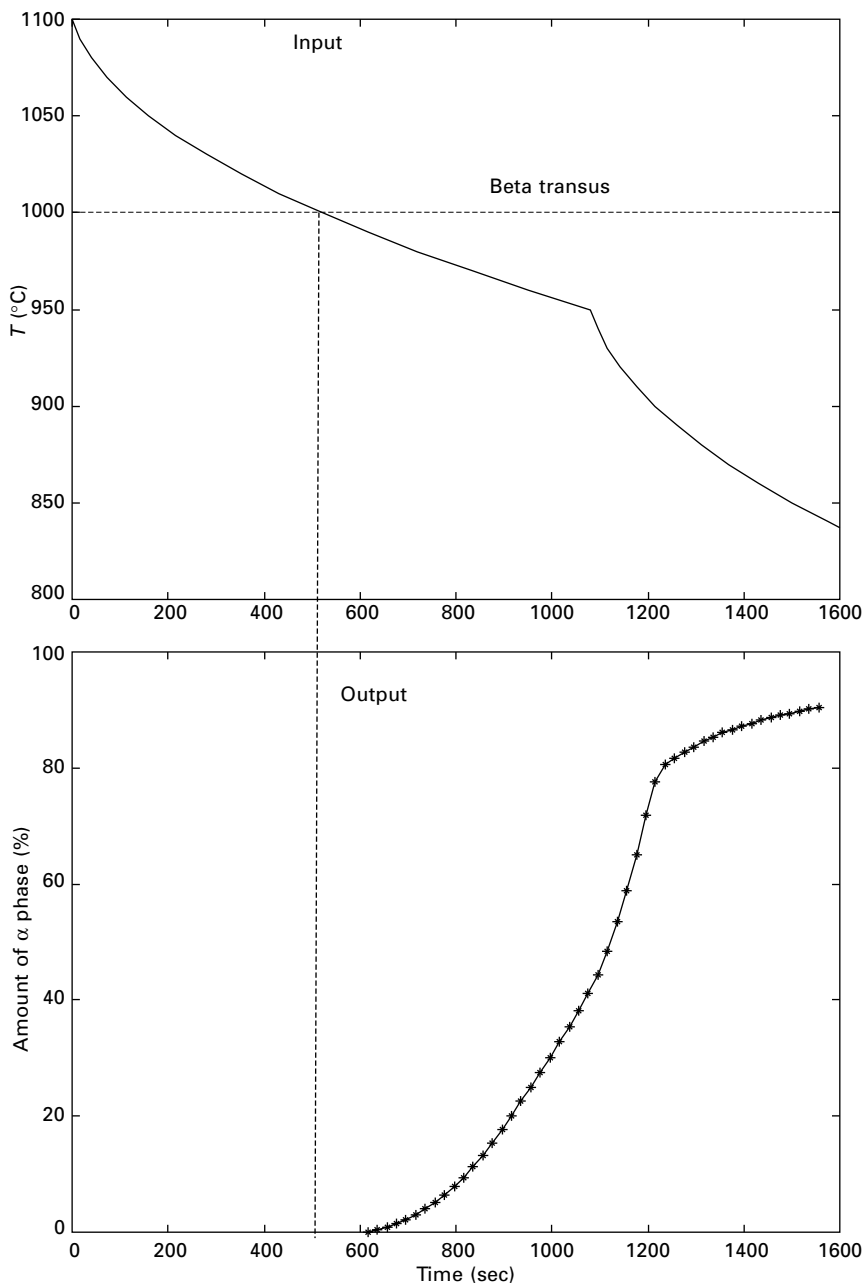
7.20 Block diagram of model for tracing transformation on continuous cooling.

An option is incorporated into the model to enable it to be linked to a real furnace. In this case, the cooling path of the furnace (i.e. time–temperature curve) is read into the model as an ASCII data file. Thus, the transformation process is monitored in real-time. This kind of model could provide a useful insight into such processes.

7.8 Summary

The DSC technique is suitable for quantitative description of transformations in titanium alloys during continuous cooling. Using DSC data, CCT diagrams with lines of iso-degree of transformation are proposed. The cooling rate is shown to influence the lattice parameter of the α phase in conventional titanium alloys.

The JMA theory can be adapted to describe and model the kinetics of transformations in titanium alloys as functions of the temperature. The kinetic parameters can be derived. Good agreement between the calculated and the experimental transformed fractions is demonstrated. Using the derived kinetic parameters, the transformations can be described for any cooling path and conditions. A model has been developed to monitor the transformation process for complex cooling paths.



7.21 Calculated kinetics of β to α transformation in Ti-6Al-2Sn-4Zr-2Mo-0.08Si for continuous cooling with an arbitrary cooling path.

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Finite element method: morphology of β to α phase transformation

Abstract: A mathematical model and computer programs are described for numerical simulation of the processes of nucleation and growth of the α phase Widmanstätten plates during the course of the β to α phase transformation in titanium alloys. The α phase appearance at the grain boundary of β phase is described by a numerical procedure for random nucleation as a function of the β stabiliser concentration and the temperature. The rate at which an interface moves depends both on the intrinsic mobility and on the rate at which diffusion can remove the excess of β stabiliser atoms ahead of the interface.

Key words: microstructure evolution, finite element method, diffusion, thermodynamics, nucleation.

8.1 Introduction

The modelling of phase transformations in titanium alloys described in the last three chapters was about the thermodynamics and the kinetics during processing without taking into account their morphology and geometry.

The morphology, distribution and geometry of the fine microstructure cannot be described in the framework of the Johnson–Mehl–Avrami theory. The problem for predicting the morphology of titanium alloys, formed during phase transformations, can be solved with the development of mathematical models describing the nucleation and growth processes of the new phase. If the mathematical formulation of the problem is known as a system of partial differential equations, one of the most powerful numerical techniques for obtaining its solution is the finite element method (FEM).

In this chapter, we extend the kinetics modelling in the last two chapters. We will show a mathematical model and one-dimensional and two-dimensional finite element computer simulation of the nucleation and growth processes of the α phase Widmanstätten plates lamella structure during the β to $\alpha + \beta$ phase transformation on cooling from homogeneous β range, and the morphology, distribution, and geometry of the fine microstructure. This type of cooling is the practical case of cooling after β solution treatment of α , near- α and $\alpha + \beta$ alloys (see the alloy classification in Chapter 1). The model has been adjusted and verified to simulate the microstructure evolution in Ti-6Al-4V (Ti 6-4), Ti-6Al-2Sn-4Zr-2Mo (Ti 6-2-4-2) and Ti-8Al-1Mo-1V (Ti 8-1-1) alloys. It is generally based on the fundamental metallurgical theories for phase nucleation and diffusion controlled growth. The FEM will be used

to obtain numerical solution of the problem for localisation and evolution of the α/β interface. The model is a general and powerful tool for optimisation of the processing parameters in order to obtain pre-defined microstructure and properties for different applications.

8.2 Experimental and modelling methodology

During the course of the model development, many unknown parameters need to be derived or fitted. This can be done with the help of data from experiential work and integrating different modelling techniques.

Experimental data are used to feed and verify the models developed. Once developed, the models are capable of giving predictions and simulations for new processing conditions for which experimental data do not exist. The experimental and materials conditions used for developing the model presented in this chapter are described in an original research paper (Malinov *et al.*, 2005).

The phase transformations and microstructure evolution taking place at different processing conditions are studied after heat treatment of furnace cooling from the β field. Optical, including high-temperature *in situ*, microscopy is used to characterise the morphology of the phases present and to study the mechanisms of phase nucleation and growth in different heat treatment conditions. Experiments using room-temperature microscopy on alloys after different heat treatments are useful for studying the correlations between the processing parameters and the fine microstructure. Experiments with high-temperature microscopy are useful for studying *in situ* the morphology of the $\alpha \leftrightarrow \beta$ phase transformations in titanium alloys. Information on the specimens and further details on the microscopy study are given by Malinov *et al.* (2002).

Differential scanning calorimetry (DSC) is used to *in situ* study the kinetics of the β to α phase transformation at various conditions of continuous cooling. The data from the DSC can be used to compare and fit the numerical simulations for microstructure evolution in terms of the amounts of phases at different temperatures during a continuous cooling process. The following time–temperature cycle has been found particularly useful: heating up to β -field using a heating rate of 20 °C/min; isothermally holding for 20 min for homogenisation; and thereafter cooling with varying cooling rates of 5, 10, 20, 30, 40 and 50 °C/min.

The α phase appearance at the grain boundary of β phase is described by a numerical procedure for random nucleation as a function of the alloy composition and the temperature. The rate at which an interface moves depends both on the intrinsic mobility and on the rate at which diffusion can remove the excess of β stabilising atoms ahead of the interface. The finite element method is used for solving the diffusion equation on the domain

occupied by β phase. The elements chosen have dimensions in both space and time. A computer code based on finite element modelling and the volume of fluids method is used.

8.3 Experimental observation of the morphology of the phase transformation

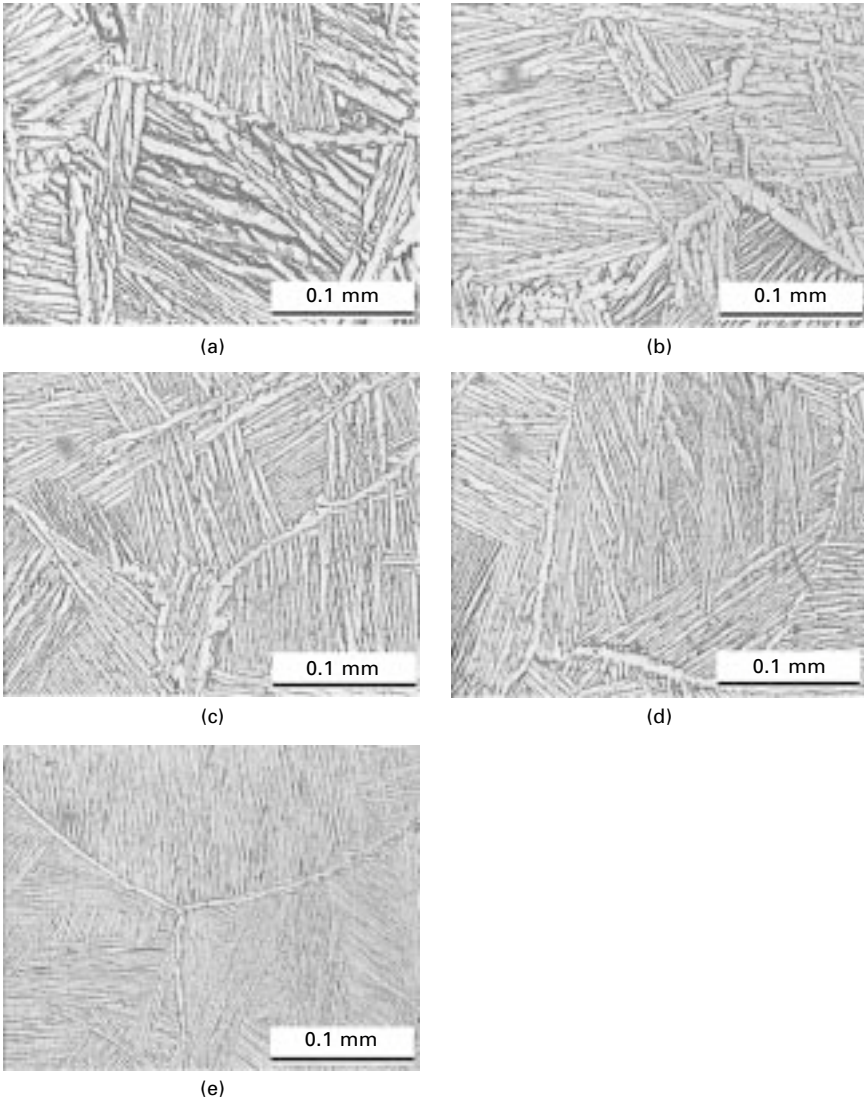
Thermodynamics and kinetics of the phase transformation process consider mainly the amounts of phases present. However, different morphologies of the phases and characteristics of the microstructure determine completely different combination of mechanical properties, and therefore the application of the alloys, even if the amounts of the phases present are the same. The microstructure of the different alloys is formed during manufacturing and subsequent thermomechanical and/or heat treatment processes. Usually, any change of the heat treatment parameters, such as temperature, time, heating/cooling rates, results in significant change in the characteristics of the microstructure. Considering these, we discuss in this chapter experimental study and computer modelling of the morphology of the phase transformations in titanium alloys at different processing conditions.

In Fig. 8.1, examples are given for microstructure from a same alloy (Ti 6-2-4-2) and same processing history, with only difference in the final cooling rate. The difference in the morphology is obvious and would result in difference in the properties. All cooling rates given in Fig. 8.1 are within the range of usual cooling in industrial conditions, ranging between furnace and air cooling. The final cooling rate plays an essential role on the microstructure formation.

A technique was developed for *in situ* microscopy study of titanium alloys based on the effect of thermal etching, which can be used to study the morphology of the $\alpha \leftrightarrow \beta$ phase transformation in different processing conditions including isothermal treatment and continuous heating/cooling. Figure 8.2 shows examples of *in situ* high temperature microscopy images taken at 780 and 840 °C for Ti 6-4 and Ti 6-2-4-2 alloys, respectively, upon cooling from 1100 °C. The data from this type of study are discussed in detail in Chapter 2 and are used to verify the model for the microstructure evolution in titanium alloys.

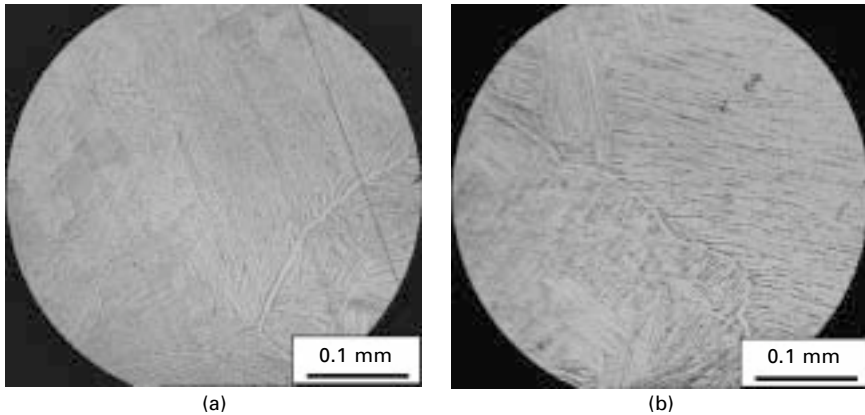
8.4 Mathematical formulation in the model for the microstructure of Ti-6Al-4V

The microstructure of the Ti-6Al-4V alloy after heat or thermomechanical treatment in the β phase field depends strongly on the cooling rate from the β region. When the alloy is slowly cooled below the β -transus temperature, the α phase is nucleated and grown in plate form, starting from β -grain boundaries. The resulting lamellar structure is referred to as plate-like α .



8.1 Microstructure of the Ti-6Al-2Sn-4Zr-2Mo alloy after continuous cooling at different cooling rates. (a) 5 °C/min; (b) 10 °C/min; (c) 20 °C/min; (d) 30 °C/min; and (e) 40 °C/min.

Faster cooling (air cooling) results in a fine needle-like α phase referred to as acicular α phase. Certain intermediate cooling rates develop Widmanstätten structures, which become finer with increasing cooling rate. The β phase remains as a thin layer between the Widmanstätten α plates. The α plates grow with their long dimension parallel to $\{110\}\beta$ plane.



8.2 *In situ* high temperature microscopy images of (a) the Ti-6Al-4V alloy at 780 °C and (b) the Ti-6Al-2Sn-4Zr-2Mo alloy at 840 °C. The images were taken at these temperatures during continuous cooling from 1100 °C at a cooling rate of 20 °C/min.

The β to α transformation in Ti-6Al-4V begins when a nucleus of α phase forms preferentially at β grain boundary. Since the vanadium content in the β phase is greater than in the α phase (Fig. 5.1) and because of the low diffusivity of the vanadium in the β phase, partial enrichment of vanadium is observed along the α phase boundary. This phenomenon produces a locally-stabilised β phase, and results in the formation of plate-like morphology of the α grain boundary. The α phase grain boundary presents a morphology with concave parts rich in vanadium that hinder the growth and with convex parts rich in aluminium where the Widmanstätten α plate can grow easily. The observations by transmission electron microscopy and the data of energy dispersive spectrometry analysis indicate that the β to α phase transformation is controlled mainly by vanadium diffusion. The Widmanstätten α plates obtained at slower cooling rates are thicker than the plates obtained at faster cooling rates due to the longer diffusion periods (Chapter 7).

The β to α phase transformation in titanium alloys including Ti-6Al-4V, as stated above, follows the classical way of phase transformations, namely nucleation and growth of the new α phase. The first appearance of the α phase at the grain boundary within the metastable β phase is followed by the growth of this nucleus into the surrounding matrix. An interface is created during the nucleation stage and then migrates into the surrounding parent phase during the growth stage by the transfer of atoms across the interface.

8.4.1 Nucleation

The free energy change associated with the process of nucleation of the α phase has the following three main contributions:

- (i) The creation of a volume V of α phase will cause a free energy reduction of $V\Delta g$ where Δg is the free volume energy of nucleation or driving force;
- (ii) The creation of area S of interface will give a free energy increase of $S\gamma$;
- (iii) The transformed volume will not fit perfectly into the space originally occupied by the matrix and this gives rise to a misfit strain energy ΔG_S per unit volume of α .

Summing all of these gives the total free energy change as

$$\Delta G^* = -V\Delta g + S\gamma + V\Delta G_S \quad [8.1]$$

The nucleus of the α phase forms preferentially at a β grain boundary because the interfacial energy term will be reduced and some free energy will be released, thereby reducing the activation energy barrier. Ignoring any misfit strain energy, the optimum embryo shape should be that which minimises the total interfacial free energy – two abutted spherical caps with wetting angle θ given by

$$\cos\theta = \frac{\gamma_{\beta\beta}}{2\gamma_{\alpha\beta}} \quad [8.2]$$

The excess free energy associated with the embryo will be given by

$$\Delta G^* = -V\Delta g + S_{\alpha\beta}\gamma_{\alpha\beta} - S_{\beta\beta}\gamma_{\beta\beta} \quad [8.3]$$

where V is the volume of the embryo, $S_{\alpha\beta}$ is the area of α/β interface of free interface energy $\gamma_{\alpha\beta}$ created, and $S_{\beta\beta}$ the area of β/β grain boundary of energy $\gamma_{\beta\beta}$ destroyed during the process.

The above equation can be written in terms of the wetting angle θ and the cap radius r as

$$\Delta G^* = \left(-\frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma_{\alpha\beta} \right) S(\theta) \quad [8.4]$$

where $S(\theta)$ is a shape factor given by

$$S(\theta) = \frac{1}{2}(2 + \cos\theta)(1 - \cos\theta)^2 \quad [8.5]$$

By differentiation of Eq. [8.4], it can be shown that the critical radius for nucleation is

$$r_c = \frac{2\gamma_{\alpha\beta}}{\Delta g} \quad [8.6]$$

and the activation barrier for nucleation is

$$\Delta G_c^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3\Delta g^2} S(\theta) \quad [8.7]$$

The nucleation rate is given by an equation of the form

$$N = N_v \frac{k_b T}{\hbar} \exp\left(-\frac{\Delta G_m}{k_b T}\right) \exp\left(-\frac{\Delta G_C^*}{k_b T}\right) \quad [8.8]$$

where N_v is the number of nucleation sites (atoms) per unit volume, ΔG_m , the activation energy for atomic migration across the interface, k_b , the Boltzmann constant, T , the temperature in Kelvin, and $\hbar$, the Planck constant.

N_v can be assumed to be constant. ΔG_m is usually assumed to be half of the activation energy for diffusion (Wilkinson, 2000). Note that the diffusion of vanadium away from the interface is considered in the growth theory further below, where the activation energy for bulk diffusion is used. ΔG_C^* strongly depends on the temperature and the concentration of vanadium in the β phase. The interface energy $\gamma_{\alpha\beta}$ can be considered as temperature and vanadium concentration independent and is a free parameter in the model, which is obtained by fitting the calculated results to the microstructural observations.

At each time-step, we calculate the number of nuclei on the grain boundary area S_β occupied by the β -phase using

$$J_0 = \int_{t_0}^{t_n} \int_{S_\beta} N_v \frac{k_b T}{\hbar} \exp\left(-\frac{\Delta G_m}{k_b T}\right) \exp\left(-\frac{\Delta G_C^*}{k_b T}\right) ds dt \quad [8.9]$$

At the moment that the number of nuclei increases by one, a new nucleus is generated on the β phase surface. The probability for a nucleus to appear at a point x of the grain boundary area S_β , occupied by the β phase, is proportional to the exponent of the activation energy and depends on the temperature and vanadium (the alloying element to be redistributed) concentration C :

$$P(x) = P_0 \exp\left[-\frac{\Delta G_C^*(T, C(x))}{k_b T}\right] \quad [8.10]$$

The coefficient P_0 is determined from the requirement that the total probability for a new nucleus occurring on the grain boundary area S_β at the moment t_n is equal to 1:

$$1 = P_0 \int_{S_\beta} \exp\left[-\frac{\Delta G_C^*(T, C(x))}{k_b T}\right] dx \quad [8.11]$$

8.4.2 Growth of α phase lamellae

The evaluation of aluminium and vanadium contents in the α and the β phases indicates that the migration of the interface is controlled mainly by the transfer of vanadium atoms (Fig. 5.1 and Chapter 6). For simplicity, we

consider the migration of the interface separating the two phases as a result of the flux of vanadium atoms from α to β phase. As the precipitate grows, the α becomes depleted of vanadium so that the β vanadium concentration adjacent to the interface C_i increases above the initial vanadium concentration in the β phase C_0 (see Fig. 8.3).

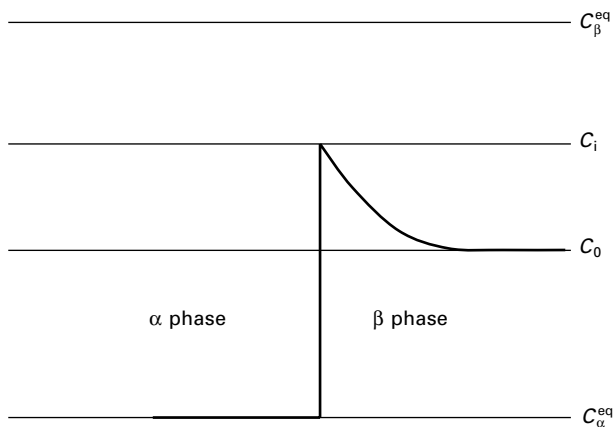
The rate at which an interface moves depends both upon intrinsic mobility, which is related to the process of vanadium atom transfer across the interface, and on the rate at which lattice diffusion can remove the excess of vanadium atoms ahead of the interface. If the interfacial reaction is fast, i.e. the transfer of atoms through the interface is an easy process, the growth is known as diffusion controlled. However, if, for some reasons, the interfacial reaction is much slower than the rate of diffusion, the growth rate will be governed by interface kinetics. The growth is said to be interface controlled.

The two processes are in series so that the interface flux calculated from the interface mobility always equals the flux calculated from the diffusion ahead of the interface.

Since the growth of the precipitate requires a flux of vanadium atoms from α to β phase, there must be a positive driving force across the interface – difference in the chemical potential that drives the vanadium atoms across the boundary $\Delta\mu_V$. Clearly, for growth to occur, the interface composition C_i must be lower than the equilibrium vanadium concentration in the β phase C_β^{eq} . The corresponding flux across the interface will be given by

$$J_V^i = \frac{M\Delta\mu_V}{V_m^2} \quad [8.12]$$

where M is the interface mobility and V_m is the molar volume of the α phase.



8.3 Vanadium concentration profile at the α/β interface.

As a result of the concentration gradient in the β phase, there will also be a flux of vanadium atoms removing the excess of vanadium ahead of the interface given by

$$J_V^\beta = D \nabla C|_{\text{interface}} \quad [8.13]$$

where D is the diffusion coefficient of vanadium. If a steady state exists at the interface, these two fluxes must balance:

$$J_V^i = J_V^\beta \quad [8.14]$$

The diffusion process and the concentration of vanadium in the β phase can be calculated by solving the classical diffusion equation in appropriate initial and boundary conditions:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) \quad [8.15]$$

Ignoring the heat absorbed or evolved and volume changes during the process of phase transformation, the free energy change is due only to the change in entropy. In this case the driving force $\Delta\mu_V$ is given as

$$\Delta\mu_V = \frac{RT}{C_\beta^{\text{eq}}} (C_\beta^{\text{eq}} - C_i) \quad [8.16]$$

Then, the boundary condition Eq. [8.12] can be written in the form

$$J_V^\beta|_{\text{int}} = \frac{MRT}{C_\beta^{\text{eq}} V_m^2} (C_\beta^{\text{eq}} - C_i) \quad [8.17]$$

The α/β interface is not stationary but moves as diffusion progresses. If a unit area of the α/β interface advances a small distance dx , a volume $dx \cdot 1$ will be converted from α containing C_α amount of vanadium to α containing C_i , where C_α and C_i are the concentrations of vanadium at the interface in α and β phases, respectively. This means that the amount of vanadium removed from α phase and partitioned into β is given by

$$(C_i - C_\alpha) dx \quad [8.18]$$

In order to maintain the mass balance at the interface, this amount of vanadium must equal the product $(J_V^\beta \cdot \mathbf{n}) \cdot dt$, where $J_V^\beta \cdot \mathbf{n}$ is the flux of vanadium atoms diffusing away from the interface in a direction $\mathbf{n}$ normal to the interface (Borgenstam *et al.*, 2000). Therefore,

$$(C_i - C_\alpha) dx = D(\mathbf{n} \cdot \nabla C)|_{\text{int}} dt \quad [8.19]$$

The growth rate is then given by

$$\frac{dx}{dt} = \frac{D}{(C_i - C_\alpha)} (\mathbf{n} \cdot \nabla C)|_{\text{int}} \quad [8.20]$$

If the interface mobility M is very high, $\Delta\mu_V$ can be very small and $C_i \approx C_\beta^{\text{eq}}$. Under these circumstances, there is effectively local equilibrium at the interface. The interface will then move as fast as diffusion allows, and growth will take place under diffusion control. The growth rate then can be evaluated as a function of time t by solving the diffusion equation in the area occupied by the β phase with the boundary condition at the α/β interface given by

$$C_i = C_\beta^{\text{eq}} \quad [8.21]$$

When the interface has a lower mobility, a greater chemical potential difference $\Delta\mu_V$ is required to drive the interface reaction and there will be a departure from the local equilibrium at the interface. The value of C_i will be that which satisfies the flux balance equation Eq. [8.14]. The growth rate then can be evaluated by solving the diffusion equation in the area occupied by the β phase with the boundary condition at the α/β interface given by Eq. [8.17].

8.4.3 Localisation of the α/β interface

The most important task in the analysis of the β to α transformation is the determination of the location of the moving α/β interfaces for all of the Widmanstätten α plates. Methods employed to solve such a problem can be classified into two groups: Lagrangian and Eulerian schemes. The Lagrangian scheme is characterised by the mesh which is moved or deformed with the progress of the calculation. The mesh boundaries coincide with the free surface. However, over-distorted meshes due to the growth of the great number of Widmanstätten α plates in different directions may result in numerical errors. In Eulerian schemes, computational meshes are generated beforehand and fixed during the entire calculation. Therefore, they are free from the difficulties due to the deforming of meshes. However, a special treatment is necessary to track the moving free surface. The volume of fluid (VOF) method, introduced by Hirt and Nichols, is popular in flow problems with moving free surface. In this method, the entire domain is divided into cells and the volume fraction of fluid in each cell is defined. The flow front is advanced by solving the following transport equation:

$$\frac{\partial F}{\partial t} + \nabla(\mathbf{v} \cdot F) = 0 \quad [8.22]$$

Here F is the volume fraction of the fluid in a cell and $\mathbf{v}$ is the flow velocity vector.

A computer code based on the finite element method and the VOF method is developed to trace the moving α/β interface. Instead of fluid, we consider the volume fraction F of the α phase in the finite elements. Depending on the value of the α phase volume fraction F in an element, the entire domain is divided into three categories by the following criterion:

$$F(x, t) = \frac{\text{volume of } \alpha \text{ phase}}{\text{volume of element}} = \begin{cases} 1 & \text{filled} \\ > 0 \text{ and } < 1 & \text{partially filled} \\ 0 & \text{empty} \end{cases} \quad [8.23]$$

F is unity in the α phase regions and zero in the β phase region. Therefore, the α/β interface can be considered to exist in the partially filled elements with F values between 0 and 1. In order to represent the interfaces, it is convenient to use nodal values. A control volume is associated with each nodal point and the α phase fraction of a nodal control volume is taken as the average of the α -phase fractions of the elements surrounding the corresponding node

$$F_{CV}^i = \frac{\sum F_k^i V_k^i}{\sum V_k^i} \quad [8.24]$$

where superscript i denotes the i th nodal point, and subscript k indicates a surrounding element. V_k^i is the volume of the corresponding element, and F_k^i is its α phase fraction. The shape of the α/β interface is represented by contour lines connecting nodal points along which the volume fractions are such that $0.5 \leq F_{CV}^i < 1$.

In order to locate the interface precisely, the number of partially filled elements should be kept as small as possible. However, as Eq. [8.22] is solved numerically, the interface region becomes wider as time progresses due to false numerical diffusion of F . The donor-acceptor scheme is a popular method for overcoming such smearing of the free surface. Instead of solving Eq. [8.22] directly, volume flux across the element boundary is estimated and the change in F of the element is monitored.

For the location of the α/β interface, we integrate the equation of the α phase volume fraction Eq. [8.22] only for partially filled elements. Discretisation by the explicit scheme gives

$$F_k^{\text{new}} = F_k^{\text{old}} + \frac{\Delta t}{V_k} \left[- \int_{S_k} (F_S \mathbf{v} \cdot \mathbf{n}) dS \right] \quad [8.25]$$

where F_k^{new} and F_k^{old} are the volume fractions of α phase in element k at previous and present times, Δt is the calculation time step, $\mathbf{v}$ is the growth rate and S_k is the boundary of the element. The last term in Eq. [8.25] represents the increase of F due to the incoming flux of vanadium atoms across the α/β interface. F_S is the value of F on the boundary, defined as

$$F_{S_{ik}} = \frac{\alpha \text{ phase volume transferred through } S_{ik}}{\text{total value transferred through } S_{kl}} \quad [8.26]$$

where l denotes the l th boundary of the k th element. Once F_S is known, the

integral in Eq. [8.25] can be evaluated to give the net flux of F into the element i . F values after time interval Δt can then be updated and the α/β interface location can be determined. Therefore, the problem is simplified down to the determination of the value of F_S . We use an algorithm proposed by Shin and Lee (2000) to determine the α phase flux across the boundary F_S . The proposed scheme uses the concept of the donor–acceptor method and is modified to make compatible with FEM.

8.4.4 FEM formulation of the diffusion problem

The finite element method is used for solving the diffusion equation on the domain occupied by β phase. The elements chosen have dimensions in both space and time, which allows for the easy determination of the position of the free surface and also incorporate the natural boundary conditions in a straightforward manner. The method is essentially an implicit time stepping technique and therefore is stable even for relatively large time steps.

The finite element approximation is based on the weak form of the diffusion equation [8.15], which may be written as

$$\int_V \phi \left(\frac{\partial C}{\partial t} - D \sum_{i=1}^3 \frac{\partial^2 C}{\partial x_i^2} \right) dv dt = 0 \quad [8.27]$$

where V is the space–time domain for $t > 0$

$$V = \{(x_i, t): x_i \in V_0, t > 0\}$$

V_0 is the volume occupied by β phase. The function ϕ is required to be measurable in the Sobolev sense.

From a computational viewpoint, a more useful weak form is the Galerkin form, which is derived from Eq. [8.27] by the use of Stock's theorem. This form requires minimum continuity of the solutions for C .

$$\int_V \phi \frac{\partial C}{\partial t} dv dt + D \int_V \frac{\partial \phi}{\partial x_i} \frac{\partial C}{\partial x_i} dv dt - D \int_E \phi \frac{\partial C}{\partial x_i} n_i ds dt = 0 \quad [8.28]$$

where the integration in s is over the boundary δV_0 of V_0 and E is the domain

$$E = \{(x, t): x \in \delta V_0, t > 0\} \quad [8.29]$$

The boundary conditions on the α/β interface are incorporated by the replacement of the flux $D \frac{\partial C}{\partial x_i} n_i$ of vanadium atoms diffusing away from the interface in a direction $\mathbf{n}$ normal to it with the corresponding flux across

the interface $J_V^{\text{int}} = \frac{MRT}{C_\beta^{\text{eq}} V_m^2} (C_\beta^{\text{eq}} - C)$. Then, Eq. [8.28] is written in the form

$$\int_V \phi \frac{\partial C}{\partial t} dv dt + D \int_V \frac{\partial \phi}{\partial x_i} \frac{\partial C}{\partial x_i} dv dt + \frac{MRT}{C_\beta^{\text{eq}} V_m^2} \int_E \phi (C_\beta^{\text{eq}} - C) ds dt = 0 \quad [8.30]$$

Let us assume that the solution of the Eq. [8.30] is given at time t and the solution at some later time is desired. V^n is defined as a region in the space-time containing the β phase domain between the times t_n and t_{n+1}

$$V^n = \{(x_i, t): x_i \in V_0, t_n \leq t \leq t_{n+1}\} \quad [8.31]$$

Then, Eq. [8.30] may be rewritten as

$$\int_{V^n} \phi \frac{\partial C}{\partial t} dv dt + D \int_{V^n} \frac{\partial \phi}{\partial x_i} \frac{\partial C}{\partial x_i} dv dt + \frac{MRT}{C_E V_m^2} \int_{E^n} \phi (C_E - C) ds dt = 0 \quad [8.32]$$

where

$$E^n = \{(x_i, t): x_i \in \delta V_0, t_n \leq t \leq t_{n+1}\} \quad [8.33]$$

We approximate the region V_0 by a set of finite elements, in particular a set of four node elements in the two-dimensional case, and introduce parametric approximations, which map these elements onto a standard square. Clearly, the elements approximating the regions V_0 are the quadrilateral bases of the prisms that approximate the region V^n . The subdivision of the domain V^n into a set of finite elements reduces the original problem to one which is finite dimensional and the values of the concentration are calculated only at the nodes of the elements. In terms of basic function expansion, the concentration field is taken to be of the form

$$C \cong \tilde{C} = \sum_{k=1}^N \phi^k(x, y) C_k(t) \quad [8.34]$$

where N is the number of FE mesh nodes, and

$$C_k(t) = \frac{1}{(t_{n+1} - t_n)} [(t_{n+1} - t) C_k^n + (t - t_n) C_k^{n+1}]; t_n \leq t \leq t_{n+1} \quad [8.35]$$

where C_k^n are the nodal values of C at time t_n ; ϕ^k are the basic functions, which are assumed to form a complete set of functions over the β phase domain volume. The interpolating functions ϕ^k must be chosen to preserve continuity of concentration between the elements because of the first order derivatives in Eq. [8.32]. Here, ϕ^k are chosen to be a set of bilinear pyramid functions:

$$\phi^k(P_l) = \delta_l^k = \begin{cases} 1 & k = l \\ 0 & k \neq l \end{cases} \quad [8.36]$$

The Galerkin approximation satisfies

$$\begin{aligned} \int_{V^n} \phi^k \frac{\partial \tilde{C}}{\partial t} dv dt + D \int_{V^n} \frac{\partial \phi^k}{\partial x_i} \frac{\partial \tilde{C}}{\partial x_i} dv dt \\ + \frac{MRT}{C_\beta^{\text{eq}} V_m^2} \int_{C^n} \phi^k (C_\beta^{\text{eq}} - \tilde{C}) ds dt = 0 \end{aligned} \quad [8.37]$$

The derivatives of $\tilde{C}$ are calculated in the form

$$\frac{\partial \tilde{C}}{\partial t} = \sum_{k=1}^N \phi^k \frac{1}{(t_{n+1} - t_n)} (C_k^{n+1} - C_k^n) \quad [8.38a]$$

$$\frac{\partial \tilde{C}}{\partial x_j} = \sum_{k=1}^N \frac{\partial \phi^k}{\partial x_j} \frac{1}{(t_{n+1} - t_n)} [(t_{n+1} - t) C_k^n + (t - t_n) C_k^{n+1}] \quad [8.38b]$$

Substituting the derivatives [8.38] into Eq. [8.37], we obtain a system of linear equations:

$$\begin{aligned} \frac{1}{(t_{n+1} - t_n)} \sum_{l=1}^N (C_l^{n+1} - C_l^n) \int_{V_0} \phi^k \phi^l dv \\ + \frac{D}{2} \sum_{l=1}^N (C_l^n + C_l^{n+1}) \int_{V_0} \frac{\partial \phi^k}{\partial x_i} \frac{\partial \phi^l}{\partial x_i} dv \\ - \frac{MRT}{2C_\beta^{\text{eq}} V_m^2} \sum_{l=1}^N (C_l^n + C_l^{n+1}) \int_{S_0} \phi^k \phi^l ds + \frac{MRT}{C_\beta^{\text{eq}} V_m^2} C_\beta^{\text{eq}} \int_{S_0} \phi^k ds = 0 \end{aligned} \quad [8.39]$$

which can be solved for the unknown nodal values C_k^{n+1} of the concentration field.

The overall numerical procedure is summarised as follows:

- (i) Divide the entire domain into meshes.
- (ii) Solve the diffusion equation of vanadium in β phase domain by FEM.
- (iii) Determine the growth rate of the α/β interface by solving Eq. [8.20].
- (iv) Determine the value of F_s at each boundary of the partially filled element.
- (v) Calculate the α phase flux into the element.
- (vi) Determine the α phase fraction at the new time.
- (vii) Define the β phase domain using the updated α phase volume fraction of the elements.
- (viii) Repeat steps (ii) through (vii) until the final temperature is reached.

In summary, the following main assumptions are accepted in the model:

- (i) The β to α phase transformation in the Ti-6Al-4V alloy is diffusional. This assumption is reasonable for the cooling rates (from 5 to 50 °C/min)

and the temperature intervals (from 750 to 1000 °C) applied. However, this also means that the model simulations cannot be used for higher cooling rates when a martensitic transformation is involved.

- (ii) The diffusional β to α phase transformation at cooling is mainly controlled by the diffusional redistribution of vanadium between the α and the β phases toward enrichment of vanadium in the β phase. This assumption is based on the following.
 - (a) Thermodynamic calculations performed using the titanium database show that the major difference in the compositions of the α and the β phases at different temperatures is their vanadium contents while the aluminium contents in the two phases are similar (see Fig. 5.1b).
 - (b) The diffusion coefficient of vanadium in the titanium matrix is 2 to 3 times lower than that of aluminium in the temperature range.

It is possible to incorporate into the model simultaneous aluminium redistribution. This, however, would increase significantly the requirements for computational resources without worthy improvement of the model simulations.

- (iii) The diffusion coefficient, used for the calculation of the vanadium concentration in the β phase, depends on the temperature by an Arrhenius-type equation:

$$D = A \exp\left(-\frac{Q}{RT}\right) \quad [8.40]$$

where $A = 1.6 \times 10^{-4} \text{ cm}^2/\text{s}$ and the activation energy $Q = 123.9 \text{ kJ/mol}$.

- (iv) In our case we use a value of 62 kJ/mole for ΔG_m which is half of the activation energy for diffusion of vanadium in the β phase.

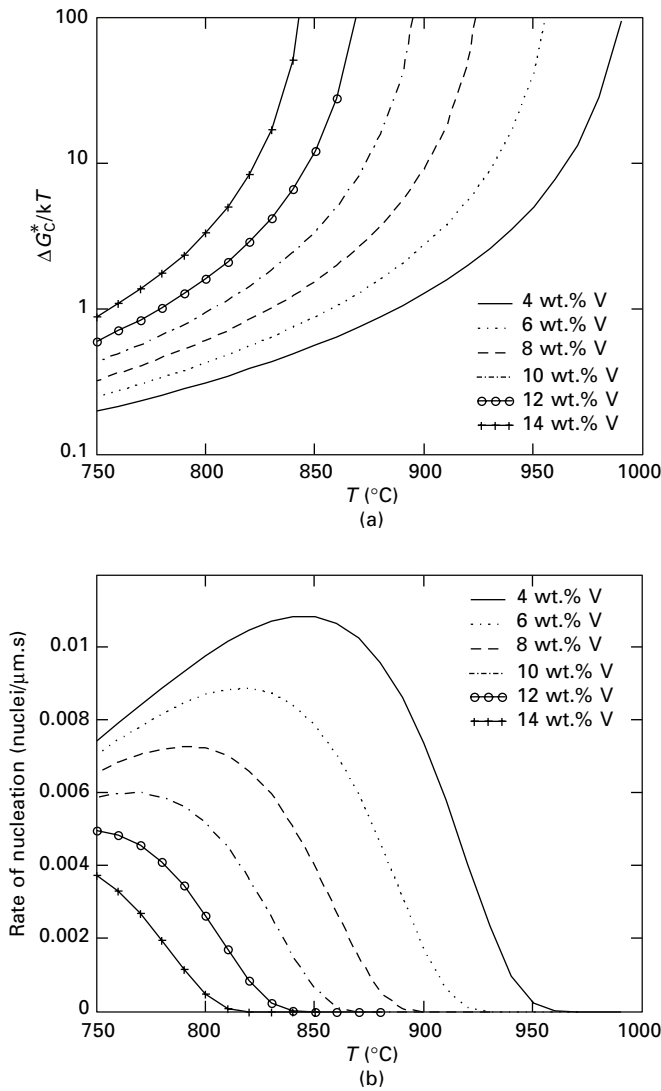
In the following sections, some of the simulations from the model will be discussed.

8.5 The 1-D model

The first step is to develop a 1-D model for the β to α phase transformation in the Ti-6Al-4V alloy. The 1-D model can be used for a description of the nucleation and growth of the α phase at the grain boundary and for prediction of the thickness distribution of a group of Widmanstätten plates growing in parallel direction. We will now simulate the processes of nucleation and growth for different cooling rates.

Using Thermo-Calc and the titanium database, we calculate the volume driving force for formation of the α phase for a wide range of temperatures

and different vanadium concentrations. Subsequently, the difference in the energies of the two phases, Δg , and the activation barrier for nucleation, ΔG_C^* , are calculated using Eq. [8.7] (see Fig. 8.4a). In order to limit the number of unknown parameters in the model, we make the assumption that the interface mobility is high, so that the atoms are able to move freely



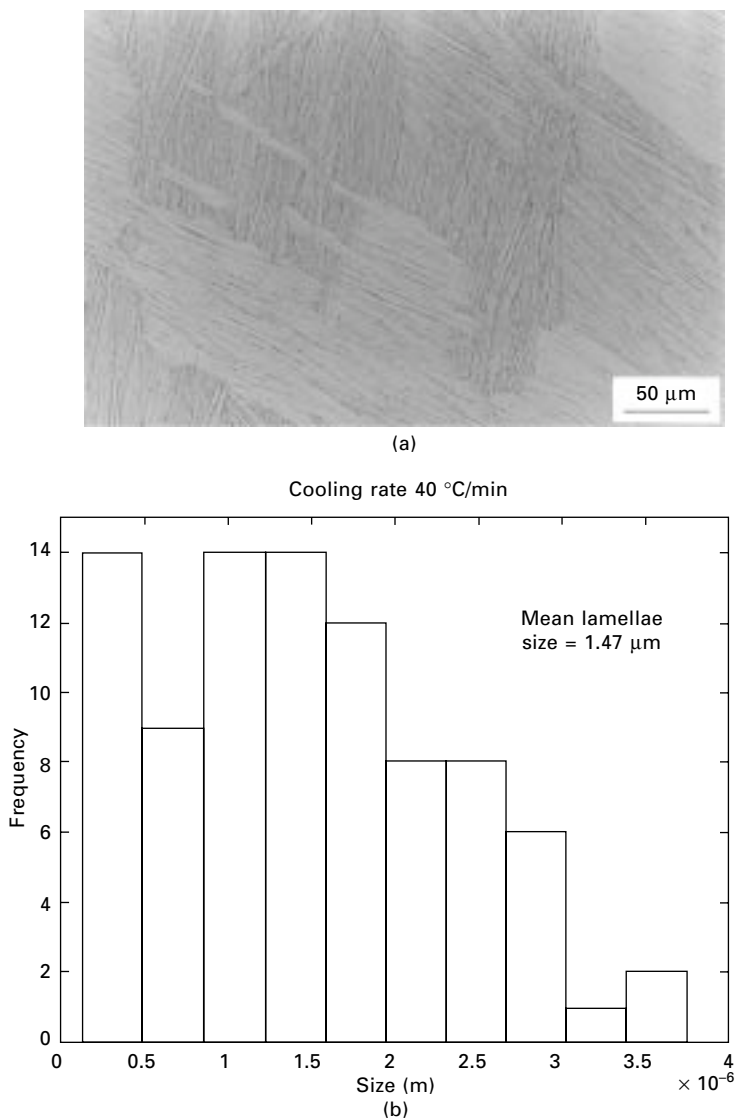
8.4 Calculated (a) barrier for nucleation and (b) rate of nucleation for the β to α transformation in Ti-6Al-4V alloy as functions of the vanadium content and the temperature. In calculating $\Delta G/kT$, T in Kelvin is used.

across the interface. The diffusion controls the growth and the lamella grows just as fast as the diffusion allows. In this case, the vanadium concentration in β phase at the interface is equal to equilibrium concentration (see Fig. 5.1b) and the free parameters in the model are the number of nucleation sites N_v and the surface energy γ . The next step is to fit the calculated thickness of the α plates to the experimental data by setting the N_v and γ values free but constant for all the temperatures, concentrations and cooling rates used. From the fitting of the free parameters, the values of $N_v \frac{k_b}{h} = 1.3 \times 10^4 \text{ nucleus}/(\text{s} \cdot \text{m})$ and $\gamma \sqrt[3]{S(\theta)} = 0.012 \text{ J/m}^2$ for the β to α phase transformation in Ti-6Al-4V alloy are obtained. The plots of the calculated barrier for nucleation (Fig. 8.4a) and the rate of nucleation (Fig. 8.4b) are for these values of $N_v \frac{k_b}{h}$ and $\gamma \sqrt[3]{S(\theta)}$ and applying Eqs. [8.7] and [8.8], respectively.

The simulated distribution of the α lamellae thickness for the above values of N_v and γ is plotted in Fig. 8.5b. This simulation from the model is compared with the experimentally observed microstructure of the Ti-6Al-4V alloy after cooling with the same cooling rate (Fig. 8.5a). A good agreement between the experimental mean lamellae size and the prediction from the FEM is obtained. The 1-D model predicts the existence of a notable fraction of lamellae with small thickness, which nucleate at the end of the process of transformation and do not have enough driving force and time to grow. Perhaps such lamellae really exist, but they cannot be observed in the optical microstructure because of their small thickness. Similar good agreement between the FEM simulations for the α lamellae thickness and experimental observations is obtained for other cooling rates. The model predictions for the average thickness of the α lamellae for cooling rates of 20 and 10 °C/min are 1.7 and 2.1 μm , respectively.

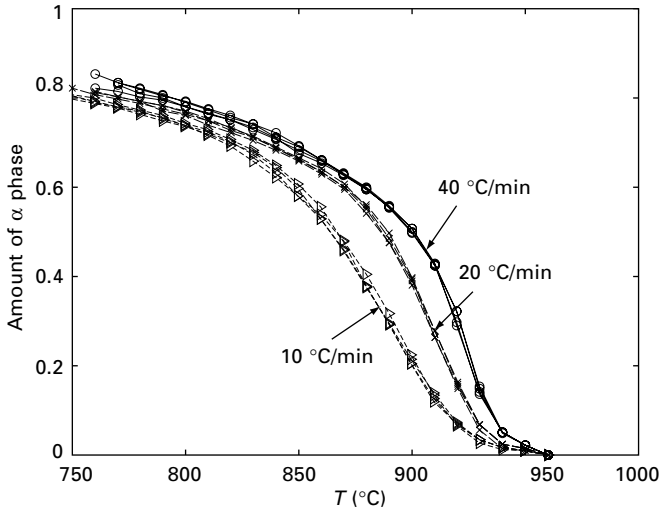
The 1-D model is further used to simulate the kinetics of the β to α phase transformation in the Ti-6Al-4V alloy. Figure 8.6 shows the model simulations for the amount of the α phase as a function of the temperature for different constant cooling rates. For each cooling rate a number of runs were performed, and the results are reproducible. The shapes of the curves tracing the kinetics of the β to α phase transformation are classical. The simulated influence of the cooling rate on the kinetics of the transformation is in agreement with the experimental data from the differential scanning calorimetry study of the same transformation (Chapter 7). There are some differences between the experimental calorimetry kinetics curves in Chapter 7 and the FEM simulations here. A possible reason for this difference is that the processes of the 2-D and 3-D impingement cannot be taken into account in the 1-D model.

The 1-D model is also used for analysis of the nucleation rate of the β to α phase transformation in Ti-6Al-4V alloys. Figure 8.7 presents the FEM

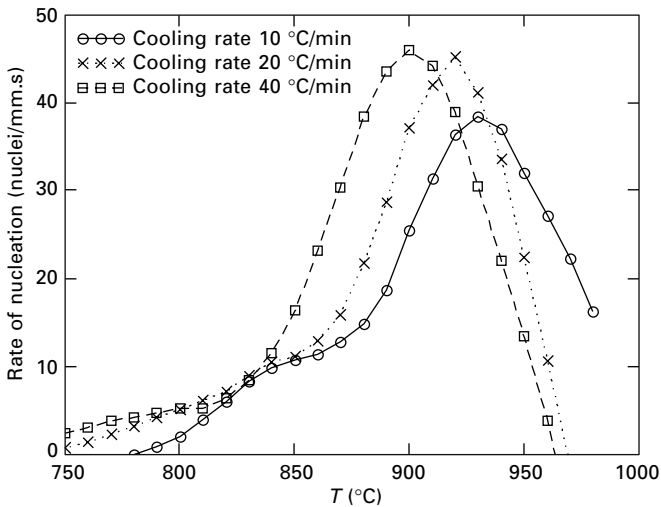


8.5 (a) Microstructure of Ti-6Al-4V alloy after cooling at a cooling rate of 40 °C/min and (b) distribution of the lamellae thickness of the α phase for the same cooling rate calculated from the FEM.

simulations for the real nucleation rate for different cooling rates. The nucleation rates presented in Figs. 8.4b and 8.7 should be well distinguished. Figs. 8.4b shows the theoretical nucleation rate for different temperatures and vanadium concentrations and is obtained by the plotting of Eq. [8.8]. Figure 8.7 shows the model simulations for the real nucleation rate for the current temperature



8.6 Kinetics of the β to α transformation in Ti-6Al-4V alloy for different cooling rates calculated from the FEM.



8.7 FEM simulation for the real rate of nucleation at different cooling rates.

and the vanadium concentration profile in the residual β phase at the corresponding moment in the β phase. The simulated rate of nucleation first increases with the decrease in the temperature (increase in the degree of undercooling below β -transus temperature). The reason for this is that the barrier for nucleation of α phase significantly decreases with the undercooling. The maximum of the nucleation rate is around 900 °C. This observation is in

agreement with the TTT diagram for the Ti-6Al-4V alloys (Chapter 14) according to which the nose point is in the range of 850–900 °C, depending on the alloy composition. Naturally, higher cooling rates shift the maximum of the nucleation rate to lower temperatures. Further decrease in the temperature leads to decrease in the rate of nucleation. There are three concurrent reasons for this: (i) the diffusion and the migration of the atoms across the interface are slower, (ii) the amount of the β phase is decreased, and (iii) the vanadium concentration in the residual β phase is increased.

8.6 The 2-D model

In order to describe more realistically the β to α phase transformation, we will show 2-D simulation of the nucleation and growth of the α phase lamellae within a former β grain. We assume that the nucleus of α phase is formed at the β grain boundary and then grows to the grain interior. The mechanism of nucleation of the α phase at the β grain boundary, used in 2-D model, is the same as the mechanism used in the 1-D problem.

After the α/β interface is created during the nucleation stage, it starts migrating into the surrounding β phase, by the transfer of vanadium atoms across the interface. Since the α plates grow mainly parallel to $\{110\}\beta$ plane, the mobility M_1 of vanadium across the interface in the direction of the longitudinal dimension is much higher than the mobility M_2 across the interface in the transverse direction. Hence, the growth oriented parallel to the $\{110\}\beta$ plane can be expected to be mainly diffusion controlled, whilst the growth in the transverse direction is mixed or even interface controlled. The mobility determines the corresponding flux of vanadium atoms across the interface, Eq. [8.12], which in its turn defines the boundary conditions at the α/β interface for the vanadium diffusion in the β phase.

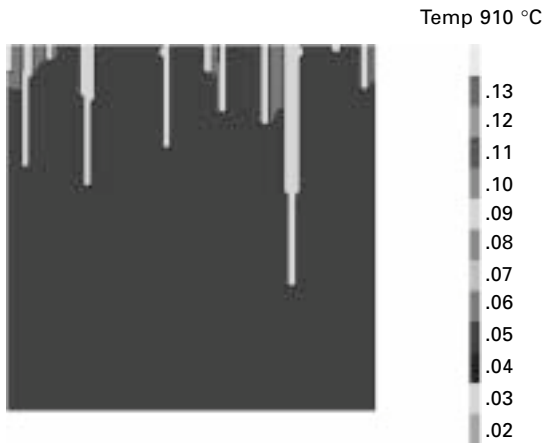
The growth rate can be evaluated by solving the diffusion equation [8.15] in the domain occupied by the β phase. The value of vanadium concentration at any point of the interface C_i will be that which satisfies the boundary condition Eq. [8.17]. The mobility of vanadium atoms M_1 and M_2 in the two directions are free parameters in the model and are determined by fitting the calculated shape of the α plates to the metallographic observations (Chapters

6 and 7). The following values of $\frac{M_1 R}{V_m^2} = 6.4 \times 10^{-5} \mu\text{m} \cdot \text{wt.}\% / (\text{K} \cdot \text{s})$ and

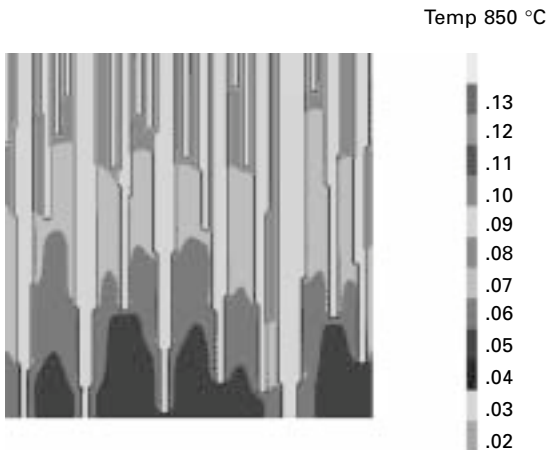
$\frac{M_2 R}{V_m^2} = 3.5 \times 10^{-7} \mu\text{m} \cdot \text{wt.}\% / (\text{K} \cdot \text{s})$ for the β to α phase transformation in Ti-6Al-4V are obtained.

Using the computer package, we simulate the process of nucleation and growth of a colony of α phase lamellae on a square with length 40 μm for constant cooling rates of 10 °C/min (Fig. 8.8a–d) and 30 °C/min (Fig. 8.8e–h). Two observations are apparent from the comparison of the simulations:

- (i) The degree of the β to α phase transformation at the same temperatures is at much advanced stage when the lower cooling rate is applied (compare Fig. 8.8a with 8.8e, 8.8b with 8.8f, etc.). This is in agreement with the experimental study of the kinetics of the same phase transformation at the same cooling rates using differential scanning calorimetry (Chapter 7).

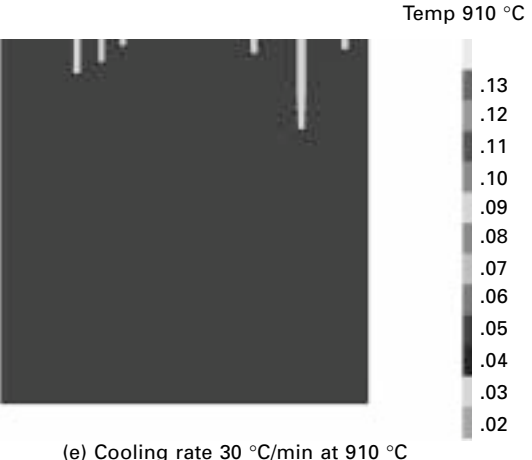
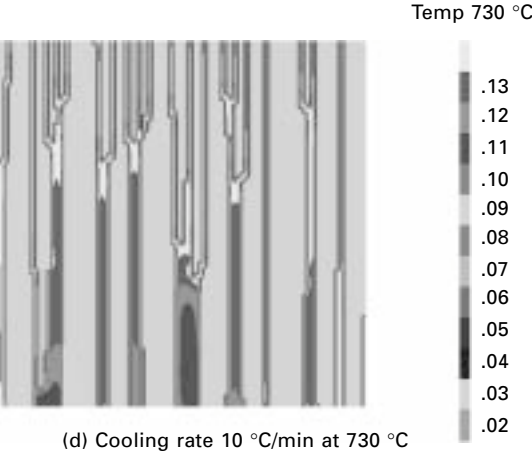
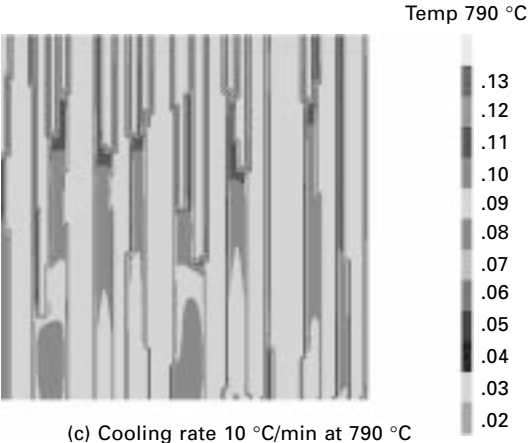


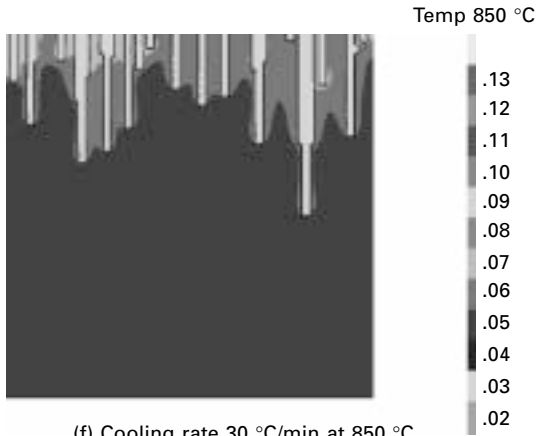
(a) Cooling rate 10 °C/min at 910 °C



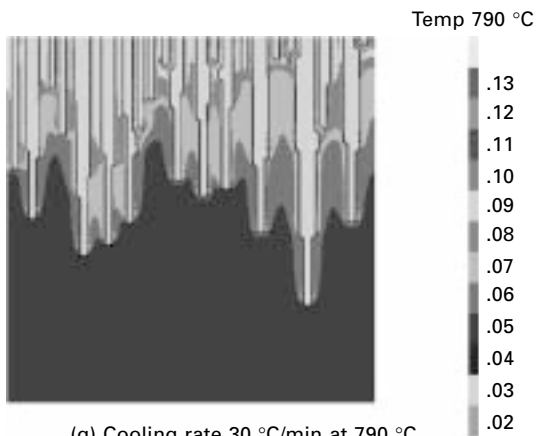
(b) Cooling rate 10 °C/min at 850 °C

8.8 FEM simulations for the microstructure evolution of the β to α phase transformation in Ti-6Al-4V alloy at continuous cooling with constant cooling rate. The scales to the right of each figure represent vanadium concentration. (a)-(d) 10 °C/min; (e)-(h) 30 °C/min; (a) and (e) $T = 910$ °C; (b) and (f) $T = 850$ °C; (c) and (g) $T = 790$ °C; and (d) and (h) $T = 730$ °C.

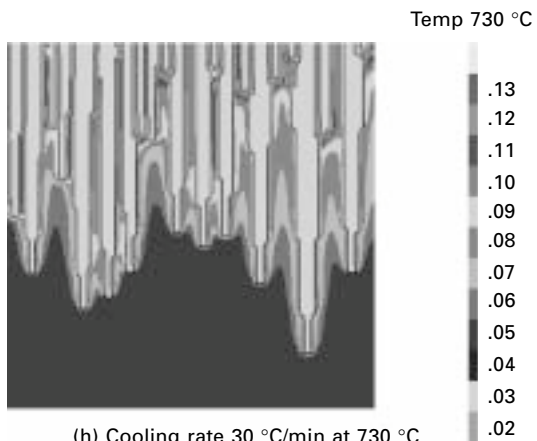




(f) Cooling rate 30 °C/min at 850 °C



(g) Cooling rate 30 °C/min at 790 °C



(h) Cooling rate 30 °C/min at 730 °C

8.8 Continued

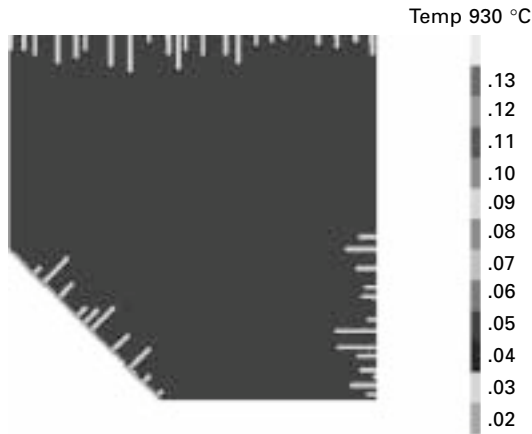
- (ii) The thickness of the grain boundary α phase lamellae of the Widmanstätten morphology is larger and their number is smaller when the slower cooling rate is applied (compare Fig. 8.8a–d with Fig. 8.8e–h). This is in agreement with the metallographic observation of the features of the phase transformation and a general knowledge of the influence of the cooling rate on the α phase lamellae morphology and the size and distribution of the fine microstructure in the Ti-6Al-4V alloys.

A more realistic numerical simulation of the β to α phase transformation, when the grain boundary α phase colonies grow in different directions, is presented in Fig. 8.9. This case takes into account the 2-D impingement of the colonies growing in the different directions. We consider the nucleation and growth of α plates on a sector of a β phase grain with a long dimension of 150 μm . The evolution of the morphology of the microstructure at different stages (temperatures) simulated from the model is traced in Fig. 8.9a–e. The transformation starts with the first nucleus at around 960 °C. With further decrease of the temperature, α phase colonies grow in the different directions until the transformation is nearly completed at about 800 °C. The calculated average thickness of the α plates is about 6 μm , which is in good agreement with the metallographic observations (Chapters 6 and 7).

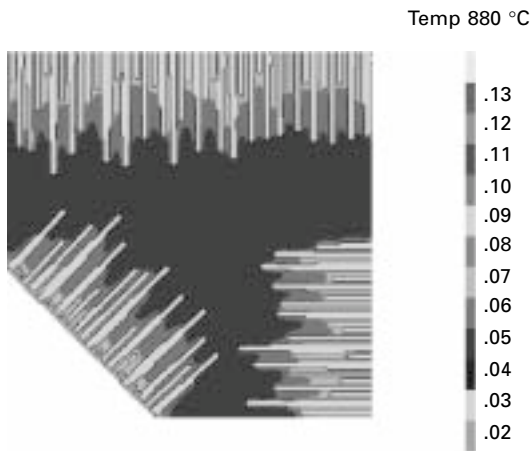
As the next step, we simulate the evolution of the β to α phase transformation under isothermal conditions. The starting microstructure is β phase domain and the temperature is instantly set at any constant temperature in the $\alpha + \beta$ equilibrium range. Figure 8.10a–d traces the morphology and the kinetics of growth for colony of α phase lamellae on a square with length 40 μm . After long periods of time, the concentration gradients in the β phase decrease, the interface vanadium concentration converges to the equilibrium concentration and the chemical potential difference $\Delta\mu_V$ driving the vanadium atoms across the interface converges to zero. At this stage, it can be said that the equilibrium in respect to the amounts of the α and the β phases, as well as their chemical compositions at this temperature, is reached, and the transformation process is completed. Note here that the β to α phase transformation at isothermal conditions predicted from the FEM kinetics does not fit well to the experimental data. The model presented here shows that, at 900 °C, the transformation is completed between the 20th and the 30th minute (Fig. 8.10d). However, the experimental data in Chapter 6 and the TTT diagram of this alloy conclude that, at the same temperature, the transformation should complete between the first and the sixth minute, depending on the real composition of the alloy. There are at least two reasons for this difference: (i) in this model we consider nucleation and growth of only one α colony, which is far from the realistic case of simultaneous nucleation and growth from real starting microstructure with many grains in both direction of each grain boundary; and (ii) we

consider the 2-D case, which does not take into account the diffusional redistribution and the growth in the third direction.

In this respect it is worth mentioning that it was possible to fit the kinetics under isothermal conditions predicted from the FEM to the experimental one when the diffusion coefficient of vanadium in the β phase was increased by from 10 to 50 times.

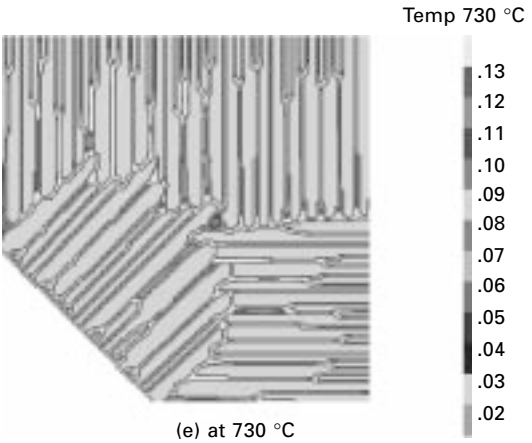
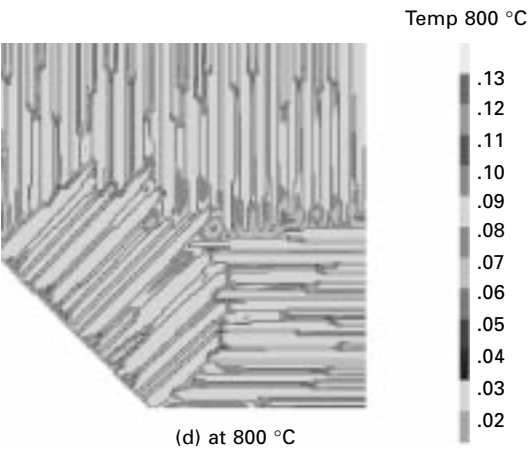
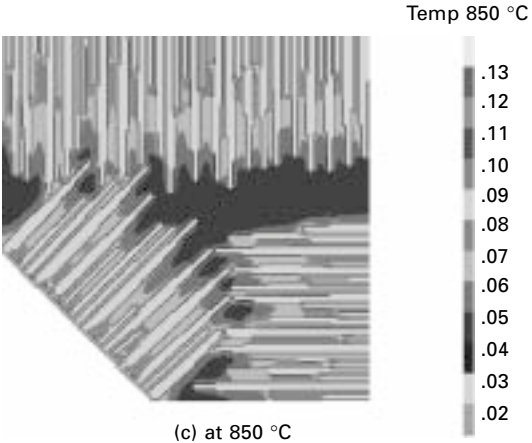


(a) at 930 °C



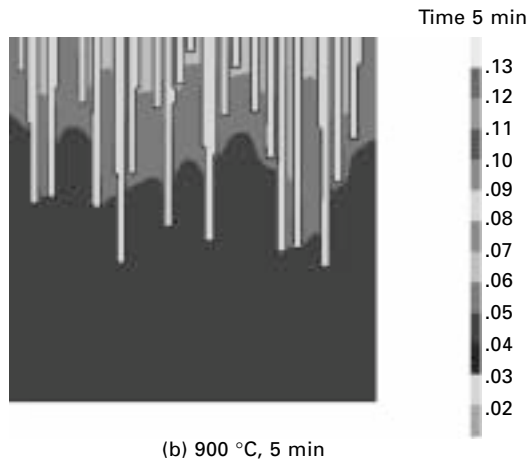
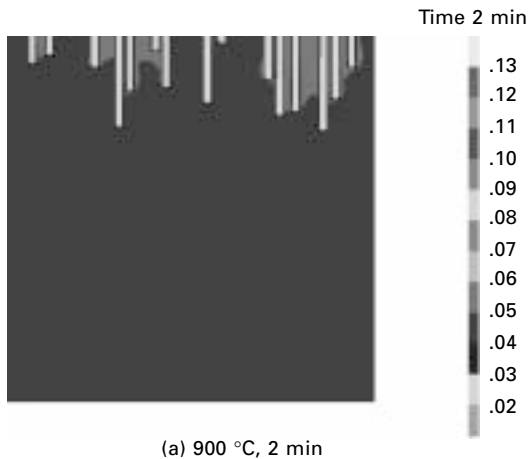
(b) at 880 °C

8.9 FEM simulations for the microstructure evolution of the β to α phase transformation in Ti-6Al-4V alloy at continuous cooling with constant cooling rate of 5 °C/min, assuming α colony growth in three different directions. The scales to the right of each figure represent vanadium concentration. (a) 930 °C; (b) 880 °C; (c) 850 °C; (d) 800 °C; (e) 730 °C.

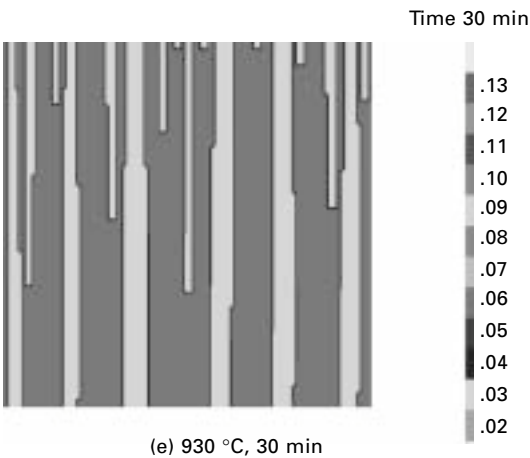
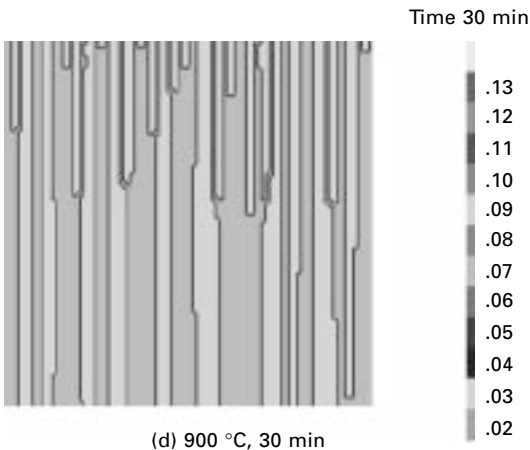
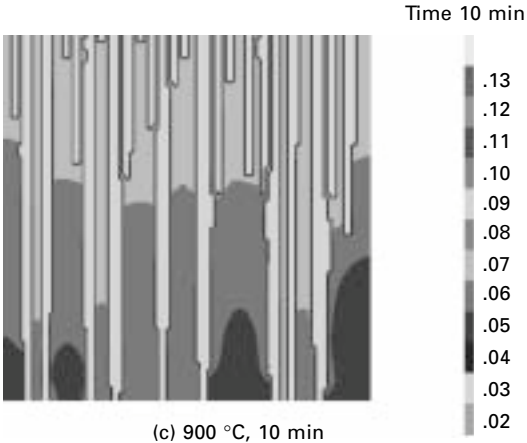


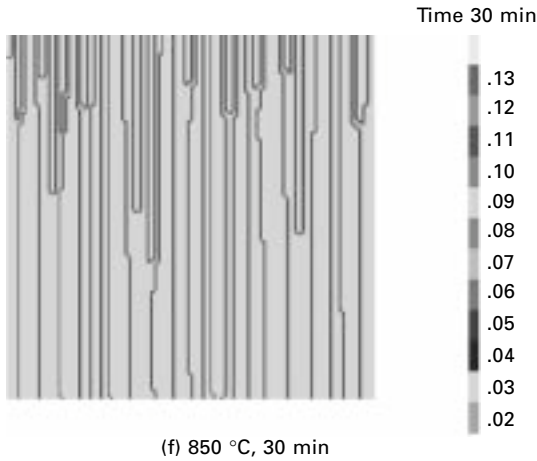
The isothermal simulations are also performed at different temperatures, in order to study the difference in the morphology of the α phase after the transformation has completed. Fig. 8.10d,e and f show the final morphology of the α colony after isothermal exposures at 900, 930 and 850 °C, respectively. The model simulations showed that lower temperature of isothermal exposure results in the following:

- (i) Finer microstructure with thinner α lamellae (Fig. 8.10f). This is in agreement with the results from metallographic examination of



8.10 FEM simulations for the microstructure evolution of the β to α phase transformation in Ti-6Al-4V alloy under isothermal conditions. The scales to the right of each figure represent vanadium concentration. (a) 900 °C, 2 min; (b) 900 °C, 5 min; (c) 900 °C, 10 min; (d) 900 °C, 30 min; (e) 930 °C, 30 min; (f) 850 °C, 30 min.





8.10 Continued

Table 8.1 Equilibrium (Thermo-Calc) and calculated (FEM) amounts of the α phase

T (°C)	Thermo-Calc (vol.%)	FEM (vol.%)
950	23	22
930	36	35
900	53	45
850	73	59

samples quenched after different temperatures of isothermal exposure (Chapter 6).

- (ii) Larger amount of the α phase. This is in agreement with the knowledge of the phase equilibria in the Ti-6Al-4V alloy, and the calculations performed on the equilibrium α phase volume fractions (see Fig. 5.1a). We obtain good agreement between the FEM simulations and the thermodynamic calculations in the amounts of α phase, especially at the relatively high temperatures (Table 8.1).

Using the 1-D and 2-D models, we are able to predict the main features of the Widmanstätten morphology formed during thermal treatment – the distribution and geometry of α phase lamellae and their dependence on the processing route. However, since the real microstructure formation problem is a 3-D one, a precise description of the evolution of the α/β interface, α -phase transformed fraction and vanadium concentration in the β phase can be obtained only by solving the 3-D problem for nucleation and growth of the Widmanstätten α plates. The development of a 3-D model, as well as

extension of the model to predict for larger domain with initial real β grain and even group of β grains, however, requires a dramatic increase of computational resources.

Finally, it should be mentioned that the simulation discussed above is obtained either for cooling with constant cooling rate or for isothermal exposure. However, the models developed and program packages are capable of 1-D and 2-D simulations of the morphology of the β to α phase transformation in Ti-6Al-4V alloy for continuous cooling with any cooling path (not necessarily constant cooling rate) as well as for an arbitrary combination and mix between continuous cooling and isothermal exposure. In this way, real production time-temperature routes can be modelled.

8.7 Summary of the models for Ti-6Al-4V

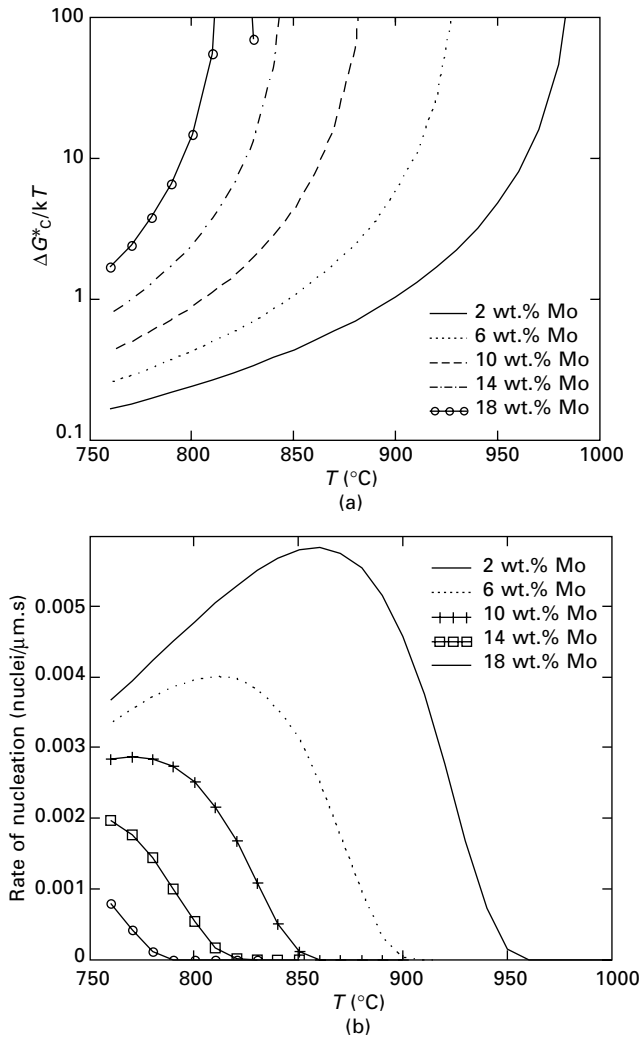
The morphology, distribution and geometry of the fine microstructure of Ti-6Al-4V alloy, formed during heat treatment, and their dependence on the processing route are simulated in the framework of a mathematical model describing the nucleation and growth processes of the new phase. The finite element modelling and the volume of fluids method are used for obtaining a numerical solution of the problem for localisation and evolution of the α/β interface. Computer program packages are developed for solving the 1-D and 2-D problems for nucleation and growth of the α phase Widmanstätten plates in the β phase.

The packages are used to simulate the morphology of the microstructure evolution during different heat treatment conditions. The effects of the cooling rate and the temperature on the microstructure are predicted and analysed. A good agreement between the model simulations and experimental data is observed regarding (i) the α lamellae thickness obtained with different heat treatment conditions; (ii) the kinetics of the β to α phase transformation; (iii) the rate of nucleation of the α phase; and (iv) the simulated phase equilibria.

The model can be used for predictions of the morphology of the β to α phase transformation in Ti-6Al-4V alloy in a real processing route.

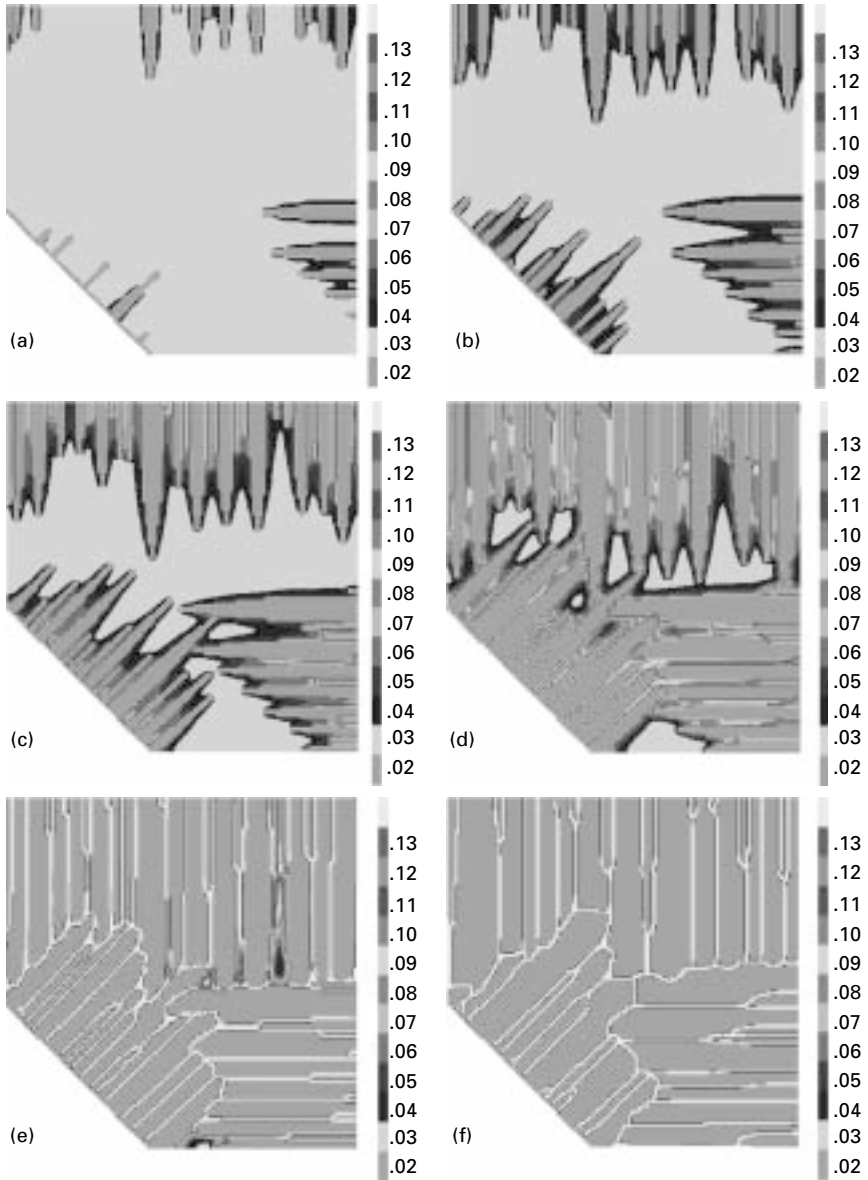
8.8 Extending to other alloys

The values for the driving force obtained by thermodynamic calculations (see Chapter 5) are used in deriving Δg . The unknown parameters, such as number of nucleation sites per unit volume, free interface energy of nucleation and shape factor, are derived by fitting the model simulation to the experimental data from the microstructural observations (Figs. 8.1 and 8.2b) and kinetics of phase transformations under different conditions (Fig. 7.7). The calculated barrier and rate of nucleation for the β to α transformation in Ti 6-2-4-2 alloy are given in Fig. 8.11.



8.11 Calculated (a) barrier for nucleation and (b) rate of nucleation for the β to α transformation in Ti-6Al-2Sn-4Zr-2Mo alloy as functions of the molybdenum content and the temperature. In calculating $\Delta G/kT$, T in Kelvin is used.

The process of α phase growth is simulated based on the assumption that the migration of the interface separating the two phases is a result of flux of alloying element atoms across the interface. As the precipitate grows, the β alloying element concentration adjacent to the interface C_i increases above the initial concentration C_0 . In this way, the process of diffusion redistribution between the α and the β phases takes place, leading to enrichment of the β phase with different alloying elements depending on the alloy composition (see Chapter 5).



8.12 FEM simulations for the microstructure evolution of the β to α phase transformation in Ti-6Al-2Sn-4Zr-2Mo alloy at continuous cooling with constant cooling rate of (a) – (e) 10 °C/min and (f) 5 °C/min, assuming α colony growth in three different directions. The scales to the right of each figure represent molybdenum concentration. (a) 960 °C; (b) 940 °C; (c) 920 °C; (d) 880 °C; (e) 760 °C; and (f) 5 °C/min, 760 °C.

The model described in previous sections is adjusted and used to simulate the phase transformation morphology in Ti 6-4 alloy only. In the Ti 6-4 alloy, the β to α phase transformation is controlled by the diffusion redistribution of vanadium between the two phases (see Fig. 5.1). The model can be further developed and adjusted for simulation of other α , near- α and $\alpha + \beta$ alloys, where the process of phase transformation may be controlled by diffusion redistribution of other elements, e.g. molybdenum in the Ti 6-2-4-2 and Ti 8-1-1 alloys.

One numerical simulation of the β to α phase transformation in the Ti 6-2-4-2 alloy, when the grain boundary α phase colonies grow in different directions, is presented in Fig. 8.12. The microstructure evolution at cooling from β region is shown (Fig. 8.12a–e).

8.9 Summary

Models and modules for simulation of the microstructure evolution during the course of the β to α phase transformation at cooling in α , near- α and $\alpha + \beta$ titanium alloys have been developed. The models are based on classical theory for nucleation and diffusion controlled growth. Experimental data are used to build and verify the models. The models and program packages developed are capable of 1-D and 2-D simulations of the morphology of the β to α phase transformation in titanium alloys for continuous cooling with any cooling path and for an arbitrary combination between continuous cooling and isothermal exposure, including that representing a real processing route. The models are convenient and powerful tools for optimisation of the processing parameters in titanium alloys. The programs have potential for direct practical applications in solving various problems in titanium alloys and for a significant reduction of the experimental work.

The model cannot be used straightforwardly to simulate the β to $\alpha + \beta$ phase transformation in β or near- β alloys because these alloys are usually quenched after solution treatment and the β to $\alpha + \beta$ phase transformation takes place during additional ageing after quenching. The phase nucleation and growth may have significantly different mechanisms.

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Phase-field method: lamellar structure formation in γ -TiAl

Abstract: This chapter describes a phase-field model for simulating the formation evolution of the lamellar microstructure in γ -TiAl alloys. The mechanism of formation of TiAl lamellae proposed by Denquin and Naka is incorporated into the model. The model describes the formation and evolution of the face-centred cubic (fcc) stacking lamellar zone followed by the subsequent appearance and growth of the γ phase, involving both the chemical composition change by atom transfer and the ordering of the fcc lattice. This chapter describes the model in detail to enable the reader to undertake similar modelling.

Key words: phase field models, titanium aluminides, phase transformation, modelling, simulation.

9.1 Introduction

Alloys based on the aluminides of titanium that contain large volume fractions of the γ -TiAl phase have attracted particular interest. For single-phase γ -TiAl alloys, the ductility is limited, giving poor formability and fracture toughness. These problems are ameliorated partially by adjusting the composition and heat-treatment to give a lamellar mixture of γ -TiAl and α_2 -Ti₃Al phases. Alloys with such a microstructure usually exhibit slightly improved ductility and even higher strength than single-phase alloys.

The lamellar structure is generally characterised by a set of several γ lamellae alternating with a single α_2 lamella, following the orientation relationship: $(0001)_{\alpha_2} // \{111\}_{\gamma}$, and $\langle 11\bar{2}0 \rangle_{\alpha_2} // \langle 1\bar{1}0 \rangle_{\gamma}$. The lamellar microstructure is formed by decomposition of either disordered α -phase (hexagonal structure, A3) or ordered α_2 (hexagonal structure, DO₁₉) matrix into lamellar precipitates of γ -phase (ordered tetragonal structure, L1₀), following one of the two transformation paths: $\alpha \rightarrow \alpha_2 \rightarrow \alpha_2 + \gamma$ or $\alpha \rightarrow \alpha_2 + \gamma$. Each γ lamella is divided into numerous order domains. These domains are generated due to the fact that the $\langle 1\bar{1}0 \rangle$ and $\langle 01\bar{1} \rangle$ directions of the L1₀ structure are not equivalent to each other.

Transmission electron microscopy studies on the initial stages of the precipitation have shown the existence of large stacking faults (SF), which originate at prior grain boundaries or grain boundary γ allotriomorphs. The mechanism of the formation of lamellar structure supposes the formation of γ lamellae at these faults. The whole sequence of the lamellar structure formation involves: (i) a crystal structure change from hexagonal close-

packed (hcp) type to face-centred cubic (fcc) type; (ii) a chemical composition change through atom transfer; (iii) an ordering reaction of the fcc type structure leading to the final $L1_0$ phase. The formation of the pre-nucleus corresponding to an fcc stacking lamellar zone can lower the nucleation barrier to the γ -phase formation, and takes place towards the grain interior through the propagation of Shockley partial dislocations starting from grain boundaries. During the formation of the stacking faults, the ABABAB... stacking sequence of the hexagonal structure is transformed into either the ABCABC... or ACBACB... stacking sequences of the fcc structure.

The nucleation of the γ -phase involves both the chemical composition change by atom transfer and the ordering of the fcc zone. The ordering process consists of nucleation of orientation variants at a number of separate sites in the metastable fcc, followed by independent growth of the variants and their encounter, resulting in the formation of order domain boundaries (ODBs) or anti-phase boundaries (APBs).

The longitudinal and lateral growth of the lamellar precipitates occurs through the ledge mechanism (Pond *et al.*, 2000), which can be described as a change from a shear process involving the motion of partial dislocations to diffusion-controlled ledge migration, which produces the required change in both stacking and composition. The growth of the lamellar γ -phase slows down and can stop with a gradually decreasing solute supersaturation in the matrix, reducing the driving force for the ledge movement.

Such a multi-phase and multi-domain lamellar structure is what gives the alloys their remarkable properties. The statistical distributions of the lamellae, their thickness, the orientation domains size and relationship have a direct effect on the mechanical properties.

The problem for predicting the morphology of γ -TiAl alloys, formed during heat treatment, can be solved with the development of computer models describing the phase transformations and microstructural evolution. One physics-based modelling technique that has gained much attention lately is the phase-field method, which has been used to simulate microstructural development under site saturation conditions. A phase-field model of the $\alpha_2 \rightarrow \alpha_2 + \gamma$ transformation was developed to simulate the formation of the lamellar structure in γ -TiAl alloy (Wen *et al.*, 2001b). Some essential features of the lamellar structure have been predicted. However, the formation of stacking faults at intermediate stages of the transformation was not included in the model and the heterogeneous nucleation of γ -phase on the stacking faults was ignored. The shear deformation, which transforms hcp to fcc, and the deformation modes associated with the ordering process were assumed to occur simultaneously.

To tackle this problem properly, we need to have a simulation model which can take into account not only the precipitation of γ from α_2 but also the formation and evolution of the fcc stacking lamellar zone, and the

appearance and growth of the γ -phase involving both the chemical composition change by atom transfer and the ordering of the fcc zone. In this chapter, a computer model is given describing the formation and evolution of lamellar microstructure in γ -TiAl alloy. We have developed a phase-field model for simulation of: (i) crystal structure changes from hcp type to fcc type and formation of a fcc stacking lamellar zone; (ii) nucleation of $L1_0$ orientation variants at a number of separate sites in the metastable fcc-type structure during the growth and the coarsening of the lamellae; (iii) encounter of the orientation variants after their growth, leading to the formation of ODBs. Within the phase-field model, the spatial distribution of the fcc stacking lamellar zone and the γ orientation variants are described by the introduction of structural field variables. The thermodynamics of the model system and the interaction between the displacive and diffusional transformations are described by a non-equilibrium free energy formulated as a function of concentration and structural order parameter fields. The long-range elastic interactions, arising from the lattice misfit between the α (A3), fcc (A1) and the various orientation variants of the γ -phase are taken into account by incorporating the elastic strain energy into the total free energy.

The mathematical description of the phase transformation path in γ -TiAl and formation of lamellar structure was introduced in Section 9.2. The computer simulation was discussed in Section 9.3. Finally, the major simulation conclusions were summarised in Section 9.4.

9.2 Mathematical formulation

9.2.1 Phase-field model

The phase-field approach is based on a simple idea that an arbitrary multi-phase microstructure with compositional and structural heterogeneities can be described by continuous functions (field variables), $\theta_1(\mathbf{r})$, $\theta_2(\mathbf{r})$, ..., $\theta_n(\mathbf{r})$, where $\mathbf{r}$ is the spatial coordinate vector. Each of them characterises the spatial distribution of one of the phases or orientation variants. Thus, the total number of functions is equal to the number of all possible coexisting phases or orientation variants, which are determined by the compositional variation and crystal lattice rearrangement. Each function assumes a non-zero value within the corresponding domain and vanishes within the parent phase or other domains.

As discussed earlier, the precipitation of γ from α involves the formation of two groups of stacking sequences of the fcc structure and six orientation variants of the γ -phase. In the present approach, the spatial distributions of the two groups of fcc domains with different stacking sequences and the six orientation variants are described by eight field variables

$$\theta_1(\mathbf{r}, t), \theta_2(\mathbf{r}, t), \dots, \theta_8(\mathbf{r}, t)$$

where t is time and $\mathbf{r}$ is the spatial coordinate vector. The six structural order parameter fields $\theta_3(\mathbf{r}, t)$, $\theta_4(\mathbf{r}, t)$, $\dots$, $\theta_8(\mathbf{r}, t)$, describing the six orientation variants of γ , are arranged in two groups (three for each stacking sequence) and assume a non-zero value only within the domains where the corresponding stacking fault is formed, i.e. $\theta_i(\mathbf{r}, t) \neq 0$, $i = 1$ or 2 . The field variables $\theta_3(\mathbf{r})$, $\theta_4(\mathbf{r})$, $\dots$, $\theta_8(\mathbf{r})$ corresponding to the six orientation variants of γ -phase can be presented in the form

$$\theta_p(\mathbf{r}) = \theta'_p(\mathbf{r}) \cdot \theta_s(\mathbf{r}); \quad s = 1; \quad p = 3, 4, 5; \quad \text{or} \quad s = 2; \quad p = 6, 7, 8$$

where the continuous fields $\theta'_p(\mathbf{r})$ can be considered as long-range order parameter fields, describing the ordering of the fcc lattice into the $L1_0$ structure. The temporal dependence of the field functions describes the temporal evolution of the microstructure. Therefore, if the time-dependent equations for those field variables are formulated, the problem of the theoretical description of microstructural dynamics is simply reduced to a solution of these equations.

The simplest form of kinetic equation of this type is the stochastic Langevin equation based on the phenomenological time-dependent Ginzburg–Landau kinetic equation, which assumes that the rate of evolution of a field is a linear function with respect to the transformation driving forces

$$\frac{\partial \theta_p(\mathbf{r}, t)}{\partial t} = \sum_{q=1}^n L_{pq} \frac{\delta F}{\delta \theta_q(\mathbf{r}, t)} + \xi_p(\mathbf{r}, t) \quad [9.1]$$

where the indexes $p, q = 1, 2, \dots, 8$, F is the free energy functional, $\delta F / \delta \theta_q(\mathbf{r}, t)$ is the thermodynamic driving force and $\xi_p(\mathbf{r}, t)$ is the Langevin noise term. L_{pq} is an operator of the kinetic coefficients related to interface mobility. Here, only diagonal terms of the kinetic coefficients tensor are assumed non-zero, i.e. the rate of evolution of a field θ_p is a linear function only with respect to the corresponding driving force $\delta F / \delta \theta_p$. The interface mobility is assumed to be phase-field and orientation variant independent, i.e.

$$L_p = \begin{cases} L & p = 1, 2, \\ L' & p = 3, \dots, 8, \end{cases} \quad \text{and} \quad L_{pq} = -L_p \delta_{pq}$$

Since, for non-conserved fields like θ_p , the first non-vanishing term in the long wave approximation for the kinetic coefficient matrix is a constant, we simply choose coefficients L and L' , related to interface mobility of the two stacking sequences of the fcc structure and six orientation variants of the γ -phase, to be constants (isotropic interfacial boundary mobility). $\xi_p(\mathbf{r}, t)$ is taken to be Gaussian distributed and its correlation properties meet the requirements of the fluctuation–dissipation theorem

$$\langle \xi_p(\mathbf{r}, t), \xi_q(\mathbf{r}', t') \rangle = 2k_B T L_{pq} \delta_{pq} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'),$$

where k_B is the Boltzmann constant. The origin of the noise term is related

to the microscopic degrees of freedom, e.g. to the thermal vibrations (phonons), high-order correlations with short relaxation time.

The temporal evolution of the concentration field can be obtained by solving the Cahn–Hilliard diffusion equation

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = M \nabla^2 \frac{\delta F}{\delta c(\mathbf{r}, t)} + \zeta(\mathbf{r}, t) \quad [9.2]$$

where M is a kinetic coefficient characterising diffusional mobility and $\zeta(\mathbf{r}, t)$ is the Langevin noise term.

9.2.2 Free energy functional

The thermodynamic driving force in Eqs. [9.1] and [9.2] is determined by the total free energy functional F formulated as a functional of the concentration and the field variables. For coherent phase transformations, the total free energy consists of two terms: the chemical free energy and the elastic strain energy

$$F = F_{\text{ch}} + E_{\text{el}}.$$

Chemical free energy

The total non-equilibrium chemical free energy as a function of the field variables is given by the Ginzburg–Landau free energy functional, which contains a local specific free energy $f(c, \theta_1, \theta_2, \dots, \theta_8)$ and gradient energy terms (Wen *et al.*, 2000; 2001a,b)

$$F_{\text{ch}} = \int_V \left[\frac{1}{2} \rho (\nabla c)^2 + \frac{1}{2} \sum_{i,j,p} \lambda_{ij}^{(p)} \left(\frac{\partial \theta_p}{\partial r_i} \right) \left(\frac{\partial \theta_p}{\partial r_j} \right) + f(c, \theta_1, \theta_2, \dots, \theta_8) \right] dV \quad [9.3]$$

where ρ and $\lambda_{ij}^{(p)}$ are gradient energy coefficients. The inclusion of the gradient terms in Eq. [9.3] automatically takes into account the interface energy contribution. Here, the gradient energy coefficients ($\lambda_{ij}^{(p)}$ tensor) are assumed to be phase-fields and orientation variants-independent and only diagonal terms are non-zero, i.e. $\lambda_{ij}^{(p)} = \lambda_i^{(p)} \delta_{ij}$. The anisotropy of the gradient coefficients results in the crystallographic anisotropy of the interfacial boundary. Taking into account the processes of crystal structure change from hcp type to fcc type, formation of lamellar precipitates, their shape and growth mechanism, we assume that the specific interfacial energies in the close-packed plane are higher than those in the direction perpendicular to the close-packed plane x_3 and a smaller $\lambda_3^{(p)}$, $p = 1, 2$ should be chosen. Because the parent phase (DO₁₉) is transversely isotropic in the close-packed plane (x_1 ox₂ plane for the chosen reference system), we further assume that

$\lambda_1^{(p)} = \lambda_2^{(p)}$ when $p = 1, 2$. The ordering of the fcc lamellar zone is assumed to be isotropic and the gradient energy coefficients are chosen to be $\lambda_1^{(p)} = \lambda_2^{(p)} = \lambda_3^{(p)}$ when $p = 3, \dots, 8$.

The integration in Eq. [9.3] is carried out over the entire system volume V . The local specific free energy in Eq. [9.3] describes the thermodynamics of the model system. It is usually approximated by a Landau-type polynomial expansion as a function of field variables. The order of the polynomial is determined by the desired accuracy of the model. In principle, the polynomial should include all the terms that are allowed by the parent phase symmetry and the number of allowed terms will depend on the nature of a specific transformation.

For the $\alpha_2 \rightarrow \alpha_2 + \gamma$ transformation considered by Wen *et al.* (2001b), an expansion up to the sixth order in the expanded parameters describing the six orientation variants, contains quadratic, fourth, and sixth-order terms. Here, we employ a similar strategy but we add terms corresponding to the disordered fcc phase

$$f(c, \theta_1, \theta_2, \dots, \theta_8) = \frac{A_1}{2}(c - c_1)^2 + \frac{A_2}{2}(c_2 - c) \sum_{s=1}^2 \theta_s^2 - \frac{A_3}{4} \sum_{s=1}^2 \theta_s^4 + \frac{A_4}{6} \left(\sum_{s=1}^2 \theta_s^2 \right)^3 + \frac{A_5}{2}(c_3 - c) \sum_{p=3}^8 \theta_p^2 - \frac{A_6}{4} \sum_{p=3}^8 \theta_p^4 + \frac{A_7}{6} \left(\sum_{p=3}^8 \theta_p^2 \right)^3 \quad [9.4]$$

where $c_1 - c_3$ and $A_1 - A_7$ are positive parameters. The plots of free energies of the metastable fcc and γ -phases versus composition can be obtained by minimising the above functional with respect to the field parameters and then substituting the corresponding equilibrium parameter as a function of composition back into the free energy expression. In addition to the local minima at $\theta_i = 0$; $i = 1, \dots, 8$ corresponding to the metastable parent phase, the free energy functional Eq. [9.4] has two local minima at $\theta_i = \pm \theta'_c$, $\theta_{j \neq i} = \theta_p = 0$; $i, j = 1, 2$; $p = 3, \dots, 8$ corresponding to the two stacking sequences of the fcc structure and six global minima at $\theta_p = \pm \theta''_c$, $\theta_{q \neq p} = 0$; $p, q = 3, \dots, 8$; $\theta_1 = \theta_2 = \pm \theta'_c$ corresponding to the six orientation variants of the γ -phase. From here on, we will designate by $\theta_i(\mathbf{r}, t)$ the normalised field variables $\frac{\theta_i}{|\theta'_c|}$, where $i = 1, 2$ and $\frac{\theta_i}{|\theta''_c|}$, where $i = 3, \dots, 8$.

As mentioned earlier, the local specific free energy provides the driving force for the $\alpha \rightarrow \gamma$ transformation. The temperature effect on the local free energy has to be taken into account in a perfect, comprehensive model. The available thermodynamic data, in our opinion, do not provide reliable information about the temperature dependency of the free energy functional, especially for the free energy of the metastable fcc phase. Here the constants

$A_2 - A_4$, which determine the specific free energy of the metastable fcc, are chosen to give a qualitatively correct description of the thermodynamics of the system. The parameters $A_1, A_5 - A_7$ are chosen to fit the local specific free energies of α - and γ -phases based on the available thermodynamic data of the Ti–Al system (Ohnuma *et al.*, 2000).

Elastic strain energy

The elastic energy of an arbitrary coherent multi-phase mixture is

$$E_{\text{el}} = \frac{1}{2} \int_V \sigma_{ij}^{\text{el}}(\mathbf{r}) \epsilon_{ij}^{\text{el}} dV$$

where $\sigma_{ij}^{\text{el}}(\mathbf{r}) = C_{ijkl} \epsilon_{kl}^{\text{el}}(\mathbf{r})$ is the local stress, and the local strain $\epsilon_{ij}^{\text{el}}(\mathbf{r})$ can be written in the form

$$\epsilon_{kl}^{\text{el}}(\mathbf{r}) = \epsilon_{kl}(\mathbf{r}) - \epsilon_{kl}^0(\mathbf{r})$$

where $\epsilon_{ij}(\mathbf{r})$ is the total local strain and $\epsilon_{ij}^0(\mathbf{r})$ is the local stress-free transformation strain (SFTS).

Since the transformation $\theta \rightarrow -\theta$ describes rigid body translation leading to anti-phase domains, and the free energy is invariant with respect to this transition, the first non-zero term of the stress-free strain expansion is quadratic with respect to $\theta_p(\mathbf{r})$

$$\epsilon_{ij}^0(\mathbf{r}) = \sum_{p=1}^n \theta_p^2(\mathbf{r}) \epsilon_{ij}^0(p) \quad [9.5]$$

where $\epsilon_{ij}^0(p)$ is the stress-free strain of the p th product phase when $\theta_p(\mathbf{r}) = 1$. The above expression can be used for the description of the local stress-free transformation strain of the stacking sequences of the fcc structure.

The appearance of the γ -phase consists of nucleation of three different orientation variants at a number of separate sites in a given stacking sequence of the metastable fcc, accompanied by independent growth of the variants. The ordering of the fcc lattice into the $L1_0$ structure is followed by a strain energy change due to the misfit between fcc and $L1_0$ crystal lattices.

To incorporate the strain energy change due to formation of γ -phase, we modify Eq. [9.5] by expressing the stress-free strain through the continuum fields $\theta_3(\mathbf{r}), \theta_4(\mathbf{r}), \dots, \theta_8(\mathbf{r})$ corresponding to six possible orientation variants for γ lamellae

$$\begin{aligned} \epsilon_{ij}^0(\mathbf{r}) = & \sum_{s=1}^2 \epsilon_{ij}^0(s) \theta_s^2(\mathbf{r}) + \sum_{p=3}^5 (\epsilon_{ij}^0(p) - \epsilon_{ij}^0(1)) \theta_p^2(\mathbf{r}) \\ & + \sum_{p=6}^8 (\epsilon_{ij}^0(p) - \epsilon_{ij}^0(2)) \theta_p^2(\mathbf{r}) \end{aligned} \quad [9.6]$$

where $\epsilon_{ij}^0(p)$ is the transformation-induced stress-free strain accompanying the transformation of hcp phase into the p th orientation variant of the product γ -phase. $\delta\epsilon_{ij}^0(p) = \epsilon_{ij}^0(p) - \epsilon_{ij}^0(s)$; $s = 1$; $p = 3, 4, 5$; or $s = 2$; $p = 6, 7, 8$ can be considered as the transformation-induced stress-free strain accompanying the ordering of the parent fcc A1 phase into the p th orientation variant of the γ -phase. We will write Eq. [9.6] in the form

$$\epsilon_{ij}^0(\mathbf{r}) = \sum_{p=1}^8 \tilde{\epsilon}_{ij}^0(p) \theta_p^2(\mathbf{r}) \quad [9.7]$$

where

$$\tilde{\epsilon}_{ij}^0(p) = \begin{cases} \epsilon_{ij}^0(s) & \text{if } s = 1, 2 \text{ (replace } p \text{ with } s) \\ \epsilon_{ij}^0(p) - \epsilon_{ij}^0(1) & \text{if } p = 3, 4, 5 \\ \epsilon_{ij}^0(p) - \epsilon_{ij}^0(2) & \text{if } p = 6, 7, 8 \end{cases} \quad [9.8]$$

$\theta_p(\mathbf{r})$ is not zero if a point $\mathbf{r}$, in the corresponding stacking fault ($\theta_i(\mathbf{r}) \neq 0$, $i = 1$ or 2), is within an orientation variant of γ -phase of type p , and zero outside it.

Using the local stress-free transformation strain (Eq. [9.7]) we have:

$$\begin{aligned} E_{el} = & \frac{V}{2} C_{ijkl} \bar{\epsilon}_{ij} \bar{\epsilon}_{kl} - V C_{ijkl} \bar{\epsilon}_{ij} \sum_{p=1}^8 \tilde{\epsilon}_{kl}^0(p) \overline{\theta_p^2(\mathbf{r})} \\ & + \frac{V}{2} C_{ijkl} \sum_{p,q=1}^8 \tilde{\epsilon}_{ij}^0(q) \tilde{\epsilon}_{kl}^0(q) \overline{\theta_p^2(\mathbf{r}) \theta_q^2(\mathbf{r})} \\ & - \frac{1}{2} \sum_{p,q=1}^8 \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \tilde{B}_{pq}(\mathbf{e}) \{\theta_p^2(\mathbf{r})\}_k^* \{\theta_q^2(\mathbf{r})\}_k \end{aligned} \quad [9.9]$$

where V is the total volume of the system; C_{ijkl} is the elastic modulus tensor; $\overline{(\dots)}$ represents the volume average of $(\dots)$; $\{\theta_p^2(\mathbf{r})\}_k = \int \frac{d^3 r}{(2\pi)^3} \theta_p^2(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r})$ is the Fourier transformation of $\theta_p^2(\mathbf{r})$; $(\dots)^*$ is complex conjugate of $(\dots)$; $\tilde{B}_{pq}(\mathbf{e})$ is a two-body interaction potential given by

$$\tilde{B}_{pq}(\mathbf{e}) = e_i \tilde{\sigma}_{ij}^0(p) \Omega_{jk}(\mathbf{e}) \tilde{\sigma}_{kl}^0(q) e_l$$

where $\mathbf{e} = \mathbf{k}/k$ is a unit vector in the reciprocal space, $\tilde{\sigma}_{ij}^0(p) = C_{ijkl} \tilde{\epsilon}_{kl}^0(p)$ and $\Omega_{ij}(\mathbf{e})$ is a Green function tensor which is inverse to the tensor

$$\Omega_{ij}^{-1}(e) = C_{ijkl} e_k e_l$$

The integration in Eq. [9.9] is carried out over the first Brillouin zone and the volume $(2\pi)^3/V$ is excluded from the integration.

The quantity $\bar{\epsilon}_{ij}$ is the homogeneous strain determining the macroscopic shape deformation of the crystal as a whole produced due to the presence of new phase particles. Here, the macroscopic homogeneous strain $\bar{\epsilon}_{ij}$ is assumed

to be zero, which corresponds to a fixed boundary condition which does not allow any macroscopic shape changes of the crystal. This condition is a good approximation for describing the boundary condition of a system of a single grain embedded in a polycrystalline material (Wen *et al.*, 2001b). As a result, the first two terms in Eq. [9.9] are zero.

9.2.3 Stress-free transformation strain

In view of the similarity of microstructures formed following the two transformation paths $\alpha \rightarrow \alpha_2 \rightarrow \alpha_2 + \gamma$ or $\alpha \rightarrow \alpha_2 + \gamma$, the mechanisms of nucleation and growth should be the same irrespective of the ordered or disordered character of the matrix. Since the $\alpha \rightarrow \alpha_2$ ordering does not change the major characteristics of the microstructure, we consider only $\alpha_2 \rightarrow \alpha_2 + \gamma$ transformation here.

The hcp $\rightarrow$ fcc structure change during $\alpha_2 \rightarrow \alpha_2 + \gamma$ transformation is a combination of $\langle 10\bar{1}0 \rangle_{\alpha_2}$ shuffling along close-packed planes, accompanied by homogeneous isotropic strain in $(0001)_{\alpha_2}$ planes, and change of the interplanar distance c_{hcp} between $(0001)_{\alpha_2}$ planes. We take α_2 -phase as a reference state and set x_1, x_2 and x_3 axes parallel to $\langle 11\bar{2}0 \rangle_{\alpha_2}$, $\langle \bar{1}100 \rangle_{\alpha_2}$ and $\langle 0001 \rangle_{\alpha_2}$, respectively. The crystal lattice correspondence

$$a_{\text{hcp}} \rightarrow a_{\text{fcc}} \sqrt{2} \quad \text{and} \quad c_{\text{hcp}} \rightarrow 2d_{(111)} \quad [9.10]$$

enables us to calculate the isotropic strain in the $(0001)_{\alpha_2} // (111)_{\text{fcc}}$ planes and the strain value associated with the mismatch between the d -spacing along the $\langle 0001 \rangle_{\alpha}$ direction

$$\varepsilon = \begin{pmatrix} \varepsilon_{\text{SF}} & 0 & 0 \\ 0 & \varepsilon_{\text{SF}} & 0 \\ 0 & 0 & v_{\text{SF}} \end{pmatrix} \quad [9.11]$$

where $v_{\text{SF}} = \frac{2a_{\text{fcc}}}{c_{\text{hcp}} \sqrt{3}} - 1$ is the elastic strain associated with the mismatch between the d -spacing along the $\langle 0001 \rangle_{\alpha_2}$ direction and $\varepsilon_{\text{SF}} = (a_{\text{fcc}} \sqrt{2} - a_{\text{hcp}})/a_{\text{hcp}}$. The change of stacking sequence $AB \rightarrow ABC$ and $AB \rightarrow ACB$ associated with the hcp $\rightarrow$ fcc transition induces fields of opposite shear strain along $\langle 10\bar{1}0 \rangle_{\alpha_2}$. The transformation shear strain corresponding to the two types of stacking sequences can be obtained in the form (Wen *et al.*, 2001b)

$$\varepsilon_s^0(1) = \begin{pmatrix} 0 & 0 & -s\sqrt{3}/4 \\ 0 & 0 & -s/4 \\ -s\sqrt{3}/4 & -s/4 & s^2/2 \end{pmatrix},$$

$$\epsilon_s^0(2) = \begin{pmatrix} 0 & 0 & s\sqrt{3}/4 \\ 0 & 0 & s/4 \\ s\sqrt{3}/4 & s/4 & s^2/2 \end{pmatrix} \quad [9.12]$$

where $s \approx 1/(2\sqrt{2})$ is the shear magnitude corresponding to the Shockley partials bordering the stacking fault.

Taking all these into consideration, the SFTS for the two types of stacking sequences can be expressed as

$$\epsilon^0(1) = \begin{pmatrix} \epsilon_{SF} & 0 & -s\sqrt{3}/4 \\ 0 & \epsilon_{SF} & -s/4 \\ -s\sqrt{3}/4 & -s/4 & v_{SF} + s^2/2 \end{pmatrix}$$

$$\epsilon^0(2) = \begin{pmatrix} \epsilon_{SF} & 0 & s\sqrt{3}/4 \\ 0 & \epsilon_{SF} & s/4 \\ s\sqrt{3}/4 & s/4 & v_{SF} + s^2/2 \end{pmatrix} \quad [9.13]$$

There are three pairs of orientation variants of the γ -phase, denoted as (γ^0, γ^{180}) , $(\gamma^{120}, \gamma^{300})$ and $(\gamma^{240}, \gamma^{60})$ (Wen *et al.*, 2001b), where three of them, γ^0 , γ^{120} and γ^{240} , belong to stacking sequence group (1) and the others, γ^{180} , γ^{300} and γ^{60} , to group (2). The six orientation variants can be described by shears along $\pm\langle\bar{1}100\rangle_{\alpha 2}$, $\pm\langle 10\bar{1}0\rangle_{\alpha 2}$ and $\pm\langle 01\bar{1}0\rangle_{\alpha 2}$ on $(0001)_{\alpha 2}$. The elastic strain associated with the crystal lattice mismatch between α and $L1_0$, corresponding to the six variants can be expressed as (Wen *et al.*, 2001b)

$$\epsilon^0(3) = \begin{pmatrix} \epsilon'_\gamma & 0 & 0 \\ 0 & 2\epsilon_\gamma/3 + \epsilon'_\gamma & s/2 \\ 0 & s/2 & s^2/2 + v_\gamma \end{pmatrix},$$

$$\epsilon^0(4) = \begin{pmatrix} \epsilon_\gamma/2 + \epsilon'_\gamma & \epsilon_\gamma\sqrt{3}/6 & -s\sqrt{3}/4 \\ \epsilon_\gamma\sqrt{3}/6 & \epsilon_\gamma/6 + \epsilon'_\gamma & -s/4 \\ -s\sqrt{3}/4 & -s/4 & s^2/2 + v_\gamma \end{pmatrix},$$

$$\epsilon^0(5) = \begin{pmatrix} \epsilon_\gamma/2 + \epsilon'_\gamma & -\epsilon_\gamma\sqrt{3}/6 & s\sqrt{3}/4 \\ -\epsilon_\gamma\sqrt{3}/6 & \epsilon_\gamma/6 + \epsilon'_\gamma & -s/4 \\ s\sqrt{3}/4 & -s/4 & s^2/2 + v_\gamma \end{pmatrix},$$

$$\epsilon^0(6) = \begin{pmatrix} \epsilon'_\gamma & 0 & 0 \\ 0 & 2\epsilon_\gamma/3 + \epsilon'_\gamma & -s/2 \\ 0 & -s/2 & s^2/2 + v_\gamma \end{pmatrix},$$

$$\varepsilon^0(7) = \begin{pmatrix} \varepsilon_\gamma/2 + \varepsilon'_\gamma & \varepsilon_\gamma \sqrt{3}/6 & s\sqrt{3}/4 \\ \varepsilon_\gamma \sqrt{3}/6 & \varepsilon_\gamma/6 + \varepsilon'_\gamma & s/4 \\ s\sqrt{3}/4 & s/4 & s^2/2 + v_\gamma \end{pmatrix},$$

$$\varepsilon^0(8) = \begin{pmatrix} \varepsilon_\gamma/2 + \varepsilon'_\gamma & -\varepsilon_\gamma \sqrt{3}/6 & -s\sqrt{3}/4 \\ -\varepsilon_\gamma \sqrt{3}/6 & \varepsilon_\gamma/6 + \varepsilon'_\gamma & s/4 \\ -s\sqrt{3}/4 & s/4 & s^2/2 + v_\gamma \end{pmatrix},$$

where $v_\gamma = \frac{2c_\gamma a_\gamma}{c_{\text{hcp}} \sqrt{a_\gamma^2 + 2c_\gamma^2}} - 1$ is the elastic strain associated with the mismatch between the d -spacing along the $\langle 0001 \rangle_{\alpha 2}$ direction, $\varepsilon_\gamma = (c_\gamma/a_\gamma - 1)$ and $\varepsilon'_\gamma = (\sqrt{2}a_\gamma - a_{\text{hcp}})/a_{\text{hcp}}$.

9.2.4 Nucleation

In the usual formulation of the phase-field model, nucleation is simulated with Langevin noise terms. Though an elegant treatment, this becomes computationally expensive, since it requires sampling at a very high frequency in order to observe nucleation events, which are very rare. In addition, to distinguish the critical and non-critical heterogeneities, the noise terms in Eqs. [9.1] and [9.2] are artificially turned off after a certain number of nuclei have been generated and the microstructural evolution is controlled by growth and coarsening of the nuclei.

The Langevin noise terms allow homogeneous nucleation. Here, we consider a hypothesis for nucleation of the γ -phase on the fcc stacking lamellar zone. According to this hypothesis, the formation of γ nuclei takes place during the entire process of growth of the fcc lamellae. In this case, we cannot divide the processes of nucleation and growth and distinguish the critical and non-critical heterogeneities by turning off the noise terms after a number of time steps. In order to describe the heterogeneous nucleation of γ -phase, we have to consider simultaneously the processes of nucleation of γ and the growth of the fcc lamellae and γ orientation variants.

Chapter 8 has developed an approach for treating processes including simultaneous precipitation and growth. The approach includes two algorithms, which alternate, one for nucleation and one for growth and coarsening. The nucleation rate varies independently, according to the depletion of the matrix, to account for the constantly changing state of supersaturation. Here, we use a similar approach to adapt the phase-field method to processes involving simultaneous nucleation and growth. This is accomplished through a hybrid model, in which stochastic nucleation events are explicitly introduced into

the phase-field model. In this model, nucleation and growth take place by a cyclic process. During the nucleation phase, the nucleation rates are determined as functions of local supersaturation. These rates are then used to determine the behaviour of the nucleation events. Since there are, in general, multiple atomic sites within each cell and multiple characteristic nucleation time scales in each phase-field time step, both time and length dimensions need to be scaled up. To adjust the time scale to that of the phase-field method, we assume that no nuclei form at any of the atomic sites within a cell for any of the nucleation time steps for a period of time smaller than one phase-field time step.

The formation of the primary fcc A1 type lamellar structure takes place towards the grain interior, through the propagation of Shockley partial dislocations, starting from grain boundaries. The nucleus of the stacking faults forms preferentially at a grain boundary, because the interfacial energy term will be reduced, and some free energy will be released, thereby reducing the activation energy barrier. At each phase-field time step, we calculate the number J_0 of fcc A1 nucleus on the grain boundary area S_α occupied by the α -phase, using:

$$J_0 = \int_{t_0}^t \int_{S_\alpha} k_1 \exp(-k_2 \Delta G^*) ds dt \quad [9.14]$$

where $k_1 = N_v \frac{k_B T}{\hbar} \exp\left(-\frac{\Delta G_m}{k_B T}\right)$, $k_2 = \frac{1}{k_B T}$, N_v is the number of nucleation sites (atoms) per unit volume, ΔG_m is the activation energy for atomic migration across the interface, ΔG^* is the excess free energy associated with the creation of embryo of the transformed phase, t_0 is the time when the previous nucleus is formed, and $\hbar$ is the Planck constant. The moment that the number of nuclei increases by one, a new nucleus is generated. The generation of a nucleus on the area occupied by α is modelled here with a random number generator that produces a random variable whose value is 1 with probability $P(x)$, where $P(x)$ is the probability of forming one nucleus at a point x . The probability of a nucleus appearing at a point x of the volume occupied by the α -phase, is proportional to the exponent of the activation energy and depends on the temperature and concentration (Chapter 8)

$$P(x) = P_0 \exp(-k_2 \Delta G^*) \quad [9.15]$$

The coefficient P_0 is determined from the requirement that the total probability for a new nucleus occurring on the grain boundary area S_α at the moment t_n is equal to 1. The same approach is used for the simulation of the nucleation of the different orientation variants of the γ -phase in the stacking lamellar zone.

The drawback in using the classical nucleation theory to distinguish the

critical and non-critical heterogeneities is the introduction of a number of unknown parameters. The most significant parameter affecting the nucleation kinetics is the free energy for formation of a critical nucleus ΔG^* . The local free energy reduction Δf and the misfit elastic strain energy ΔE_{el} associated with the process of nucleation can be evaluated by the methods described in Section 9.2.2. The only unknowns in the calculation of ΔG^* are the interfacial energies $\sigma_{\alpha\alpha}$, $\sigma_{\alpha A1}$ and $\sigma_{A1\gamma}$. There are no experimental values available for these interfacial energies, but data from other systems (Veeraraghavan *et al.*, 2003) suggest that the α - α interface energy $\sigma_{\alpha\alpha}$ typically varies from 400 to 1000 mJ/m² and coherent α - γ energy ranges from 25 to 200 mJ/m². Following Veeraraghavan *et al.* (2003), a value of $\sigma_{\alpha\alpha} = 500$ mJ/m² is chosen here. Since Veeraraghavan *et al.* (2003) indicates that typical ratios of coherent interface boundary energies range from 0.15 to 0.4 times the grain boundary energy, values of $\sigma_{\alpha A1} = 175$ mJ/m² and $\sigma_{A1\gamma} = 75$ mJ/m² are chosen. Since the nucleation rate is very strongly dependent on the interfacial energies, a shortcoming of the model is that small errors in these quantities will lead to significant differences in nucleation rates.

Here, the Langevin noise terms $\xi_i(\mathbf{r}, t)$ and $\zeta(\mathbf{r}, t)$ are set to zero, since the periodic introduction of particles described above accounts for nucleation.

9.2.5 Normalisation of the kinetic equations and choice of the input parameters

Following Wen *et al.* (2000, 2001a,b), we transform the kinetics Eqs. [9.1] and [9.2] into a dimensionless form through the introduction of a reduced time, defined as $\tau = L |\Delta f| t$, and reduced spatial coordinates, defined as $u_i = x_i/l$. In these definitions, $|\Delta f| = 1$ kJ mol⁻¹ and l is the length unit of the computational grid size. Since the orientation variants of γ -phase are formed as result of the ordering of the fcc lattice into the L1₀ structure, it is more suitable to formulate Eq. [9.1] in terms of the long-range order parameter fields $\theta'_p(\mathbf{r})$ $\theta'_p(\mathbf{r})$ for $p = 3, \dots, 8$. In this case, Eq. [9.1] is formulated in the volume occupied by the fcc phase $\theta_i(\mathbf{r}) \neq 0$, $i = 1$ or 2 . Substituting the above variables into Eqs. [9.1] and [9.2], the dimensionless form of the kinetic equations is

$$\frac{\partial \tilde{\theta}_p(\mathbf{u}, \tau)}{\partial \tau} = - \left[- \sum_{ij=1}^3 \beta_{ij}^{(p)} \frac{\partial^2 \tilde{\theta}_p(\mathbf{u}, \tau)}{\partial u_i \partial u_j} + \frac{\partial f_a}{\partial \tilde{\theta}_p(\mathbf{u}, \tau)} + \phi \frac{\delta E_{el}}{\delta \tilde{\theta}_p(\mathbf{u}, \tau)} \right] \quad [9.16]$$

$$\frac{\partial c(\mathbf{u}, \tau)}{\partial \tau} = \phi \nabla^2 \left[-\alpha \nabla^2 c(\mathbf{u}, \tau) + \frac{\partial f_a}{\partial c(\mathbf{u}, \tau)} \right] \quad [9.17]$$

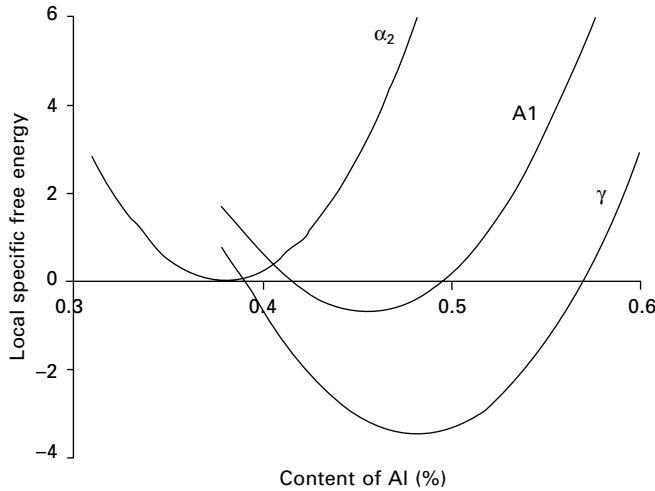
where $\tilde{\theta}p(\mathbf{u}, \tau) = \theta p(\mathbf{u}, \tau)$, $p = 1, 2$, $\tilde{\theta}'p(\mathbf{u}, \tau) = \theta'p(\mathbf{u}, \tau)$, $p = 3, \dots, 8$,

$$\beta_{ij}^{(p)} = \frac{\lambda_{ij}^{(p)}}{l^2 |\Delta f|}, p = 1, 2; \beta_{ij}^{(p)} = \frac{L'}{L} \frac{\lambda_{ij}^{(p)}}{l^2 |\Delta f|}, p = 3, \dots, 8;$$

$$\phi = \frac{1}{|\Delta f|}; \varphi = \frac{M}{Ll^2}; \alpha = \frac{\rho}{|\Delta f|l^2}$$

and $f_a(c, \theta_1, \theta_2, \dots, \theta_8)$ is given by Eq. [9.4], where the constants A_i are replaced by $a_i = A_i/|\Delta f|$. Those phenomenological polynomial expansion coefficients in Eq. [9.4] should be chosen properly to provide a qualitatively correct description of the specific free energy of the system. Although accurate free energy curves of α , γ and especially of A1 fcc phase are not available, we have chosen $(a_1, a_2, a_3, a_4, a_5, a_6, a_7, c_1, c_2, c_3) = (1149.43, 137.93, 40.52, 29.95, 34.82, 20.11, 14.87, 0.38, 0.48, 0.48)$ to fit the available thermodynamic data of the Ti–Al system (Ohnuma *et al.*, 2000). The temperature effects are not taken into account, but the accuracy of the specific free energy is not critical as long as the sequence of the morphological transformation rather than the quantitative values of the transformation rate is concerned. The local free energy minima defined by Eq. [9.4] with the above chosen parameters are projected onto the f – c plane and plotted in Fig. 9.1. Following Wen *et al.* (2001b), φ and α are assumed to be 1 and 3, respectively.

Since the gradient energy coefficients $\lambda_{ij}^{(p)}$ are assumed to be field variables independent, only diagonal terms of $\beta_{ij}^{(p)}$ are non-zero, i.e. $\beta_{ij}^{(p)} = \beta_i^{(p)}\delta_{ij}$. Due to the mechanism of longitudinal and lateral growth of the lamellar



9.1 Local specific free energy for α_2 , fcc (A1) and γ -phases as a function of aluminium concentration.

precipitates, we assume that $\beta_1^{(p)} = \beta_2^{(p)} = 25$ and $\beta_3^{(p)} = 0.6$ when $p = 1, 2$. By taking into account a comparison of the growth rate of an order domain V_{OD} and the velocity of the kink responsible for the longitudinal growth of stacking faults V_S , it is established that $V_{OD} < V_S$. Taking into account this limitation, we assume that the ordering of the fcc lamellar zone is isotropic and the gradient energy coefficients are chosen to be $\beta_1^{(p)} = \beta_2^{(p)} = \beta_3^{(p)} = 0.6$ when $p = 3, \dots, 8$.

The elastic moduli tensor of the system is assumed to be homogeneous and those for the α_2 -phase at 290 K are employed to represent the elastic moduli of the system. All the Voigt elastic constants are zero except that: $C_{11} = C_{22} = 175$ GPa; $C_{33} = 220$ GPa; $C_{12} = 88.7$ GPa; $C_{13} = C_{23} = 62.3$ GPa; $C_{44} = C_{55} = 62.2$ GPa; $C_{66} = (C_{11} - C_{12})/2$, which are taken from experimental data (Tanaka *et al.*, 1996).

The disordered A1 structure is characterised by lattice parameters $a_{fcc} = c_{fcc} = 0.405$ nm. With the ordering, the structure changes from fcc to tetragonal $L1_0$ with lattice parameters $a_\gamma = 0.396$ nm, $c_\gamma = 0.418$ nm (Chen *et al.*, 2004). The lattice parameters characterising hcp structure are $a_{hcp} = 0.576$ nm, $c_{hcp} = 0.456$ nm (Yoo *et al.*, 1995).

The coefficients k_1 and k_2 in Eq. [9.14], describing the nucleation rate of the stacking faults and the order variants of γ , are assumed to be $k_2 = 5 \times 10^{19} \text{ J}^{-1}$, $k_1(\text{SF}) = 1.39 \times 10^{-2}$ and $k_1(\gamma) = 1.12$.

The phase-field model for the formation and dynamic evolution of lamellar structures in two-phase TiAl alloys, described in this section, is formulated in 3D. The simulation of the microstructural evolution and formation of the multi-phase and multi-domain lamellar structure in 3D, however, requires considerable computational resources. In order to reduce the number of calculations and taking into account that the growth of the lamellar structure is isotropic on the close-packed plane ($x_1o x_2$ plane for the chosen coordinate system), all computations in the next section are made in a 2D unit cell on the $x_2o x_3$ plane, although the algorithm can be extended in a straightforward fashion to 3D. Finally, all computations have been made under isothermal conditions. However, for the purpose of alloy design, the simulations should be carried out in 3D and take into account the influence of the temperature effects on the local free energy.

Eqs. [9.16] and [9.17] are solved numerically on a 2D unit cell with 64×64 mesh points. The spatial and time increments in our numerical solution have been chosen as $du_2 = du_3 = 0.5$ and $d\tau = 0.01$.

9.3 Computer simulation of lamellar structure formation in γ -TiAl

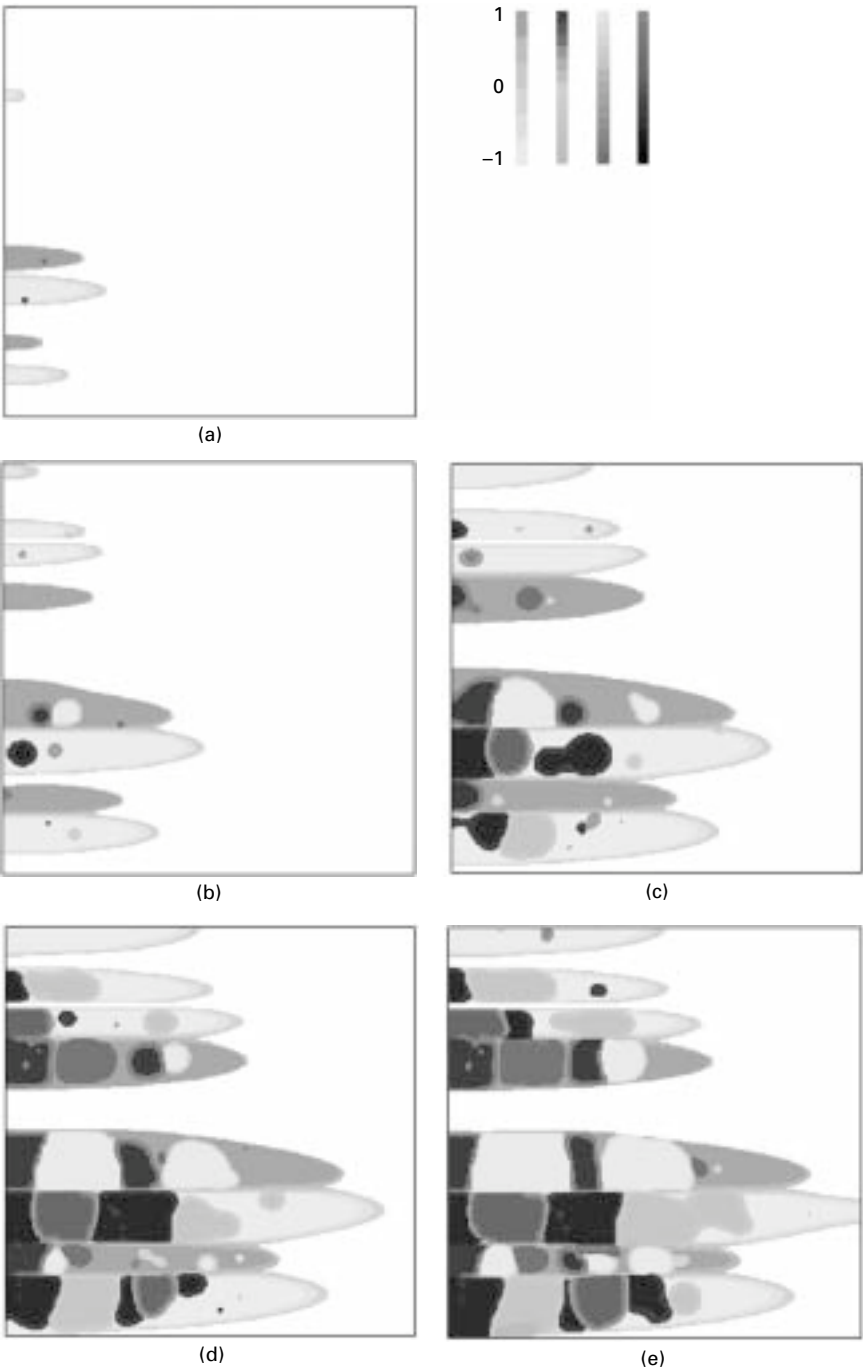
The composition dependency of the free energies of α_2 -, A1- and γ -phases used for the computer simulation of the lamellar structure formation is shown in Fig. 9.1.

The initial condition for the simulation is a homogeneous supersaturated α_2 -phase with a mean aluminium composition of the alloy $\bar{c} = 0.46$. According to the local specific free energy curve in Fig. 9.1, with the parameters given in Section 9.2.5, the initial hexagonal phase is unstable. The transformation takes place through a nucleation and growth mechanism. In the simulations, the nucleation process is simulated through the model proposed in Section 9.2.4. In accordance with the experimental observations, the formation of the primary fcc lamellar structure takes place towards the grain interior starting from grain boundaries because the activation energy barrier will be reduced. We assume that one of the sides of the area under consideration is a part of the grain boundary. The gradually decreasing solute supersaturation in the matrix leads to reducing the driving force for SF nucleation and the local free energy, Eq. [9.4]. Further evolution of the fcc lamellar microstructure is controlled by growth and coarsening. The simulated 2D fcc evolution is shown in Fig. 9.2, where the shades of grey represent the values of $\theta_1^2 - \theta_2^2$.

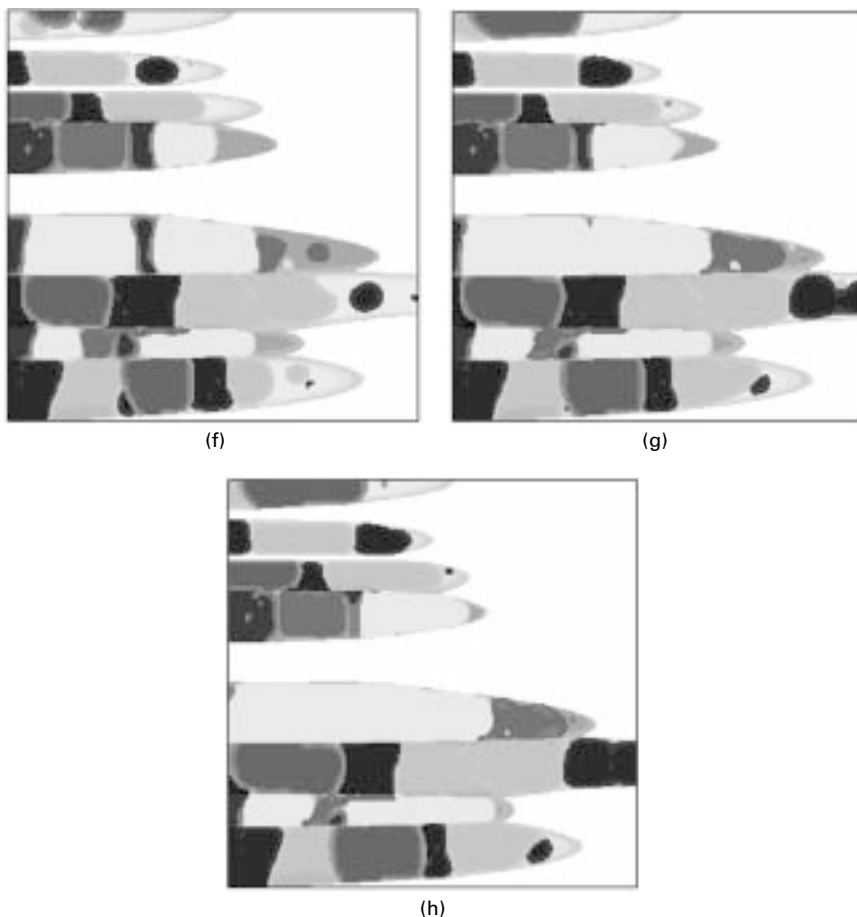
The appearance of the γ -phase consists of nucleation of three different orientation variants at a number of separate sites in a given stacking sequence of the metastable fcc, followed by independent growth of the variants and their encounter, resulting in the formation of ODBs and other types of boundaries as discussed further below. The values of $\theta_3^2 - \theta_6^2$, $\theta_4^2 - \theta_7^2$ and $\theta_5^2 - \theta_8^2$, corresponding to the twin-related pairs (3, 6), (4, 7), and (5, 8), are shown in Fig. 9.2 by iso-surfaces with different grey scales. The grey scale scheme is illustrated in Fig. 9.2, by the grey scale bars, each with two major grey scales. In such a grey scale scheme, variants 3–8 correspond to three grey scales from the right hand side, respectively. The two stacking groups 1 and 2 correspond to light and dark grey. Therefore, the white background represents the α_2 -phase.

Some of the main features of the lamellar structure are obtained as results of the computer simulation of the process of $\alpha_2 \rightarrow \gamma$ transformation:

- The interfaces between two γ lamellae are flat, lying parallel to the (0001) plane.
- These interfaces are order domain (if the lamellae are of the same stacking group), twin or pseudo-twin boundaries (the boundaries between the order domains 3–7, 3–8, 4–6, 4–8, 5–6 and 5–7).
- Inside a lamella there are also order domain boundaries, separating lamella into several areas having different orientations and belonging to the same orientation group. The order domain boundaries are wavy, contrary to those found for lamellar interfaces.
- Most of the interfaces separating γ – γ lamellae belong to different orientation groups.
- Most of α_2 lamellae are bordered by γ lamellae of the same group.
- Joining of two lamellae of the same group is more difficult than joining



9.2 Simulated evolution of the lamellar structure. (a) $\tau = 0.48$; (b) $\tau = 1$; (c) $\tau = 1.8$; (d) $\tau = 2.5$; (e) $\tau = 3$; (f) $\tau = 3.5$; (g) $\tau = 4$; (h) $\tau = 4.5$.



9.2 Continued

of lamellae of different groups. Two lamellae of the same group tend to leave α_2 -phase between them due to the repulsive component in the expression for the elastic strain energy, Eq. [9.9].

Because of the tetragonality of the $L1_0$ structure, the interfaces corresponding to twin relationship are fully coherent, whereas those corresponding to the pseudo-twin relationship should generate a mismatch. Therefore, the relatively higher proportion found for the twin boundaries is most likely due to the minimisation of the elastic energy of the interfaces. This minimisation may be achieved through the following two processes. One happens during the nucleation when collective or sympathetic ordering takes place, involving several adjacent lamellae; in this case, adjacent variants are twin related to each other due to the lower activation barrier for nucleation ΔG^* . The other

process takes place during the growth when the migration of the boundaries separating two variants within each gamma lamella tends to reduce the pseudo-twin portion of the interface in favour of the twin relationship due to the minimisation of the elastic energy term in Eq. [9.16].

Formation of an intermediate disordered fcc structure and subsequent ordering is one plausible mechanism which could explain the formation of lamellar Ti-Al structure. This mechanism is incorporated here through the proposed form of the local energy function, Eq. [9.4]. While most of the input parameters (the elastic constants, lattice parameters, crystallographic relationship, etc.) are based on experimental work, the local specific free energy is not based on experimental data. Using the local energy, Eq. [9.4], we have obtained some of the main features of the lamellar structure. However, the present level of knowledge of the free energy of the system under consideration as a function of the temperature, concentration and field variables does not allow us to provide additional information to support the mechanism hypothesis. For the same reason, we do not consider the processing condition in the model. In order to solve this problem, we need a more comprehensive model in which the temperature dependency of the local free energy has to be taken into account.

9.4 Summary

Here, a phase-field model has been developed for simulating the formation and evolution of lamellar microstructure in γ -TiAl alloy. The model describes the crystal structure change from hcp type to fcc type, formation of fcc stacking lamellar zone and nucleation and growth of $L1_0$ orientation variants at a number of separate sites in the metastable fcc-type structure during the growth and the coarsening of the lamellae. The interaction between the displacive and diffusional transformations taking place is described by a non-equilibrium free energy, formulated as a function of concentration and structural order parameter fields. The long-range elastic interactions, arising from the lattice misfit between the α (A3), fcc (A1) and the various orientation variants of the γ -phase, are taken into account by incorporation of the elastic strain energy into the total free energy.

Using the mechanism of formation of TiAl lamellae can predict the main features of the lamellar structure discussed in the literature. The elastic interaction between domains plays a critical role in determining the morphology of γ lamellae and their mutual arrangement. The joining of two lamellae of the same stacking group is more difficult than that of lamellae of different groups due to the accommodation of the coherency elastic strain, arising from the lattice misfit between the disordered fcc, low-symmetry product phase γ and the high-symmetry α -phase, as well as among the various orientation variants of the product phase. Also, the relatively higher proportion

of the interfaces between twin-related domains over pseudo-twin-related domains is related to the strain-induced correlated nucleation and the minimisation of the elastic energy of the interfaces.

9.5 References

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Cellular automata method for microstructural evolution modelling

Abstract: The microstructural evolution of the Ti-6Al-4V alloy during thermomechanical processing in the β phase field, investigated both experimentally and via modelling, is the subject of this chapter. The influence of strain rate and temperature is considered. Experimental data show that dynamic or metadynamic recrystallisation occurs when processed in the β phase field. Simulation data show that both the degree of dynamic recrystallisation and the mean size of the dynamically recrystallised grains increase with increasing temperature and decreasing strain rate. The predicted mean dislocation density fluctuates at low strain rates or high temperatures, and gradually stabilises with increasing strain rate or decreasing temperatures.

Key words: recrystallisation, deformation effects, strain rate, grain size, thermomechanical treatment.

10.1 Introduction

Although the microstructural characteristics of the Ti-6Al-4V alloy during thermomechanical processing in the β phase field have been experimentally studied extensively by many researchers, there has been little theoretical and modelling activity to understand quantitatively the evolution of microstructure, particularly that involving the dynamic recrystallisation process in the β phase field.

The subject of this chapter is the microstructural variation of the Ti-6Al-4V alloy during high-temperature β -processing in the single-phase field, and the influence of thermomechanical processing parameters, e.g. strain rate and temperature, on the characteristics of dynamic recrystallisation (DRX). We will simulate accurately plastic flow characteristics, by coupling fundamental metallurgical principles with an appropriate modelling approach (Ding and Guo, 2001). The type of technique developed is the cellular automaton (CA) method.

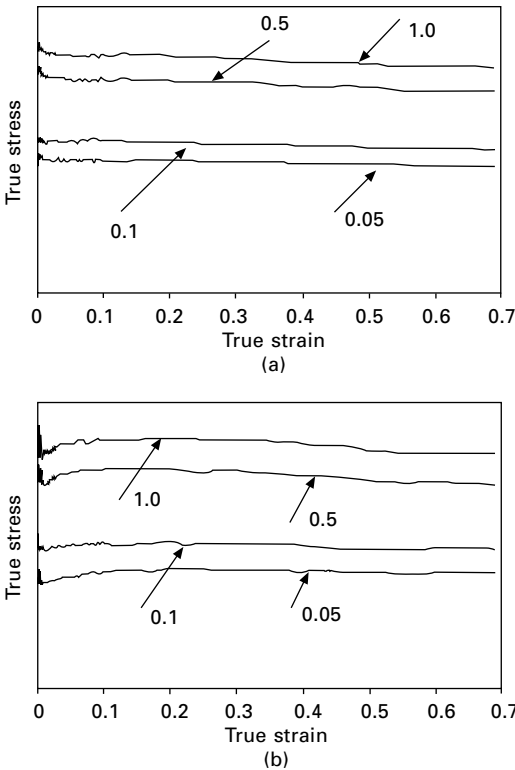
In order to provide experimental and microstructural evidence for simulation, an experimental investigation will be shown for the microstructural evolution under a range of hot working conditions, with temperatures ranging 850–1050 °C and strain rates ranging 0.05–1 s⁻¹. The influences of hot working parameters on deformation localisation, width of α platelets, α to β phase transformation, and (meta)dynamic recrystallisation are systematically examined by optical microscopy and scanning electron microscopy.

The novel approach of combining CA with theoretical principles of DRX links meso- and micro- structural features with continuum flow properties of metallic materials and with processing conditions. The influences of hot deformation parameters, e.g. strain, strain rate and deformation temperature, on the characteristics of DRX, e.g. the microstructural evolution and the flow stress–strain behaviour, are analysed in this chapter.

10.2 Microstructural evolution of Ti-6Al-4V during thermomechanical processing

10.2.1 Flow stress–strain curves

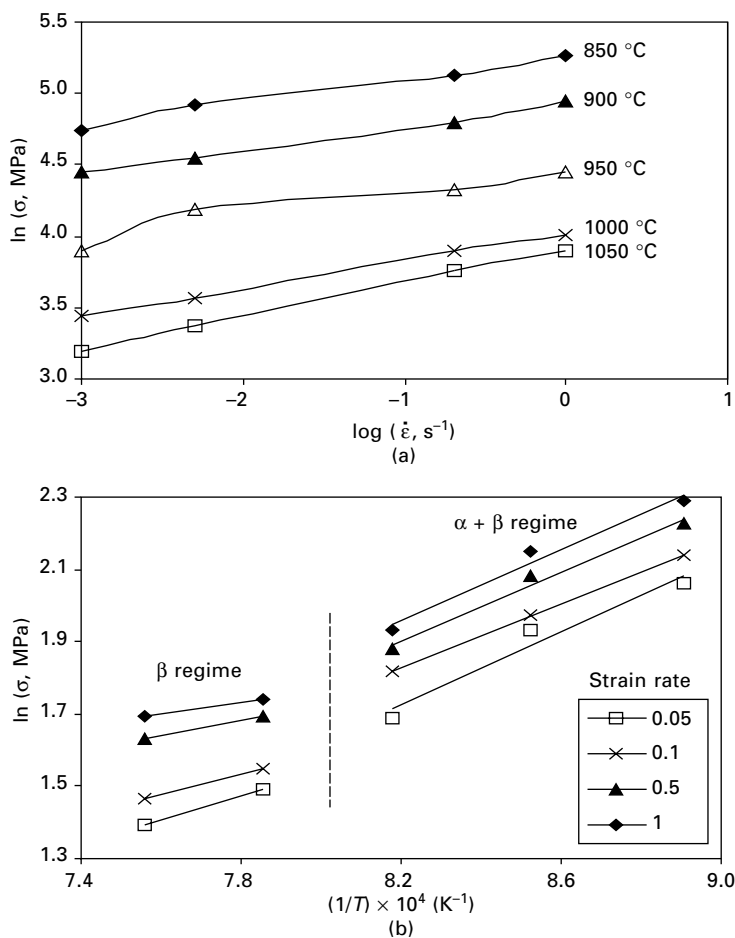
The flow stress is almost constant under all conditions, as shown in typical curves of the hot-pressed specimens in Fig. 10.1. The stress–strain characteristics may be attributed to the microstructural changes due to phase



10.1 Stress–strain curves for different hot working temperatures and strain rates. (a) 1000 °C; and (b) 1050 °C. The vertical axis scale is obscured due to proprietary data.

transformation, adiabatic heating and evolution of dynamic recovery or dynamic recrystallisation during hot processing. Further evidence for these is provided in later sections.

The experimental stress-strain curves show that the flow stress increases with strain rate at a given temperature and decreases with increasing temperature at a given strain rate (Fig. 10.2). Significant flow softening occurs for hot-pressing at the lower temperatures. There are two possible mechanisms responsible for the flow softening: (i) adiabatic heating during hot-pressing; and (ii) α to β phase transformation during hot-pressing.

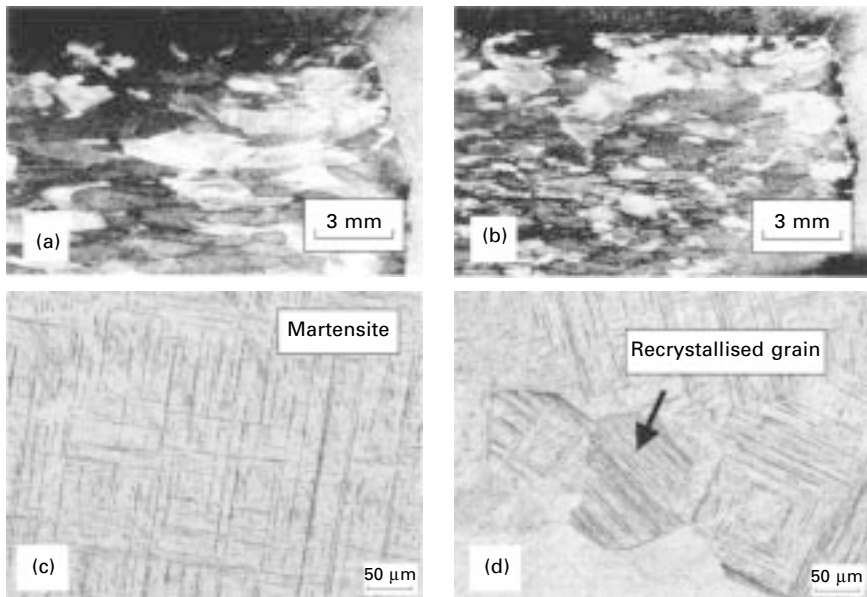


10.2 Variation of flow stress of Ti-6Al-4V with (a) strain rate at different processing temperatures and (b) temperature at different strain rates.

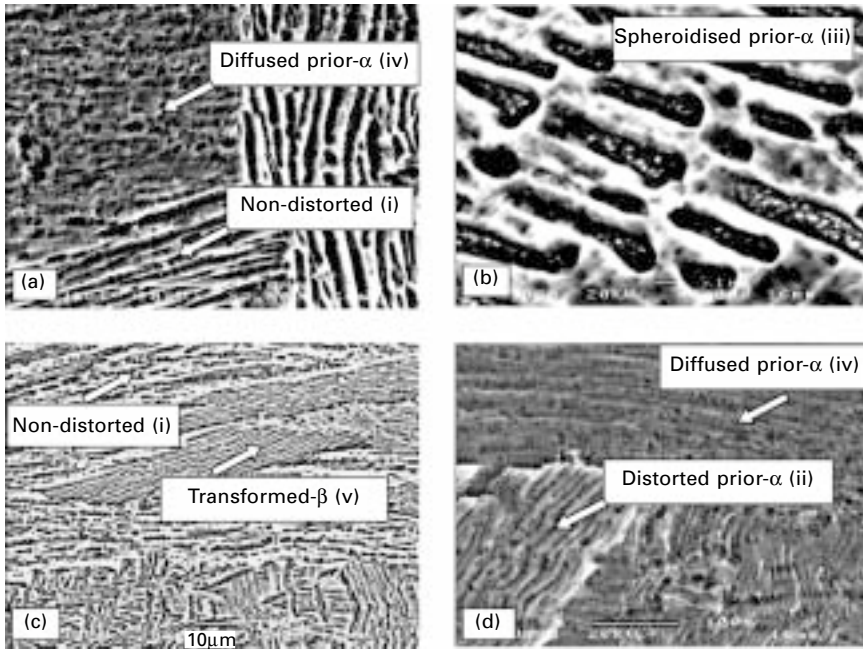
10.2.2 Phase transformation

Phase transformation during thermomechanical processing is an important feature for $\alpha + \beta$ titanium alloys. The microstructure of the non-deformed samples shows that all the prior- α lamellar phase has transformed into equiaxed grains prior to hot working. After quenching from the β -processing temperatures, the β -grains transformed into martensite. The features are shown in Fig. 10.3 where two samples were processed at $\dot{\epsilon} = 0.1 \text{ s}^{-1}$.

The experimental results show that the behaviour of deformation and transformation of the prior- α lamellar phase is very complex at the processing temperatures. Phase transformation of the prior α lamellar phase may be distinguished by three stages: non-transformed, partially-transformed and completely transformed, respectively. The final microstructural morphology of the samples deformed in the $\alpha + \beta$ phase field is characterised by at least five different types (Fig. 10.4). These are: (i) non-distorted prior- α platelets with an interplatelet β phase (prior- α microstructure before hot deformation); (ii) distorted prior- α platelets with an interplatelet β phase; (iii) spheroidised prior- α lamella zone; (iv) diffused prior- α phase zone; and (v) transformed- β phase zone, respectively. The morphology depends on the local thermomechanical history corresponding to different stages of transformation (Ding *et al.*, 2002).



10.3 Micrographs of two hot-pressed samples for the strain rate of 0.1 s^{-1} . The conditions are: (a, c) 1000°C ; and (b, d) 1050°C .



10.4 Five different morphologies of α phase after hot working in the $\alpha + \beta$ field (850 °C, 0.5 s⁻¹) after post-deformation quenching.

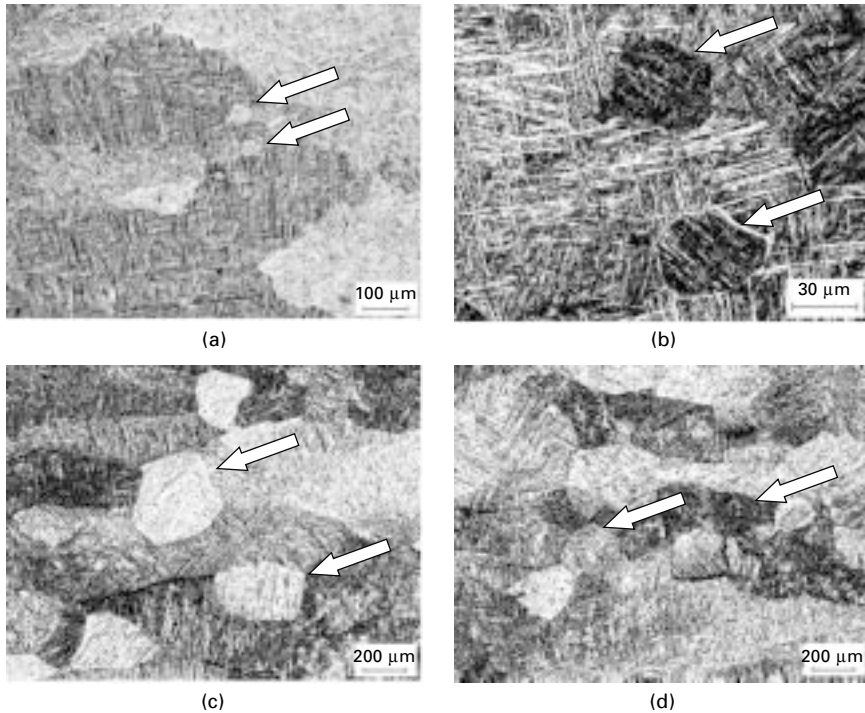
10.2.3 Dynamic recrystallisation

Microstructural observations confirm that dynamic recrystallisation occurs during hot working of the Ti-6Al-4V alloy in the β phase field at the temperatures of 1000 and 1050 °C. Figure 10.5 presents representative micrographs that exhibit various levels of dynamic recrystallisation. The extent is relatively small at 1000 °C. The percentage increases with temperature. When the processing is at 1050 °C, relatively high levels of dynamic or metadynamic recrystallisation are evident for strain rates of 0.5 and 1 s⁻¹.

According to literature, the mean size of dynamically recrystallised (DRXed) grains increases monotonically with decreasing stress. It remains constant during hot deformation, and can be calculated according to the following equation:

$$\frac{\sigma}{\mu} \left(\frac{D}{b} \right)^n = K \quad [10.1]$$

where σ is the flow stress, μ is the shear modulus, b is Burger's vector, D is the mean stable size of the DRXed grains, the exponent n is 2/3, and K is a constant in the range of 1–10. Taking $K = 10$ and $b = 0.286$ nm, the calculated mean sizes of the stable dynamic recrystallised grains are around 53 and



10.5 Micrographs showing dynamic recrystallisation. The conditions are: (a) 1000 °C and 0.05 s⁻¹; (b) dark field photo of (a) at higher magnification; (c) 1050 °C and 0.5 s⁻¹; and (d) 1050 °C and 1 s⁻¹. Arrows point to recrystallised prior-β grains.

42 μm, respectively, at the temperature of 1050 °C and the strain rates of 0.5 and 1 s⁻¹. The measured mean sizes of the DRXed grains in Fig. 10.5c and d are 336 and 320 μm, respectively, which are much greater than the calculated values. The reason for the discrepancy may be attributed to meta-dynamic recrystallisation or rapid grain growth occurring immediately after the hot deformation at the relatively high processing temperature.

10.3 The simulation model

The CA method is an algorithm describing the discrete spatial and/or time evolution in a physical system by applying a deterministic or probabilistic transformation rule. The space of interest is divided into finite cells, and the state of every cell is determined by the states of its neighbouring sites according to a given transformation rule. Here, the CA method is used to simulate the equiaxed growth of the DRXed grains, and the theoretical model of DRX is used to calculate its characteristics, e.g. the critical nucleation condition and

the nucleation rate, the dislocation density variation in the primary grains, and the growth kinetics of the DRXed grains (R-grains), which are all closely associated with the practical hot working parameters.

A continuous nucleation model is used to simulate the DRX. It is assumed that a constant nucleation rate exists during the entire thermomechanical processing if DRX occurs. The nucleation rate for DRX is assumed to be a function of both the temperature and the strain rate:

$$\dot{n}(\dot{\epsilon}, T) = C\dot{\epsilon}^m \exp\left(-\frac{Q_{\text{act}}}{RT}\right) \quad [10.2]$$

where C is constant, $\dot{\epsilon}$ is the strain rate, T is the deformation temperature, Q_{act} is the activation energy, R is the gas constant, and the exponent m is constant. The constant C can be obtained according to experimental results.

The driving force for the nucleation of DRX and the growth of the nuclei originates from the strain energy induced by dislocations during thermomechanical processing. Variation of the dislocation density during hot working is dependent on two competing processes: work hardening and dynamic recovery (softening). There is a phenomenological approach (KM model) to predict the variation of dislocation density with strain for Stage III hardening of metals. The model is based on the assumption that the kinetics of plastic flow are determined by a single structural parameter, the dislocation density ρ . The dislocation density variation can be expressed as:

$$\frac{d\rho}{d\epsilon} = k_1 \sqrt{\rho} - k_2 \rho \quad [10.3]$$

where ϵ is true strain, k_1 is a constant, and k_2 is the softening parameter which is a function of temperature and strain rate, $k_2 = k_2(\dot{\epsilon}, T)$. The strain-dependent dislocation component of the flow stress, due to the dislocation–dislocation interaction, can be expressed as:

$$\sigma = \alpha(\dot{\epsilon}, T)\mu b \sqrt{\rho} \quad [10.4]$$

where $\alpha(\dot{\epsilon}, T)$ is a dislocation interaction term that approaches 0.5 as $T \rightarrow 0$.

For a deforming matrix, the variation of its dislocation density can be calculated using Eq. [10.3] from the beginning of deformation. When its value exceeds the critical dislocation density for the nucleation of DRX, DRXed nuclei appear on the grain boundaries. For the newly formed grain, the initial dislocation density is set to be zero inside the DRXed grain, but increases when the grain grows with continuous deformation. When the dislocation density of the DRXed grain reaches the density of the matrix, the driving force for its growth becomes zero, and the grain ceases to grow.

The driving force for growth of the DRXed grains comes from the stored

strain energy difference between the DRXed grains and the matrix. The growth velocity V is proportional to the driving force F , where $V = MF$ and M is the grain boundary mobility. If the DRXed grain is assumed to be spherical, the driving force F can be expressed as:

$$F = 4\pi r_d^2 \tau(\rho_m - \rho_d) - 8\pi r_d \gamma \quad [10.5]$$

where ρ_m and ρ_d are dislocation densities of the matrix and the DRXed grain, respectively, r_d is the radius of the DRXed grain, τ is the dislocation line energy, γ is the grain boundary energy, which can be calculated from the Read-Shockley equation:

$$\gamma = \gamma_m \cdot \frac{\theta}{\theta_m} \left(1 - \ln \frac{\theta}{\theta_m} \right) \quad [10.6]$$

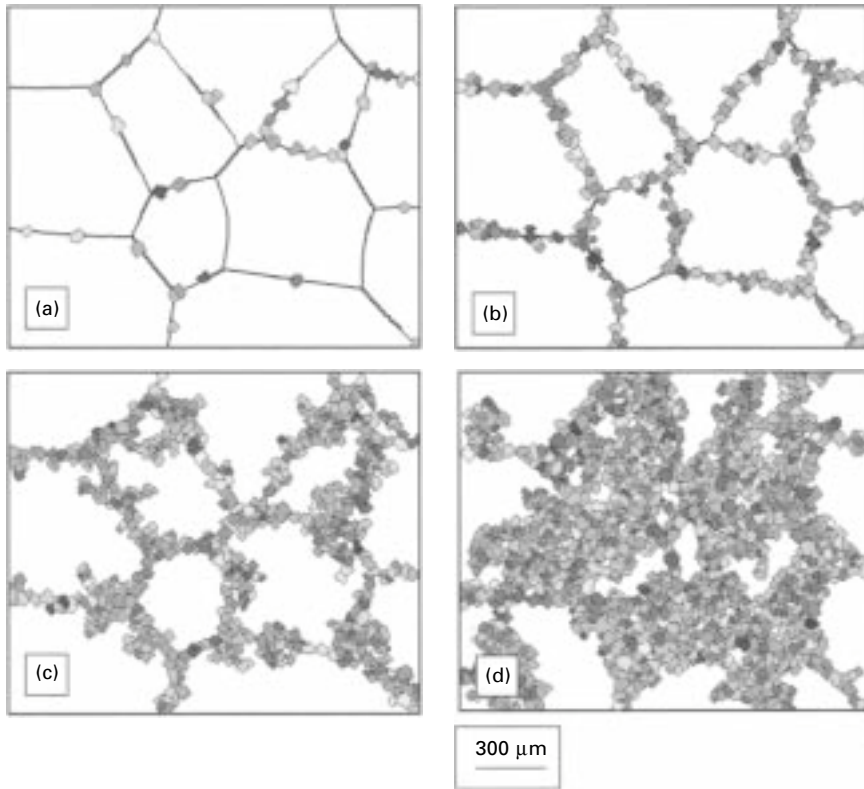
where θ is the grain boundary misorientation, γ_m and θ_m are the boundary energy and misorientation when the grain boundary becomes a high angle boundary (taken as 15°), respectively.

10.4 Simulated microstructural evolution during dynamic recrystallisation

Figure 10.6 shows the simulated microstructure for the alloy hot-pressed under specific deformation conditions ($\dot{\epsilon} = 1 \text{ s}^{-1}$, $T = 1050^\circ \text{C}$). In order to simulate the experimental observations, the initial mean diameter of the prior grains in the calculation is controlled to be around 1.06 mm, close to the actual prior grain size of 1.1 mm. The simulated percentage of DRX at a strain of 0.7 is 3.2%, which agrees well with the actual percentage of DRX, 3.1%, under the experimental conditions. From Fig. 10.6d, a large strain of 45 is needed for the percentage of DRX to reach 65.6%.

In the following, we investigate the influences of temperature and strain rate on DRX, using simulation carried out under various deformation conditions. The DRXed grain size decreases with increasing strain rate (Fig. 10.7). The mean size of the DRXed grains is $62 \mu\text{m}$ at the strain rate of 0.3 s^{-1} , but decreases to $30 \mu\text{m}$ at the strain rate of 3 s^{-1} . The percentage of DRX decreases from 34.5% to 15.2% when the strain rate varies from 0.3 to 3 s^{-1} . The percentage of DRX increases with increasing deformation temperature, and the mean size of the DRXed grains increases from $37 \mu\text{m}$ at 1000°C to $49 \mu\text{m}$ at 1100°C (Fig. 10.8).

The experimental and simulated microstructures of the Ti-6Al-4V after hot-pressing in the β phase field are compared in Fig. 10.9, (Ding and Guo, 2002).



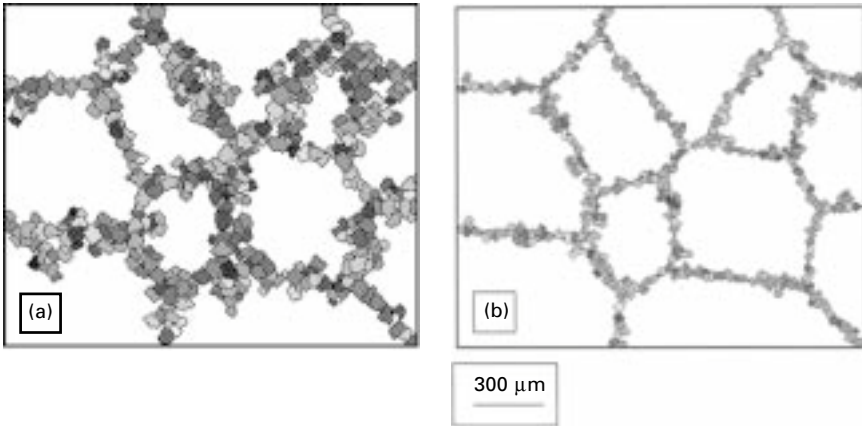
10.6 Simulated microstructure of the Ti-6Al-4V alloy during thermomechanical processing in the β phase field at 1050 °C and a strain rate of 1 s^{-1} . The strains are: (a) 0.7 (mean size of the DRXed grains 42.8 μm); (b) 5 (43.6 μm); (c) 15 (43.2 μm); and (d) 45 (43.5 μm).

10.5 Simulated flow stress–strain behaviour

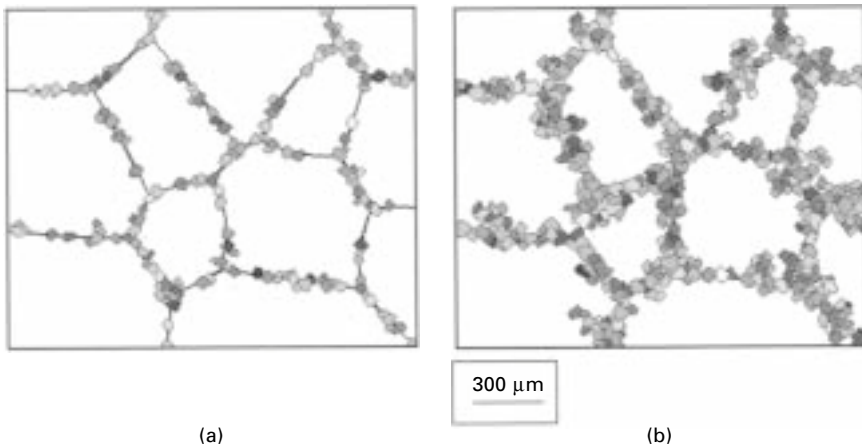
The calculated stress evolution curves are very close to the experimental results (Fig. 10.10). The flow stress fluctuates at low strain rates in the small strain range. When the strain rate is higher than 0.1 s^{-1} , the stress reaches the steady-state regime very rapidly at a small strain (< 0.01).

The phenomenon of flow stress oscillation is frequently observed during DRX. The flow stress depends not only on the rate of dislocation accumulation in the R-grains, which is influenced by the thermomechanical processing parameters (strain rate and temperature), but also on the grain size.

The dislocation density fluctuates at small strain rates and small strains (Fig. 10.11). When the strain rate reaches 0.5 s^{-1} , the dislocation density rapidly achieves a stable value. The dislocation density exhibits pronounced



10.7 Simulated microstructure of the Ti-6Al-4V alloy during thermomechanical processing in the β phase field at 1050 °C and a true strain of 10. The strain rates are: (a) 0.3 s^{-1} ; and (b) 3 s^{-1} . True strain is $\ln(\text{original length}/\text{final length})$

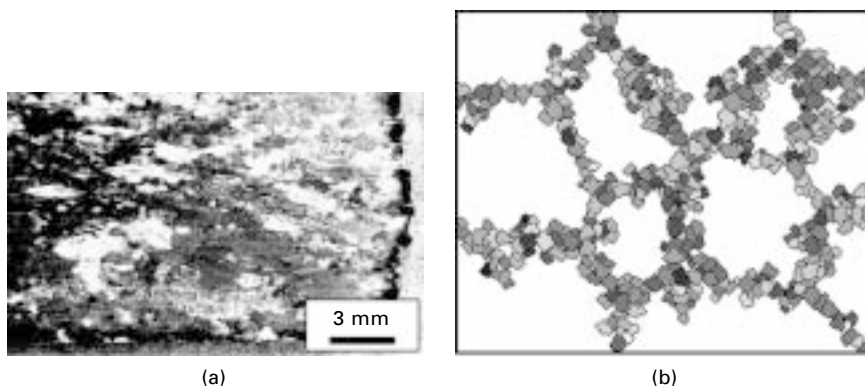


10.8 Simulated microstructure of the Ti-6Al-4V alloy during thermomechanical processing in the β phase field at different temperatures for a given strain rate of 1 s^{-1} and a true strain of 6. The deformation temperatures are: (a) 1000 °C; and (b) 1100 °C.

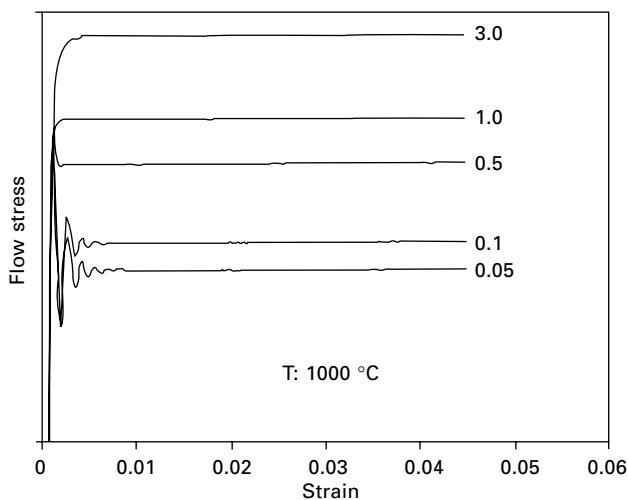
fluctuations at relatively high temperatures, and reaches stable values rapidly when the temperature is only 1000 °C.

10.6 Summary of the simulation method and its capabilities

Dynamic recrystallisation and/or rapid grain growth occurs after hot deformation. Both the percentage of DRX and the mean size of the DRXed



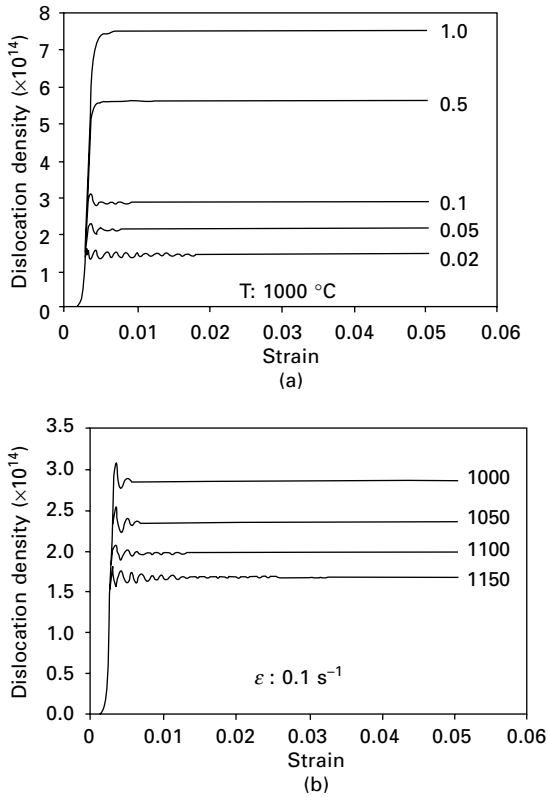
10.9 Microstructure of the Ti-6Al-4V alloy after hot pressing at 1050 °C with a strain rate of 0.5 s^{-1} and strain of 0.7: (a) experimental; and (b) simulated.



10.10 Calculated variation of flow stress with strain at a deformation temperature of 1000 °C and different strain rates ($0.05\text{--}3 \text{ s}^{-1}$). The vertical axis scale is obscured due to proprietary data.

grains increase with increasing temperature and decreasing strain rate. The mean dislocation density fluctuates at lower strain rates, and gradually stabilises with increasing strain rate. Conversely, it fluctuates more severely at a higher temperature and reaches a stable state with reduced fluctuation at a lower temperature.

The cellular automaton approach described in this chapter provides an essential link for future multiscale modelling to bridge mesoscopic dislocation activities to microscopic grain boundary dynamics, allowing accurate



10.11 Predicted variation of the dislocation density with strain under different deformation conditions, (a) at different strain rates ($0.02\text{--}1\text{ s}^{-1}$) and a fixed temperature of $1000\text{ }^{\circ}\text{C}$, (b) at different temperatures ($1000\text{--}1150\text{ }^{\circ}\text{C}$) and a fixed strain rate of 0.1 s^{-1} .

predictions of materials properties with a reduced level of empiricism. Almost all the important phenomena associated with DRX are taken into account in the quantitative model. More realistic relationships are proposed to determine accurately the nucleation rate, growth kinetics, and the effect of processing parameters, such as strain rate and the temperature. The model enables both quantitative and topographic simulations of microstructure evolution during DRX. The growth kinetics of each recrystallised grain (R-grain), including variation of its dislocation density, growth velocity, grain topology, and direction of growth, can be calculated and tracked during the entire deformation process. The flow stress–strain curve is determined directly from the averaged current dislocation density of all the grains in the considered field. The growth direction and the shape of each R-grain are determined using the CA method, and the equiaxed growth behaviour of R-grains can be predicted. The simulated microstructure closely resembles the actual DRX microstructure.

Predictions for the Ti-6Al-4V alloy agree well with the corresponding experimental findings, including the microstructure evolution and the plastic flow behaviour at a range of thermomechanical processing conditions.

10.7 References

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- Ding R and Guo Z X (2002), 'Microstructural modelling of dynamic recrystallisation using an extended cellular automaton approach', *Comp Mater Sci*, 23 (1–4), 209–18.
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Crystallographic and fracture behaviour of titanium aluminide

Abstract: The chapter presents a crystallogeometrical analysis of the geometry of micro- and macrocracks in a Ti_3Al single crystal with an orientation where the basal slip is operative. The basal and $\{10\bar{1}1\}$, $\{10\bar{1}2\}$, $\{\bar{1}\bar{1}23\}$ pyramidal planes are the planes of micro- and macrocracks facets. The coalescence of shear microcracks in the basal plane leads to the zigzag crack formation on the fracture surface. A model for shear microcrack nucleation with screw a -superdislocations interacting in the slip band of the basal planes is described. The macrocracks path behaviour in the Ti_3Al single crystal is discussed based on the model.

Key words: titanium aluminides based on Ti_3Al , fracture, dislocation geometry and arrangement, defects, superdislocations.

11.1 Introduction

In Ti_3Al single crystals, there is a strong dependence of the yield stress on the orientation, complex slip geometry, and dislocation structure. The difference in temperature dependence of the deformation characteristic is evident, namely: (i) normal behaviour of shear stress $\sigma_y(T)$ for the basal and prism slip planes, and (ii) anomalous dependence with a maximum in the $\sigma_y(T)$ curve for the pyramidal slip plane. The orientation dependence of the fracture behaviour of the Ti_3Al single crystals has also been discovered: the deformation before fracture reaches a value of about 250% for prism slip, while for basal slip brittle fracture happens immediately after loading, even in compression. The α_2 phase plays a major role in fracture processes of α_2/γ alloys with lamellar structure.

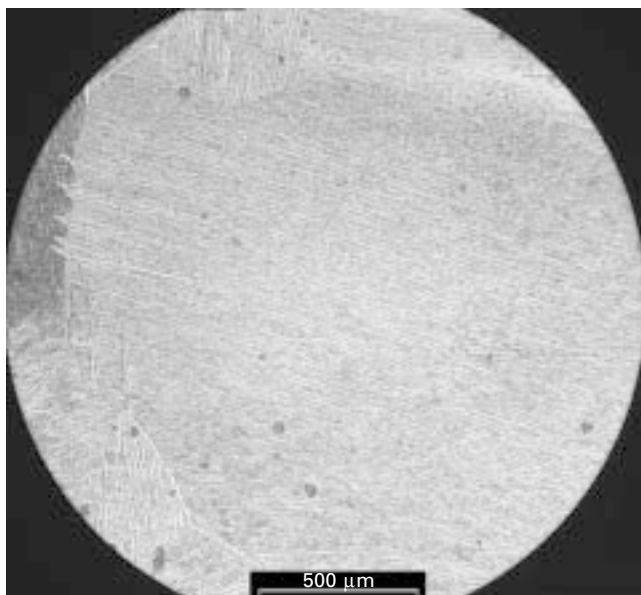
For an orientation where basal slip is operative, the slip lines are rough and widely spaced. Electron microscopy reveals microcracks of shear type along the basal slip planes. When loaded with a notch cut along the planes close to the (0001) plane, brittle fracture occurs not only along the basal plane, but also along the $\{1\bar{1}02\}$ and $\{\bar{1}\bar{1}23\}$ pyramidal planes. The reasons for such low plasticity and brittle fracture in the (0001) basal plane compared with the high plasticity and ductile fracture of Ti_3Al in the prism plane $\{1\bar{1}00\}$ need to be investigated, although in both cases the deformation is accomplished by moving of a -superdislocations with Burgers vector $\frac{1}{3}\langle\bar{1}\bar{1}20\rangle$. In order to understand the nature of the brittle fracture of a Ti_3Al single crystal with basal slip, it is necessary to reveal the correlation between the type and planes of brittle cleavage with micro- and macro-experimental findings.

This chapter presents both experimental and theoretical findings of the deformation morphology, geometry, and the peculiarities of micro- and macrocracks in a Ti_3Al single crystal with the deformation axis orientated for a basal slip. Statistical treatment allows us to recognise the most probable types of macrocleavage and microcrack planes. TEM study on the deformed material helps us to determine the cause of the step-like macrocleavage surface forming. Establishing the decohesion plane types allows us to better understand the reasons for brittle fracture in a single crystal Ti_3Al with an orientation where basal slip is operative.

11.2 Single crystal characteristic

The alloy under study has a composition of Ti-28.4Al (at.%). Single crystals of the alloy were grown from a master ingot using a floating zone furnace under an argon gas flow. Figure 11.1 shows a typical micrograph. The central part of a cylinder (diameter about 7 mm and height 0.4 mm) consists of large single crystal grains (average size 3–5 mm), while the periphery consists of grains with smaller size and large angle boundaries.

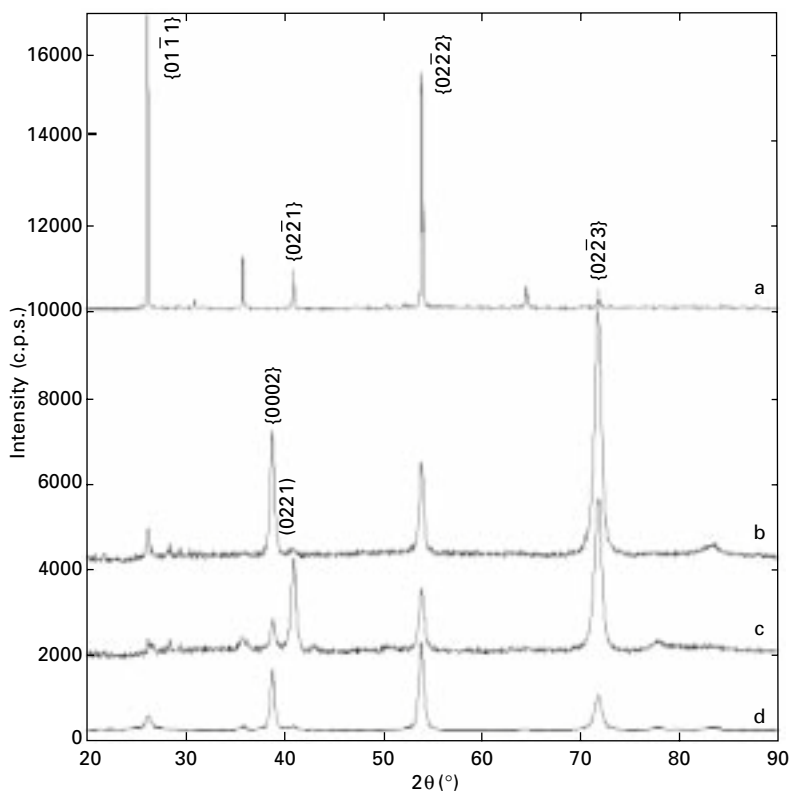
X-ray diffraction analysis proves that the material in its as-grown state is mostly in a single crystal state with $(10\bar{1}1)$ orientation, i.e. $(10\bar{1}1)$ plane perpendicular to the cylinder axis which is also the direction of compression



11.1 Optical microscope image of the microstructure of as-grown Ti_3Al single crystal.

deformation, with a small number of grains of other orientations (Fig. 11.2a). To study the peculiarities of deformation and fracture for basal slip, the single crystals with $(10\bar{1}1)$ orientation are chosen.

The maximum intensity of diffraction peaks decreases with increasing deformation (Fig. 11.2b–d). At the same time, the peak width increases as a result of the defect density increase in the material. The formation of small angle grain boundaries in the single crystal manifests itself in the appearance of two additional peaks, $\{20\bar{2}3\}$ and $\{20\bar{2}1\}$, of noticeable intensity along with the main $\{20\bar{2}2\}$ peak. One can also see the formation of the grains of (0001) orientation, (0002) peaks in Fig. 11.2b–d, which is a pronounced deviation from the initial orientation of a single crystal. The compression axis is rotated towards the $[0001]$ direction for the single crystals with $(10\bar{1}1)$ orientation (the maximum Schmid factor for this orientation corresponds to the $[\bar{1}\bar{1}20]$ (0001) and the $[2\bar{1}\bar{1}0]$ (0001) slip systems, $f = 0.43$). The



11.2 X-ray diffraction patterns for (a) an as-grown state Ti_3Al single crystal and (b–d) three deformed crystals, respectively. For clarity, the diffraction patterns are shifted with respect to each other along the vertical axis.

formation of grains with this orientation is observed experimentally in deformed crystals (Fig. 11.2).

For the chosen orientation, the operating slip system with maximum Schmid factor would be the $(0001)[\bar{1}\bar{2}10]$ and the $(0001)[\bar{2}110]$ basal slip systems (Table 11.1). Yakovenkova *et al.* (2003b) show that orientations in the range of $24\text{--}60^\circ$ from $[0001]$ direction are those where basal slip is preferred, i.e. maximum Schmid factors correspond to basal slip systems. The orientation chosen here for the single crystal Ti_3Al lies within this range.

11.3 Crack path analyses

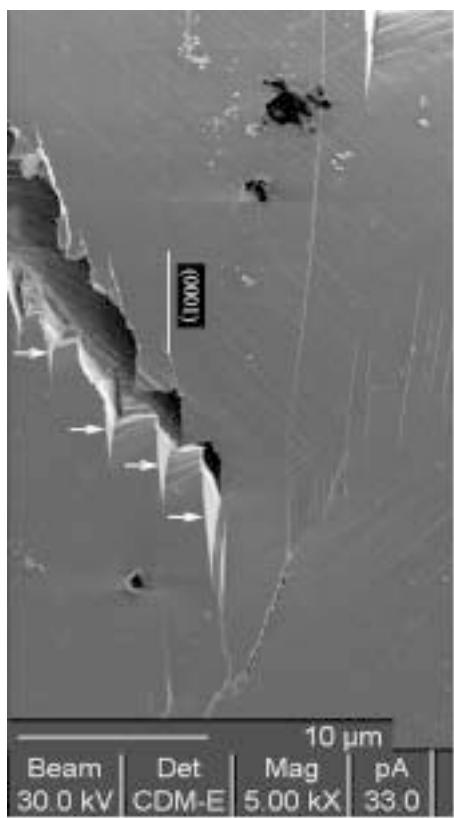
Figure 11.3 shows the fracture surface, deformed by compression perpendicular to the $(10\bar{1}1)$ plane. The basal slip, which has the maximum Schmid factor for this orientation (Table 11.1), is coarse with big distances between slip lines. The coarse basal slip lines result in the formation of deep microcracks in the basal slip planes. In Fig. 11.3b, the microcracks of shear type are just the extension of coarse slip bands. Consecutive coalescence of microcracks in the basal plane results in macrocrack nucleation. The fracture surface is stepped and the average fracture surface does not coincide with the basal plane. The plane of the picture in Fig. 11.3b is parallel to the $(10\bar{1}1)$ plane. The line direction $[\bar{1}210]$ is parallel to a projection of the basal plane into the $(10\bar{1}0)$ plane. As in Fig. 11.3a, along the $[\bar{1}210]$ line direction there are coarse basal slip lines. The fracture trace, on average, coincides with the $[\bar{1}321]$ direction. The stepped nature of this surface is very pronounced, with the zigzag projection into the $(10\bar{1}1)$ plane parallel to the $[\bar{1}210]$ and $[\bar{1}012]$ line directions.

A crystallogometrical analysis of microcracks formed after deformation will be shown for grains with orientations close to the $(10\bar{1}1)$, $(20\bar{2}3)$ and $(20\bar{2}1)$ planes. The deformation in these grains occurs in the basal slip systems. Table 11.1 presents the maximum Schmid factors for the chosen deformation axis. In basal slip systems $(0001)[\bar{2}110]$ and $(0001)[\bar{1}\bar{1}20]$, the Schmid factor is maximum for $(10\bar{1}1)$ and $(20\bar{2}1)$ orientations. For $(20\bar{2}3)$ orientation, the Schmid factor ($f = 0.46$) is maximum in the case of pyramidal slip systems. Deformation in these slip systems occurs when a deformation axis is orientated close to the $[0001]$ direction and the Schmid factors in the basal and prism slip systems are close to zero. An analysis of slip traces shows that for all the orientations included in Table 11.1, the main operating slip system is the basal one. Optical micrographs (Fig. 11.4) show the pronounced rough traces of basal slip on the polished surface, which are formed during deformation. The chosen grain orientations (Table 11.1) makes it possible to obtain a representative set of micro- and macrocleavage paths, which are formed in presence of basal slip.

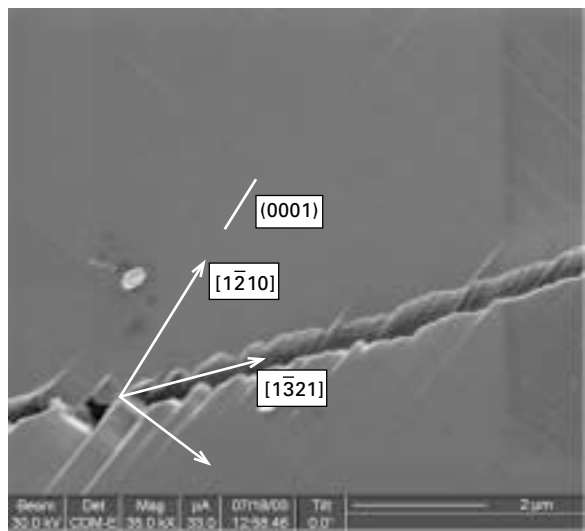
A macrocrack, shown in Fig. 11.4a, has a stepped path. The several straight

Table 11.1 Maximum Schmid factor for basal, prism and pyramid slip systems

Plane, compression axis	Basal slip	Schmid factor	Prism slip	Schmid factor	Pyramid slip	Schmid factor
$(10\bar{1}1)$, $[10\bar{1}2]$	$(0001)[\bar{2}110]$	0.43	$(0\bar{1}10)[2\bar{1}\bar{1}0]$	0.23	$(\bar{1}\bar{1}21)[11\bar{2}6]$	0.37
	$(0001)[\bar{1}\bar{1}20]$		$(1\bar{1}00)[\bar{1}\bar{1}20]$		$(2111)[2\bar{1}\bar{1}6]$ $(1\bar{2}11)[\bar{1}\bar{1}26]$	0.34
$(20\bar{2}1)$, $[60\bar{6}7]$	$(0001)[\bar{2}110]$	0.36	$(0\bar{1}10)[2\bar{1}\bar{1}0]$	0.33	$(\bar{1}\bar{1}21)[11\bar{2}6]$	0.32
	$(0001)[\bar{1}\bar{1}20]$		$(1\bar{1}00)[\bar{1}\bar{1}20]$		$(2111)[2\bar{1}\bar{1}6]$	
$(20\bar{2}3)$, $[20\bar{2}7]$	$(0001)[\bar{2}110]$	0.39	$(0\bar{1}10)[2\bar{1}\bar{1}0]$	0.12	$(\bar{1}\bar{1}21)[11\bar{2}6]$	0.46
	$(0001)[\bar{1}\bar{1}20]$		$(1\bar{1}00)[\bar{1}\bar{1}20]$		$(2111)[2\bar{1}\bar{1}6]$	

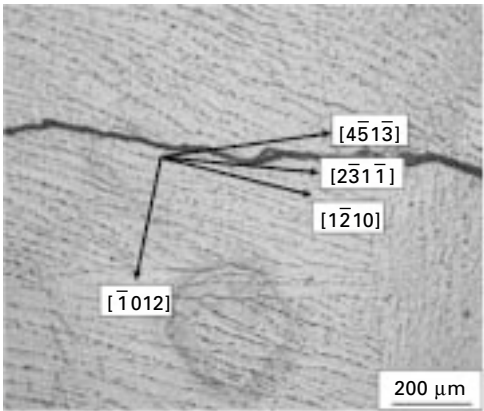


(a)

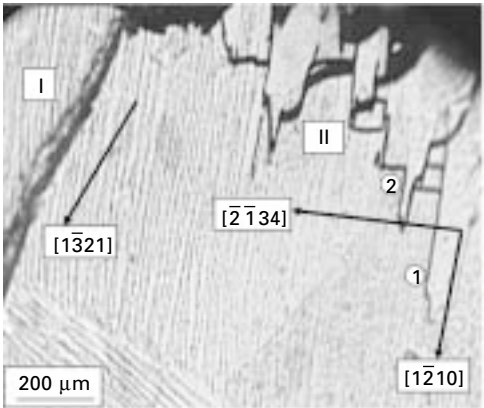


(b)

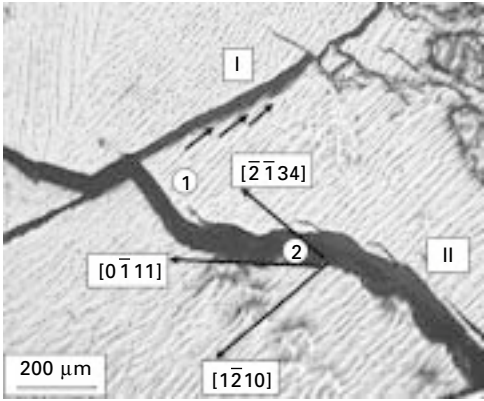
11.3 Focused ion beam (FIB) image of the surface of a Ti_3Al single crystal after deformation, showing (a) the basal slip lines (arrows) and (b) crystallogeometry of the shear type microcrack.



(a)



(b)



(c)

11.4 Optical microscope image of the surface of deformed Ti_3Al single crystals at $(10\bar{1}1)$ planes: (a) crystal 1; (b) crystal 2 and (c) crystal 3.

segments of the crack lie along the $[1\bar{2}10]$ direction and form consecutive steps of (0001) plane traces. The main crack path lies close to the $[2\bar{3}1\bar{1}]$ direction. These segments are connected by comparatively short parallel cracks with traces approximately $[4\bar{5}1\bar{3}]$ (Table 11.2).

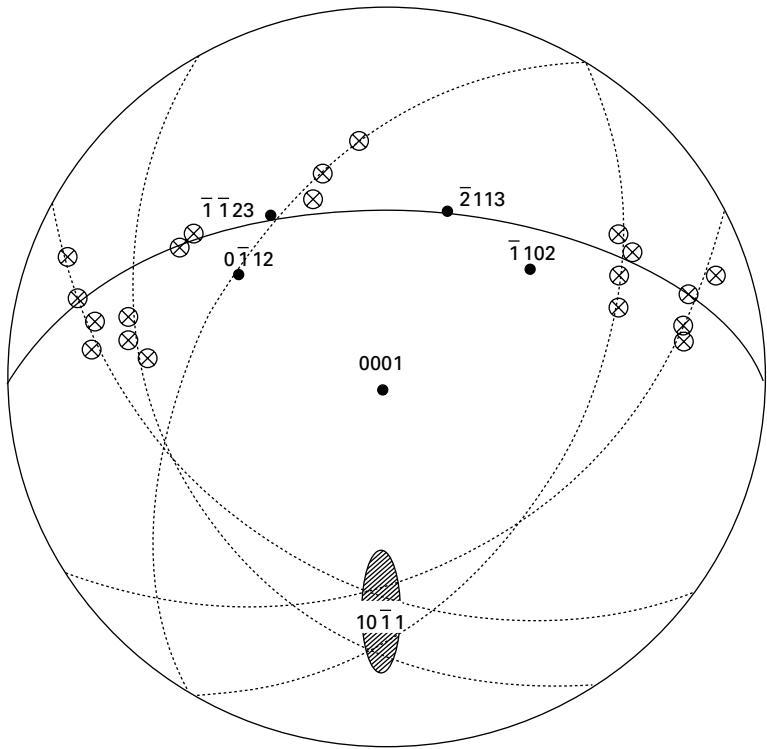
Figure 11.4b shows one of the fragments of the crystal surface, which contains Crack I and Crack II, consisting of short straight segments. The Crack I trace is parallel to the $[1\bar{3}21]$ direction (Table 11.2). For Crack II, part of the segments is parallel to the $[1\bar{2}10]$ direction (Segment 1 in Fig. 11.4b), i.e. lies in the basal plane, and the other part of the segments is parallel approximately to the $[2\bar{1}34]$ direction (Segment 2 in Fig. 11.4b).

In Fig. 11.4c, two intersecting main cracks are marked as Crack I and Crack II. The trace of Crack I on average is parallel to the $[1\bar{3}21]$ direction, and contains several microcracks (marked by arrows in Fig. 11.4c) in the basal plane (the trace along the $[1\bar{2}10]$ direction). Crack II contains several straight segments. One of the straight segments (marked as 1 in Fig. 11.4c) is formed by a crack which has a trace parallel approximately to the $[2\bar{1}34]$ direction; the other straight segment (marked as 2 in Fig. 11.4c) is parallel approximately to the $[0\bar{1}11]$ direction (Table 11.2).

In Fig. 11.5, the hatched region corresponds to the orientation of the grains. The solid line is the trace of the $(10\bar{1}1)$ plane. The directions corresponding to the traces of the 20 cracks are marked with crosses (some cracks shown in Fig. 11.4). Dashed lines, traversing the crosses correspond to the planes in which the traces of the microcracks lie (within the limits of $2-5^\circ$). The indexes of the cracks' planes $(0\bar{1}12)$, $(\bar{1}\bar{1}23)$, $(2\bar{1}13)$, $(\bar{1}102)$, $(01\bar{1}1)$ are depicted by solid dots. The main crack planes of $\{0\bar{1}12\}$ and $\{\bar{1}\bar{1}23\}$ type have been observed before, where the crystals were loaded with a notch cut.

Table 11.2 Typical experimentally observed traces of micro- and macrocracks on the $(10\bar{1}1)$ plane

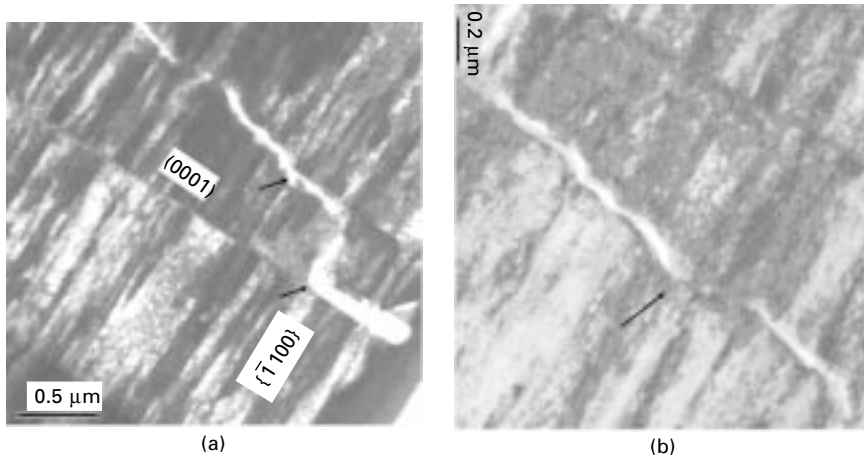
Sample number	Crack trace on $(10\bar{1}1)$ plane	Crack plane
1	$[1\bar{2}10]$	(0001)
	$[4\bar{5}1\bar{3}]$	$(0\bar{1}12)$
	$[2\bar{3}1\bar{1}]$	$(\bar{1}\bar{1}23)$
2	$[1\bar{2}10]$	(0001)
	$[2\bar{1}34]$	$(01\bar{1}1)$
	$[1\bar{3}21]$	$(2\bar{1}13)$
3	$[1\bar{2}10]$	(0001)
	$[0\bar{1}11]$	$(01\bar{1}2)$, $(11\bar{2}3)$, $(\bar{1}2\bar{1}3)$
	$[1\bar{3}21]$	$(2\bar{1}13)$
	$[2\bar{1}34]$	$(01\bar{1}1)$



11.5 Stereographic projection for the DO_{19} lattice. The traces and planes of crack openings are presented.

The analysis allows us to determine all possible microcrack planes for crystals 1–3 (Fig. 11.4a–c and Table 11.2). The plane of the macrocrack shown in Fig. 11.4a, coincides with the $(\bar{1}\bar{1}23)$ plane, and the planes of its cleavage microfacets are the (0001) and $(01\bar{1}2)$ planes, respectively. Crack II in Fig. 11.4b contains cleavage microfacets in the basal plane and pyramidal $(01\bar{1}1)$ plane. In Fig. 11.4c, Crack I propagates along the $(\bar{2}113)$ plane, and Crack II is formed by cleavage microfacets in the $(01\bar{1}1)$ planes and in $(01\bar{1}2)$, $(11\bar{2}3)$, $(\bar{1}2\bar{1}3)$ or $(\bar{1}101)$ planes.

Figure 11.6 shows the microstructure near the top of the microcrack stopped in the crystal bulk. The crack has a stepped path with the straight segments parallel to the rough slip bands in the basal plane (0001). The regions in which the crack trace has a zigzag path due to the plastic zone formation in the prism plane $(1\bar{1}00)$ are marked by the arrows in Fig. 11.6a. The crack shifts from one basal plane to a parallel one. The region where the crack stops within the bulk of the crystal is marked with the arrow in Fig. 11.6b. The high dislocation density in the prism plane is very pronounced. Therefore, the stepped nature of the cracks in (0001), $\{01\bar{1}2\}$ and $\{01\bar{1}1\}$ planes is



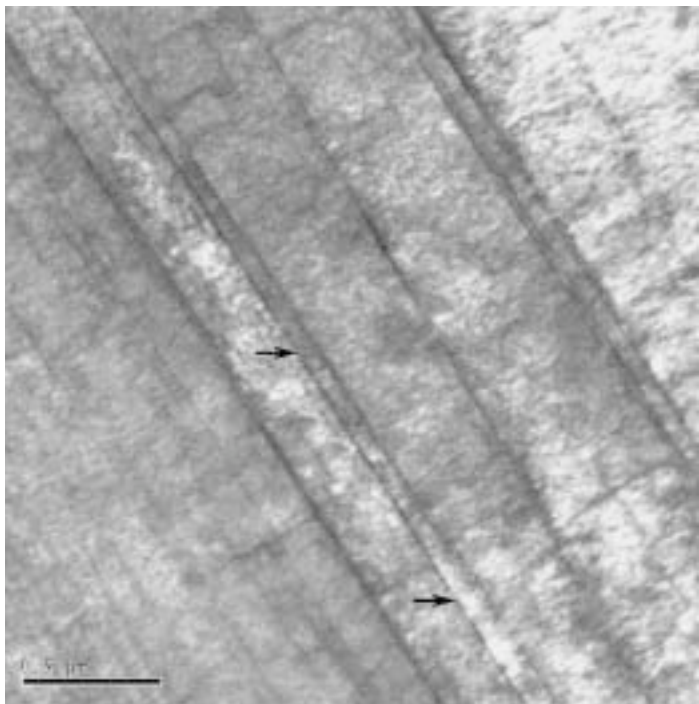
11.6 Bright-field TEM images of the microstructure of a single crystal Ti_3Al after compression deformation (Crystal 1).

stipulated by their stopping and blunting as a result of plastic zone formation in the prism slip systems.

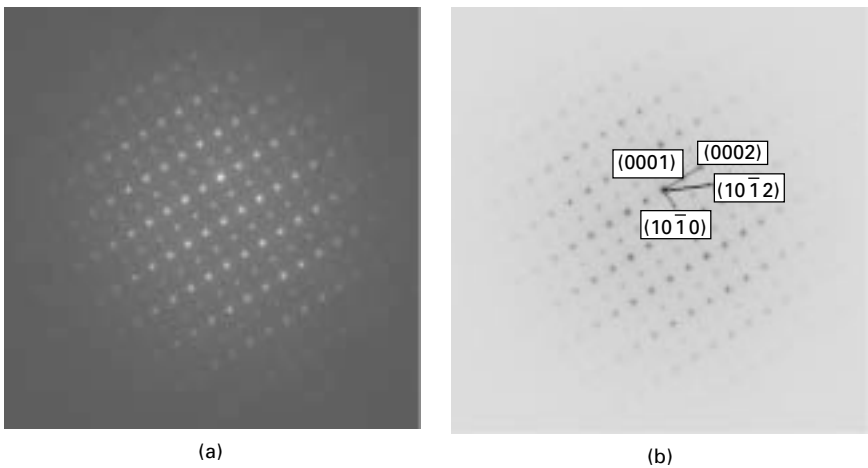
The above presents the geometry of micro- and macrocracks in a single crystal Ti_3Al with an orientation where basal slip is operative. Most of the cracks observed have a stepped path. The indexes of the traces on straight fragments of microcracks are determined using a statistical method. The directions determined are shown by crosses on the stereographic projection (Fig. 11.5). They can be divided into several groups which belong to the pyramidal planes of different types. Therefore, we have proved, experimentally, that the stepped-like macrocleavage surface is formed by microcracks of shear type along the basal planes, bound with the opening fracture mode cracks in the pyramidal planes. The analysis shows that the cleavage microfacets of the cracks are formed by the (0001) , $\{10\bar{1}2\}$, $\{\bar{1}011\}$ and, $\{\bar{1}\bar{1}23\}$ planes. The fracture on the pyramidal planes of $\{\bar{1}011\}$ type is observed. The most frequently observed planes of main cracks are the pyramidal planes of $\{\bar{1}\bar{1}23\}$ type, while the planes (0001) , $\{10\bar{1}2\}$ and $\{\bar{1}011\}$ form short cleavage microfacets.

11.4 Transmission electron microscopy

Straight lines of slip band traces (Figs. 11.7 and 11.8) are parallel to the $[\bar{1}010]$ direction. We can see only dot contrast of dislocations, which belong to the slip bands (pointed by arrows in Fig. 11.7), and a projection of the dislocation line coincides with the $[\bar{1}010]$ direction. One can suppose, therefore, that the slip bands are perpendicular to the surface of the image, while its normal coincides with the $[0001]$ direction. The experimentally



11.7 Bright-field TEM image of microstructure of a single crystal Ti_3Al after deformation.



11.8 (a) Electron diffraction pattern of deformed Ti_3Al , and (b) the corresponding reciprocal lattice plane $(\bar{1}210)$ with selected directions indicated.

observed basal slip is in agreement with calculated values of Schmid factors (Table 11.1), because the choice of compression axis orientation defines the maximum Schmid factor to correspond to basal slip.

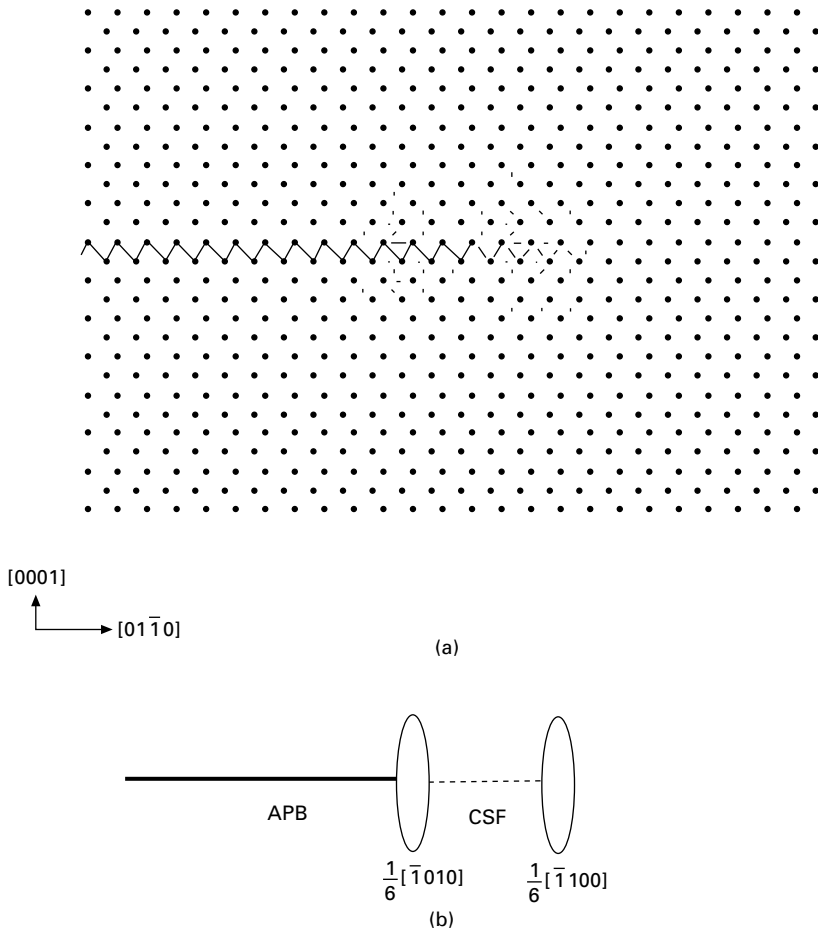
The dislocations located in between the slip bands are in Fig. 11.7 besides the dislocations in basal plane. The number density of these dislocations is higher near the basal planes. A part of the dislocations is located in short slip bands in the $(10\bar{1}0)$ prism plane, which initiate at basal planes. The prism slip was observed before for the material oriented for basal slip. The short bands of prism slip form and initiate at more coarse basal slip bands, having zero Schmid factor. Why these short traces of prism slip form, initiated by basal slip, is not clear.

The microstructure near a basal slip plane shows quite noticeable prism slip. The macrocleavage surface is stepped-like, as it consists of microcracks of shear type along the basal planes (0001), and decohesion in some other planes. Ti_3Al single crystals are soft and quite deformable with respect to prism slip. The reason why the macrocleavage surface is stepped-like might be the stopping and blunting of microcracks of shear type along basal slip planes due to the previously mentioned prism slip.

11.5 A model for microcracks nucleation in basal slip

The main experimental facts on basal slip study in a single crystal of Ti_3Al are: (i) quite low yield stress; (ii) coarse bands of basal slip with fine short bands of prism slip formation; (iii) low strain to failure with formation of shear cracks in a basal plane. A theoretical model on deformation behaviour of Ti_3Al for basal slip has to explain all the above experimental facts.

Yakovenkova *et al.* (2003b) have determined the structure and energies of *a*-superdislocations of different orientations with $\frac{1}{3}\langle 11\bar{2}0 \rangle$ Burgers vector in the basal plane by molecular dynamics calculations, having *N*-atom interaction potentials for Ti_3Al found by the embedded atom method (Kar'kina *et al.*, 2002; Yakovenkova *et al.*, 2000). The analysis of the results from computer modelling of screw, 30° , 60° and edge superdislocations in the basal plane, separated by an anti-phase boundary (APB), shows that the changes in partial core structure are to be observed only for superdislocations of screw orientation (Fig. 11.9a and b). The core of each Shockley partial with $\frac{1}{6}\langle 1\bar{1}00 \rangle$ Burgers vector, confining a complex stacking fault (CSF), acquires quite pronounced displacement in the $\{1\bar{1}00\}$ prism plane, propagated on 2–3 interplanar spacing. The analogous core structure for a screw *a*-superdislocation, split into Shockley partials in the basal plane is proved to have the minimal energy value (Fig. 11.3). The increasing of Peierls stress for Shockley superpartials slip is stipulated by the core structure of nonplanar partial dislocations in the basal plane. It also explains the experimental observation



11.9 (a) Core structure of the $\frac{1}{6}\langle\bar{2}110\rangle$ screw dislocation in basal plane after relaxation, and (b) scheme of split dislocation.

that the yield stress in the basal plane is higher than in the prism plane. A sufficiently high Peierls stress for the motion of the $\frac{1}{6}\langle\bar{2}1\bar{1}0\rangle$ superpartial dislocation was also reported, and it was shown that the motion of the α -superdislocation connected by APB in the basal plane occurs jump-wise and is characterised by a sufficiently high Peierls stress for the motion of the $\frac{1}{6}\langle\bar{2}1\bar{1}0\rangle$ superpartial dislocation.

On the basis of available experimental data, a model for shear microcracks nucleation in the basal slip band is introduced here, taking into account the processes of cross-slip into the prism plane. A dislocation might undergo cross-slip only in case that its axis is parallel to an intersection line of initial slip plane and cross-slip plane. The basal and prism planes intersect along

the $\langle 2\bar{1}\bar{1}0 \rangle$ direction, which is the axis of a 60° or screw a -superdislocation. The energy advantage of the reactions is estimated with the use of the expressions for the dislocation interaction energy, adjusted to the unit of its length. In Fig. 11.10, the consecutive stages of microcracks nucleation in the slip bands of the basal plane are depicted, taking into account the long-distance elastic interaction of a -superdislocations and all superpartial dislocations taking part in the reaction. If we examine the analogous scheme for 60° orientated a -superdislocations, we will find that the rearrangement of a superdislocation with cross-slip into the prism plane is energetically unfavourable. Thus, the nucleation of a microcrack of shear type is possible only on screw dislocations.

Figure 11.10a presents a fragment of two interacting split a -superdislocations with $\frac{1}{3}[\bar{2}110]$ Burgers vector of screw orientation. The superdislocation is split into two superpartials with $\frac{1}{6}[\bar{2}110]$ Burgers vector with APB formation:

$$\frac{1}{3}[\bar{2}110] \rightarrow \frac{1}{6}[\bar{2}110] + \text{APB}_{(0001)} + \frac{1}{6}[\bar{2}110] \quad [11.1a]$$

Each of the superpartial dislocations further dissociates, with the formation of a CSF:

$$\frac{1}{6}[\bar{2}110] \rightarrow \frac{1}{6}[\bar{1}100] + \text{CSF}_{(0001)} + \frac{1}{6}[\bar{1}010] \quad [11.1b]$$

In Fig. 11.10a, the Dislocations 1 and 2 move in the slip plane under the orientation of the external stress.

Figure 11.10b shows the result of a rearrangement of Shockley dislocations with $\frac{1}{6}[\bar{1}100]$ and $\frac{1}{6}[\bar{1}010]$ Burgers vectors, which belong to Superdislocation 1 in a stress field of Superdislocation 2. As a result of the rearrangement, the splitting of each Shockley dislocation occurs in the prism plane with SF band formation, confined by the partial with $\frac{1}{12}[\bar{2}110]$ Burgers vector:

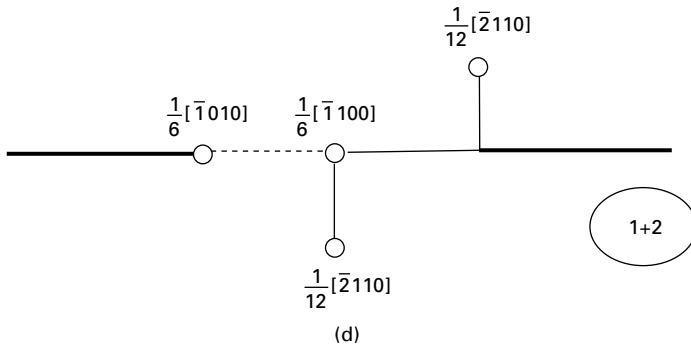
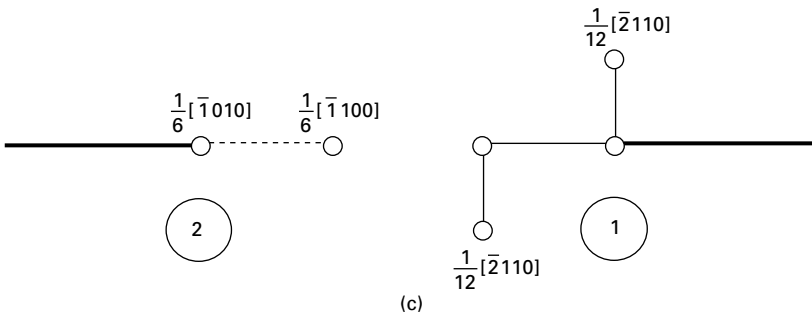
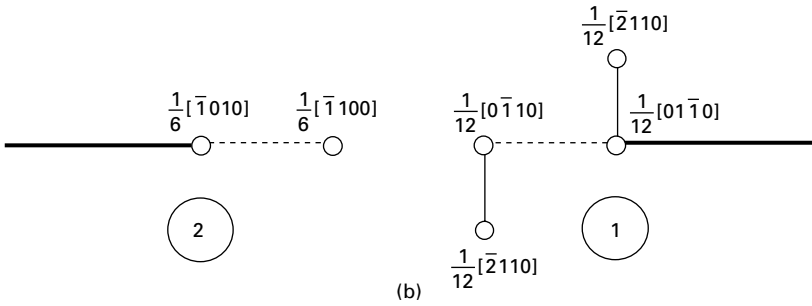
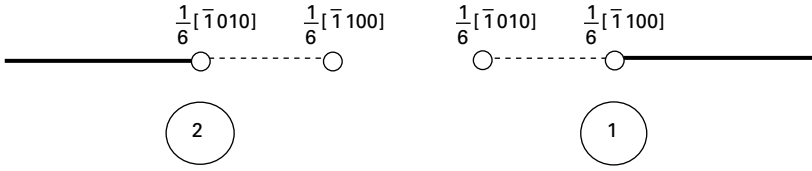
$$\frac{1}{6}[\bar{1}010] \rightarrow \frac{1}{12}[\bar{2}110] + \text{SF}_{(0\bar{1}10)} + \frac{1}{12}[0\bar{1}10] \quad [11.2a]$$

$$\frac{1}{6}[\bar{1}100] \rightarrow \frac{1}{12}[\bar{2}110] + \text{SF}_{(0\bar{1}10)} + \frac{1}{12}[01\bar{1}0] \quad [11.2b]$$

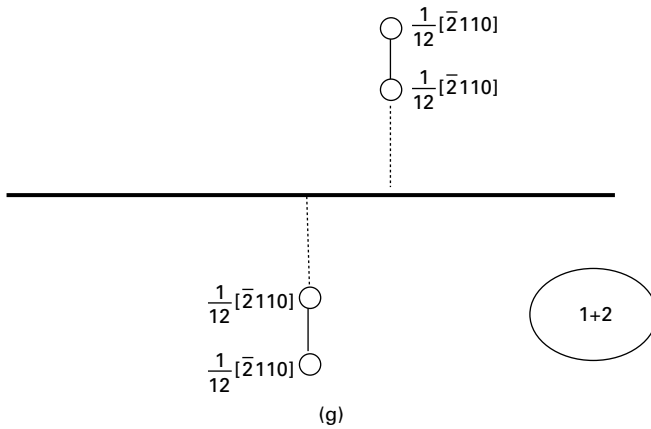
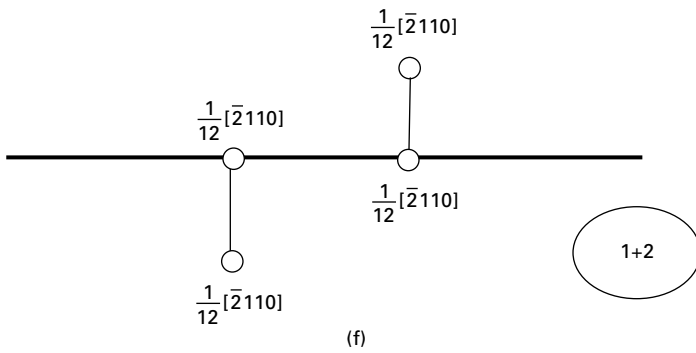
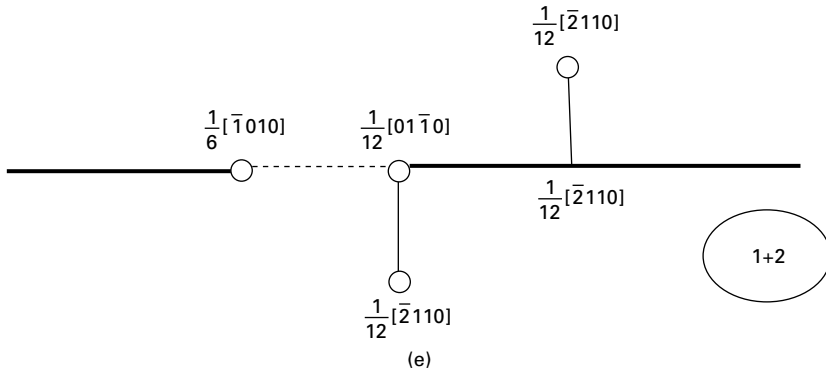
The reactions of splitting, Eqs. [11.2a] and [11.2b], are energy indifferent, and their realisation is possible only due to the repulsion of the partials belonging to other superdislocations in the slip band, as mentioned above.

Experimentally, the splitting of a $a/2$ -superdislocation into two partials in the prism plane was observed, but the Burgers vector magnitudes of the partials were not determined. As a result of computer modelling (Yakovenkova *et al.*, 2000), the Burgers vectors of the partial dislocations were found to be equal to $\frac{1}{12}[\bar{2}110]$. These Burgers vectors are used in reactions Eqs. [11.2a] and [11.2b].

The dislocation configuration formed (Fig. 11.10b) is not stable, because



11.10 Scheme of a shear microcrack formation.



$\text{— APB}_{(0001)}$ $\text{--- CSF}_{(0001)}$
 $\text{--- APB}_{(\bar{1}100)}$ $\text{— SF}_{(\bar{1}100)}$

the partials with $\frac{1}{12}[0\bar{1}10]$ and $\frac{1}{12}[01\bar{1}0]$ Burgers vectors belonging to the Superdislocation 1, attract in the basal plane and can recombine with the formation of the configuration shown in Fig. 11.10c. As a result of these dislocation rearrangements for Superdislocation 1, there is no partial along the intersection of the basal and prism planes to prevent superdislocation approaching. The partial dislocations $\frac{1}{12}[\bar{2}110]$ of Superdislocation 1 do not interact with the partial dislocation $\frac{1}{6}[\bar{1}100]$ and thus do not hamper the coalescence of Superdislocations 2 and 1. The configuration shown in Fig. 11.10d becomes possible under the action of the external stress and the stress imposed by other superdislocations of the slip band. The total Burgers vector of the configuration is twice as big in this case.

Consecutive stages of internal dislocation rearrangements of the 1+2 configuration (Fig. 11.10d) are shown in Fig. 11.10e–g. As a result of these rearrangements, the total energy of the configuration decreases because of the reactions occurring between attracting partials (the dislocations with the Burgers vectors $\frac{1}{12}[01\bar{1}0]$ and $\frac{1}{6}[\bar{1}010]$ in Fig. 11.10e). When the change of the configuration of Fig. 11.10d to the configuration of Fig. 11.10e occurs, the energy decreases due to the change of a planar defect type ($\text{CSF}_{(0001)} \rightarrow \text{APB}_{(0001)}$), because the energy of complex SF is lower than the energy of APB in the basal plane (Yakovenkova *et al.*, 2000). Similarly, the decrease of energy while the configuration of Fig. 11.10f changes to configuration of Fig. 11.10g is due to the $\text{SF}_{(\bar{1}100)} \rightarrow \text{APB}_{(\bar{1}100)}$ change. The final configuration (Fig. 11.10g) is stable. It consists of bands of anti-phase boundaries in the initial basal plane and in the planes of cross slip – the prism planes. The considerable anisotropy in anti-phase boundaries energies for prism and basal planes ($\text{APB}_{(0\bar{1}10)} \ll \text{APB}_{(0001)}$) is characteristic of Ti_3Al , and is the consequence of DO_{19} superstructure features (Yakovenkova *et al.*, 2003a).

Thus, we have examined the sequence of dislocation transformations (Fig. 11.10a–g) on Superdislocations 1 and 2, as a result of which the configuration with total Burgers vector of $2a$ magnitude is formed. An interaction of this configuration with following a -superdislocation coalescence may be described with the help of the same chain of dislocation transformations. This will result in total Burgers vector magnitude being equal to $3a$, etc. The configuration developed may be considered as a microcrack nucleus of shear type because the total Burgers vector of the configuration lies on the basal plane. The number of dislocations which form a microcrack depends on both the number of dislocations in an array and their distribution in the slip band. This may lead to a microcrack nucleation in different places of the slip band.

Kar'kina *et al.* (2002) have shown an a -superdislocation to be split into two superpartial dislocations with Burgers vector $\frac{1}{6}[\bar{2}110]$ connected by an APB band. The atom arrangement of the neighbouring layers in the basal plane of DO_{19} superstructure is equivalent to the one in the octahedron plane of the L1_2 superstructure. This allows us to compare the results on the

computer modelling of the core structure of the superdislocations $\frac{1}{3}\langle\bar{2}110\rangle$ and $\langle 110\rangle$ in these two superstructures. A superdislocation with the Burgers vector $\langle 110\rangle$ splits in the octahedral plane into four Shockley partial dislocations, connected by APB bands and CSF, similarly to the superdislocations $\frac{1}{3}\langle\bar{2}110\rangle$ in the basal plane. The core structure of Shockley partial dislocations differs essentially in these cases. For a screw superdislocation in Ti_3Al , the core of a Shockley partial dislocation is nonplanar, and noticeable displacements take place in the prism plane (Fig. 11.9), whereas for L_{12} superstructure the displacements near the core of Shockley superpartial dislocations are localised in the octahedron plane. This makes the configuration considered to be a gliding one for L_{12} superstructure, while the motion of a superpartial dislocation is impeded for DO_{19} superstructure. The stress field of other a -superdislocations in a slip band of the basal plane causes the lowering of Peierls stress, and, apparently, results in coarse slip band formation in this plane.

External stress and the stress imposed on a dislocation in the slip band might change the core structure of the dislocation. For instance, in L_{12} superstructure, the stress imposed by the array dislocations might promote the Shockley partial dislocations recombination, as a result of a decreasing of the distance between the partial dislocations, and facilitate the process of cross-slip of screw superdislocations. For Ti_3Al , this stress can both promote and impede the process recombination and cross-slip of a superpartial dislocation, depending on the relation between the components of stress effective in the basal and prism planes. If stress, caused by the other dislocations in the slip band, promotes the widening of Shockley partial dislocation splitting in the prism plane, the processes of recombination and cross-slip become difficult, but coalescence of a -superdislocations with microcracks nucleation by the mechanism introduced here is easy to initiate. If the stress in the prism plane is small, it is possible to activate thermally the process of a -superdislocations cross-slip. Thus, in the slip band both processes of shear microcracks nucleation and slip-cross process might take place. In fact, the cross-slip of the a -superdislocations into the prism plane in a slip band when the basal slip is operative has been observed experimentally, along with shear microcrack nucleation.

In Section 11.2, the surface of macrocleavage is shown to be stepped. One of the steps is parallel to the basal plane; the trace of the other one on the crystal surface $(10\bar{1}1)$ coincides with $[1\bar{2}10]$ line direction (Fig. 11.3b). Thus, the cleavage-like crack propagation might be due to consecutive processes of shear along the basal plane and decohesion in the $(1\bar{2}10)$ prism plane. It might be suggested that the microcracks of shear type nucleate first in the basal planes. These microcracks nucleate in the places of high concentration of local stress in one or several parallel slip bands. When the density of shear microcracks is comparatively high, the macrocrack is nucleated due to some

processes of decohesion (along $(\bar{1}2\bar{1}0)$ plane in our case). Here, the trace of a macrocrack plane coincides with the $[1\bar{3}21]$ line direction. In a Ti_3Al single crystal with operative basal slip, cracks propagate along macroscopic habit planes parallel to $\{10\bar{1}2\}$, $\{2\bar{1}\bar{1}3\}$ and $\{4311\}$. Taking into account only these types of planes, it is possible to demonstrate that the $[1\bar{3}21]$ line direction coincides with the $(\bar{2}113)$ plane projection into the surface foil $(10\bar{1}1)$. Thus, the accumulation of shear microcracks in (0001) slip bands, being the initiating mechanism of macrocleavage, ultimately determines the low plasticity of a single crystal Ti_3Al with operative basal slip.

It is noted that stresses generated by superdislocations in a slip band might promote both microcrack nucleation and transversal slip of screw superdislocations in the prism plane. Formation of plastic zones in the prism plane leads to microcrack blunting and coming to a stop. These processes are observed experimentally (Fig. 11.6). Therefore, in the slip band within several parallel basal planes, a microcrack system forms. A main crack forms as a result of the coalescence of these microcracks.

The type of the forming macrocleavage surface is determined by the values of applied stresses and decohesion energy for the crack plane. The experimental data prove that decohesion occurs in pyramidal planes. Normals to the experimentally observed pyramidal planes lie on the stereographical projection near the arc of the big circle which depicts the trace of the $(10\bar{1}1)$ plane with the $[10\bar{1}2]$ normal. When a single crystal is compressed along the $[10\bar{1}2]$ direction, the maximum normal tensile stress appears in the planes whose normals lie in the $(10\bar{1}1)$ plane, i.e. they belong to the above arc of the big circle. Thus, a cleavage in the pyramidal planes with maximum normal stress is observed experimentally. Although external normal stress is high, we did not observe microcracks in prism planes of the $\{\bar{1}2\bar{1}0\}$ type, for instance, suggesting that they are caused by the difference in cohesion characteristic of these planes (cleavage stress, surface energy, etc.). This matter requires additional investigation.

There is one more significant element which facilitates microcrack nucleation. In this section, we have described the model of shear microcrack nucleation in the basal plane. According to this model, a microcrack nucleates as a result of coalescence of several a -superdislocations of screw orientation, i.e. the top of a formed microcrack is parallel to the Burgers vector $\frac{1}{3}\langle\bar{1}\bar{1}20\rangle$ of superdislocation. This direction $\langle\bar{1}\bar{1}20\rangle$ belongs to cleavage microfacets on the (0001) , $\{10\bar{1}2\}$ and $\{10\bar{1}1\}$ planes of the zigzag cracks, observed experimentally (Fig. 11.4 and Table 11.2). The $\{\bar{1}\bar{1}23\}$ plane is often the main plane of a crack. One can suppose that in the top of the crack in the planes of $\{\bar{1}\bar{1}23\}$ type, a plastic zone does not form by the dislocations of prism slip systems. This prevents the blunting of the crack and promotes its spreading through the bulk of the crystal.

11.6 Summary

Transmission electron microscopy shows that the (0001) basal slip is accompanied by short bands of $\{1\bar{1}00\}$ prism slip formation. The macrocleavage surface is a step-like one, consisting of microcracks of shear type along the (0001) basal planes and decohesion in the $\{1\bar{2}10\}$ prism planes. In a Ti_3Al single crystal orientated for basal slip, the planes of micro- and macrocracks cleavage are the basal and pyramidal planes of $\{10\bar{1}1\}$, $\{10\bar{1}2\}$ and $\{\bar{1}\bar{1}23\}$ types. The shear microcracks' coalescence in the basal plane results in the formation of the step-like fracture surface, consisting of (0001), $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ planes. The most probable plane of the main crack is the $\{\bar{1}\bar{1}23\}$ plane. The microcrack stopping and blunting in the (0001) plane is due to plastic zone formation in the prism slip systems.

A model of shear microcracks nucleation in basal planes, with screw a -superdislocations coalescence, has demonstrated that long-range stress of dislocations in a slip band plays an important part in the process of microcrack nucleation. Both theoretically and experimentally, brittle fracture is initiated by nucleation of microcracks of shear type along basal slip planes.

11.7 References

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Atomistic simulations of interfaces and dislocations relevant to TiAl

Abstract: TiAl alloys for high temperature applications usually have the form of lamellar structures composed of γ -TiAl and α_2 -Ti₃Al phases. Refinement of the lamellar size is a promising way of generally improving the yield strength of such alloys, but this does not work when the lamellae are too thin. This chapter takes the first steps towards an understanding of the variation of yield strength with lamellar size based on atomistic modelling. Topics discussed include bond-order potentials for the Ti–Al system, the structures and energies of γ/α_2 interfaces, simulations with and without misfit dislocations, and with stoichiometry variations at the interface, and the structures of dislocation cores.

Key words: interatomic potential, dislocations, dislocation pile-ups, molecular statics, lamellae.

12.1 Introduction

Regarding the mechanical properties of lamellar TiAl alloys, both a Hall–Petch relation between yield stress σ_y and lamellar thickness λ , and saturation of yield stress with decreasing lamellae width have been observed experimentally (Maruyama *et al.*, 2001, 2002). The Hall–Petch relation and the upper limit to the hardening are predicted on the basis of a pile-up model of dislocations. The multiple pile-up model considers that, during the early stage of deformation, a dislocation pile-up is formed in a lamella due to the blockage by an interlamellar interface. To eventually defeat the interface, the applied shear stress τ is raised, enabling more dislocations to enter the pile-up. Yielding occurs when the leading dislocation in a pile-up can overcome the barrier stress at an interface.

However, the $\sigma_y - \lambda$ curve of the lamellar TiAl alloy exhibits complex behaviour in the transition region from the Hall–Petch relation to the upper limit, which cannot be explained by the simple pile-up model. Maruyama *et al.* (2004) considered the distribution of lamellar thickness based on measurement of a real lamellar microstructure. However, the distribution of lamellar thickness by itself cannot explain the complex transition from the Hall–Petch relation to the saturation.

To understand the complex $\sigma_y - \lambda$ relation, we have to take account of the change in the structure of a γ/α_2 boundary in the transition region. In a thick lamellar structure, misfit dislocations are introduced into γ/α_2 lamellar boundaries to relieve the lattice misfit between γ and α_2 and are found on the lamellar boundaries (Maruyama *et al.*, 2004). We refer to these boundaries

as semi-coherent. On the other hand, in an alloy with a thin lamellar structure, the γ/α_2 boundaries are found to be perfectly coherent (Maruyama *et al.*, 2004).

The entire curve of yield stress versus lamellar thickness can be explained by taking account of the difference in lamellar boundary structure between a dislocated boundary and a coherent one (Maruyama *et al.*, 2004). The difference in lamellar boundary structures, specifically the absence or presence of misfit dislocations, may be associated with a difference in the barrier stress at an interface. The $\sigma_y - \lambda$ curve was explained assuming the boundary resistance τ^* to be 440 MPa for γ lamellae thicker than 50 nm, and 260 MPa for those thinner than 50 nm (Maruyama *et al.*, 2004). It was conjectured that dislocation sources in lamellar boundaries interacted with the misfit dislocations, and the misfit dislocations acted as obstacles to the operation of the dislocation sources. The dislocated boundaries are more resistant to dislocation motion across the boundaries.

In its present form, the Hall–Petch model is far from providing a complete theory of yield in a multilayer, since it pays no attention to the operation of dislocation sources, and it uses estimates, mostly based on elasticity, for the barrier stress. It is important to understand the mechanisms of deformation and transition of dislocation across the γ/α_2 interface at the atomic scale. In particular, in order to improve the model, a key requirement is a more accurate calculation of barrier strengths in a multilayer.

Modelling of the dislocation– γ/α_2 interface interactions in lamellar TiAl has been generally carried out using the continuum approach in which no account is taken of the material's microstructure. Recent advances in computational materials science have enabled atomistic modelling of the dislocation–interface interactions to become a respectable alternative for elucidation of the role of atomic-scale effects on the transmission of plastic deformation across the interface. Based on such calculations, one hopes that ultimately it will be possible to design new, lighter alloys with both room-temperature ductility, and strength that increases with temperature as close to the melting point as possible.

12.2 Tasks

Many simulations can be carried out with the Oxford order–N (OXON) program package using the bond order potential (BOP), discussed in more detail below.

The following research tasks are of increasing complexity and will require an increasing number of atoms in the simulation, with a corresponding increase in the cost of computation, visualization and analysis:

- (i) possible γ/α_2 boundary structures (coherent and partially coherent) by molecular statics, including the role of local stoichiometry variations

- (ii) mobile dislocation core structures in γ and α_2 crystals by molecular statics
- (iii) application of shear stress to the dislocation model to study the friction barrier
- (iv) molecular statics and dynamics study of the blocking strength of a coherent γ/α_2 interface using BOP
- (v) molecular statics simulations of the interaction of misfit dislocations with mobile dislocations and evaluation of the influence of the misfit dislocations on the blocking strength of the γ/α_2 interface
- (vi) introduction of a queue of mobile dislocations in γ or α_2 layers, which will be pushed against the γ/α_2 interface in order to study the mechanisms of pile-up formation and eventually the penetration of the interface.

Detailed methodologies are discussed in the next two sections.

12.3 Computational procedure

The calculations can be carried out using a molecular statics method, whereby the internal energy of the system studied is minimised by moving the particles according to the conjugate gradients algorithm so as to attain zero forces on each atom. An initial phase of molecular dynamics simulation and quenching may be carried out in order to avoid trapping in local minima.

The microstructure of TiAl lamellar alloys is formed by a succession of γ ($L1_0$ structure) and α_2 (DO_{19} structure) parallel lamellae related by $(0001)_{\alpha_2} // (111)_{\gamma}$, and $\langle \bar{2}110 \rangle_{\alpha_2} // \langle 1\bar{1}0 \rangle_{\gamma}$. The γ lamellae have three orientation groups with respect to the interface plane (two orientation variants in each group) corresponding to the three possible positions of the $\langle 110 \rangle$ direction in the habit plane. We refer to them as Groups I, II and III.

A first set of simulations should be carried out to explore the structures and energies of these interfaces. They can be constructed initially to be perfectly coherent, and then relaxed energies and structures are obtained. With much larger supercells, the corresponding semi-coherent interfaces can be studied by introducing misfit dislocations, the nature of which is described below. The boundary structures obtained will be used in simulations of the dislocation–boundary interactions.

Since several types of dislocation can be activated in the α_2 and γ phases, numerous crystallographic situations can be encountered. They differ in the nature of the interface, and in the incident system, which depends on the orientations of γ lamellae with respect to the interface plane. The events occurring at an interface can also be different for a given crystallographic situation as a function of the orientation of the applied stress. Atomistic simulations of the structures of the main dislocations observed in α_2 and γ can be used to investigate their interaction and subsequently to study the

transfer of deformation across the interface between α_2 and each of the three γ lamellae orientation groups.

The simulations should be designed in the light of experimental work. In α_2 -Ti₃Al, deformation occurs by glide of dislocations with $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ on $\{10\bar{1}0\}$, and less favourably on (0001) , and with $\mathbf{b} = \frac{1}{6}\langle 11\bar{2}6 \rangle$ on either $\{11\bar{2}1\}$ or $\{20\bar{2}1\}$. The $\frac{1}{2}\langle 110 \rangle\{111\}$ ordinary slip system is dominant in the γ phase.

The transfer mechanisms of the deformation at the γ/α_2 interface have been studied by *in situ* straining experiments. Different types of behaviour have been found, depending on the nature of the interface, on the involved deformation systems and/or on the lamella orientation. The results of these studies may be summarised as follows:

- (i) Transmission of shears through γ/α_2 interfaces at the intersection of these interfaces and certain cross-lamellar twins is effected by slip of dislocations with $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ in the α_2 phase, which may glide on either $\{10\bar{1}0\}$ or $\{20\bar{2}1\}$.
- (ii) Such shear transmission events that result in dislocations with $\mathbf{b} = \frac{1}{6}\langle 11\bar{2}6 \rangle$ appear to be very difficult.
- (iii) Dislocations with $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ and $\mathbf{b} = \frac{1}{6}\langle 11\bar{2}6 \rangle$ can be generated by stress-induced activation of sources in γ/α_2 interfaces. The latter dislocations glide on either $\{11\bar{2}1\}$ or $\{20\bar{2}1\}$, although mostly slip occurs on $\{11\bar{2}1\}$.
- (iv) In γ orientation variants of Group I, the Burgers vector $\mathbf{b} = \frac{1}{2}\langle 1\bar{1}0 \rangle$ of the ordinary dislocation is parallel to the Burgers vector $\mathbf{b} = \frac{1}{3}\langle \bar{2}110 \rangle$ in the α_2 phase. The movement of dislocations from the α_2 lamella to the next γ (I) lamella and further to the other α_2 lamella occurs by a cross slip process. The γ/α_2 boundaries between an α_2 lamella and the γ variant of Group II and III behave in a similar way to usual grain boundaries because $\langle 110 \rangle$ is not parallel with $\langle \bar{2}110 \rangle$. One of the following two slip systems may operate in the four γ variants of Groups II and III – the activation of a $\frac{1}{2}\langle 1\bar{1}0 \rangle$ dislocation whose glide plane is continuous with the primary slip plane of α_2 lamella or the activation of a $\frac{1}{2}\langle 110 \rangle$ dislocation and its glide on a $\{111\}$ plane not continuous with the primary slip plane. This slip in γ may activate a $\frac{1}{3}\langle 11\bar{2}0 \rangle\{10\bar{1}0\}$ slip system in the next α_2 lamella.

Based on these results, the focus of attention is on the movement of a $\mathbf{b} = \frac{1}{3}\langle 11\bar{2}0 \rangle$ dislocation in the α_2 phase and the ordinary dislocation $\mathbf{b} = \frac{1}{2}\langle 110 \rangle$ in the orientation variants of the γ phase.

Besides the coherent and incoherent interfaces, other issues include the core structures, and possibly also the friction stresses, of the mobile dislocations. A simulation cell with at least one lattice repeat distance along the dislocation line is necessary. The dislocations are introduced into the centre of the

simulation cell by displacing all the atoms from their perfect lattice positions according to their anisotropic elastic displacement field. All atoms in an outer shell with radius R_{out} in width (greater than $2R_{\text{cut}}$, where R_{cut} is the cut-off range of the BOP) should be fixed at their original elasticity positions during the relaxation. Atoms within an inner radius are then allowed to relax, using the BOP interactions employing periodic boundary conditions along the dislocation line direction. The relaxation calculations are performed by minimising the energy of the atomistic model using a molecular statics method.

To study the motion of dislocations, we apply homogenous shear stresses to our atomistic model. The stresses are actually imposed via homogeneous shear strains by displacement boundary conditions and are increased in a stepwise manner. After every step, the entire system is relaxed and examined for changes in the core structure using differential displacement plots. The minimum stress at which the dislocation moved by a translational unit is defined to be the friction stress of the dislocation. Increments corresponding to about a tenth of the estimated strain at the friction stress are applied until the dislocation core moves by at least one lattice repeat distance normal to the dislocation line in the glide plane.

A rectangular parallelepiped consisting of a two-part computational cell is used in all simulations of interfaces and dislocation–interface interactions. Before introducing an incident dislocation in the γ or α_2 crystals, the interface simulation cells are relaxed using periodic boundary conditions along the γ/α_2 interface directions. In the direction perpendicular to the interface, the boundary conditions are expected to simulate the bulk media on either side of the interface. Along the interface normal, atoms within two slabs of width $2R_{\text{cut}}$, one at the upper surface and the other at the lower surface, are fixed at their perfect lattice positions. The atoms between these slabs are allowed to relax.

After this initial relaxation of the γ/α_2 interface, the corresponding dislocations are introduced into the simulation cell by displacing all atoms according to the anisotropic elastic displacement field. As before, atoms within an inner radius are relaxed using the BOP interactions with the outer shell fixed. The relaxed structures of the dislocation cores are examined using differential displacement plots. To determine the blocking strength of the interface to dislocations, a pure shear strain is applied on the previously relaxed cell. The sense of the shear strain is such that the force on the dislocation pushes it towards the interface from the corresponding γ or α_2 layer. Increasing amounts of shear strain are applied to the initially relaxed configurations. When slip dislocations collide with the interface, there are three fundamental reactions that may take place – the dislocation may be absorbed, transmitted, or rejected. In order to understand the nature of the nucleation of the dislocations and their interaction with the lamellar interfaces, we need to answer the following questions: (i) will the dislocation be completely

transmitted through the interface into the adjacent lamella or order domain; (ii) will it retain its integrity in the interface but undergo core reconstruction; (iii) will the dislocation dissociate into discrete interfacial defects, which may subsequently disperse along the interface due to their mutual repulsion. The stress at which the dislocations overcome the interface obstacle (the dislocation moves freely through the bilayer simulation cell) is the barrier strength of the interface.

To investigate the blocking strength of the γ/α_2 interface against a dislocation pile-up, we introduce a queue of dislocations in our atomistic model. After the initial relaxation in the absence of external applied stress, the pile-up is pushed against the interface by a shear stress, which is increased in a stepwise manner. The incremental shear stress enables more dislocations to enter the pile-up, until the total stress at the head of the pile-up is so concentrated that slip occurs in the adjacent lamella and one or more dislocations are driven away from the head of the existing pile-up. Stresses required for the above process are evaluated.

The blocking strength of the γ/α_2 interfaces depends on the presence of interfacial dislocations. Crystal lattice images of a γ/α_2 lamellar boundary observed in a coarse lamellar structure show that the interface contains several ledges of two atomic plane heights. Analyses of their Burgers vector indicate that the ledges correspond to a $\frac{1}{6}\langle 01\bar{1}0 \rangle$ ($\frac{1}{6}\langle \bar{1}\bar{1}2 \rangle$) or $\frac{1}{6}\langle \bar{1}010 \rangle$ ($\frac{1}{6}\langle 2\bar{1}\bar{1} \rangle$) dislocation. All the ledges have the same sign on a lamellar boundary and are distributed regularly with similar spacing, indicating that they are misfit dislocations introduced to accommodate the lattice misfit.

Guided by the experimental observations, we introduce $\frac{1}{6}\langle 01\bar{1}0 \rangle$ ($\frac{1}{6}\langle \bar{1}\bar{1}2 \rangle$) misfit dislocation into our atomistic model and simulate the interaction of the misfit dislocation in γ/α_2 boundaries with mobile dislocations. The dislocation is created by removal or addition of two layers of atoms. In order to analyse the role of the misfit dislocation, increasing amounts of shear strain are applied to the initially relaxed configurations both in the presence and in the absence of mobile dislocations in γ or α_2 crystals. This will show how the misfit dislocation affects the resistance of the γ/α_2 interface. The purposes of such simulations are: (i) to determine the critical load required to induce or transfer plastic deformation at γ/α_2 interfaces; and (ii) to elucidate the mechanisms of such deformations. Questions to be answered include which particular lamellar boundary and orientation of the applied stress leads to the emission or transfer of dislocations at the boundary, and a migration of the boundary itself due to the stresses.

12.4 Choice of interatomic potential

Since titanium is a transition element with a partially filled d-band, it can be expected that bonding in Ti–Al alloys will possess a significant covalent

component. Atomistic calculations of γ/α_2 interfaces were carried out using the Finnis–Sinclair type many-body potentials. Such central force schemes are not predictive as far as the energies of the planar faults are concerned and underestimate both the antiphase boundary (APB) energy on $\{100\}$ planes and the energy of superlattice intrinsic stacking faults (SISF). While this could be corrected empirically by introducing longer ranged (third and further neighbours) functions, the physical reason for the problem is the neglect of covalent contributions. A higher value is achieved if the non-central character of atomic bonding is considered, which is the case in BOPs. Embedded-atom method (EAM) interatomic potentials were constructed for the Ti–Al system and employed in studies of dislocations, interfaces and point defects. These calculations describe a number of general features of lattice defects but neglect the strong covalent and directional bonding that is characteristic for the Ti–Al alloys. Another telling feature of TiAl is the negative value of Cauchy pressures, which are the combinations of elastic constants $C_{13} - C_{44}$ and $C_{12} - C_{66}$. With potentials of the EAM or Finnis–Sinclair type, these pressures are always positive, and even the earlier BOP formulations could not correct this problem, which was solved only within the new BOP scheme in which the environmental dependence of the repulsive energy is taken into account.

A general description of BOPs and the tight-binding model on which they are based is given by Finnis (2003). BOPs were first formulated by Pettifor and coworkers and represent a numerically efficient scheme that works within the orthogonal tight-binding approximation. A further advantage of BOPs is that they allow the evaluation of the energy in a time that scales linearly with the number of atoms, so that it is feasible to simulate the tens of thousands of atoms needed to study the interaction between dislocations and γ/α_2 interfaces. Variants of the BOP method were implemented in the OXON.

A remarkable property of the BOP for $L1_0$ TiAl developed by Znam *et al.* (2003) is that it can be used not only for 1:1 stoichiometry of TiAl but shows excellent transferability to the 3:1 stoichiometry of Ti_3Al which is vital for the investigation of γ/α_2 interface. All the parameters of this model were fitted only to TiAl, which makes its transferability a genuine test that it is physically meaningful. The most important test of the potential was the calculation of the stacking-fault-like defects APB, complex stacking fault and SISF on $\{111\}$ planes in $L1_0$ TiAl. The calculated energies of these faults are in good agreement with those evaluated by *ab initio* methods.

The characteristics of the BOP constructed by Znam *et al.* (2003) mentioned above show that it is the most suitable atomistic model for atomistic study of dislocations not only in TiAl but also in Ti_3Al , as well as the interactions between them and the interfaces between these phases.

12.5 References

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Abstract: Models and software products have been developed for simulation and prediction of the correlation between processing parameters and properties, time–temperature–transformation diagrams, and fatigue stress life (S–N) diagrams, based on trained artificial neural networks. Graphical user interfaces are created for easy use of the models. The models designed are combined and integrated in a software package that is built up in a modular fashion. A description of the software products is given, to demonstrate that they are convenient and powerful tools for practical applications. Examples for optimisation of the alloy composition, processing parameters and working conditions are given. An option for use of the software in materials selection procedure is described.

Key words: neural network, software, properties, optimisation, materials selection.

13.1 Introduction

Many computer-based models and software packages have been developed, to aid the understanding of the physical metallurgical process, and to help reduce investment of time and money for experimental work. Generally, the modelling techniques can be classified into two large groups – physical modelling and statistical modelling. Each of them has advantages and areas of applications. Both are being constantly improved and applied to a variety of processes and correlation in physical metallurgy and materials science.

The physical models and software are usually based on fundamental theory and laws describing the physical nature of the process. There are major achievements in the field of physical modelling of the correlations between processing parameters and the microstructure formation of metals and alloys, mainly on thermodynamics and kinetics modelling.

At present, there is no physical theory or model that comprehensively covers the correlations for the entire path of processing parameter – microstructure – properties for all types of materials. The statistical models, from the other side, have applications in areas where large quantities of data exist and there are not physical models to well describe the process. A huge amount of data for various correlations in metals and alloys, including mechanical properties of titanium alloys (especially Ti-6Al-4V) under different conditions, is currently available in the literature; however, these data are sometimes rather confusing for use in engineering practice. Artificial neural network (ANN) is currently one of the most powerful and advanced modern modelling techniques based on a statistical approach with a very quick return

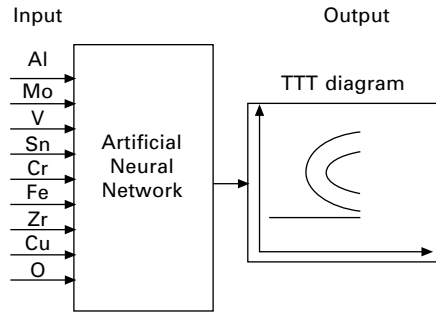
for the practice. Neural network (NN) modelling is suitable for simulations of correlations which are hard to describe or cannot be accurately predicted by physical models. Since artificial neural network modelling is a non-linear statistical technique, it can be used to solve problems that are not amenable to conventional statistical methods. ANNs have been applied to model complicated processes in many engineering fields: aerospace, automotive, electronic, manufacturing, robotics, telecommunication, etc., and the method is now a standard modelling technique. Since the 1990s, there has been increasing interest in ANN modelling in different fields of materials science (Bhadeshia, 2001; Huang *et al.*, 2002; Keong *et al.*, 2004; Wang *et al.*, 2000). ANN models have been developed to model various correlations and phenomena in steels (Cole and Bhadeshia, 2001; Guo and Sha, 2004; Lalam *et al.*, 2000a,b; Malinova *et al.*, 2001a,b; Metzbower *et al.*, 2001a,b; Yescas *et al.*, 2001), aluminium alloys (Gundersen *et al.*, 2001), nickel-base superalloys, mechanically alloyed materials, etc. A special feature of the models is the ability to provide upper and lower limits of the predicted value, thanks to the introduction of probability theory into non-linear data statistical analysis. ANN modelling has also been employed to study the mechanical properties of microalloyed steels as functions of alloy composition and rolling process parameters, the effect of carbon content on the hot strength of austenitic steels, and continuous-cooling-transformation (CCT) diagrams of vanadium containing steels. These are relevant to Chapters 14 and 15.

One direction of titanium research has been dedicated to artificial neural network modelling and software development for simulation of processes, correlations and phenomena in titanium (Guo and Sha, 2000; Malinov and Sha, 2004; Malinov *et al.*, 2000, 2001a,b; McShane *et al.*, 2001). The software products are largely based on trained artificial neural networks. This chapter describes the NN technique, and its software development. The organisation and the features of the software products are presented. The effectiveness and applications of the programs are discussed. Examples of the use of the software for modelling, simulation and optimisation of different processes are demonstrated. Ways for improvement and upgrade of the models are given. Finally, an integration of the models is outlined.

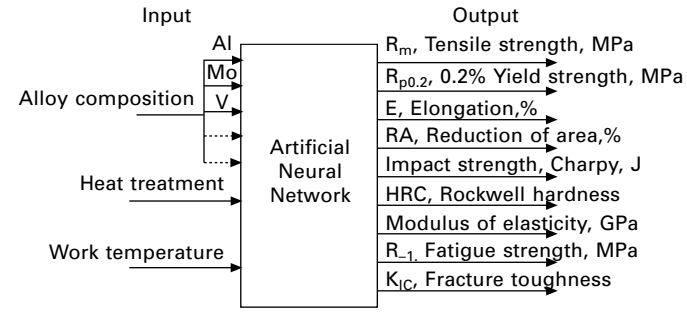
13.2 Software description

13.2.1 The models

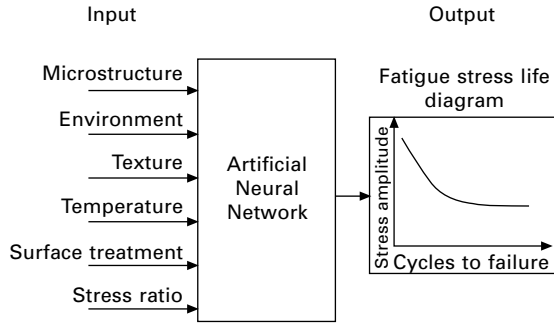
The models for different correlations are schematically summarised in Fig. 13.1. The input parameters for each particular case of output are chosen based on the physical background of the process; all relevant input parameters must be represented. The graphical user interfaces of the software products are shown in Fig. 13.2. In addition to these, neural network models and



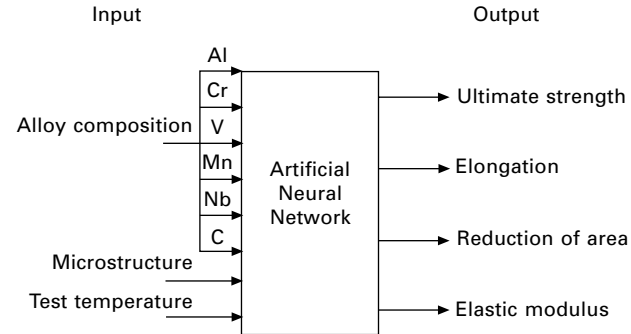
(a)



(b)

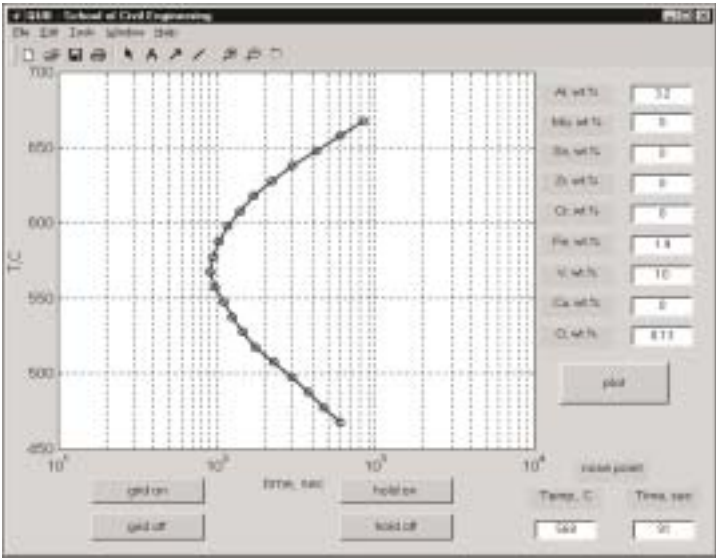


(c)

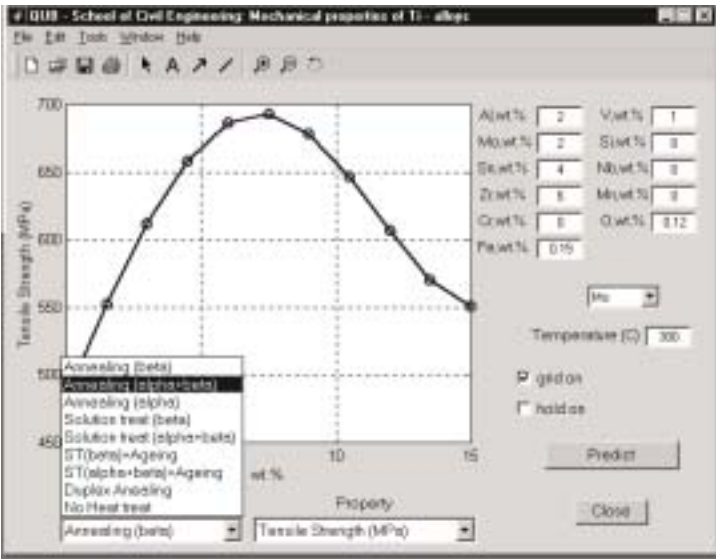


(d)

13.1 Schematic models of artificial neural networks for simulation and prediction of different correlations in titanium alloys: (a) time–temperature–transformation diagrams; (b) mechanical properties of titanium alloys; (c) fatigue stress life diagrams; (d) mechanical properties of titanium aluminides.

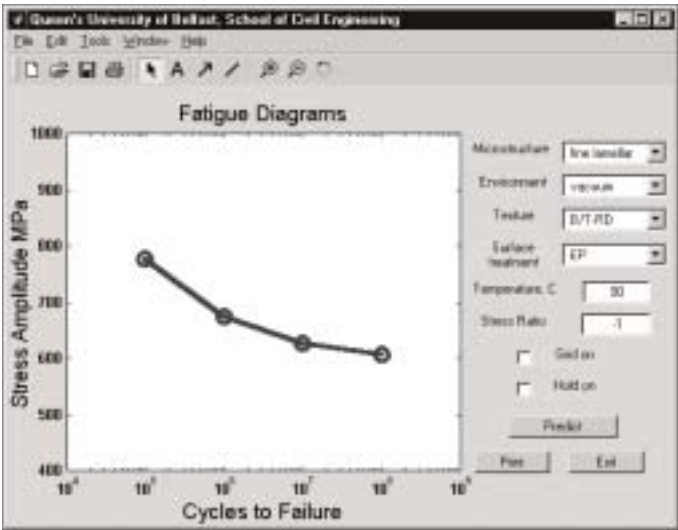


(a)

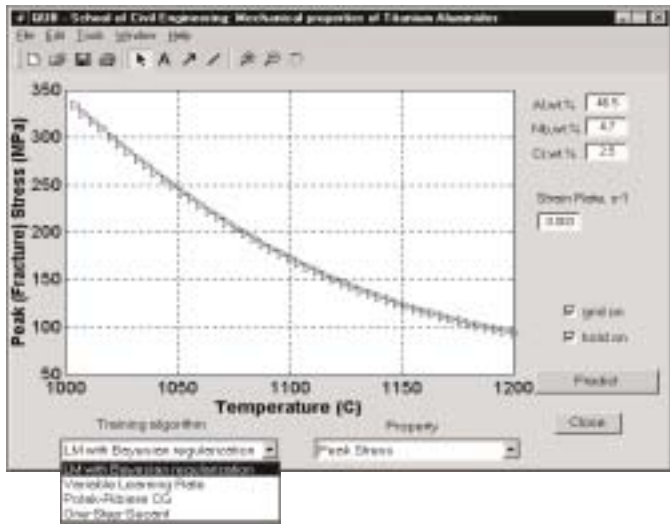


(b)

13.2 Graphical user interfaces of software for modelling different correlations in titanium alloys: (a) time–temperature–transformation diagrams; (b) mechanical properties of titanium alloys; (c) fatigue stress life diagrams; (d) mechanical properties of titanium aluminides.



(c)



(d)

13.2 Continued

software have been developed for calculating the hardness after surface nitriding of titanium alloys (Chapter 18). The basic principles of the neural network modelling and the algorithms of the software programs will be discussed in the following sections. The use of graphical user interfaces will be discussed further below.

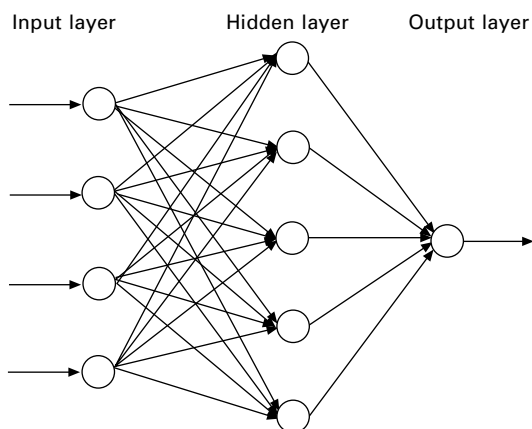
13.2.2 Basic principles of neural network modelling

In this section, the basic principles of neural network modelling are given so that the reader can understand the software products developed without having to refer to dedicated neural network books.

Artificial neural network modelling is essentially an operation linking input to output data, by using a particular set of non-linear basis functions. A neural network consists of simple synchronous processing elements, which are inspired by the biological central nervous systems of living organisms. It comes to a conclusion given the relevant information, or stimuli, and experience. The basic unit, or building block, in the artificial neural network is the neuron. Neurons are connected to each other by links known as synapses. Figure 13.3 shows the schematic layout of the neurons within a network, with each arrow representing a link, or a synapse, between neurons. Each of these synapses has a weight attached to it, which governs the output of the neuron. As the synapses are built up, a network is formed. For modelling processes, such as in the software shown in this part of the book, hierarchical types of networks are most suited. In all our cases, feedforward hierarchical artificial neural networks are used (Fig. 13.3). In a feedforward neural network, the input information is processed in a one-way direction – from input to output – and the neurons are ordered in layers, with an input set, hidden set(s) and an output set of neurons (input layer, hidden layer(s) and output layer, see Fig. 13.3). Most of the neural networks for metallurgical studies follow this structure, fully-connected and feedforward.

In all the models developed, these steps are followed:

- (i) determination of input/output parameters;
- (ii) database collection;



13.3 A schematic model of the structure of a feedforward hierarchical artificial neural network.

- (iii) analysis and pre-processing of the data;
- (iv) training of the neural network;
- (v) test of the trained network;
- (vi) use of the trained network for simulation and prediction.

The designed NN must be trained. The training procedure is the most significant part of the neural network modelling. Training is a procedure whereby a network is adjusted to do a particular job. Usually, neural networks are trained using a large amount of data-containing input with corresponding output values, called input/output pairs, so that a particular set of known inputs produces, as nearly as possible, a specific set of known target outputs. Training involves adjusting the weight associated with each connection (synapse) between neurons within the network, by comparison of the computed outputs and the targets, until the computed outputs for each set of data inputs are as close as possible to the target data outputs. The weight of a synapse, multiplied by the strength of the signal on that synapse, defines the contribution of that synapse to the activation of the neuron for which it is input. The total activation of a neuron is then the sum of the activation of all its inputs plus a bias value, and this defines the value of the output signal for that neuron, via a transfer function. By adjusting the values of these synaptic weights throughout the network, the outputs of the neural network for any given set of inputs can be altered. Training is a continuous process, until the network correctly simulates the known behaviour of the system to be modelled. The simulation will rarely be exact; training is usually aimed at minimising the sum of the squares of the differences (the errors) between the predicted and experimentally measured values of the outputs.

The term ‘training algorithm’ (also known as learning rule) refers to the procedure for modifying the weights and biases of a network. The training algorithm is applied to train the network to perform some particular task. It is basically the mathematical apparatus by which the data are used to fit (train) the network. There are many different training algorithms. In order to achieve the best result, different training algorithms should be attempted. For feedforward NN, the most commonly used ones are batch gradient descent, batch gradient descent with momentum, one-step-secant, scaled conjugate gradient, resilient backpropagation, Polak–Ribiere conjugate gradient, Fletcher–Powell conjugate gradient, Powell–Beale conjugate gradient, variable learning rate, and Levenberg–Marquardt. These training algorithms are standard. Their mathematics can be found in many neural network books. From a comparative work (Malinov *et al.*, 2001b), the algorithms based on batch gradient descent require about 1000 times longer training time compared with the Levenberg–Marquardt training and do not give better results. The algorithms based on conjugate gradient require 20–30 times longer training time compared to the Levenberg–Marquardt training. The best result is obtained with Polak–Ribiere conjugate gradient. The Levenberg–Marquardt training algorithm is the fastest,

but the results for the test and the whole dataset for this algorithm are not acceptable. The most probable reason for this is the problem with overfitting. When Bayesian regularisation in combination with the Levenberg–Marquardt training was used, the training time was increased, but the R -values (see Section 13.2.3) for the test and the whole dataset were better. The training with variable learning rate is slower than Levenberg–Marquardt, but gives better results. Based on this analysis four training algorithms give the best NN performance, namely one-step-secant, Polak–Ribiere conjugate gradient, variable learning rate and Bayesian regularisation in combination with the Levenberg–Marquardt.

By default, we assume that the user will not aim at changing the mathematics of any of the above training algorithms. In the software products, the training algorithms are implemented in the computer code.

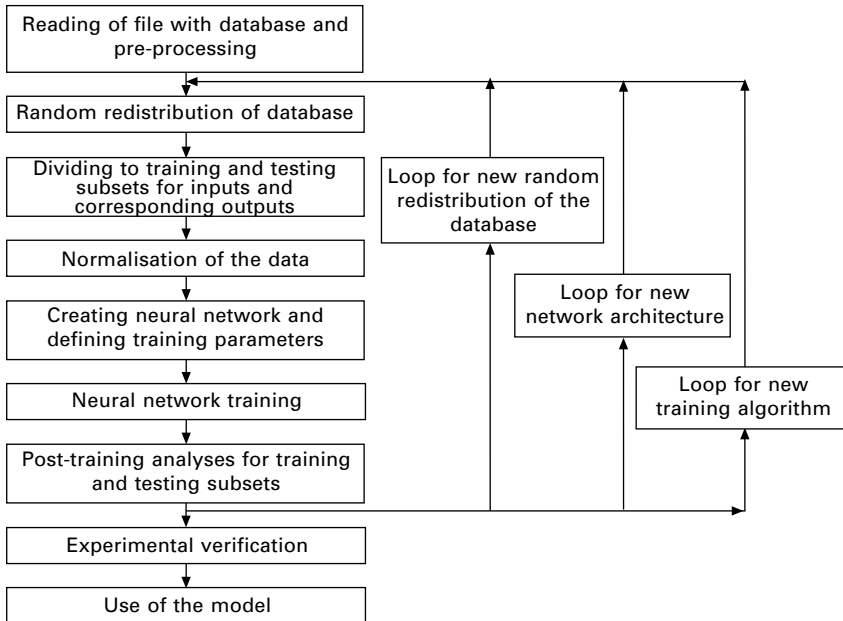
Most generally, the features of the artificial neural networks can be summarised as follows:

- The neural network models are statistical models, i.e. they are not based on any physical theory. However, they can be used to model complex processes and correlations.
- Neural network modelling is suitable for simulations of correlations that are hard to describe by physical models.
- The neural networks work with numerical characteristics (input/outputs).
- A large amount of data is required. Using such a database, we can train a neural network to perform complex functions.

13.2.3 Algorithm of computer program for neural network training

Pre-training procedures

A block diagram is given in Fig. 13.4. It starts with the accumulation of a database. The database can be constructed only by collecting available data for the correlation being modelled. The data can be from handbooks and journal papers, and usually span back over a long period of time. For the models discussed in this book, the data were collected from both Western and Russian literature. Most of the data used were for commercial Ti-alloys. The initial organisation of the data during the course of their accumulation can be in a standard spreadsheet file format. Each row in this file represents one input/output data pair. Each column in this file represents one input or output. Some of the inputs or outputs are properties that are not numbers but categories. Examples for this are heat treatment (Malinov *et al.*, 2001a), microstructure (Malinov and Sha, 2004; McShane *et al.*, 2001), material grade (Malinov and Sha, 2004), environment (Malinov and Sha, 2004; McShane *et al.*, 2001), surface treatment (McShane *et al.*, 2001), cooling method



13.4 Algorithm of computer program for creation of neural network model.

(Malinova *et al.*, 2001a), etc. At this stage of pre-training, these should be digitised by means of attributing different digits to the different categories. In some cases, the output is a graph (see Fig. 13.1a,c). In these cases, the graph should be appropriately digitised and presented as a set of numbers (Malinov *et al.*, 2000; Malinova *et al.*, 2001a; McShane *et al.*, 2001). Once the data accumulation is completed, the file containing the database is converted and saved in ASCII format. This file is read by the computer program for creation of the model (Fig. 13.4) and is put as a matrix M for further manipulations. The matrix M has dimension $m \times n$, where m is number of rows and is equal to the number of data pairs in the database and n is number of the columns and is equal to the number of inputs plus number of outputs. The spreadsheet and the ASCII files are dynamically linked, so that each change and addition in the spreadsheet file result in an automatic upgrade of the ASCII file and the matrix M to be used for the model design.

The next step in the computer program is 'random redistribution of the database' (see Fig. 13.4). In the neural network modelling, it is generally accepted that one part of the data (usually two-thirds) is used for model training and the remaining part (usually one-third) is not used in the training procedure but is used to test the model. Before training, the database is randomly divided into these two parts. In the computer program, this is done by the block for 'random redistribution of the database'. First, a vector with

random numbers between 0 and 1 is generated. The size of this vector is equal to the number of the data pairs (n). This vector is thereafter stuck as an additional ($n+1$)th column of the matrix M . The next operation is an automatic rearrangement of the rows of matrix M in ascending order of the numbers in the ($n+1$)th column. After implementation of this operation, the ($n+1$)th column is taken out and the new matrix Mr is produced. Mr is with dimension $m \times n$ and contains the same data as M . The only difference is that the rows (data pairs) in Mr are randomly redistributed as compared to the original M matrix. The computer program, written in this way, allows new random distribution of the whole database into the sub-data sets each time it is run, because each time the vector with generated random numbers will be different.

The next step in the computer program is to extract the training and the testing matrixes for input and corresponding output (Fig. 13.4). The matrix Mr is divided into two matrixes Mr_{tr} and Mr_{tst} . The first $2/3$ rows from Mr are extracted as matrix Mr_{tr} (matrix for training) and the last $1/3$ rows as matrix Mr_{tst} (matrix for testing). These new matrixes have dimensions $m_1 \times n$ and $m_2 \times n$. Obviously $m_1 + m_2 = m$; $m_1 = (2/3)m$ and $m_2 = (1/3)m$. $Mr_{tr}(m_1, n)$ and $Mr_{tst}(m_2, n)$ contain data pairs (input with corresponding output) that will be used for training and testing of the model, respectively. The next step is to divide these matrixes to matrixes containing inputs and outputs only – $M_{trin}(m_1, n_1)$, $M_{trout}(m_1, n_2)$, $M_{tstin}(m_2, n_1)$ and $M_{tstout}(m_2, n_2)$. Here $M_{trin}(m_1, n_1)$ is the matrix containing the inputs for training, $M_{trout}(m_1, n_2)$ is the matrix containing outputs for training, etc. n_1 is equal to the number of the inputs, n_2 is equal to the number of the outputs and $n_1 + n_2 = n$. These four matrixes are further used for training and testing of the model. It should be restated that, each time the program is run, a new random redistribution of the database will be executed and, as a result, these four matrixes will contain different data. It should also be mentioned that the different random redistribution of the database results in different neural network performance. This will be discussed in a following section.

The values in the matrixes for training and testing have different dimensions and ranges. To overcome this, the next block in the computer program is for normalisation of the data. Depending on the transfer function used, the data are normalised between 0 and 1 or between -1 and 1 , applying Eqs. [13.1a] or [13.1b], respectively:

$$x_N = \frac{x - x_{\min}}{x_{\max} - x_{\min}} \quad [13.1a]$$

$$x_N = 2 \frac{x - x_{\min}}{x_{\max} - x_{\min}} - 1 \quad [13.1b]$$

where x_N is the normalised value of a certain parameter, x is the measured value for this parameter, $x_{\min}$ and $x_{\max}$ are the smallest and the largest values in the database for this parameter, respectively.

Training parameters

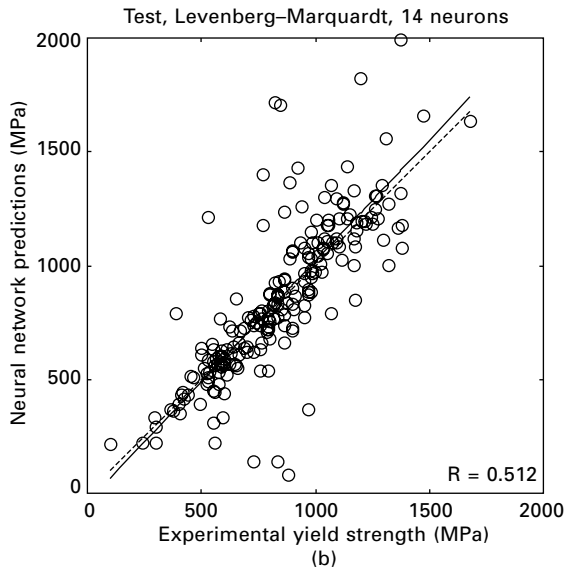
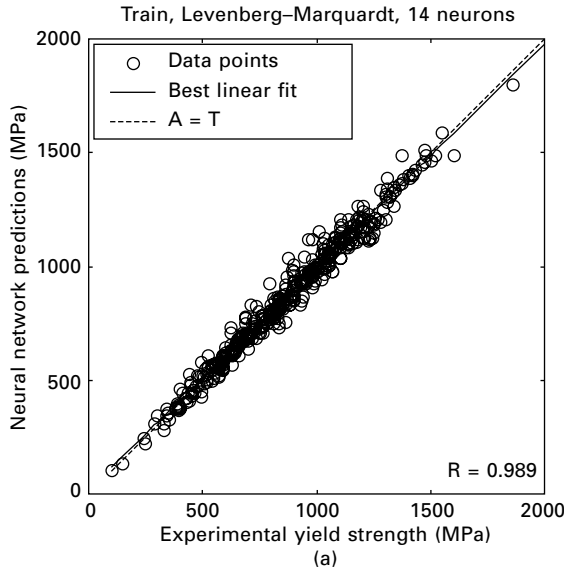
The next block in the computer program is for creating the neural network, defining the training parameters and the actual training of the model. The following matters are important in the design and training of neural networks: (i) database and its distribution, (ii) choice of architecture of the neural network, (iii) training algorithm and parameters, and (iv) transfer function. Other training parameters, such as learning rate, performance goal, and minimum performance gradient, may have a minor influence, but they aim mainly at the optimisation of the training time and computer memory use, and have little influence on the final performance of the trained model.

In the software developed on a user level, an option can be incorporated to enable users to add their own data and re-train the model. This option will be discussed in Section 13.4.1. Here, some recommendations on the selection of the important parameters and their influences on the neural network performance will be discussed. The reliability of the neural network model for any particular combination of database distribution, architecture, training algorithm and transfer function can be tested by an analysis of the network response in a form of linear regression between network outputs (predictions) and corresponding targets (experimental data) for the training and the testing datasets (Fig. 13.5).

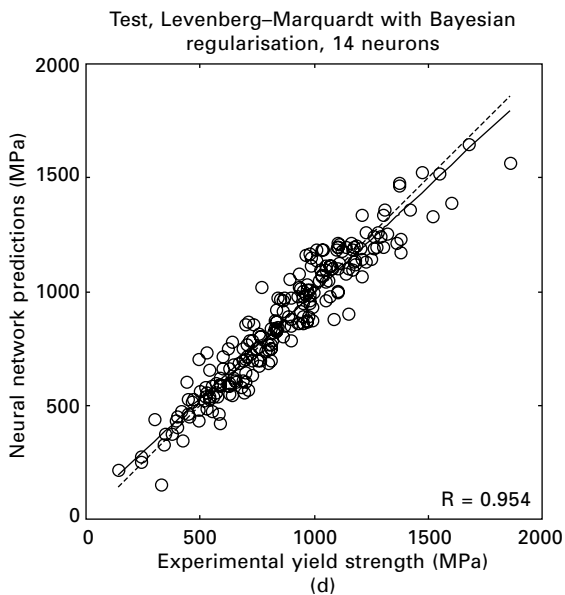
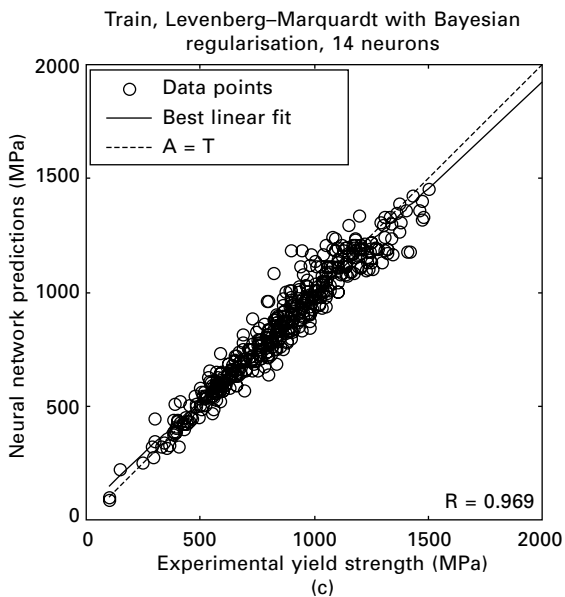
Different random division of a database into training and testing subsets, using the computer program procedure which has been described, can result in significantly different model performance for the same other parameters (architecture, training algorithm, transfer function). This difference can be explained with the ranges of input data variation for the training and the testing datasets. In some cases of random dividing, instances may happen where the range of variation of the data for the training dataset is narrow as compared to the range of variation of the test dataset. In these cases, most of the data pairs in the test datasets are new encounters for the trained NN and fall outside the range of variables for which the model has been trained. An appropriately trained NN model can give reliable predictions for new instances within the ranges it has been trained (interpolation), but appreciable errors are possible for predictions outside these ranges (extrapolation). Hence, it is recommended that not only one but a number of training sessions with the same other parameters but different random redistribution is carried out in order to find the case with the most suitable dividing of the data to training and testing sets.

The term ‘architecture of the neural network’ refers to the number of layers in the NN and the number of neurons in each layer. The numbers of neurons in the input layer and the output layer are determined by the numbers of input and output parameters, respectively, while the number(s) of neurons in the hidden layer(s) can vary. The number of the hidden layers could be

one, two or more. One hidden layer is enough for appropriate model performance. Increasing the layers to two results in a remarkable increase of the unknown parameters (connections) to be fitted, which itself increases drastically the requirements for the amount of data without any noticeable



13.5 Post-training linear regression analysis between experimental data (T) and neural network predictions (A) for training (a,c) and testing (b,d) datasets using Levenberg–Marquardt training without (a,b) and with (c,d) Bayesian regularisation.



13.5 Continued

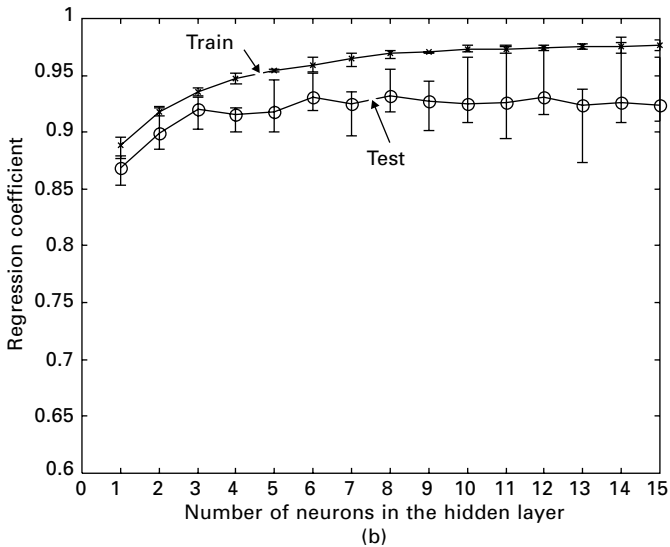
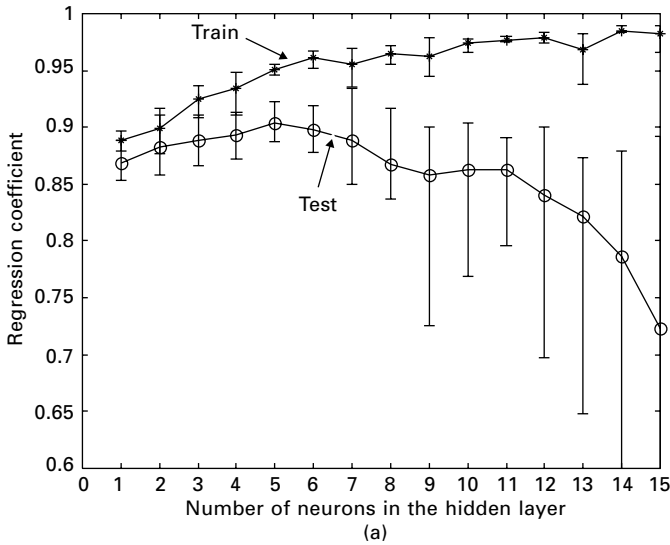
improvement in the final model performance (Malinov *et al.*, 2001a). Hence, in all the models discussed in this book (Figs 13.1 and 13.2), the general structure of input, one hidden and one output layer, is used. In order to find the optimal architecture, different numbers of neurons in the hidden layer

should be tried. The number of neurons in the hidden layer (NNHL) influences considerably the model performance. In what follows, some practical recommendations for selection of NNHL by the user when re-training the model with their own data are given. Two factors are important for determining the number of neurons.

- First, the increase of the NNHL increases the connections and weights to be fitted. The NNHL cannot be increased without limit because one may reach a case where the number of the connections to be fitted is higher than the number of the data pairs available for training. Though the neural network can still be trained in this case, it is mathematically undetermined and should be avoided. The maximum NNHL is different for each particular case and depends on the number of inputs, number of outputs and number of available data pairs. The number of the connections to be fitted can be worked out by drawing the scheme of the NN (Fig. 13.3) for the particular case of inputs, outputs and NNH, and calculating the connections to be fitted (Sha and Edwards, 2007).
- Second, the initial increase of the NNHL usually results in an improvement of the model performance. However, one problem that can occur when training with a large number of neurons is that the network can overfit on the training set and not generalise well to new data. In other words, the network is too flexible and the error of the training set is driven to very small values, but when new data are presented to the network, the error is large. The optimal NNHL depends on the database, nature of the problem to be modelled and the training algorithm, and should be determined for each particular case. The overfitting can be prevented by different techniques aiming at better generalisation of the model.

Figure 13.6 demonstrates one example of finding the optimal architecture of the NN in terms of number of neurons in the hidden layer. The case is for the prediction of yield strength of titanium alloys (Fig. 13.1b). The number of inputs is 13, the number of outputs is 1 (if just yield strength is considered) and the number of the available data pairs is 662 (441 for training and 221 for testing). In order to find the optimal architecture, different numbers of neurons in the hidden layer were tried. The Levenberg–Marquardt training algorithm was used for this study. The results for the influence of number of neurons in the hidden layer on the NN response are given in Figs. 13.5 and 13.6. The results in Fig. 13.5 are for single training with 14 neurons in the hidden layer and show the network response in a form of linear regression analysis between the network outputs (predictions) and the corresponding targets (experimental data), for two different training algorithms. The results in Fig. 13.6 are presented in the form of correlation coefficient (R) between the neural network predictions and the experimental data for the training and the testing datasets, for different numbers of neurons in the hidden layer. For

each case, the values for the R coefficient are averaged from five separate training runs under the same conditions and using different random divisions of the dataset. When the number of neurons in the hidden layer is increased from 1 to 5, the R coefficient for both training and test datasets quickly



13.6 Regression coefficients between the neural network predictions and the experimental data for different numbers of neurons in the hidden layer using Levenberg–Marquardt training (a) without and (b) with Bayesian regularisation.

increases (see Fig. 13.6a). Further increase in the number of neurons results in further increase of the R coefficient for the training dataset that is approaching the value of 1 (Figs. 13.5 and 13.6). However, the regression coefficient for the test dataset quickly decreases to average values of <0.8 with large error bars (Figs. 13.5 and 13.6). This observation shows that there is an effect of overfitting when the number of neurons is increased to six and above. One way to prevent the overfitting is by applying Bayesian regularisation in combination with the Levenberg–Marquardt training (Figs. 13.5 and 13.6). This is one of the techniques aiming at better generalisation. The results obtained for the different numbers of neurons in the hidden layer are appreciably stable (see Fig. 13.6b). Values of coefficient R for both training and test datasets increase when the number of the neurons is increased to eight. Further increase of neurons does not result in overfitting and the results for the regression analyses of both training and test datasets are comparable (see Fig. 13.5c,d). However, at the same time, increasing the number of neurons above eight does not give appreciable improvement, while the training time is significantly increased. Considering all the above, the optimal for this neural network architecture is eight neurons in the hidden layer.

The type of the training algorithm used is important for both neural network response and central processing unit (CPU) time (or computational resources) necessary for training. A summary analysis of the influence of different training algorithms on the performance of the neural network model is given below. Different training options can be carried out, including training on variations of mean square error for better generalisation, training against a validation set, and training until the gradient of the error reaches a minimum. Improvement of the generalisation can be achieved by means of regularisation and early stopping with validation. The general opinion is that automated regularisation based on Bayesian regularisation in combination with Levenberg–Marquardt training usually gives the best result, in terms of model performance and training speed. This combination is used in the neural networks described in this book unless otherwise stated. However, in some cases, other training algorithms such as one-step-secant, Polak–Ribiere conjugate gradient, and variable learning rate may give competitive results. In the software developed and described in this book, the user can choose the training algorithm to predict values or re-train the model.

The transfer function transforms the neuron input value into the output value. The most popular functions are hard limit (hardlim), linear (purelin), log sigmoid (logsig), and hyperbolic tangent sigmoid (tansig). For all cases of NN, a linear transfer function is suitable in the output layer. The transfer functions in the hidden layer are generally s-shaped curves, with the output value confined within limits of (0,1) or (−1,1), for log-sigmoid and tan-sigmoid functions, respectively. Mathematical formulations of the main transfer functions and their general shapes can be found in Chapter 14. In the model

developed and described in this book, different transfer functions in the hidden layers were attempted. Mainly, log sigmoid and tangent sigmoid functions are compared. It may be concluded that there is little influence whether log sigmoid and tangent sigmoid functions are used. Hence, this is not considered as a significant parameter for the NN response. In all models (Fig. 13.1), in their final version, hyperbolic tangent sigmoid function is used for the neurons in the hidden layer.

Optimal model parameters

The computer program for the design of the neural network model is written in a way to find the best combination of database distribution, network architecture and training algorithm, by grid search (Fig. 13.4). Loops are organised for the above parameters. By varying these, all possible combinations of network architecture and training algorithm with different database distributions are attempted and stored. For each combination, the correlation coefficients between the neural network predictions and the experimental data for the training and the testing datasets are stored and used for further evaluation. The program realisation is as follows. First, the number of neurons in the hidden layer is put equal to one, and the first training algorithm, for example one-step-secant, is used. For this combination, at least five sessions of training with different random redistributions of the database are executed. Next, the number of the neurons is increased to two, and again five sessions of training with different random redistributions (but the same as those for the above case and for all cases) of the database are executed. The same is executed for three, four, five, etc. number of neurons in the hidden layer. The NNHL is increased as far as the case remains mathematically determined (see above). The next loop is to change the training algorithm and the same procedure is repeated for the new and for all the training algorithms given above. In this way, we have stored neural networks trained with all possible combinations of network architecture and training algorithm and different random redistributions of the datasets. The next is to find the best case. To do this, the following procedure is applied. First, using the runs with different random redistributions, the average regression coefficients between neural network predictions and the experimental data for the training and the testing datasets, for different network architecture and training algorithms, are calculated. For one training algorithm, the regression coefficients after training with different NNHL are compared, and the best case (the winner), in terms of best architecture for this training algorithm, is found. This procedure is executed for each training algorithm. The winners for the different training algorithms are thereafter compared and the best combination of network architecture and training algorithm is found. For this combination, the best case among the five sessions of training with different random redistributions

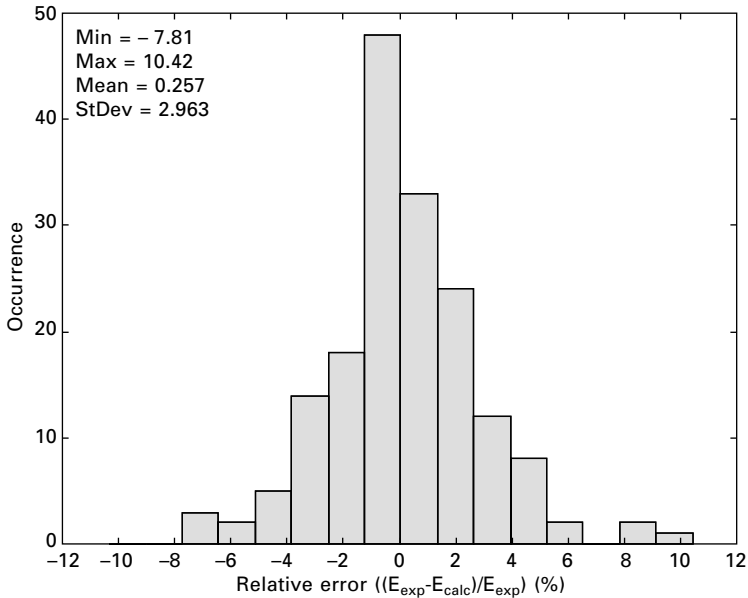
is extracted and this is the final winner in the sense of best database distribution, network architecture and training algorithm. This case is then stored and the neural network trained with these parameters is used for further simulations and predictions. The above procedure is executed for all the models in Fig. 13.1, and the best cases are used with the corresponding graphical user interface (GUI), in Fig. 13.2. Readers should be reminded that the optimal combination of database distribution, network architecture and training algorithm depends on many factors, such as the nature of the problem to be modelled, the number of inputs and outputs, and the database available, and can differ considerably from case to case. The computer program and the procedure described above for finding the optimal case of trained neural network, and reliable neural network modelling in general, require significant amounts of data, but, once trained and created, the model can quickly and easily be used to predict for new instances.

Post-training procedures

The next block of the computer program is for further experimental verification of the model by statistical analysis of the error of the model predictions. The relative error (relative difference between the model simulations and the experimental data) is calculated for each data pair. The results are presented by plotting them in the classical plot of occurrence versus error, also referred to as frequency versus error. This plot is more informative as compared to the plots of the linear regression analysis (Fig. 13.5). Using it, the specialists in the field can conclude whether the achieved accuracy in terms of error variation is acceptable for the phenomenon being modelled. Here, an example is given of such an analysis for modelling of the modulus of elasticity of titanium alloys (Fig. 13.7). Additional plots and analyses for other correlations are given and discussed by Malinova *et al.* (2001a).

Further verification of the model simulations can be performed by the user by means of direct comparison of the software predictions and experimental data. Users can utilise the software and the GUIs developed (Fig. 13.2) to calculate results for new input values and thereafter can compare these predictions with experimental data taken from the literature or with their own experimental data. This procedure is not part of the program and is executed manually by the user. Some comparisons of this type are given by in Malinova *et al.* (2001a).

In all the models in Figs. 13.1 and 13.2, very good performance is achieved. Good agreement between the experimental and calculated values is found.



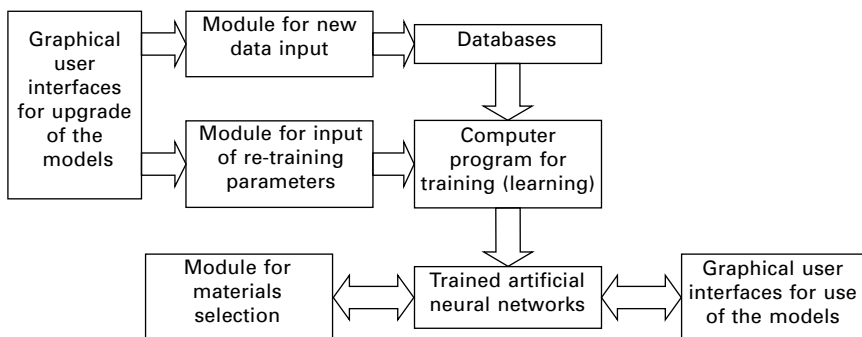
13.7 Post-training validation of the software simulations by statistical analysis of the error of model simulations for modulus of elasticity.

13.3 Use of the software

13.3.1 General organisation of the software and graphical user interfaces

The software system should be designed in a modular fashion, with each module designed in such a way that it can be upgraded by a later version without substantially affecting the operation of the remainder of the model. The different modules are linked according to the block diagram given in Fig. 13.8. The modules for databases, computer program for training and trained ANN are described in the previous section. Once the neural network models are trained and verified, they can be used for further simulations and predictions for arbitrary user defined new (unused in the training) combination of input values, in order to reveal different correlations and phenomena in titanium or during processing of titanium alloys. The interactions with the system are organised by interface modules. For each of the models in Fig. 13.1, two types of interface are developed, namely text user interface and graphical user interface (GUI). In the text version, the user is asked interactively for input of the necessary information and, once it is completed, the output from the system is generated.

On the basis of the designed models of artificial neural networks, graphical user interfaces (Fig. 13.2) are developed using MatLab programming language



13.8 Block diagram of software system for modelling of correlations in titanium alloys, based on artificial neural network approach.

that allows easy and further use of the models (Fig. 13.1). The user can run any of the GUIs in Fig. 13.2 to input the desired new combination of input values for each particular model using the textboxes, menus, list boxes, pop-up menus, radio buttons, sliders, etc., provided (see Fig. 13.2). Once the information is entered, the user can click on 'Predict' or 'plot'. The information entered is then acquired, organised and processed (see Fig. 13.8) as a new input combination to the trained neural network for the corresponding GUI. The trained artificial neural network calculates output for this combination of inputs. The output is returned to the GUI, and is visualised in a form of graph (in the cases in Fig. 13.1a,c) or dependence of the properties on a desired parameter. In this way, the user can very easily obtain and evaluate different kinds of dependence of any property involved in the models. In this way, the user can easily obtain and evaluate the dependence of the outputs from chosen input. Furthermore, the GUI provides an opportunity for easy comparison of output properties corresponding to different sets of inputs, by plotting them together. In the cases where the output is a graph, the GUIs also allow smoothing of the predicted profile with a user-defined coefficient.

The software system developed is based on trained artificial neural networks. The training of the different modules is performed using the collected databases for each particular case. However, the system is open for further upgrading from the users, by adding additional data and training (see the left part of Fig. 13.8). These features will be discussed in Section 13.4.1.

The block scheme given in Fig. 13.8 is for one of the models in Fig. 13.1 and the corresponding GUI in Fig. 13.2. In practice, in the software system developed, all the GUIs in Fig. 13.2, as well as others, are integrated and linked by an introductory GUI window. This allows easy switching between the different applications. Such organisation is convenient for the user, because once they have used any of the GUIs in Fig. 13.2 to predict a property (for

example a mechanical property), they can straightforwardly switch to others to check if the other properties (for example TTT diagram) are satisfactory.

13.3.2 Prediction of properties of existing materials

New materials with different special properties are continuously being developed to meet engineering requirements. The aim is usually to achieve desirable values of one or a combination of properties. However, most often, the other properties of these materials are unknown when they are first designed and these properties are studied by additional experiments after the materials are introduced in certain applications. The lack of knowledge of these other properties inhibits full exploitation of these new materials. The software developed (Fig. 13.2) can be used to predict unknown properties of existing materials. For this purpose, the user can input and fix the composition of the alloy and can predict the unknown property (mechanical, kinetics of phase transformation, etc., as desired) for different conditions.

One typical example for such use of the software is using the module for prediction of time–temperature–transformation diagrams (Figs. 13.1 and 13.2). Experimental investigation of TTT (and CCT) diagrams is both costly and time consuming. Hundreds of experiments are necessary to construct such diagrams for a single alloy. For this reason, when a new material is designed, its TTT diagrams are usually unknown. There is presently still a lack of such diagrams, even for widely used alloys. Using the software, TTT diagrams are predicted (Chapter 14) for many existing titanium alloys for which experimentally determined TTT diagrams are not available in the literature. These simulation results can be used for explaining the transformation kinetics during cooling of corresponding alloys. The diagrams will also be useful in the design of experimental studies of TTT diagrams for these alloys. In this way, the amount of experimental work could be significantly reduced. In this respect, it should be mentioned that, for some of the alloys, experimental TTT diagrams have become available after the simulations and good correspondence between the predictions and later available experimental diagrams is demonstrated. These agreements give us confidence in the model simulations. Other examples of using the software package developed to predict properties of existing materials are the calculation of fatigue strength S–N diagrams and mechanical properties (Chapter 15).

13.3.3 New alloy design

Neural network models are usually used to predict outputs for user-defined combination of inputs. However, very often in practice, it is necessary to solve the reverse problem, namely to find combinations of inputs which would produce a desirable output or combination of outputs. For example, it

is of great interest for the theory and the practice to find optimal alloy composition, processing and environment conditions that would give a particular desirable property or combination of properties. The background of new alloy design is the knowledge of the correlations between the alloy composition and the properties. The optimisation of one or some of the properties of the material being designed is closely related to optimisation of its composition. However, new materials are still mainly designed empirically, by carrying out expensive and time-consuming experimentation on trial alloys. The software system has assembled results from hundreds of experiments and is trained with them. As a result, it is capable of predicting properties for new alloy compositions. It can be used for optimisation of the alloy composition for the alloy being designed in order to achieve an optimal value for properties aimed for. Based on the trained neural networks, computer programs for optimisation of the input values (the alloy composition and processing) in order to obtain the desired property (or combination of properties) are developed. The trained neural network is incorporated in the body of the program and the optimisation criteria can be user defined. This approach was first applied for the model on mechanical properties of titanium alloys (Chapter 15). At a later stage, it was incorporated into the other models described above. In the first instance, the search for the best solution was based on a simple grid search. Now, the NN models are combined with efficient optimisation methods for faster discovery of the best solution. The optimisation programmes are individual for each separate NN model. There are separate modules for optimisation of mechanical properties, TTT diagrams, fatigue stress life diagram, etc. The user can use the modules (Figs. 13.1 and 13.2) in this mode by fixing the other inputs (such as temperature, environment and treatment) at certain levels and varying the composition of the alloy. The alloy composition can be altered by varying single element concentration and fixing the others on chosen values or by varying of combination and ratios of elements. In this way, the user can analyse the influence of the different elements (or combination of elements) on the output properties, and can predict the optimal composition of the new alloy that would produce the desired properties. Usage of the software package in this mode would allow the amount of experimentation for new alloy design to be reduced.

Examples for such kinds of software application are (Chapter 15): (i) influence of the aluminium and vanadium contents on the tensile properties of $\text{Ti-}x\text{Al-}y\text{V}$ alloys; (ii) influence of the contents of Al, V, O, Mo, Sn and Cr on the isothermal transformation kinetics in different alloys; (iii) influence of the aluminium content on yield strength, impact strength and hardness of $\text{Ti-}x\text{Al-}6\text{V-}2\text{Sn}$ alloys.

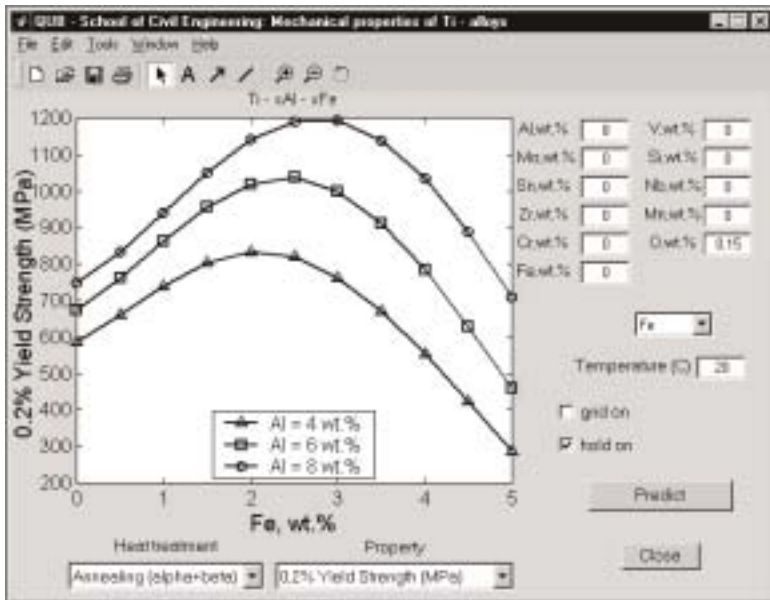
Here, we use one of the modules (Figs. 13.1 and 13.2) to demonstrate how the software can be used for alloy composition optimisation. For this purpose, the Ti–Al–Fe system is used, which is a base system for designing a new

class of low-cost titanium alloys. By varying the alloying element contents, the program can be used to find the optimal alloy composition that would result in maximum yield strength (Fig. 13.9). In a similar manner, all modules can be used to optimise the alloy composition in order to achieve other desirable properties. Integration of these models would allow simultaneous optimisation of, for example, different mechanical properties.

13.3.4 Material selection

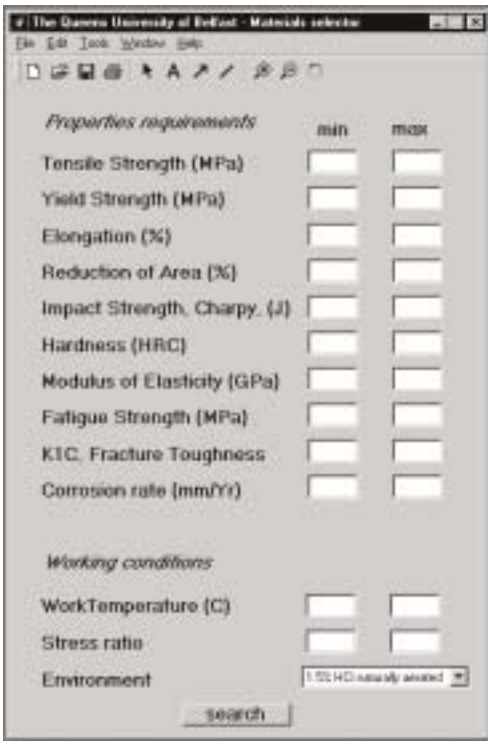
The material selection procedure has become of extreme importance for modern engineering. Over recent years, many software systems have been developed for the selection of materials for user-defined requirements. One of the popular systems of this kind is 'Cambridge Engineering Selector' (developed initially as 'Cambridge Materials Selector'). Most of these computer-based systems use a classical approach of searching a database of materials properties according to user-defined criteria for a combination of properties.

The neural network software system developed here can also be used for material selection procedures. For this purpose, a special module and GUI have been developed (see Figs. 13.8 and 13.10). The user can use the GUI



13.9 Use of the software for optimisation of the alloy composition in the Ti-Al-Fe system in order to achieve maximal room temperature yield strength.

developed (Fig. 13.10) to define the working conditions (such as temperature and environment) and the requirements for materials properties (such as strength and elasticity). Once these are defined, the user can run the module by clicking 'search'. The input information is acquired, organised and processed to the modules with the trained neural networks. Each input is processed only to the modules to which it is relevant. The trained neural networks are the core of the computer program for search of conditions that satisfy the user-defined criteria. The parameters that are fixed by the user are fixed inputs of the trained NN. The other inputs, essentially the material composition, are varied by organised loops, and the trained neural networks are used to predict properties at each loop. The predicted combination of properties is compared with the user requirements at each step, and if they are satisfied, the current combination of material composition and processing parameters is suggested as a possible solution. The loops are organised so that all possible combinations between the changeable inputs are attempted. After the completion of this procedure, material compositions that satisfied the user



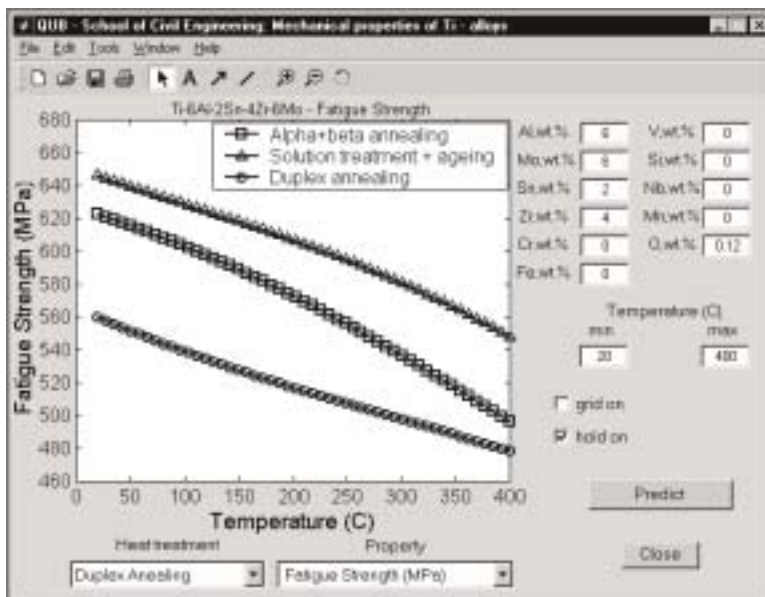
13.10 Graphical user interface of module for materials selection based on trained artificial neural network.

requirements are suggested, if such are found. In the general case, a list of possible materials compositions and processing is suggested.

In this mode, the software package developed can be used for materials selection procedures. For example, it can find material compositions that satisfy user-defined combination of mechanical properties for any work temperature. The approach used here that is based on trained artificial neural networks differs from the approaches that are based on the database search. In the latter, only a material that exists in the database can be found and suggested as a material that satisfies the user criteria. In the neural network approach, along with the existing materials, a composition of material that satisfies the criteria can be suggested even if such material does not exist. It should be restated that for this and for all modes, the software package works only within the ranges of input parameter values that are used for training.

13.3.5 Optimisation of the processing parameters

The software package can be used for optimisation of the processing parameters of a titanium alloy in order to achieve a desirable combination of properties at different working conditions. In this mode, the user can run the chosen GUI (Fig. 13.2), depending on the property concerned. The alloy composition and the working conditions (such as working temperature and environment) should be fixed on the required values. By varying the processing conditions (such as heat treatment, time, temperature, and cooling), the user can study their influence on the properties. The user can use these simulations to find optimal processing and heat treatment procedures that would produce the desired combination of properties for different working conditions and alloys. Examples for such usage of the programs are given by Malinova *et al.* (2001a), where the ANN model is used to study and optimise the influence of the processing parameters (time and temperature) on the microhardness profiles after surface nitrocarburising of steels. Here, we give an example for use of the software package for simulation of the influence of the processing route on the fatigue strength of corrosion resistant Ti-6Al-2Sn-4Zr-6Mo alloy (Fig. 13.11). The alloy composition is fixed. The desired property (in this case fatigue strength) is selected. This property is studied as a function of the temperature at different processing procedures, namely $\alpha + \beta$ annealing, solution treatment followed by ageing, and duplex annealing. In a similar way, the modules can be used to study the influences of the processing route on other selected properties for different alloy compositions.



13.11 Use of the software for optimisation of the processing procedure.

13.4 Upgrading the software system

13.4.1 Database enhancement and re-training

The model will work with sufficient accuracy within the range of the data set used in the training. If the user defines input conditions outside this range, the software will still generate an output, but it may not be correct. In such a case, the program should give a warning message that the result may not be reliable. Hence, the software system is restricted to predict with a reliable accuracy within certain ranges of input parameter values that are limited by the database used for training. As earlier mentioned, the strategy of the software developed is to create general models that will be open for constant upgrade and improvement. Following this aim, modules are developed that allow users to input their own data and to re-train the ANNs (see left part of Fig. 13.8).

Input of new data is organised in two ways. The first option is by simple adding of new data in the spreadsheet files. Since the files are dynamically linked, the new data are automatically updated in the ASCII file and introduced in the matrix M that will be used for re-training. This option is more convenient when new data are inputted in batches and the user already has the data in electronic form (as a spreadsheet). The second option is by adding data one by one using the purposely-developed graphical user interface. This option is more convenient when a single data pair is inputted.

Once the new data addition process is completed, the modules should be re-trained so they can absorb the information that is contained in the new data. This is organised by the graphical user interface for selection of the re-training parameters. The user has three options for re-training:

- Simple re-training with the optimal combination of network architecture and training algorithm that has been found in the previous training (see Section 13.2.3). This is the fastest re-training procedure. However, this option is recommended only in the cases where the amount of new data is relatively small. Input of large amounts of new data could require a different NN architecture and training algorithm.
- User-defined parameters for re-training. In this option the user can define the number of neurons in the hidden layer, training algorithm, transfer functions, etc. Advanced users who are familiar with artificial neural network modelling should use this option. Some recommendations for training parameters selection are given in Section 13.2.3.
- Re-training with all possible network architecture and training algorithms for finding the optimal combination. In this option, the program executes the entire procedure described in Section 13.2.3 for finding the optimal case of trained neural network. This is the slowest option that requires significant computational time for re-training, but it is still recommended because in this option the user can be sure that the best possible combination in terms of database distribution, network architecture and learning rule is achieved.

Organised in this way, the software system effectively accumulates and stores experience intelligently, and will constantly be improved and expanded to serve the user in the best possible way.

13.4.2 Further developments of the software

The computer programs were developed using a combination of C++ and MatLab programming language with neural network toolbox. The software products are available in versions for different platforms including Windows, UNIX and Apple Macintosh. A web-based version of the software system can be developed by implementation of Java programming.

At this stage, the models are static neural networks, i.e. they can be used for computer simulations and predictions. A properly trained and applied neural network can make decisions by itself. At later stages, the model can be developed as dynamic, i.e. it can be incorporated to control and optimise a real production technology.

13.5 Summary

Models and software products are developed for the simulation and prediction of a variety of properties of titanium alloys and correlations among processing parameters, microstructure and properties. The software programs and the models can be used for:

- prediction of mechanical properties of existing titanium alloy materials as functions of their chemical composition, heat treatment conditions and working temperature; easy comparison of mechanical properties corresponding to different conditions by plotting them together; and investigation of the influence of different factors on the mechanical properties in titanium alloys;
- simulation of TTT diagrams for titanium alloys as a function of their chemical composition and design of diagrams for new alloys; investigation of the influence of different alloying elements on β to α transformation kinetics in titanium alloys;
- simulation of S–N curves for the Ti-6Al-4V alloy under different input conditions and practical applications in solving various problems on fatigue behaviour of the titanium alloy; investigation of the influence of different factors affecting the fatigue of Ti-6Al-4V;
- significant reduction of the experimental work for measurement of TTT diagrams, S–N fatigue strength diagrams and other mechanical properties of titanium alloys;
- new alloys design;
- materials selection;
- optimisation of the alloy composition and processing parameters.

This software can benefit the industry, especially metal and alloy manufacturing companies. The models and the software are based on artificial neural network. ANN is the fastest modelling technique with a very quick return for the practice. Graphical user interfaces are developed for easy use of the models.

The models and software products developed are convenient and powerful tools for practical optimisation of the composition and processing parameters of titanium alloys in order to obtain the desired combination of properties at different working temperatures, with minimum investment in experimental work. The software products are available in versions for different platforms, including Windows, UNIX and Apple Macintosh.

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Neural network models and applications in phase transformation studies

Abstract: This chapter provides two examples of using artificial neural network (ANN) modelling for predicting, respectively, the β -transus and time-temperature-transformation diagrams as functions of alloying elements for binary and commercial titanium alloys. The first part of this chapter shows some comparisons of the ANN model developed with Thermo-Calc predictions. The second part of the chapter gives indications of how individual alloying elements will shift the C-curve and affect the martensite start temperature. This information will be of interest to persons working in the field of phase transformation of titanium alloys.

Key words: neural network, TTT diagrams, phase transformation, β -transus temperature, MatLab.

14.1 β -transus temperature

The β -transus (β_{tr}) temperature is one of the most important characteristics of titanium alloys. It is usually taken as the basic reference point when a treatment is designed. Therefore, it is very desirable to determine this temperature for a given alloy accurately, especially for some near- α alloys whose processing window is narrow. Traditionally, β_{tr} is determined experimentally by the phase disappearing method. In this method, samples are first aged to precipitate α phase. They are then reheated to various temperatures separated by 15 °C intervals, held for 15 min, followed by water quenching. The β_{tr} of the alloy studied is then no more than 15 °C above the highest temperature for which α phase is detected metallographically. The 15 °C interval can be further reduced to get a more accurate estimation of β_{tr} . β_{tr} is strongly dependent on alloy chemistry, so the measurement should be examined at a number of location points if the product to be assessed is of large scale. Such procedures are both time-consuming and costly. Since the most important influential factor on the value of β_{tr} is the alloy chemistry, it is of great importance to quantify the relationship between the β_{tr} temperature and the amount of alloying elements.

Multiple linear regression analysis has been adopted in the past, to quantify the β_{tr} temperature as a function of the alloying amounts of various elements. This type of analysis was usually developed to deal with a certain type of alloy within a certain composition range. Sometimes, results from different researchers were contradictory to each other. Moreover, linear models always suffer from the drawback that interactions between alloying elements cannot

be taken into account. Artificial neural network (ANN) modelling, which employs non-linear regression analysis tools, can overcome this disadvantage, and has found a variety of applications in materials science.

Since little prior knowledge of the physical background of the processes is required when using an ANN, and to a lesser extent when developing an ANN, this method can dramatically benefit the industry, as industrial metallurgists often have to solve their problems without full comprehension of the scientific background. This section will demonstrate using the artificial neural network modelling technique to construct a quantitative model for titanium alloys that can predict the β_{tr} temperature of a titanium alloy when the alloy chemistry is known. The β_{tr} temperature from thermodynamic calculation will also be shown, to compare with the results from ANN modelling. The influence of the database scale for ANN modelling on the model performance will also be discussed.

14.1.1 Model description

An artificial neural network provides a way of using examples of a target function to find the coefficients that make a certain mapping function approximate the target function as closely as possible. Each node (also called neuron) in the input layer represents in the network the value of one independent variable. The nodes in the hidden layer are only for computation purposes. Each of the output nodes computes one dependent variable. More details about the principles of ANN modelling can be found in Chapter 13. A three-layer (one input, one hidden and one output) ANN with sigmoid transfer functions in the hidden layer can map any function of practical interest, so a three-layer neural network model is used in this section.

Input and output parameters

The selection of the property-related parameters, or input parameters, is based on the physical background of how the target property is determined. Omitting the parameters which are not important benefits model development and simplifies further application. Because β_{tr} is mainly the function of alloy chemistry, the input for the present model is the chemical composition of the titanium alloy, whereas the output is the β_{tr} temperature.

Database construction and analysis

Construction of a reliable database is the first critical step. The data set for β_{tr} temperature modelling includes 200 input–output data pairs collected from open literature, industrial data from Timet, and the ‘Titanium and its alloys’ database compiled from data supplied by the member companies of

Titanium Information Group and Titanium Development Association and developed by MATUS Databases Engineering Information Co. Ltd. It consisted of nine input variables, and one output variable. The input variables are the concentrations of elements Al, Cr, Fe, Mo, Sn, Si, V, Zr and O. As very few alloys contain Ta and Ni, their influences are taken into account by converting their concentration to $[\text{Mo}]_{\text{eq}}$ ($[\text{Mo}]_{\text{eq}} = [\text{Mo}] + [\text{Ta}]/5 + 1.25[\text{Ni}] + \dots$), instead of considering them as individual input variables. The output variable is the β_{tr} temperature. Table 14.1 summarises some features of the data set in a statistical term.

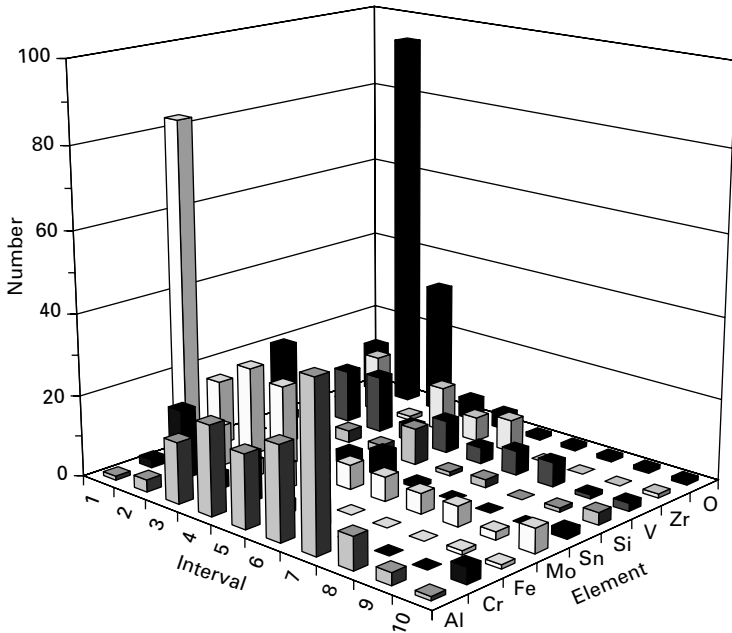
The distribution of the input values within specific concentration intervals is another very important characteristic of the data set, since it shows intervals where we can achieve higher or lower accuracy of training and prediction. The distribution here is presented as a form of histogram in ten equally spaced containers between minimal and maximal values of the alloying elements (Fig. 14.1). The model is expected to be more accurate at the places of high data density.

Training

Many parameters can be altered in order to obtain a well-trained model, an important one being the training algorithm. It has become standard for some years to train artificial neural networks by the backpropagation method. The term backpropagation refers to the manner in which the gradient is computed for non-linear multilayer networks. The early standard algorithm consists of assigning a random initial set of weights to each synapse of the neural network, then presenting the data inputs, one set at a time, and adjusting the weights with the aim of reducing the corresponding output error. This is

Table 14.1 Statistical analysis of the input and output variables for the β -transus model (concentration in wt. %)

Variable	Number of alloys containing this element	Min.	Max.	Mean	Standard deviation
Al	135	0	9.6	3.22	2.64
Cr	48	0	11.2	0.92	2.10
Fe	109	0	5.0	0.29	0.67
Mo	100	0	16.08	2.66	4.00
Sn	42	0	11.0	0.66	1.59
Si	34	0	0.5	0.03	0.09
V	64	0	20.16	2.51	4.59
Zr	41	0	11.0	0.81	1.84
O	152	0	0.9	0.12	0.13
β -transus ($^{\circ}\text{C}$)	–	670	1080	892.2	100.4



14.1 Distribution of the input data set for β -transus neural network model.

repeated for each set of data, and then the complete cycle is repeated until an acceptably low value of the sum of squares error is achieved. Such an algorithm is usually both inefficient and unreliable, requiring many iterations to converge, if it converges at all. Therefore, a number of variations of the standard algorithm have been developed, based on other optimisation techniques, with a variety of computation and storage advantages. These are detailed in The Math Works, Inc. product, Neural Network Toolbox for MatLab. One of the most popular algorithms is Bayesian regularisation (TRAINBR). TRAINBR is a MatLab command for the function. PREMNMX, POSTNMX, TRAMNMX, TANSIG, PURELIN, and NEWGRNN, which appear later, are also MatLab commands. The Bayesian regularisation (BR) algorithm usually results in ANN models which generalise well. It reduces the difficulty in determining the optimum network parameters. This algorithm itself was first used in developing the β_{tr} model, with two-thirds of the data for model training and one-third for model testing. The performance of the resulting model on the testing data was not good. Overfitting seems to have taken place. The early stopping technique was then used in combination with Bayesian regularisation. The data set was divided into three sub-data sets, which contain 100, 50 and 50 data-pairs, for training, validation and testing purposes, respectively. The model obtained this way demonstrated better

performance than using TRAINBR itself. Therefore, training was carried out by combining the early stopping technique with the TRAINBR algorithm. When dividing the three sub-data sets, the cases which contain the maximum amount of one of the alloying elements were put into the training data set. The division of the remaining cases was then done randomly.

Since backpropagation may not always find the correct weights for the optimum solution, reinitialisation and retraining of the network were carried out a number of times to obtain the best solution. Neural networks of other types may also be considered in model creation, such as radial basis function (RBF) networks. Such networks may require more neurons than standard feed-forward backpropagation networks, but often they can be designed in a fraction of the time taken to train standard feed-forward networks (The Math Works, Inc. product, Neural Network Toolbox for MatLab). In a separate work, RBF networks were created to model the M_s temperature of maraging steels (Guo and Sha, 2004). The performance was not as good as the model achieved using backpropagation algorithm, though model training took less time. RBF networks are not used here. Other new generation learning systems, such as support vector machines, are described in dedicated books (Cristianini and Shawe-Taylor, 2000; Hu and Hwang, 2001). The standard artificial neural network method used here is well-developed and comparatively has been proven to be suitable for modelling metallurgical correlations as shown in the models discussed in this chapter and in Chapter 15.

Other parameters such as data pre-processing methods, transfer functions and the number of hidden nodes were also altered to achieve the best model. A program was written to identify the model with the best performance after model training has been undertaken several hundred times with different training parameters. When each training parameter was altered manually, about 50–100 times of training were carried out to identify the best model for this new set of training parameters. This model was then stored for later comparison. Another parameter was then altered, followed by 50–100 times of training to achieve the best model corresponding to this set of training parameters. This model was then stored for later comparison. In the end, the models of best performance for different training parameters were compared with each other and the best model was chosen for use of future prediction. The optimised model for β_{tr} modelling is of 9-9-1 structure, with functions PREMNMX, POSTMNMX and TRAMNMX for pre- and post-processing. PREMNMX was used to scale inputs and targets so that they fell in the range $[-1, 1]$. Such pre-processing procedure can make the neural network training more efficient. POSTMNMX, the inverse of PREMNMX, is used to convert data back to standard units (denormalisation). TRAMNMX normalises data using previously computed minima and maxima by the PREMNMX function. It is used to pre-process new inputs to networks which have been trained with data normalised with PREMNMX. The transfer functions employed

were the hyperbolic tangent sigmoid function (TANSIG) and the linear function (PURELIN). Detailed information about these functions can be found in the manual of The Math Works, Inc. product, Neural Network Toolbox for MatLab.

14.1.2 Model performance

Two parameters are used to evaluate the performance of ANN modelling, mean error and error deviation as defined below:

$$\text{Mean error} = \frac{1}{n} \sum_{i=1}^n (A_i - T_i) \quad [14.1]$$

$$\text{Error deviation} = \sqrt{(n \sum (A_i - T_i)^2 - (\sum (A_i - T_i))^2) / n(n - 1)} \quad [14.2]$$

In the above equations, A_i is the calculated result for the i^{th} alloy, T_i is the corresponding experimental value and n is the number of alloys in the sample set. When two models have similar mean errors, both of which are smaller than the target error (10 °C in the present case), the one of smaller error deviation is considered to be better. The second column in Table 14.2 is a statistical analysis of the data sets used for different purposes. When the whole database is divided into different data sets in ANN modelling, ideally the data in each data set should be of the same distribution. The second column indicates that the data distribution is similar for the different data sets in this ANN model. Figure 14.2 illustrates the performance of this model on different data sets. It can be seen that good model performance is achieved.

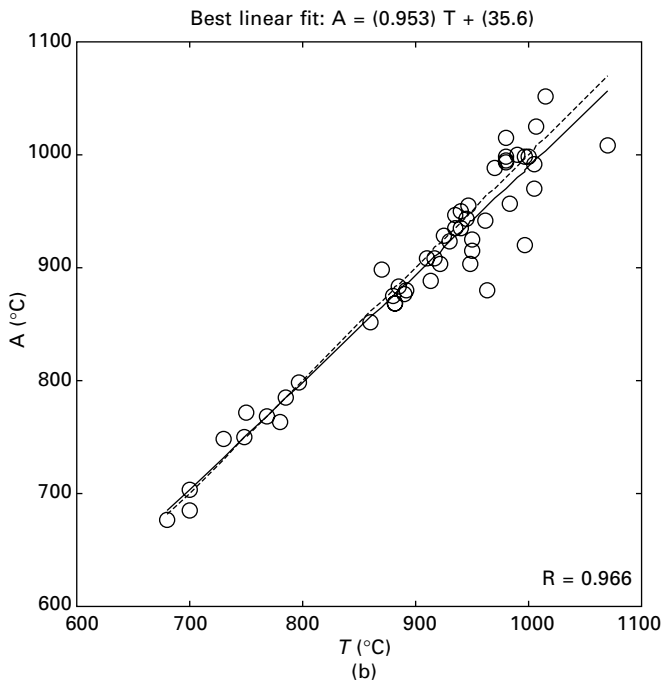
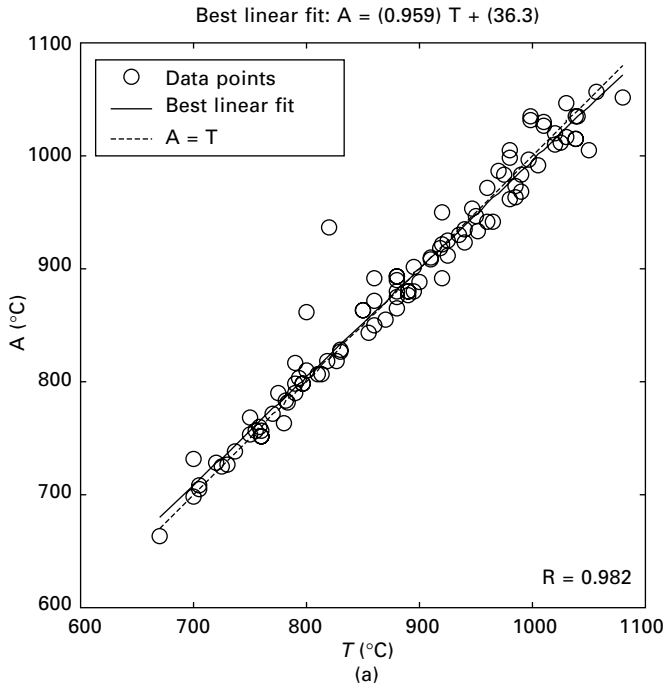
14.1.3 Phase diagram calculation of Ti–X systems

The influences of aluminium, molybdenum, vanadium, and oxygen on β_{tr} temperature are quantified using the trained model. The experimental data from literature and thermodynamic calculation using Thermo-Calc (Guo and Sha, 2000) are also plotted for comparison (Figs. 14.3–14.6). The ANN

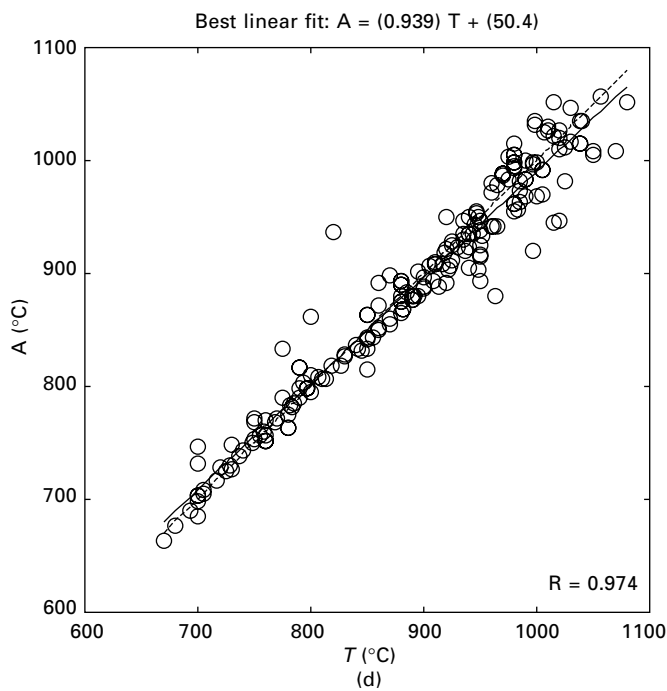
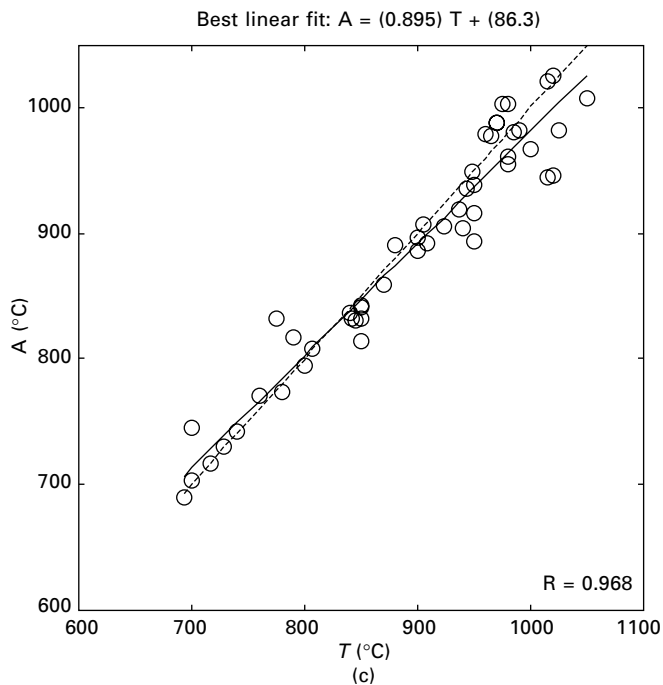
Table 14.2 Statistical analysis of ANN model (β -transus in °C)

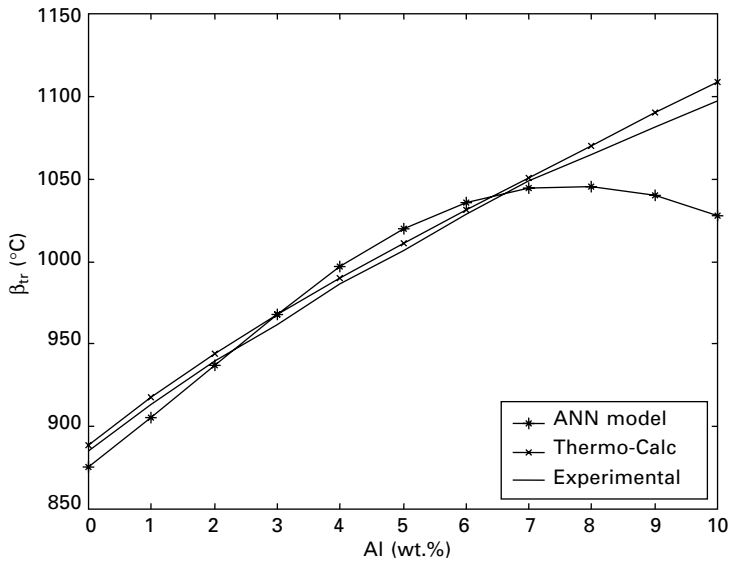
Dataset	Experimental data	Mean (A–T)*	Standard deviation (A–T)*
Training data	883 ± 104	0	20
Validation data	907 ± 94	–7	24
Testing data	894 ± 100	–8	25
Whole dataset	892 ± 100	–4	23

*A: predicted results; T: experimental results

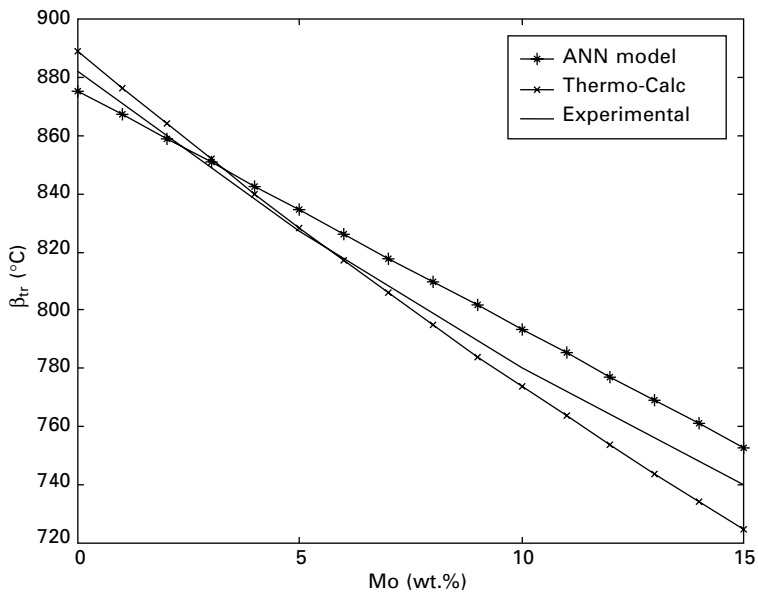


14.2 Performance of the neural network model of β -transus temperature on: (a) training, (b) validation, (c) testing, and (d) whole datasets.



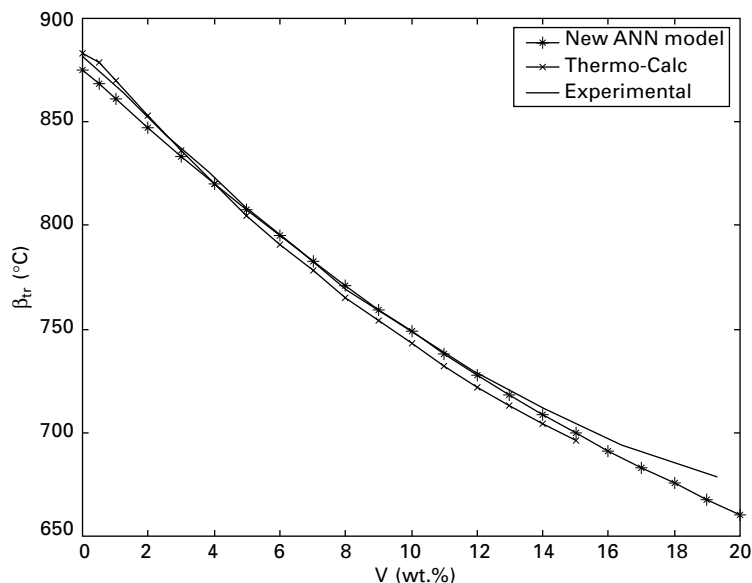


14.3 β -transus of Ti-xAl alloy.

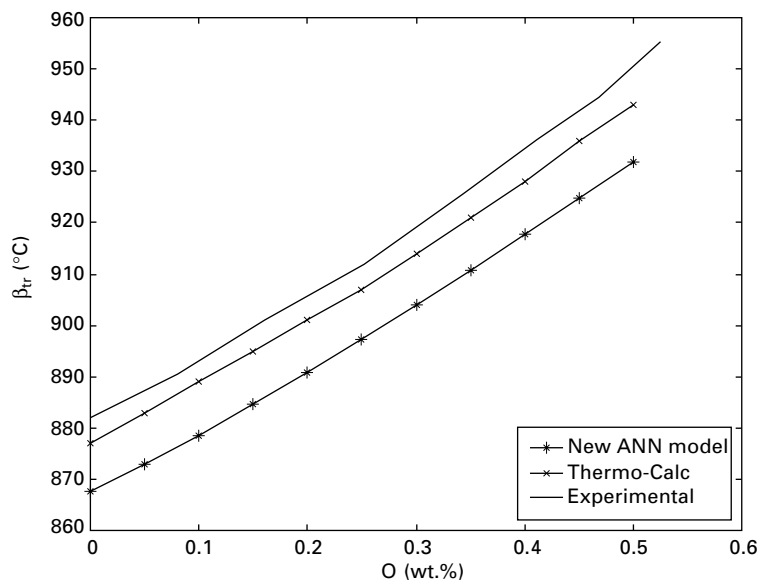


14.4 β -transus of Ti-xMo alloy.

model agrees with the experimental data very well. The error increases when the element content is out of its compositional limit. For the Ti-Al system, the error becomes very large when the amount of aluminium is over 7 wt.%. In practice, the amount of aluminium in titanium alloys is usually limited to



14.5 β -transus of Ti-xV alloy.



14.6 β -transus of Ti-xO alloy.

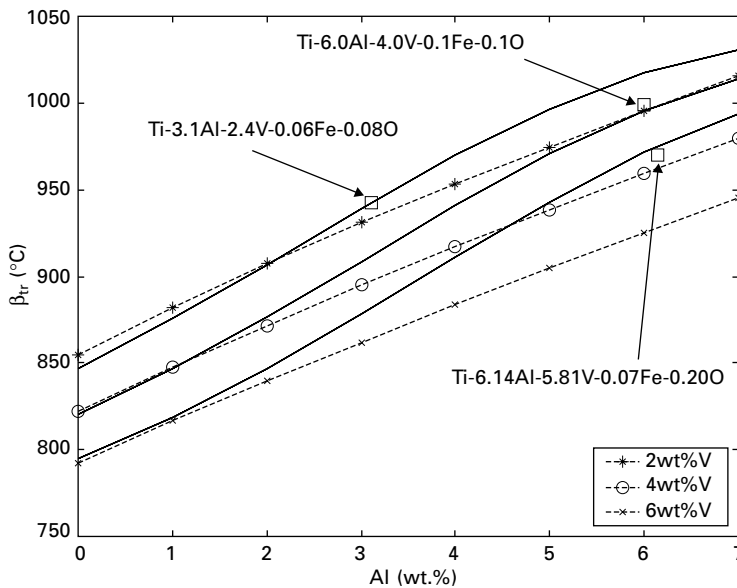
7%, and the available data for higher aluminium amount is sparse. This is thought to be the main reason for the large divergence at high aluminium content.

Generally speaking, for Ti-X (X = Al, Mo, V, O) binary phase diagrams

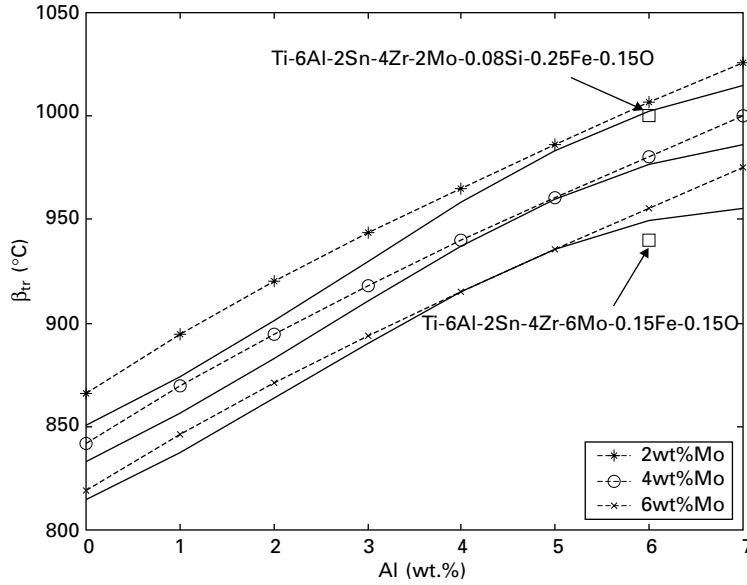
calculation, Thermo-Calc calculation gives more accurate results than ANN modelling. This might be attributed to the wide validation of the Ti-Data database during its creation and development phases, using some well-studied and commonly used phase diagrams, especially binary phase diagrams.

14.1.4 Interaction between alloying elements in multicomponent systems

The interaction between aluminium and vanadium in Ti–Al–V system is evaluated, as shown in Fig. 14.7. In this diagram, the lines with markers are results calculated using Thermo-Calc (TC), and the continuous lines show the results calculated by the ANN model. Limited experimental data are indicated in the diagram with '□' markers. The levels of iron and oxygen for both Thermo-Calc and ANN calculation were set at 0.1 wt.%. The interaction between molybdenum and aluminium in Ti-*x*Al-2Sn-4Zr-*y*Mo-0.08Si system is also evaluated (Fig. 14.8). The results calculated using Thermo-Calc are plotted in the same figure for comparison, as well as two experimental data points. From Figs. 14.7 and 14.8, the ANN model probably can give a better estimation of β_{tr} in multicomponent systems compared to Thermo-Calc calculation. However, such a conclusion should be tested by many more experimental data in the future.



14.7 Interaction between vanadium and aluminium in Ti–Al–V system.



14.8 Interaction between molybdenum and aluminium in Ti-xAl-2Sn-4Zr-yMo-0.08Si system.

14.1.5 Linear regression analysis

Linear regression analysis performed on the 200 data-pairs gives the following expression:

$$\begin{aligned} \beta_{tr} = & 882 + 21.1[Al] - 9.5[Mo] + 4.2[Sn] - 6.9[Zr] \\ & - 11.8[V] - 12.1[Cr] - 15.4[Fe] + 23.3[Si] + 123.0[O] \end{aligned} \quad [14.3]$$

The average of error in calculated β_{tr} using this equation is -1°C , and the error deviation is 27°C . Based on the above equation, two parameters $[Al]_{eq}$ and $[Mo]_{eq}$ can be used to approximately quantify the alloying effects on β_{tr} temperature of titanium alloys:

$$[Al]_{eq} = [Al] + 0.2[Sn] + 1.1[Si] + 5.8[O] \quad [14.4]$$

$$[Mo]_{eq} = [Mo] + 1.2[V] + 0.7[Zr] + 1.3[Cr] + 1.6[Fe] \quad [14.5]$$

The β_{tr} temperature can therefore be calculated using the following expression.

$$\beta_{tr} = 882 + 21.1[Al]_{eq} - 9.5[Mo]_{eq} \quad [14.6]$$

14.1.6 Summary

Artificial neural network modelling and thermodynamic calculation can accurately predict the β -transus temperature of titanium alloys when the alloy chemistry is known. The influences of the alloying elements aluminium, molybdenum, vanadium and oxygen on the β -transus temperature in binary systems can be quantitatively revealed. Thermo-Calc calculation gives a better estimation of the β -transus than the ANN model. The interactions among alloying elements V–Al, and Mo–Al are evaluated. Probably, the ANN model could give a better estimation of the β -transus than Thermo-Calc, in multicomponent systems. In addition, linear regression analysis can be used to quantify the alloying effects on β -transus.

14.2 Time–temperature–transformation diagrams

It is very important to know the kinetics of phase transformations taking place under different heat treatment regimes. The kinetics are described by time–temperature–transformation (TTT) and continuous-cooling–transformation (CCT) diagrams. The knowledge of these diagrams for different alloys would allow the optimisation of the processing parameters (temperature, time, cooling/heating rates) in order to achieve desirable microstructures.

The idea of computer modelling and prediction of these diagrams is very attractive. There is limited work on physical modelling of TTT diagrams for Ti-alloys based on the Johnson–Mehl–Avrami theory. These models, however, concern a very limited number of alloy types, and they do not predict what would happen if the composition is changed.

This section will demonstrate an artificial neural network model for the prediction of TTT diagrams of titanium alloys as a function of their composition. It also aims to better explain the influence of different alloying elements over the transformation kinetics.

14.2.1 Model description

A general scheme of the designed NN is given in Fig. 13.1a.

Database, analysis and pre-processing

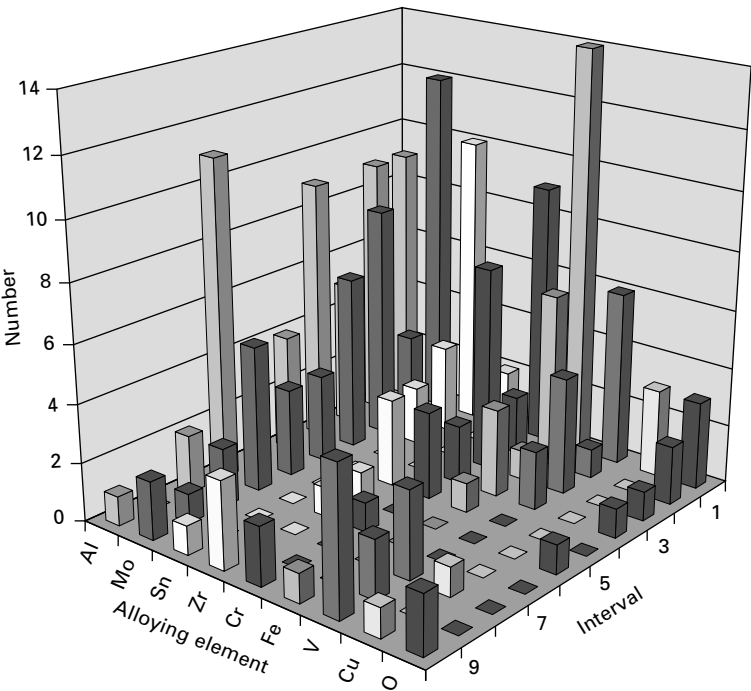
For reliable training and performance of any NN, we need an appropriate database. The data set is constructed by collecting available TTT diagrams for titanium alloys. The full list of the literature sources for these is given by Malinov *et al.* (2000). In total, 189 TTT diagrams for different Ti alloys are used fully or partly in the database. About 35% of the diagrams are for binary Ti–X alloys and the remainder concern ternary or more complex

systems. Most of the diagrams are for commercial titanium alloys. The input parameters of the NN are the chemical compositions of the alloys. Nine inputs are chosen – the eight most frequently used alloying elements (Al, Mo, Sn, Zr, Cr, Fe, V, Cu) and oxygen (see Fig. 13.1a). Some alloys also contain Nb, Co and Ni. However, since the number of the alloys containing these elements is small, either these alloys are excluded from the data set or the extra elements are converted to their molybdenum equivalent. The inputs are listed in Table 14.3, and the distribution of their values is presented in Fig. 14.9.

Table 14.3 Statistical analysis of the input variables for the TTT model

Alloying element	Al	Mo	Sn	Zr	Cr	Fe	V	Cu	O
Number of alloys containing this element	52	46	17	11	27	27	24	6	11*
Range (wt.%)	0–8.0	0–15.7	0–11.0	0–6.4	0–11.0	0–5.2	0–16.0	0–8.0	0.1–0.55

*This is the number of alloys containing more than 0.1 wt.% O; this was adopted as the minimum and inevitable oxygen level. When the oxygen level of any alloy was unknown, it was taken as 0.1wt.%.



14.9 Distribution of the input data set for TTT neural network model.

Typically, neural networks work with numerical formats of both input and output data. Therefore the output parameter, which in this particular case is a graph, has to be presented in a numerical format. Thus, all diagrams are scanned, put in electronic format and rescaled in one same scale.

Figure 14.10 shows the approach used here for digitising and presenting a diagram as a set of numbers. The nose point (n in Fig. 14.10) is used as a base point. This point is specified with its two coordinates – temperature (T_n) and time (τ_n). Thereafter, the entire curve is described by a set of numbers giving the relative increase of the time when the temperature is increased or decreased by ΔT . These values are computed using:

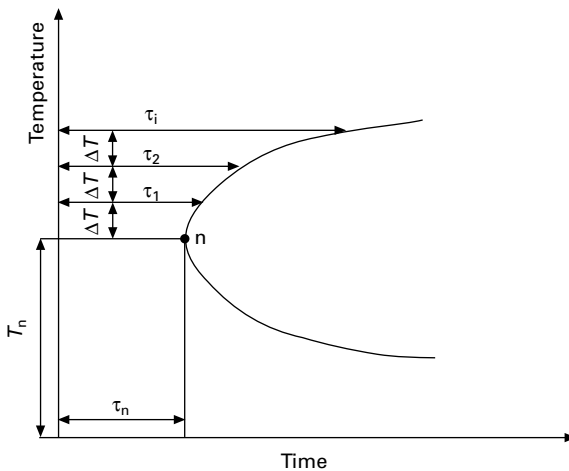
$$rt_i = \frac{\text{time}(T + \Delta T)_i}{\text{time}(T)_i} \quad [14.7]$$

for the upper part of the curve and:

$$rt_i = \frac{\text{time}(T - \Delta T)_i}{\text{time}(T)_i} \quad [14.8]$$

for the lower part of the curve, where: rt_i , is relative time; $\text{time}(T)_i$, is time corresponding to temperature T ; $\text{time}(T + \Delta T)_i$, $\text{time}(T - \Delta T)_i$, are times corresponding to temperature $T + \Delta T$ and $T - \Delta T$, respectively.

The martensite start temperature (M_s) is also included as an output to complete the TTT diagrams. In this way, 23 outputs are introduced, namely: time and temperature of the nose point (T_n and τ_n), ten numbers describing the upper part of the curve, ten numbers describing the lower part of the curve, and martensite start temperature (M_s).



14.10 Digitisation of TTT diagrams.

The following remarks are necessary:

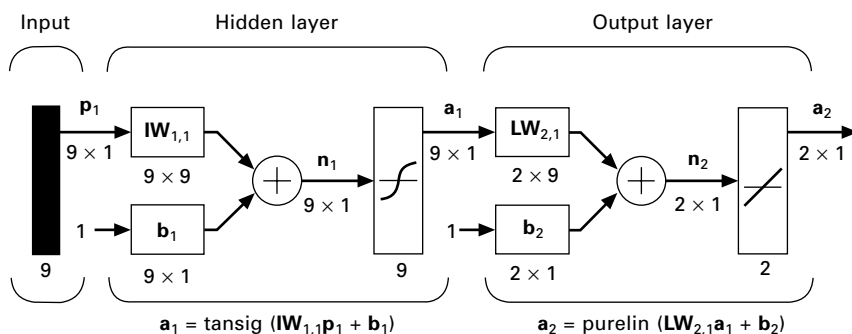
- The data for M_s temperature are mainly from binary systems. Only 30 data pairs for more complicated systems are used.
- In some cases, there is a contradiction between the TTT diagrams for the same alloy taken from different sources and authors.
- All diagrams used are for alloys after solution treatment in the homogeneous β -field (50–100 °C above β -transus for 20–30 min). No alloy had solution heat treatment within the $\alpha + \beta$ field.
- All TTT diagrams used concern the kinetics of the monovariant β to $\alpha + \beta$ transformation.
- TTT diagrams for decomposition of martensite during reheating (ageing) are not included.
- TTT diagrams describing the invariant decomposition of β through eutectoid or peritectoid transformation are not included.
- Only data for the start of the transformation are treated.

Training

The general model of the created NN (Fig. 13.1a) consists of separate networks for:

- (1) the temperature and the time of the nose point (T_n and τ_n);
- (2) description of the curve; and
- (3) M_s temperature.

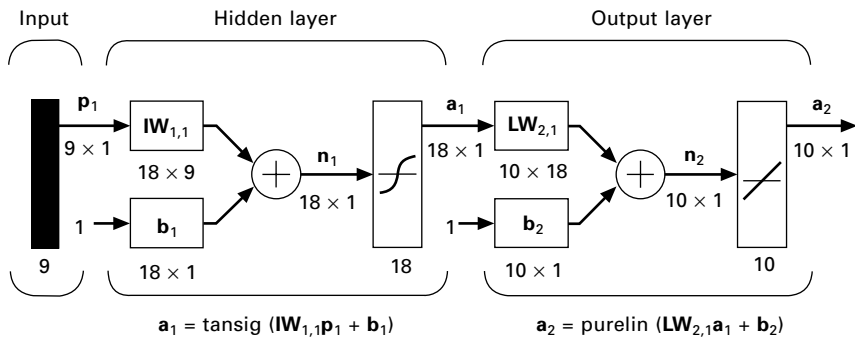
In Fig. 14.11, an example of the neural network for the prediction of the nose point is given. Figure 14.12 shows the architecture of the neural network for the prediction of the curve above and below the nose point (τ_1 , τ_2 , etc., in Fig. 14.10).



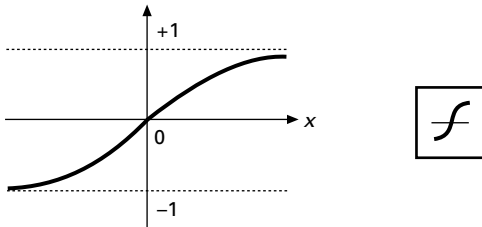
14.11 Architecture of the neural network for TTT diagram nose point simulation.

Different numbers of neurons in the layers were applied for different networks (Fig. 14.12). Before the training of the network, both input and output variables were normalised within the range from -1 to 1 using Eq. [13.1b].

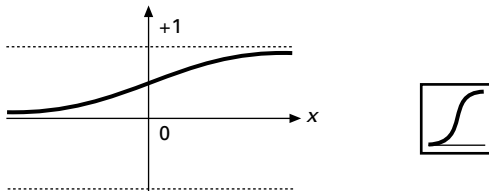
In the hidden layer, tan-sigmoid transfer function $\left(f(x) = \frac{2}{1 + e^{-2x}} - 1, \text{ Fig. 14.13}\right)$ and log-sigmoid transfer function $\left(f(x) = \frac{1}{1 + e^{-x}}, \text{ Fig. 14.14}\right)$ were attempted. When the logsig was applied, the inputs and the outputs were normalised within the range $0-1$ using



14.12 Architecture of the neural network for upper and lower part of the TTT diagram simulation.



14.13 Tan-sigmoid transfer function used in the hidden layer.



14.14 Log-sigmoid transfer function used in the hidden layer.

Eq. [13.1a]. The networks were automatically initialised with the default parameters. The Levenberg–Marquardt algorithm was used. The learning rate was 0.01 and the epoch (the number of training cycles) was 1000.

When the training was performed against a validation set, the groups were as follows: one half, training set; one quarter, validation set; and one quarter, test set. By varying all the parameters described above, trained NNs with the best performance (Fig. 14.15) were achieved.

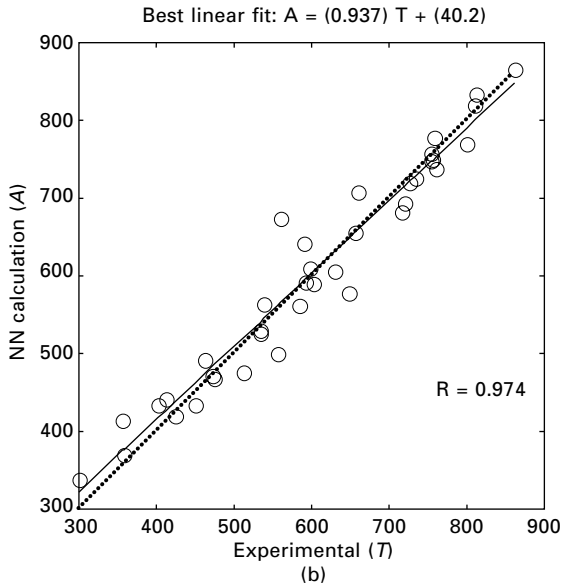
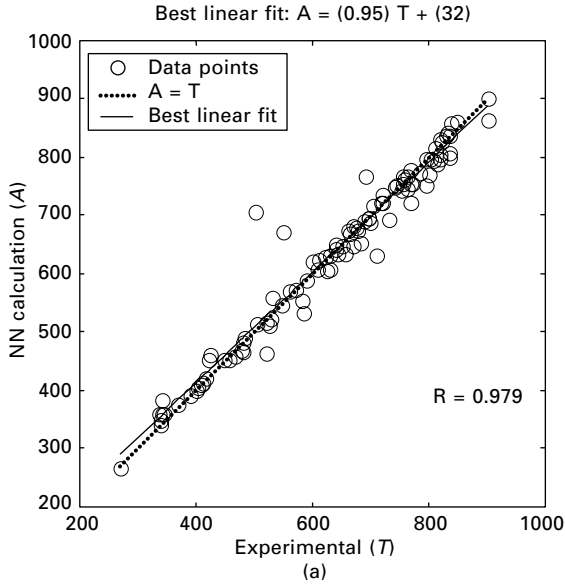
Figure 14.15 shows an analysis of the network response, using the linear regression between the network output and the corresponding targets. For all trained NNs, the outputs track the targets very well. The main source of deviation is the above mentioned contradiction in the experimental data. Similar performance is achieved for the other NNs used for the simulation of the curve description and the M_s . R -values for all cases of training, validation and test data sets are above 0.92. This means that a good performance of the NN has been achieved, and the network can be used for further simulation.

14.2.2 Calculation results and comparison with experiments

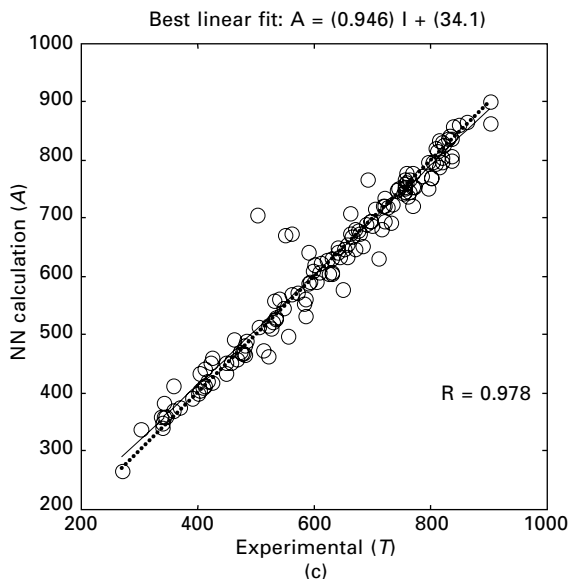
On the basis of the trained neural networks, the model for the simulation of TTT diagrams for titanium alloys has been created. This model can be used to predict diagrams with sufficient accuracy within the range of the used data set (see Table 14.3 and Fig. 14.9). In the following, some TTT diagrams for different Ti alloys are predicted by this model and are thereafter analysed by seeking some explanation of the results from the metallurgical point of view (see Figs. 14.16–14.18).

The influence of aluminium (Fig. 14.16a) and vanadium (Fig. 14.16b) on the decomposition of the β phase for one of the most popular titanium systems (Ti–Al–V) is modelled. TTT diagrams are computed assuming increased and decreased content of aluminium or vanadium from Ti–6Al–4V. With the increasing of the aluminium content, the C-curve, indicating the start of the β to $\alpha + \beta$ transformation, is shifted to higher temperatures and shorter times (see Fig. 14.16a). The influence of vanadium is the opposite; increasing the vanadium content shifts the C-curve to lower temperatures and longer times (see Fig. 14.16b). The predicted dependence of the temperature is in accordance with the well established influence of the above elements over β -transus temperature. From the metallurgical point of view, it is also not surprising that, in general, the incubation period is shorter when the transformation takes place at higher temperatures because of the higher diffusivity. The results are therefore consistent with what is expected from the theory of phase transformations.

The influence of vanadium on the martensite start temperature shows a similar tendency. With increasing vanadium content, M_s is decreased (Fig.



14.15 Performance of the neural network model of the nose point temperature, in °C, of TTT diagrams on: (a) training, (b) testing, and (c) whole datasets.



14.15 Continued

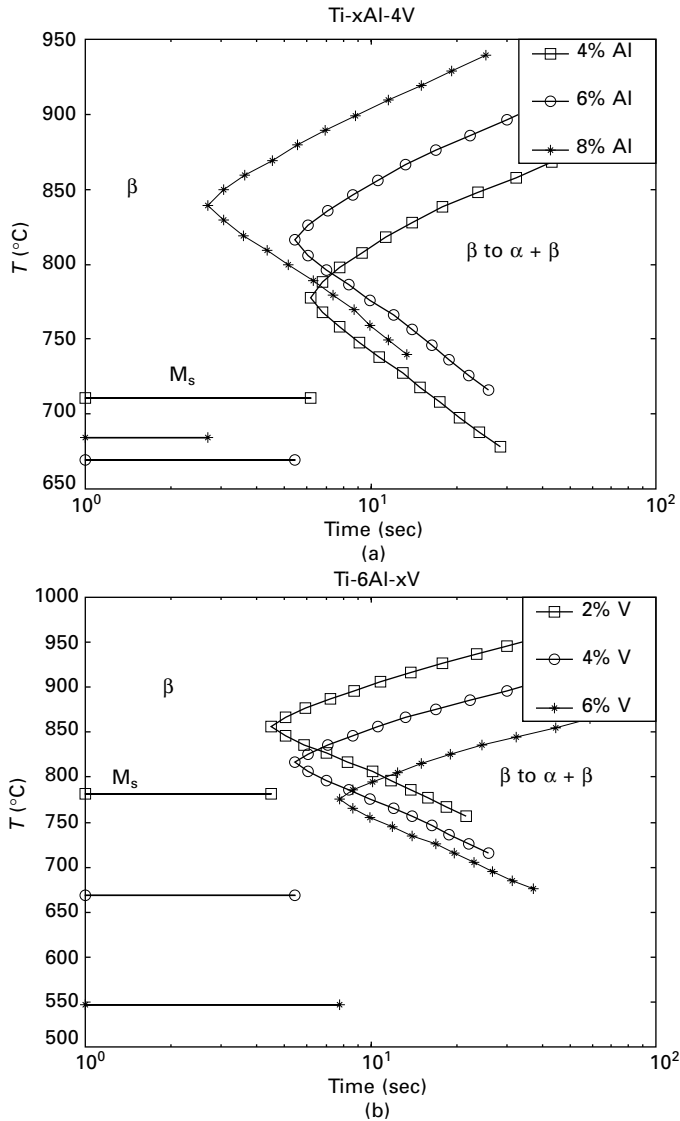
14.16b). The modelled aluminium influence on M_s seems to be more complicated. Such a character of the aluminium influence has been inducted into the model from the data set.

For Ti-6Al-4V alloy, the influence of the interstitial oxygen is also modelled (Fig. 14.17). Attention is paid to oxygen, as the level of impurities, especially oxygen, has a high influence on the behaviour of titanium and its alloys.

There is a very large influence of oxygen on the transformation kinetics. A very small increase of the oxygen content causes a significant shift of the curve to higher temperatures and shorter times (see Fig. 14.17). Hence, oxygen acts in the same direction as aluminium, but much more strongly. Such influence of oxygen over TTT diagrams (especially start curves) of titanium alloys was reported for Ti-Mo and VT15, on the basis of experimental studies. The predicted TTT diagrams for Ti-6Al-4V match well with the experimental one (Fig. 14.17).

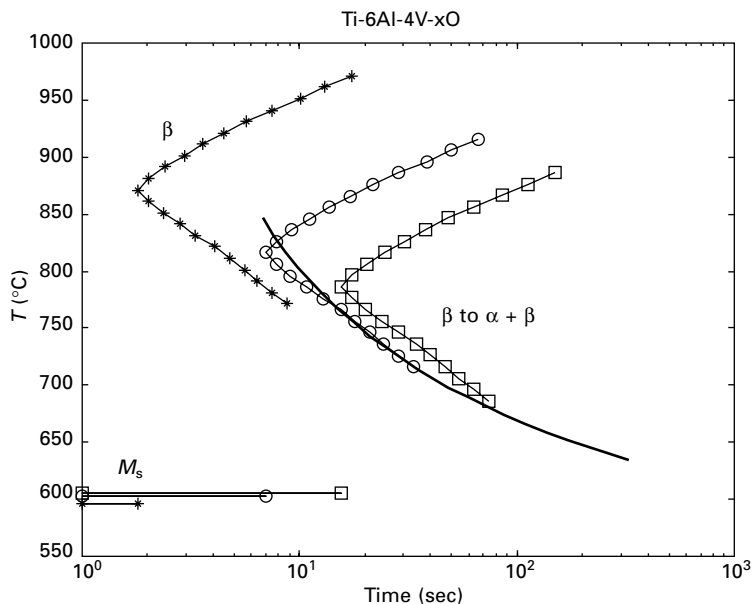
The predicted martensite start temperature is not affected so much when the oxygen content varies in the range from 0.05 to 0.2 wt.%. When the oxygen content is increased beyond 0.2 wt.%, M_s increases.

Although the calculated oxygen influence on the TTT diagram of Ti-6Al-4V is reasonable, in the data set, only 11 alloys contain oxygen. This means that the oxygen influence has been simulated on the basis of the participation of only those alloys in the training process of the model. Therefore, the modelling of the oxygen content should be performed with caution, and large deviations are possible when the model is applied.

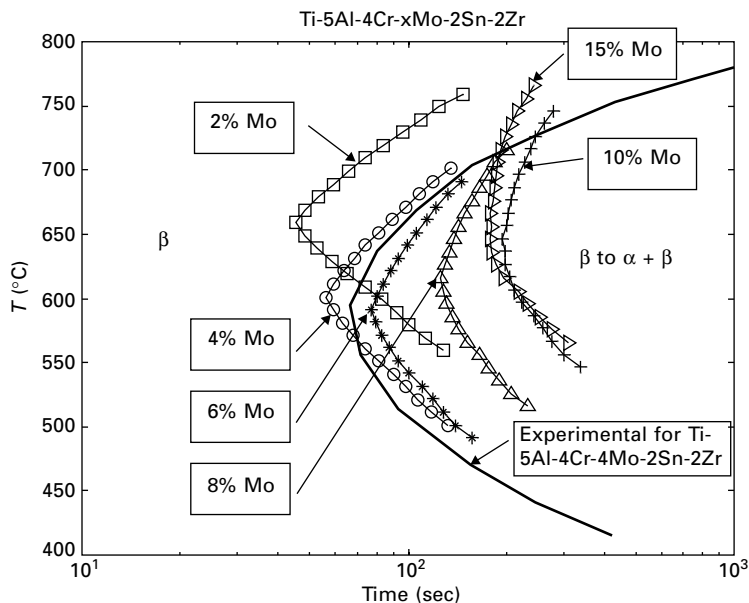


14.16 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in Ti-Al-V alloy assuming different (a) aluminium and (b) vanadium contents.

Molybdenum is another very important and frequently used alloying element in titanium alloys, and its influence is also illustrated by using the model. The well known commercial alloy Ti-5Al-4Cr-4Mo-2Sn-2Zr was chosen. TTT diagrams were calculated assuming different molybdenum contents (Fig. 14.18). They do not show any clear tendency for the influence of the



14.17 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in Ti-6Al-4V alloy with different oxygen levels: $\square$, 0.05; $\circ$, 0.10; $*$, 0.20 wt.% O. Bold line is experimental result.

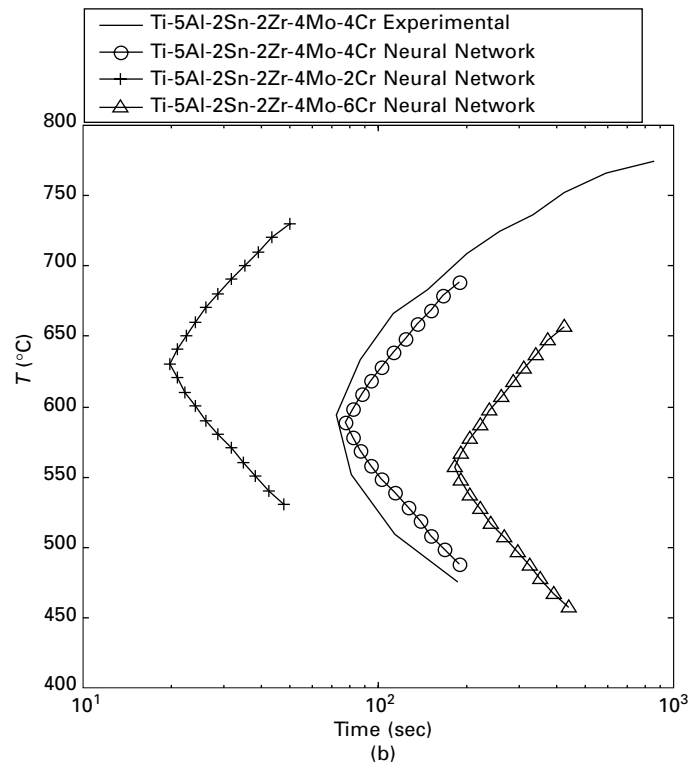
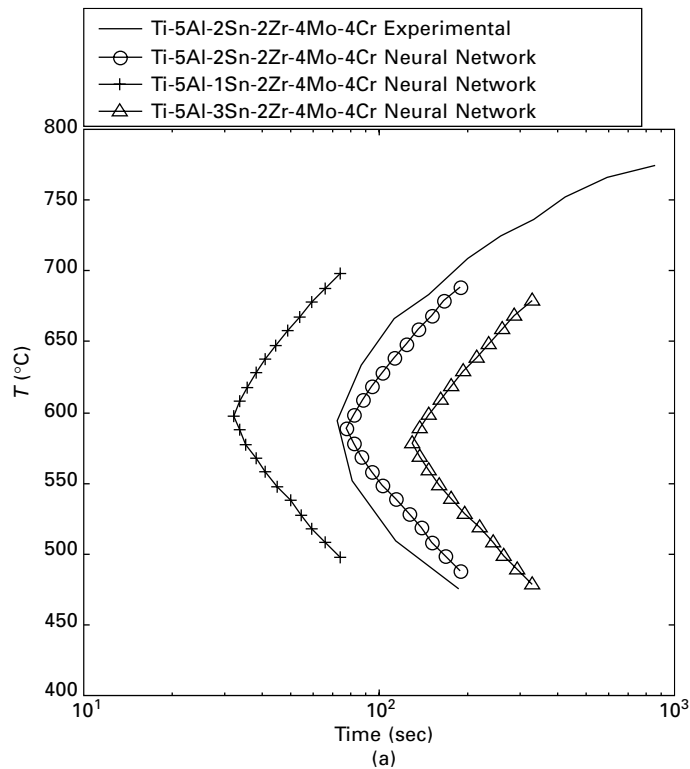


14.18 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in Ti-5Al-4Cr-xMo-2Sn-2Zr alloy assuming different molybdenum content.

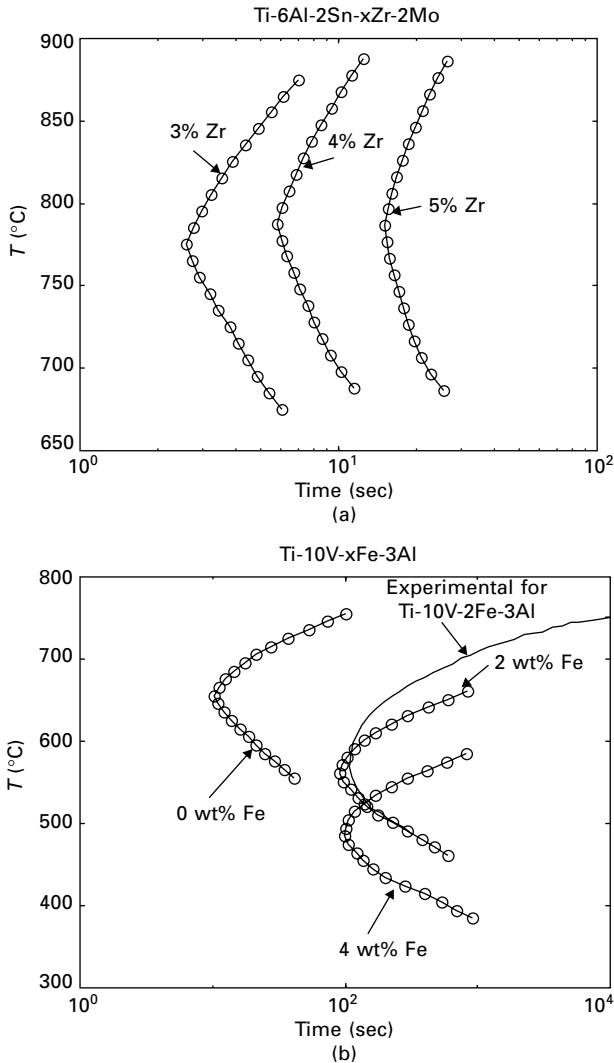
molybdenum content on the C-curve shifting. The influence is more or less unsystematic. For example, the temperature of the nose point first decreases at low content and then increases with increasing molybdenum content. The trend of the incubation time variations is also unclear. A similar, apparently erratic influence of molybdenum was reported for binary Ti–Mo alloys. This effect is most probably due to the complex and dual influence of molybdenum on the thermodynamic and the kinetic parameters. The significant changes of the C-curve shape in these cases confirm this duality.

The model was used to study the influence of other typical and commonly used alloying elements in titanium alloys. The influence of tin and chromium on the isothermal transformation kinetics is simulated. TTT diagrams are calculated by the NN model assuming increased and decreased contents of tin and chromium in the Ti-5Al-4Cr-4Mo-2Sn-2Zr alloy. With the increasing of either tin or chromium contents, the C-curve is shifted to lower temperatures and longer times (Fig. 14.19). Hence, these two elements have similar influence to vanadium. There is a good correspondence between the neural network simulations and the experimental TTT diagram for the Ti-5Al-2Sn-2Zr-4Mo-4Cr alloy.

Figure 14.20 demonstrates further examples of the use of the model developed to simulate the influence of zirconium (Fig. 14.20a) and iron (Fig. 14.20b) on the start of the β to $\alpha + \beta$ transformation in Ti 6-2-4-2 and Ti 10-2-3 alloys, respectively. TTT diagrams are calculated, assuming increased and decreased contents of zirconium and iron from their usual contents (4 wt.% zirconium in Ti 6-2-4-2 alloy and 2 wt.% iron in Ti 10-2-3 alloy). The increase of the zirconium amount shifts the C-curve to longer times, probably due to the decrease in diffusivity. At the same time, there is no appreciable effect of zirconium on shifting of the curve along the temperature scale. This simulation result is in agreement with the binary Ti–Zr phase diagram, where an increase of zirconium from 0 to 5 wt.% causes only slight decrease of the β -transus temperature, about 15 °C. The increase of iron in Ti 10-2-3 alloy causes a shift in the TTT diagram to lower temperatures and longer times (Fig. 14.20b). The nose point is shifted down by about 150 °C when the iron content is increased from 0 to 4 wt.%. Again, this simulation result is in agreement with the binary Ti–Fe phase diagram, according to which increase of iron from 0 to 4 wt.% causes decrease of the β -transus temperature by more than 100 °C. The shift of the C-curve to longer times is due to decrease in diffusivity because (i) the phase transformation takes place at lower temperatures and (ii) the presence of an alloying element decreases the diffusion coefficient. Figure 14.20b also shows good correspondence between the model simulations and experimental data for the usual composition of Ti 10-2-3 alloy. In addition, there is good correspondence between the neural network model simulations of the TTT diagram and same diagrams obtained by other methods.



14.19 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in Ti-5Al-2Sn-2Zr-4Mo-4Cr alloy assuming different (a) tin and (b) chromium contents.



14.20 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in (a) Ti-6Al-2Sn-4Zr-2Mo alloy assuming increased and decreased zirconium content, and (b) Ti-10V-2Fe-3Al alloy assuming increased and decreased iron content.

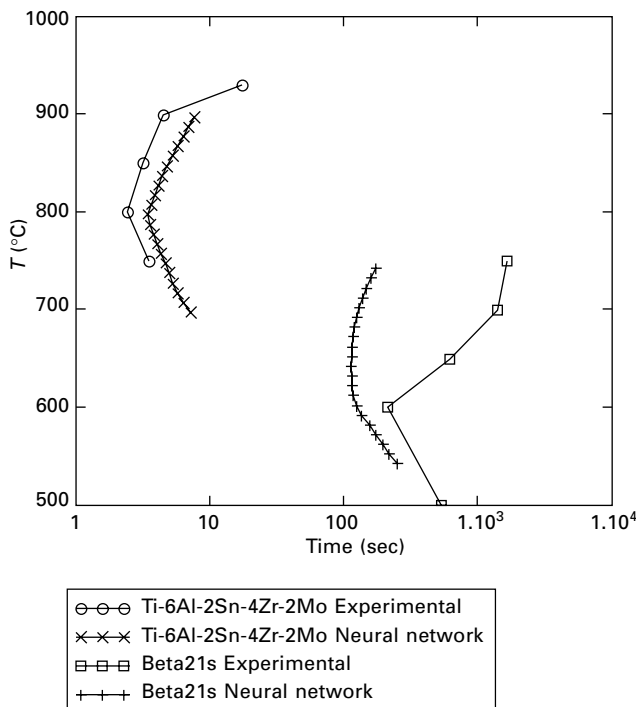
The NN model was developed based only on collected experimental TTT diagrams published by other authors. Chapter 6 has discussed experimental study of the kinetics of the β to $\alpha + \beta$ phase transformation in popular titanium alloys at isothermal conditions. Using resistivity techniques, microscopical examinations and X-ray measurements, we have designed TTT diagrams for Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo, Ti-8Al-1Mo-1V and

β 21s. These experimental TTT diagrams are compared with those predicted from the NN model (Fig. 14.21) and a good correspondence is observed.

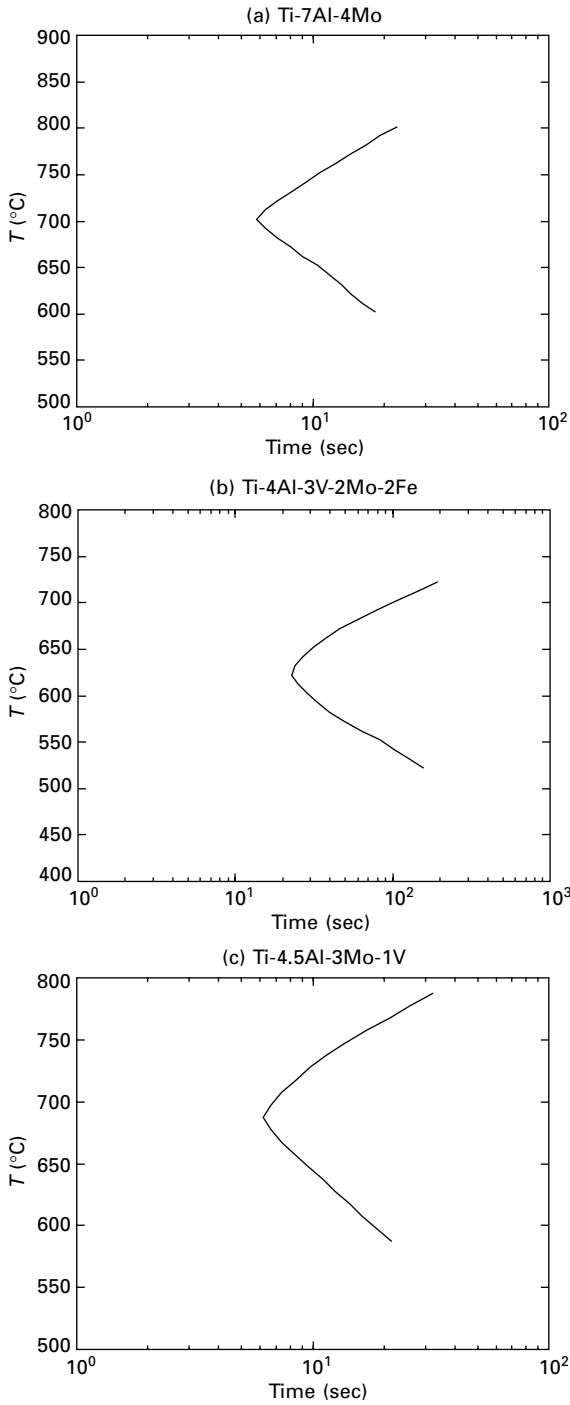
14.2.3 Prediction of TTT diagrams for commercial alloys

TTT diagrams for some commercial alloys have been calculated (see Fig. 14.22). Some of the most popular titanium alloys are chosen for which no TTT diagrams are available in the literature. In the computation of all TTT diagrams in Fig. 14.22, an oxygen level of 0.1 wt.% is assumed. When iron is not an alloying element, its content is assigned as 0.15 wt.%. The simulated TTT diagrams are consistent with what might be expected from a knowledge of the phase transformation in titanium alloys.

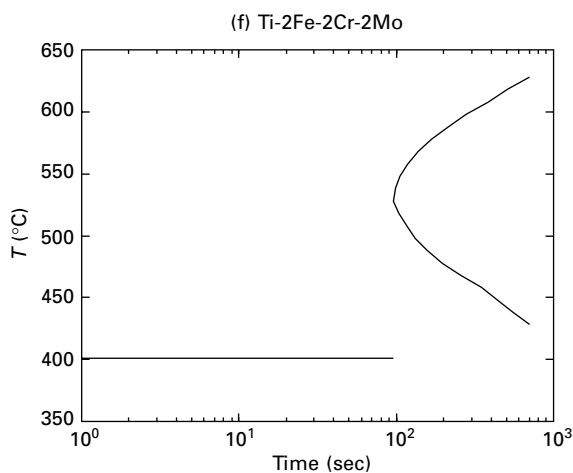
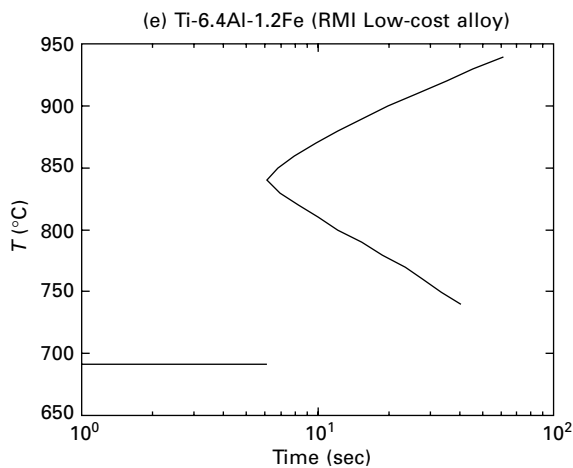
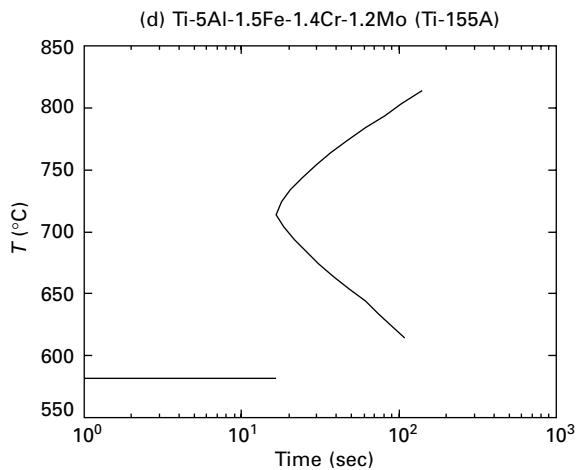
The diagrams in Fig. 14.22 could be used for explaining the transformation kinetics during cooling for corresponding alloys. In Fig. 14.23, TTT diagrams are shown for an additional set of titanium alloys for which no TTT diagrams are available in the literature, namely Ti-2.5Cu (IMI 230), Ti-12V-2.5Al-2Sn-2Zr and Ti-13V-2.7Al-7Sn-2Zr.

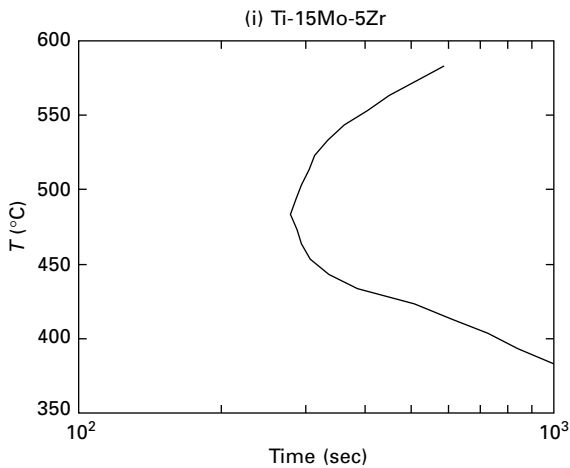
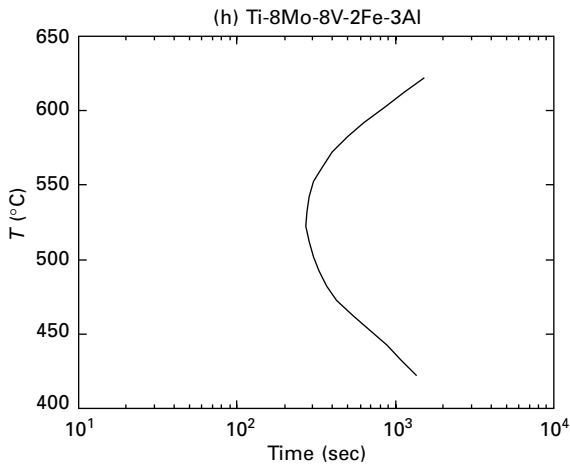
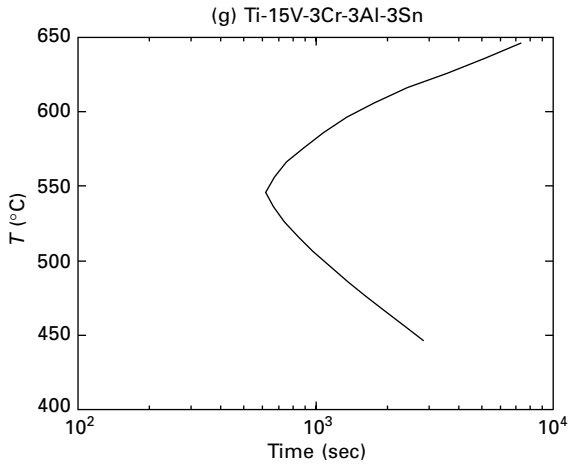


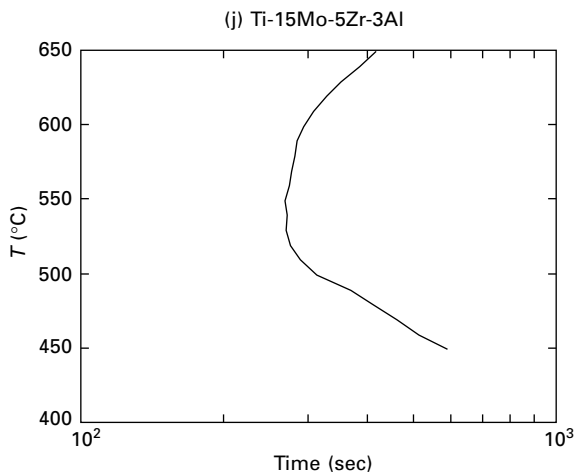
14.21 Calculated and experimental TTT diagrams for start of β to $\alpha + \beta$ transformation in Ti-6Al-2Sn-4Zr-2Mo and β 21s titanium alloys.



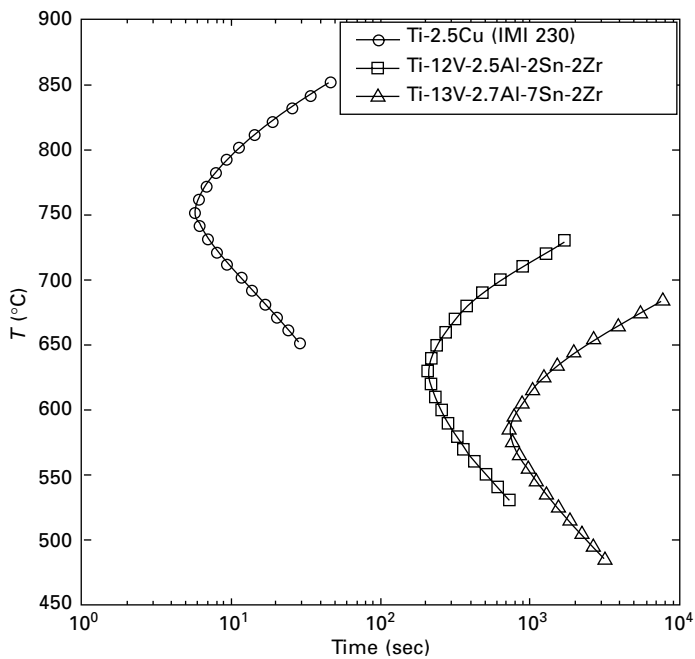
14.22 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in some commercial titanium alloys.







14.22 Continued



14.23 Calculated TTT diagrams for start of β to $\alpha + \beta$ transformation in additional commercial titanium alloys.

14.2.4 Summary

A model for prediction of TTT diagrams for titanium alloys has been created, based on a neural network analysis, using data from the published literature.

The neural network has been used to study the influence of different alloying elements on transformation kinetics in titanium alloys. It has been shown that:

- aluminium shifts the C-curve to higher temperatures and shorter times;
- vanadium shifts the C-curve to lower temperatures and longer times;
- molybdenum has a dual influence on the transformation kinetics;
- small increases in the oxygen level induce significant shifts of the C-curve to higher temperatures and shorter times.

Using the model, TTT diagrams for a number of commercial titanium alloys have been predicted. The predictions of the model are consistent with what might be expected from a knowledge of titanium alloys and phase transformation theory.

A graphical user interface for use of the model has been created. The program and the model can be used for:

- simulation of TTT diagrams for titanium alloys as a function of chemical composition;
- investigation of the influence of different alloying elements on the β to α transformation kinetics in titanium alloys;
- optimisation of the chemical composition;
- significant reduction of the experimental work for measurement of TTT diagrams for titanium alloys.

In the chapter, we have stressed the consistence between neural network predictions and a knowledge for the phase transformations in titanium alloys, especially in sections 14.2.2 and 14.2.3.

14.3 An example of MatLab program code for neural network training

The following example is for one particular combination of NN parameters, including training algorithm, transfer function and NN architecture (number of neurons in the hidden layer). During the development of the models, these parameters were changed in order to find the best combination of training algorithm, transfer function and NN architecture.

```
%This program is a part of NN for prediction of %properties
in Ti alloys
%Rm
%Training

%the following reads data file and put it into matrix M
load tb_Rm.txt;
```

```

M = tb_Rm;

%Dimensions
sz = size(M);
rws = sz(1);
cls = sz(2);

%Generates random
rnd1 = rand(rws);
rnd = rnd1(:,1);
M_r = M;
M_r(:,16) = rnd;
M_r = sortrows(M_r,16);
M = M_r(:,1:15);

%The next divide the data into train and test groups
M_all = M(1:rws,:);
M_tr = M(1:471,:);
M_val = M(471:rws,:);

%inputs
PP_all = M_all(:,2:14);
PP_tr = M_tr(:,2:14);
PP_val = M_val(:,2:14);

%outputs
TT_all = M_all(:,15);
TT_tr = M_tr(:,15);
TT_val = M_val(:,15);

p_all = PP_all';
p_tr = PP_tr';
p_val = PP_val';

t_all = TT_all';
t_tr = TT_tr';
t_val = TT_val';

%normalization
[ pn_tr,minp_Rm,maxp_Rm,tn_tr,mint_Rm,maxt_Rm] =
premnmx(p_tr,t_tr);

```



```

%min and max of the input
PR = [ min(pn_tr') ; max(pn_tr') ]' ;

%creating a network
net_Rm=newff(PR, [ 13,1], {'tansig', 'purelin'}, 'trainbr');

%training parameters
net_Rm.trainParam.show = 5;
net_Rm.trainParam.lr = 0.01;
net_Rm.trainParam.epochs = 250;
net_Rm.trainParam.goal = 0.00000001;

%training
net_Rm=train(net_Rm,pn_tr,tn_tr);

%post training analyses

an = sim(net_Rm,pn_tr);
a = postmnmx(an,mint_Rm,maxt_Rm);

figure(1)
[ m(1),b(1),r(1)] = postreg(a(1,:),t_tr(1,:));

p_val_n = tramnmx(p_val,minp_Rm,maxp_Rm);
a_val_n = sim(net_Rm,p_val_n);
a_val = postmnmx(a_val_n,mint_Rm,maxt_Rm);

figure(2)
[ m(2),b(2),r(2)] = postreg(a_val(1,:),t_val(1,:));

p_all_n = tramnmx(p_all,minp_Rm,maxp_Rm);
a_all_n = sim(net_Rm,p_all_n);
a_all = postmnmx(a_all_n,mint_Rm,maxt_Rm);

figure(3)
[ m(3),b(3),r(3)] = postreg(a_all(1,:),t_all(1,:));

%save('tr_Rm1','net_Rm','minp_Rm','maxp_Rm','mint_Rm','maxt_Rm')

```

14.4 References

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Neural network models and applications in property studies

Abstract: A model is described in detail for the prediction of properties of titanium alloys at different temperatures as functions of processing parameters and heat treatment cycles. The chapter also discusses how to use the model for the optimisation of processing and heat treatment parameters. It continues with introducing a separate model, developed for prediction of fatigue stress life S-N diagrams for Ti-6Al-4V alloy under various conditions, again using an artificial neural network. The third part of the chapter shows a model for the prediction of the correlation between alloy composition and microstructure and tensile properties in γ -based titanium aluminide alloys using ANN.

Key words: neural network, mechanical properties, fatigue, microstructure-property correlations, tensile properties.

15.1 Correlation between processing parameters and mechanical properties

We will present a systematic account of the artificial neural network models for the analysis and the prediction of the mechanical properties of titanium alloys as functions of the processing (heat treatment) parameters and alloy composition. The work is motivated by the desire to create a tool for optimisation of the processing parameters and the alloy composition.

15.1.1 Model description

A most general scheme of the model is given in Fig. 13.1b. The input parameters of the neural network are alloy composition, heat treatment parameters and work (test) temperature. The composition includes the most commonly used alloying elements in titanium alloys, namely Al, Mo, Sn, Zr, V, Cr, Fe, Cu, Bi, Si, Nb, Ta, Mn, and O. Typical heat treatments of titanium alloys are taken into account: (i) annealing in α , $\alpha + \beta$ and β regions; (ii) solution treatment in β and $\alpha + \beta$ regions followed by ageing at different temperatures; (iii) duplex annealing. Since the titanium alloys are considered as desirable and sometimes essential for many structural applications at high temperatures, the test/work temperature is included as an input in the model. In this way, the model is extended to trace the correlation ‘processing parameters – working conditions (temperature) – mechanical properties’.

The outputs of the neural network model are the nine most important mechanical properties, namely ultimate tensile strength, tensile yield strength,

elongation, reduction of area, impact strength, hardness, modulus of elasticity, fatigue strength and fracture toughness.

Data set and input/output parameters

The database was constructed by collecting available data on mechanical properties for titanium alloys with different heat treatment conditions and working temperatures. In total, 764 input/output data pairs were collected (see Appendix at the end of this chapter for list of the alloys used).

The selection of the input parameters is a very important aspect of neural network modelling. Before training, the number of input parameters should be restricted by ignoring the dependent input parameters. In this model the following were used as input parameters.

Alloy composition

After pre-processing analysis, the 14 alloying elements initially chosen (see above) were reduced to 11, namely Al, Mo, Sn, Zr, Cr, Fe, V, Si, Nb, Mn and O. Cu, Bi and Ta were each contained in only one alloy, Ti-2.5Cu (IMI 230), Ti-6Al-2Sn-1.5Zr-1Mo-0.35Bi-0.1Si and Ti-6Al-2Nb-1Ta-0.8Mo, respectively, at different conditions and temperatures. The data pairs containing Cu and Bi were excluded from the training database, while Ta, where present, was converted to Nb equivalent. When the oxygen level of the alloy was unknown, an amount of 0.15 wt.% was attributed. Modelling of the oxygen influence on the mechanical properties was based on 61 data pairs with oxygen content above 0.2 wt.% or below 0.1 wt.% (ELI alloys). For the remaining part of the database, the oxygen content was in the range 0.1–0.2 wt.%. When iron was not an alloying element in the titanium alloy, an amount of 0.15 wt.% was attributed. Analysis of the database in terms of the alloy elements present is given in Table 15.1.

Heat treatment

Nine classical heat treatment types for titanium alloys for which data in the literature exist were taken into account in the neural network model. Since neural networks operate with digits, the heat treatments are digitised by means of attributing different digits to the different heat treatments. The distribution of the heat treatments is presented in Table 15.2, showing the number of data pairs corresponding to each type of heat treatment. Large amounts of data are available for the two most popular heat treatments of titanium alloys, namely annealing in the $\alpha + \beta$ field and solution treatment in the $\alpha + \beta$ field followed by ageing.

Table 15.1 Analysis of the chemical composition (concentration in wt. %) of the alloys used for training and test

Element	Al	Mo	Sn	Zr	Cr	Fe	V	Cu ^{(a)(d)}	Bi ^{(b)(d)}	Si	Nb	Ta ^{(c)(e)}	Mn	O
Number of data pairs containing this element	699	467	247	275	163	175 ^(f)	272	3	7	150	105	39	21	61 ^(g)
Minimum	0	0	0	0	0	0.15	0	2.5	0.35	0	0	1	0	0.05
Maximum	8	15	11	11	11	5	16	2.5	0.35	0.5	7	1	8	0.33
Mean	4.91	4.89	3.38	4.73	4.78	1.36	6.49	2.5	0.35	0.20	1.98	1	4.90	0.16
Standard deviation	1.69	4.70	2.08	2.78	3.63	0.92	4.32	0.0	0.00	0.11	0.89	0	3.33	0.09

(a) Only in one alloy (Ti-2.5Cu (IMI 230));

(b) Only in one alloy (Ti-6Al-2Sn-1.5Zr-1Mo-0.35Bi-0.1Si);

(c) Only in one alloy (Ti-6Al-2Nb-1Ta-0.8Mo);

(d) Excluded from the data set;

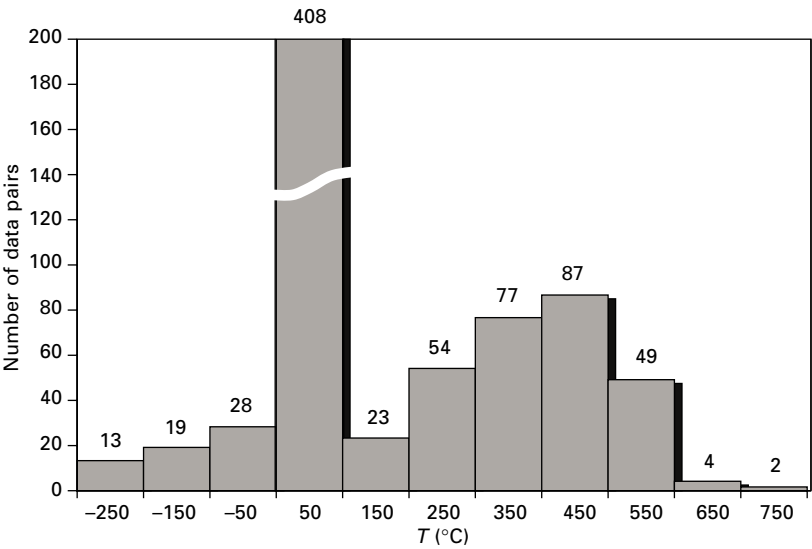
(e) Converted to niobium;

(f) Number of data pairs containing iron as an alloying element;

(g) Number of data pairs containing oxygen different from the usual.

Table 15.2 Heat treatments used in the database and their digitising

Heat treatment	Number of data pairs	Digitising
Without heat treatment	16	0
Annealing (β)	45	1
Annealing ($\alpha+\beta$)	237	2
Annealing (α)	29	3
Solution treatment (β)	18	4
Solution treatment ($\alpha+\beta$)	13	5
Solution treatment (β) and ageing	29	$6 + (1 - T_{\text{age}}/T_{\text{transus}})$
Solution treatment ($\alpha+\beta$) and ageing	247	$7 + (1 - T_{\text{age}}/T_{\text{transus}})$
Duplex annealing	130	8



15.1 Distribution in the database of mechanical properties of titanium alloys versus test/working temperature.

Temperature

Most of the data on the different mechanical properties are at room temperature (see Fig. 15.1). However, there are many data at -193 , -70 , -62 , 20 , 100 , 200 , 300 , 316 , 350 , 400 , 427 , 450 , 480 , 500 , 538 , 550 and 600 °C. Some data for mechanical properties at very low (-253 °C) as well as at very high (800 °C) temperatures were collected. The analysis of the database distribution is presented in Fig. 15.1, in a form of a histogram showing the number of data pairs in each temperature interval. This analysis shows that the model can work with sufficient accuracy within the temperature interval of -100 to $+600$ °C.

Different numbers of data pairs for the different mechanical properties were collected (Table 15.3). Most of the data are for tensile test properties, but there is also a sufficient amount of data for the other mechanical properties. The ranges of variation of the properties, as well as the conditions at which data with respect to the alloy composition, heat treatment and temperature exist, are shown in Table 15.3.

Neural network training

The choice of transfer function is one of the decisions which must be made by the user, although it is not usually a very critical factor. In their infancy, neural networks were trained using a method known as backpropagation. The method suffers from the drawback that the adjustments which reduce the errors (improvement of error) on a given set of data, may increase the errors on the other sets of data, so the process is constantly undoing the improvements made so far.

A much better approach has turned out to be to use one of the many methods of numerical optimisation which have been developed for solving nonlinear sums-of-squares problems. The nonlinearity arises because the relationships between outputs and weights of an artificial neural network are nonlinear, although well defined. It is this nonlinearity which makes it necessary to use iterative methods. The most efficient method in most cases is the Gauss–Newton algorithm, but this method can suffer from numerical instability unless the initial estimate of the weights is fairly accurate, so it is unreliable. On the other hand, the method of steepest descent is reliable, but highly inefficient. In fact, backpropagation becomes equivalent to steepest descent when adjustments are made, not for each error separately, but to all at once – so-called batch-backpropagation. The method used in this book is the Levenberg–Marquardt algorithm, which can be regarded as a compromise between Gauss–Newton and steepest descent, heavily favouring the former. Typically, the use of Levenberg–Marquardt leads to a reduction of orders of magnitude in the number of training iterations required compared with backpropagation, and is highly reliable.

The general model of the neural network (Fig. 13.1b) consists of separate neural network models for each output mechanical property. In the general case, these models include 13 neurons in the input layer, 13 neurons in the hidden layer and 1 neuron in the output layer. The most accurate predictions of the neural networks are obtained with the hyperbolic tangent sigmoid transfer function.

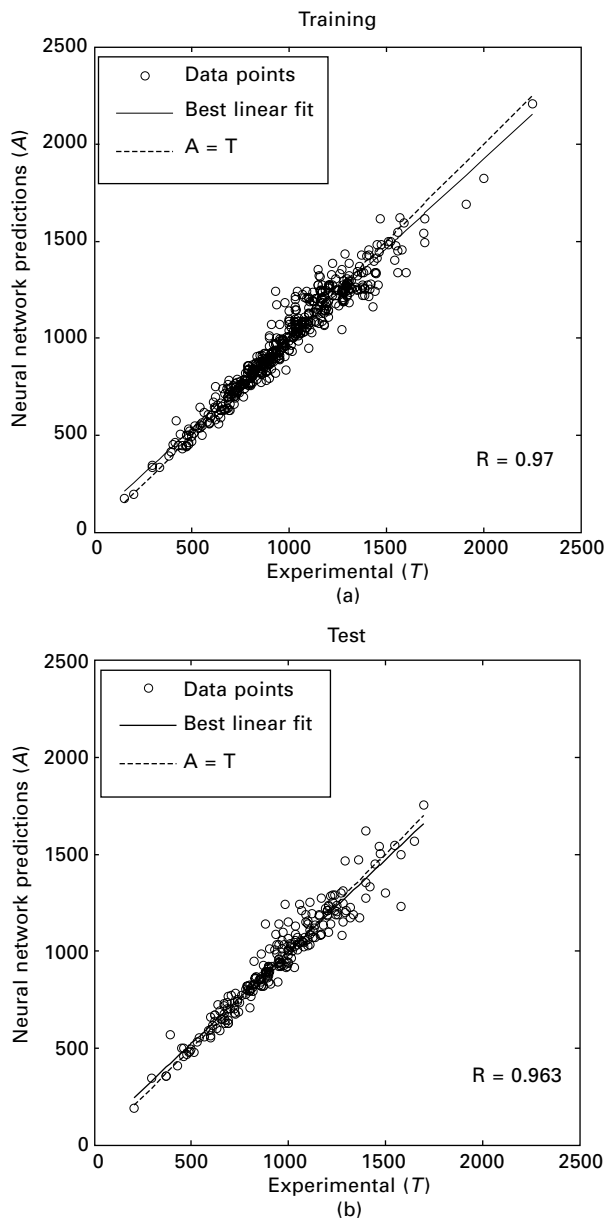
Neural network test and performance

The predicted values from the trained neural network outputs track the targets very well (see the performance example shown in Fig. 15.2). Acceptable

Table 15.3 Analysis of the output data for training and test of neural network for prediction of the mechanical properties of titanium alloys

Output	Number of data	Min.	Max.	Mean	Standard deviation	Temperature range (°C)
Tensile strength (MPa)	707	151	2250	975	282.65	−253 to 800
0.2% yield strength (MPa)	662	97	2050	859	282.89	−253 to 800
Elongation (%)	581	1	50	13	6.51	−253 to 800
Reduction of area (%)	421	4	92	38	17.80	−196 to 800
Charpy impact strength (J)	124	8	119	33	21.62	−196 to 500
Rockwell hardness (HRC)	98	24	57	36	5.56	−253 to 300
Modulus of elasticity (GPa)	259	57	140	105	13.37	−253 to 800
R_{-1} fatigue strength (MPa)*	74	220	900	537	140.07	20 to 600
K_{1C} fracture toughness (MPa·m ^{1/2})**	69	24	176	78	34.44	−253 to 316

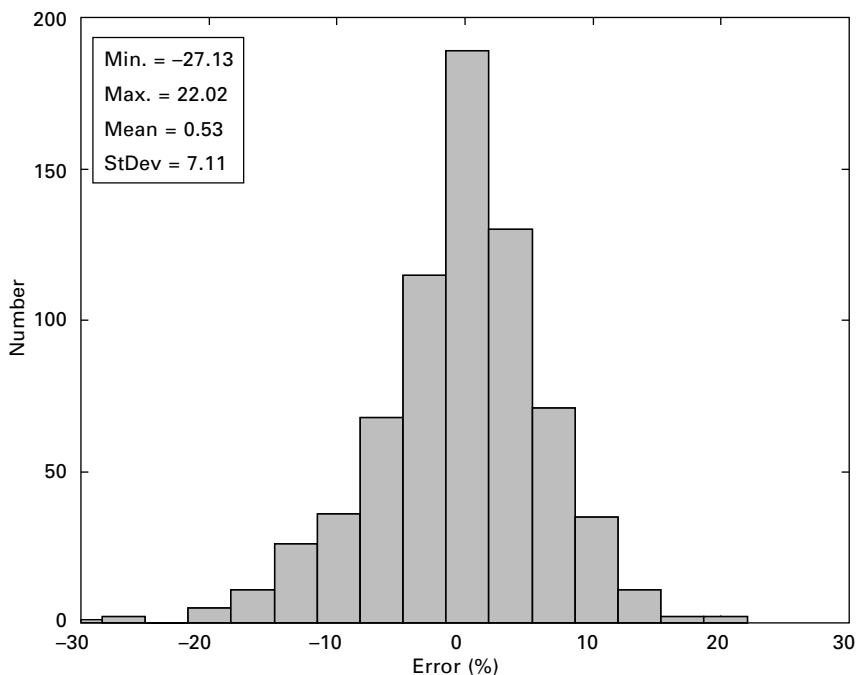
*No data for solution treatment (β).
 **No data for manganese.



15.2 Predicted tensile strength (MPa) from the neural network versus experimental values for (a) training and (b) test data sets.

performance is achieved in the neural networks for the other mechanical properties.

Additionally, the performance accuracy can be verified by the way of the analysis shown in Fig. 15.3. For the test data set, neural network predictions



15.3 Statistical analysis of the error of the neural network predictions for tensile strength.

are calculated. These are compared with the corresponding experimental values. Thereafter, the relative errors (in %) are calculated using

$$\text{Error} = \frac{Rm_{\text{Exp}} - Rm_{\text{NN}}}{Rm_{\text{Exp}}} \times 100 \quad [15.1]$$

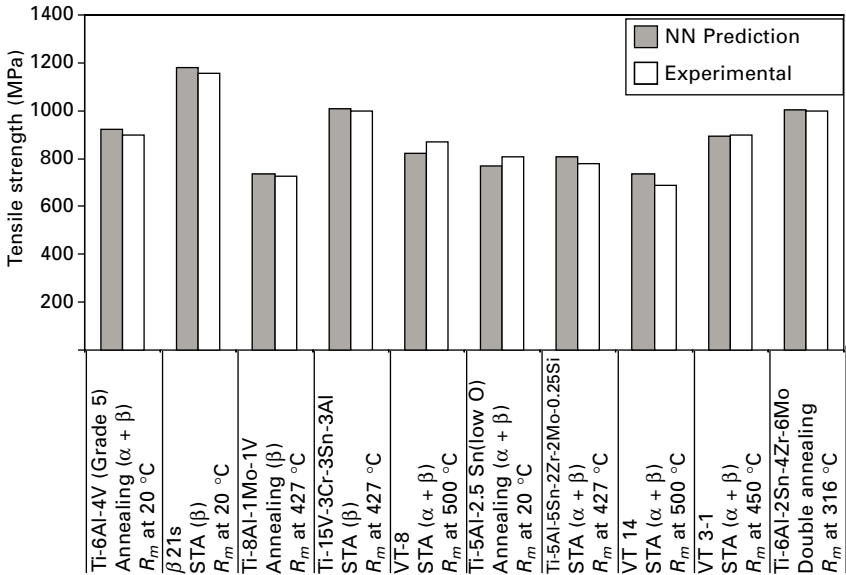
where Rm_{Exp} is the experimental (measured) tensile strength and Rm_{NN} is the predicted value from the neural network.

The error has a classical Gaussian distribution around the zero value. For more than 95% of the test data set, the error of prediction is within $\pm 10\%$, so the model can predict with sufficient accuracy for the practice.

Comparison of the prediction from the model and experimental data

Some of the results are compared with experimental data from the literature. All comparisons between neural network predictions and experimental data are for data pairs which have not been involved in the training process.

The tensile strengths for some of the most popular commercial titanium alloys are calculated (see Fig. 15.4) using the model. The neural network predictions are in good agreement with the experimental data. Similar



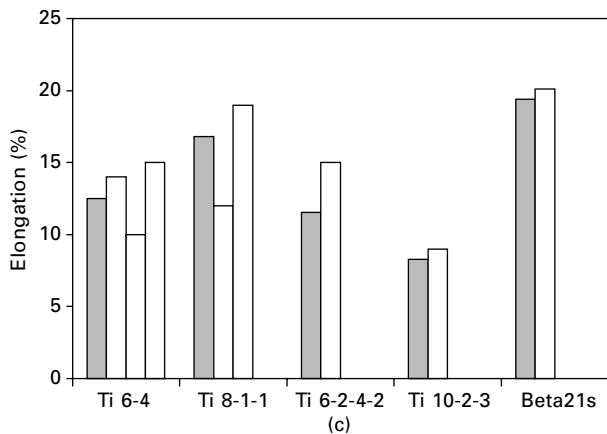
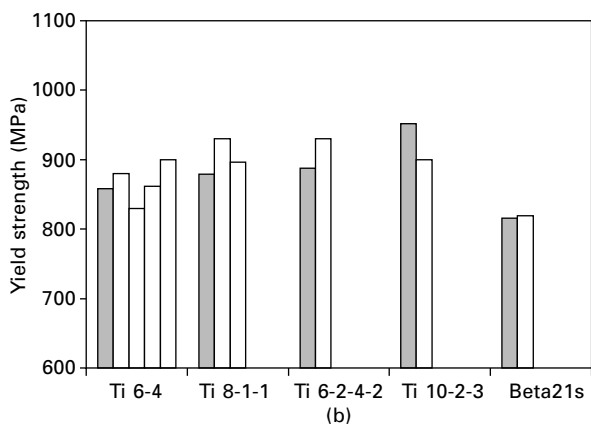
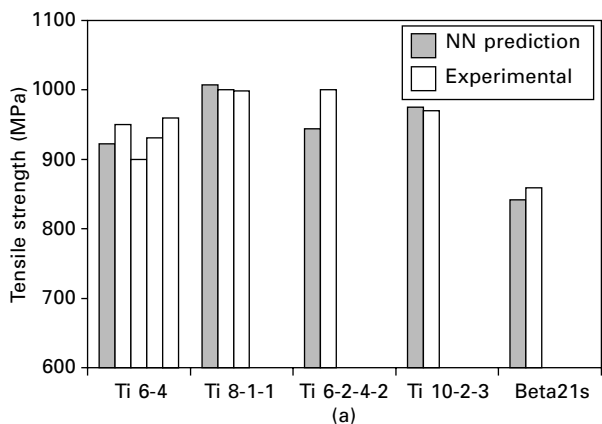
15.4 Neural network predictions and experimental tensile strengths for different alloys, heat treatments and operating temperatures.

correspondences are observed for the other mechanical properties. In fact, the accuracy of the neural network predictions is higher for the tensile test properties, because the number of training data pairs is larger for the tensile properties as compared with the other mechanical properties (see Table 15.3). However, the accuracy of the neural network predictions is within acceptable error range for all other properties. Some uncertainty exists only regarding the prediction of the fracture toughness.

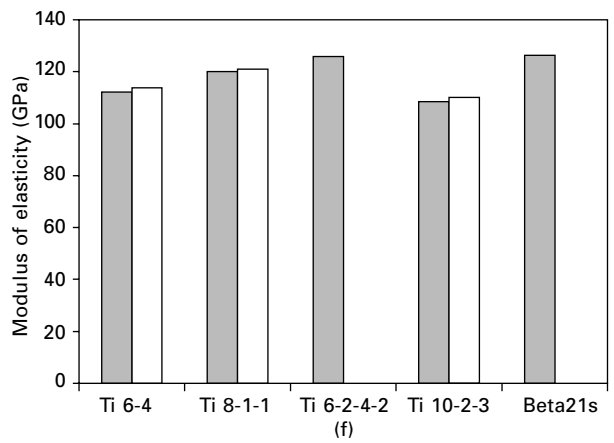
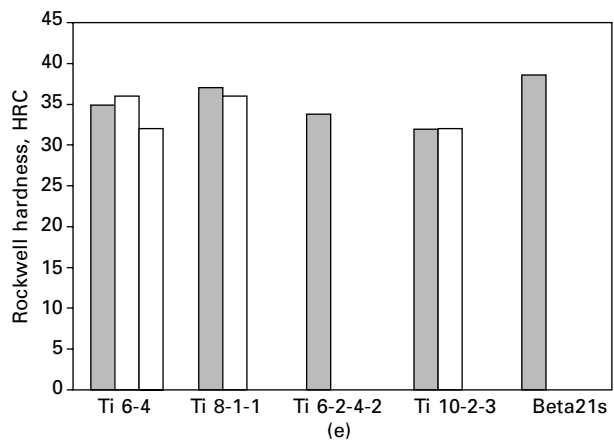
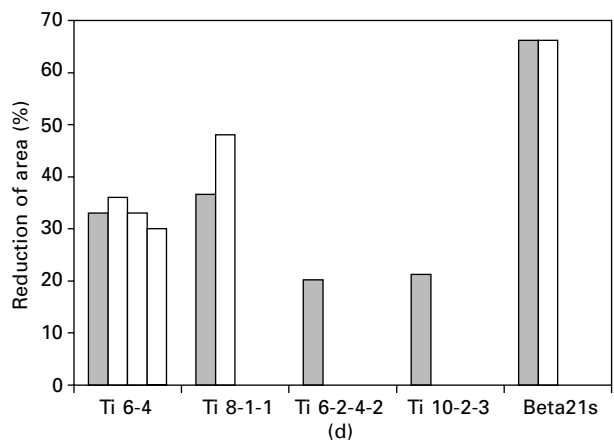
15.1.2 Prediction of mechanical properties at room temperature

Since most of the data pairs used are for mechanical properties at room temperature, the highest accuracy of the neural network is expected for the prediction of room temperature properties. The calculation results are compared with experimental data published in different sources (Fig. 15.5).

There is a very good agreement between the predicted values from the neural network and the experimental data for the various properties (Fig. 15.5). The difference between the neural network predictions and the experimental data is comparable with the difference between experimental data published in different sources. This shows the accuracy of the predictions from the model.

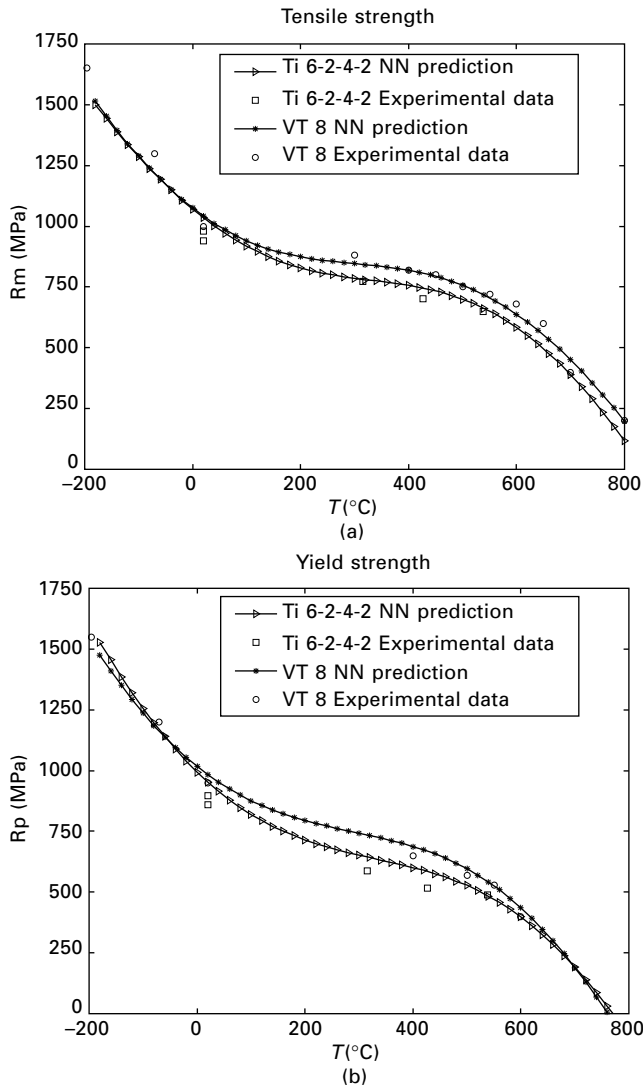


15.5 Neural network predictions of mechanical properties at room temperature for different titanium alloys after $\alpha + \beta$ annealing: (a) tensile strength; (b) yield strength; (c) elongation; (d) reduction of area; (e) hardness; (f) modulus of elasticity.

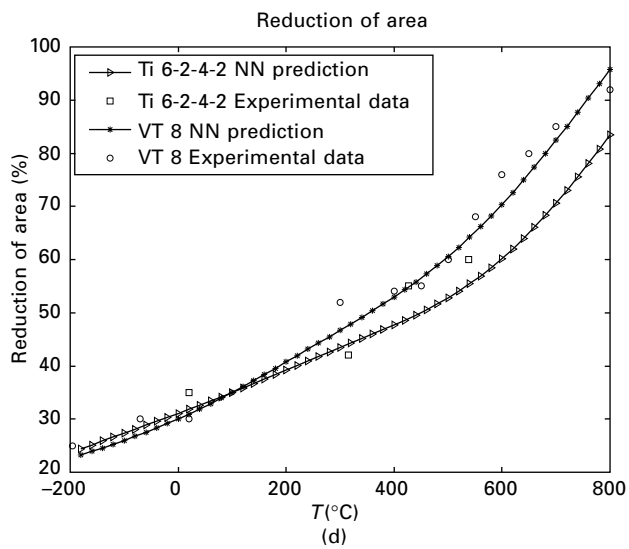
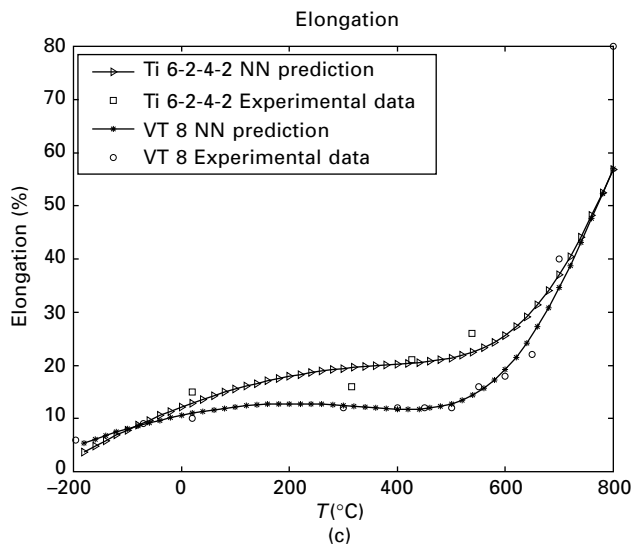


15.1.3 Prediction of mechanical properties at high and low temperatures

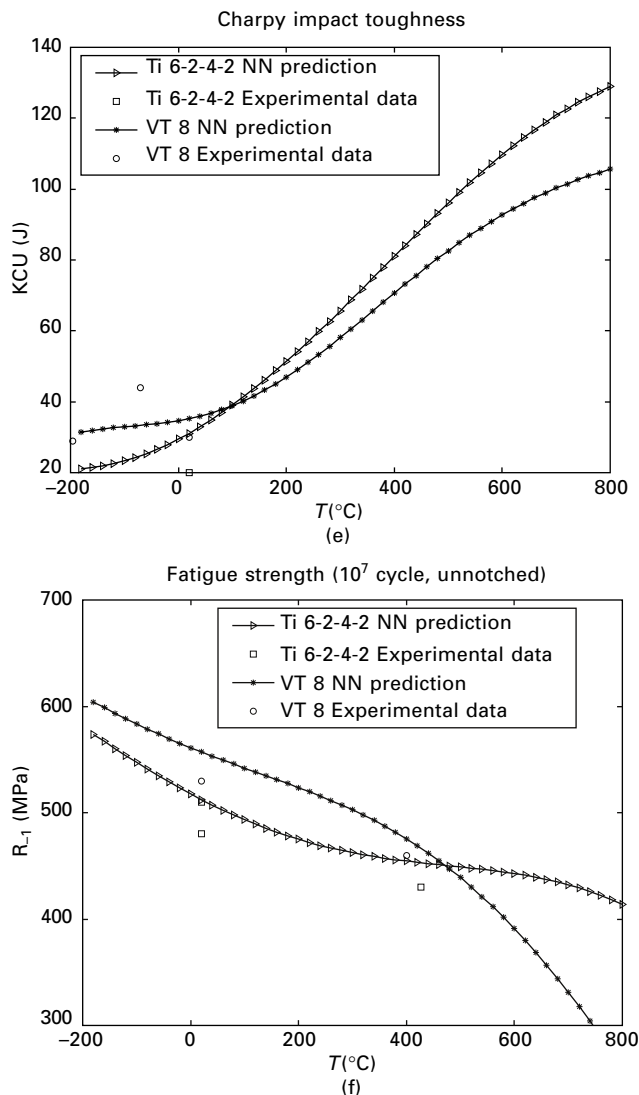
Since operating temperature is a very important factor in the application of titanium alloys, its influence is demonstrated by using the model. The well-known high-temperature commercial alloys Ti-6Al-2Sn-4Zr-2Mo (Western) and VT-8 (Russian) are chosen. Their mechanical properties are calculated in the temperature range from -200 to 800 °C (Fig. 15.6).



15.6 Neural network predictions of the influence of the temperature on the mechanical properties for Ti-6Al-2Sn-4Zr-2Mo and VT-8 alloys after double annealing heat treatment.



15.6 Continued



15.6 Continued

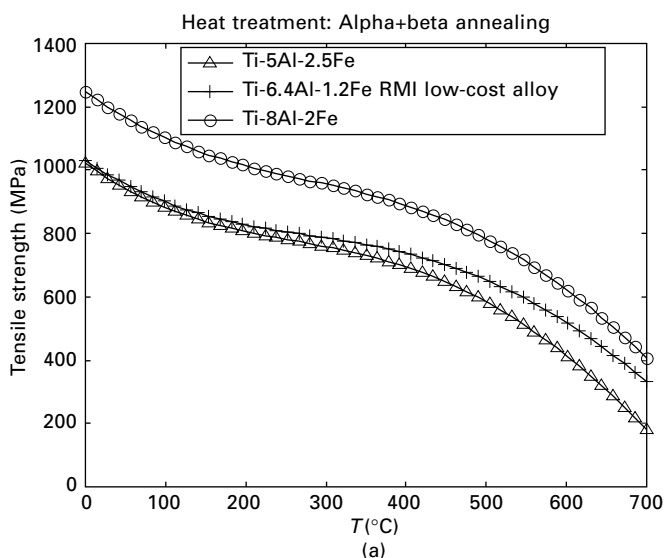
The predicted tensile and yield strength is not affected much when the temperature is increased from room temperature to 500 °C, for both alloys (see Fig. 15.6a,b). When the temperature is increased to above 600 °C, tensile and yield strength decreases significantly. The maximum operating temperature at which the strength properties are still kept stable is around 550 °C, which is in agreement with the recommendations in the literature for the temperature range of use for these alloys.

On the other hand, an increase in temperature results in significant increasing of the elongation (especially above 600 °C, see Fig. 15.6c), the reduction of area (Fig. 15.6d), and the impact toughness (Fig. 15.6e).

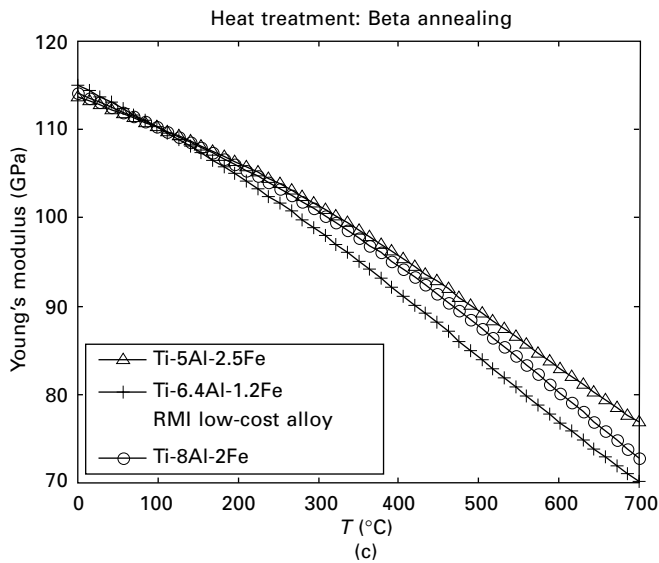
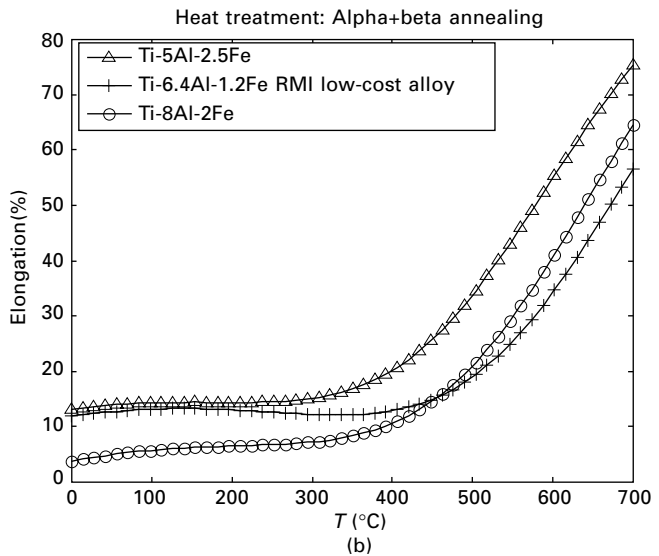
At sub-zero temperatures, naturally, the influence is the opposite. The strength properties are increased (Fig. 15.6a,b,f), while the plasticity and the toughness of the alloys are significantly decreased (Fig. 15.6c,d,e). The effect of the temperature calculated from the trained neural network on the mechanical properties is consistent with what is expected from a metallurgical point of view.

The predicted temperature dependency of the different mechanical properties matches well with the experimental data.

Further examples are demonstrated for use of the model to predict mechanical properties in different alloys and conditions. Quantitative simulations of the Ti–Al–Fe system are generated (Fig. 15.7). The model simulations show decreasing of the tensile strength and increasing of the elongation with the temperature increase. There is a critical temperature at around 450–500 °C; above that, the temperature influence in these directions is stronger. The tendency in the results for these alloys is similar to earlier modelled outcome (Fig. 15.6). The results are also consistent with a knowledge of the influence of temperature on the Young's modulus.



15.7 Neural network predictions of the influence of the temperature on (a) tensile strength, (b) elongation, and (c) Young's modulus for Ti-5Al-2.5Fe, Ti-6.4Al-1.2Fe and Ti-8Al-2Fe alloys.



15.7 Continued

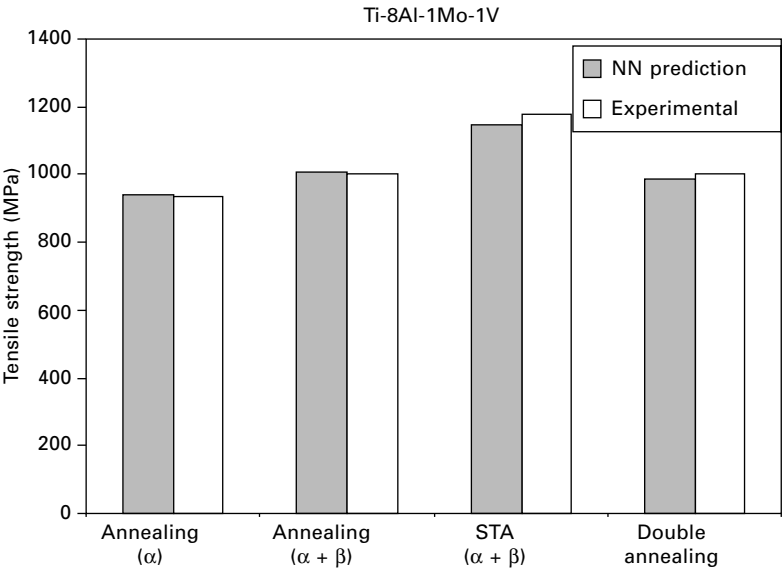
15.1.4 Prediction of mechanical properties under different heat treatment conditions

The method of heat treatment is a significant process parameter. The optimisation of the heat treatment in order to achieve desirable mechanical properties has major importance in titanium alloys practice. In the following, the neural network predictions of the influence of heat treatment on mechanical properties is discussed.

The effects of the most commonly used heat treatments for titanium alloys are shown in Fig. 15.8. A very good agreement between predicted and experimental tensile strength is illustrated. The neural network has been trained to understand the influence of the heat treatment on the microstructure, and, therefore, on the properties of titanium alloys. It must be noted, however, that the approach used is not quantitative regarding the heat treatment. The particular heat treatment parameters such as temperature of heating, time, heating/cooling rates are not taken into account in the model. The assumption is that all data are at optimal heat treatment conditions for the corresponding heat treatment procedure ($\alpha + \beta$ annealing, solution treatment and ageing, etc.) and alloy.

The model would be more accurate and precise if the particular characteristics of the microstructure (type of phases present, grain size and grain shape, morphology and distribution of the fine microstructure, e.g. $\alpha + \beta$ colonies and texture) were involved as input parameters instead of simply the type of heat treatment. However, at present, in the literature, there are not enough data for training of such a neural network.

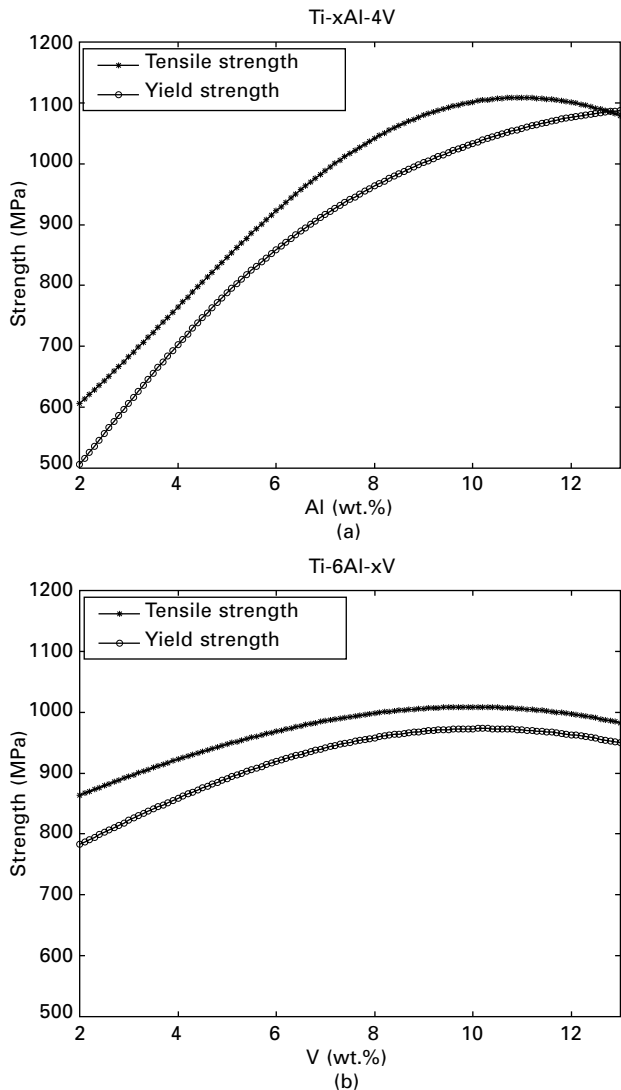
Additionally, the influence of the ageing temperature on the mechanical properties can be modelled. The tendency towards decreasing tensile strength was simulated when the ageing temperature was raised, but the accuracy of prediction was not acceptable. Apparently, more data for mechanical properties after ageing at different temperatures are needed to train the neural network to understand this effect.



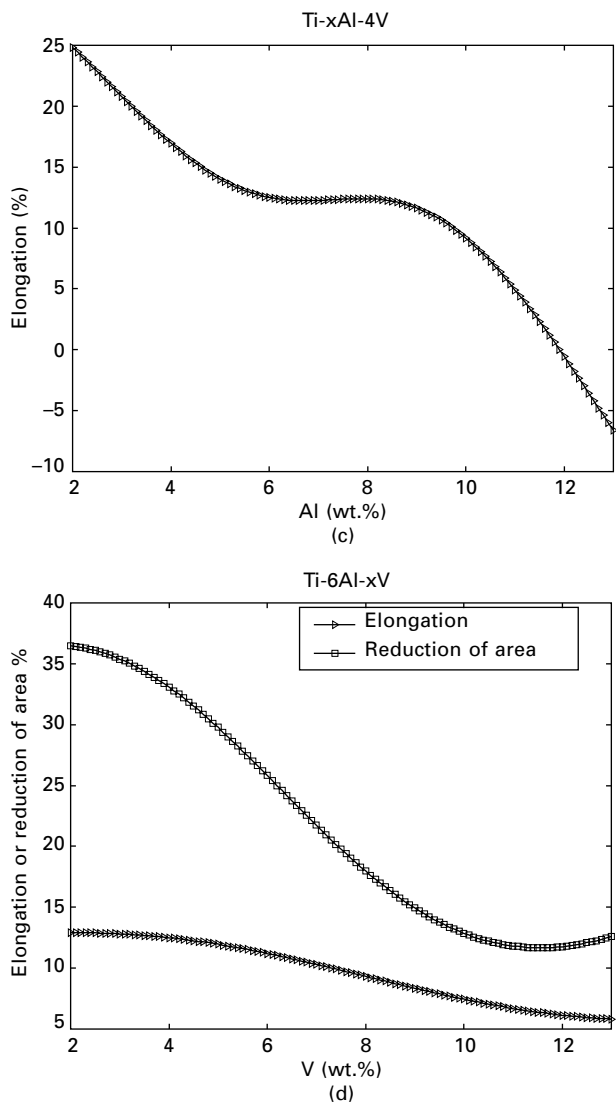
15.8 Neural network predictions and experimental tensile strength of Ti-8Al-1Mo-1V alloy after different heat treatments.

15.1.5 Prediction of mechanical properties for different alloy compositions

The influence of aluminium (Fig. 15.9a,c) and vanadium (Fig. 15.9b,d) for one of the most popular titanium systems (Ti–Al–V) is modelled. Attention



15.9 Neural network predictions of the influence of the alloy composition on the mechanical properties for the Ti–xAl–yV system: (a) tensile and yield strength for Ti–xAl–4V; (b) tensile and yield strength for Ti–6Al–yV; (c) elongation for Ti–xAl–4V; (d) elongation and reduction of area for Ti–6Al–yV.



15.9 Continued

is paid to this system since Ti-6Al-4V alloy is the most widely used titanium alloy. The mechanical properties are computed assuming increased and decreased contents of aluminium and vanadium from the Ti-6Al-4V composition, in an $\alpha + \beta$ annealing condition.

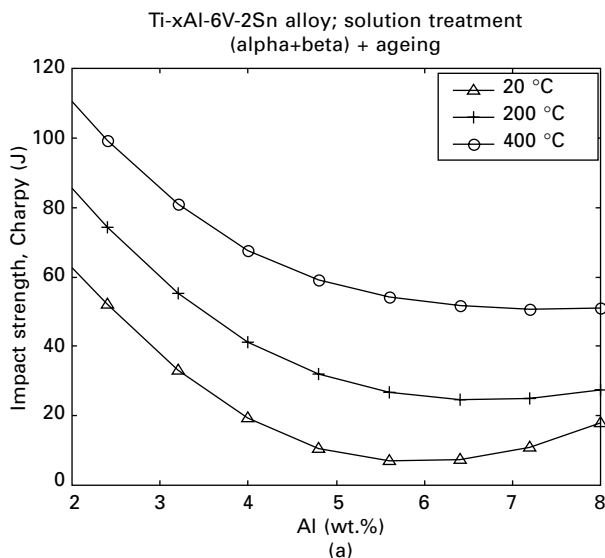
With increasing aluminium content, both tensile strength and yield strength are increased appreciably (Fig. 15.9a). Simultaneously, a very high influence of aluminium on the elongation (especially when the aluminium exceeds

8 wt.%) is found. A very small increase of the aluminium content causes a significant decrease of the elongation (see Fig. 15.9c), approaching a value of zero when the aluminium content is as high as 11 wt.%. The predicted effect of a significant decrease of the ductility properties can be explained from the metallurgical point of view with the formation of the Ti_3Al phase.

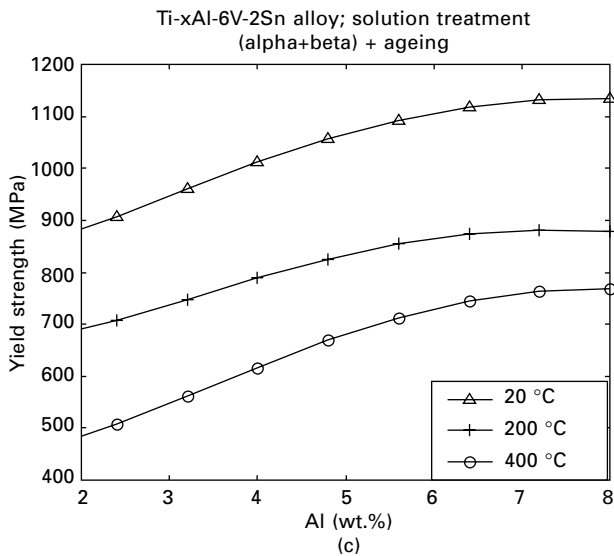
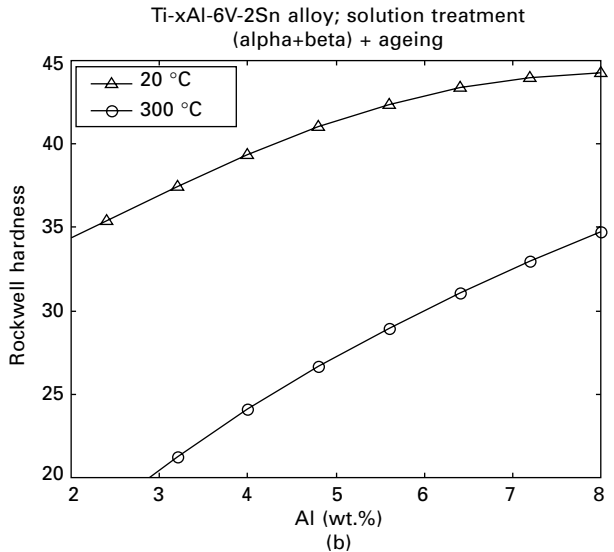
The influence of vanadium on the mechanical properties shows a similar tendency. With increasing vanadium content, tensile strength and yield strength are increased (Fig. 15.9b), while the plasticity properties (elongation and reduction of area) are decreased (Fig. 15.9d). The vanadium influence on the tensile strength is much weaker as compared to the influence of aluminium.

The predicted dependencies on aluminium and vanadium are in accordance with the well-established influence of the above elements over the mechanical properties. From the metallurgical point of view, it is also not surprising that, in general, substitutional elements increase the strength properties in titanium alloys. The simulation is therefore consistent with what is expected from the metallurgical theory and the practice of the titanium alloys.

Some mechanical properties are computed assuming increased and decreased content of aluminium from the Ti-6Al-6V-2Sn composition (Fig. 15.10). With increasing aluminium content, the impact strength is decreased appreciably. Simultaneously, the increase of the aluminium content causes an increase in the hardness. Higher operation temperature results in higher



15.10 Neural network predictions for the influence of the aluminium content on (a) impact strength, (b) Rockwell hardness, and (c) yield strength of Ti-xAl-6V-2Sn alloy at different temperatures.



15.10 Continued

impact strength and lower hardness. This is a classical example for optimisation of the alloy composition in order to maximise a property or group of properties. In similar ways, the models can be used to give quantitative predictions for all outputs in Fig. 13.1, at different alloy compositions, processing conditions and temperatures. For example, the trained neural network can be used for optimisation of the alloy composition, such as Mo, Sn, Zr, Fe and oxygen content, in order to obtain the desired combination of mechanical properties.

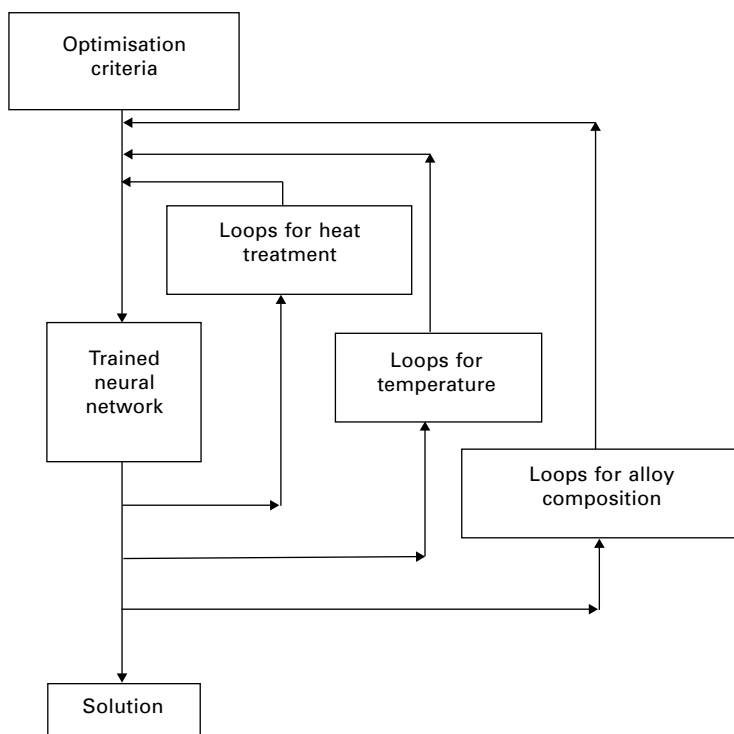
15.1.6 Optimisation of alloy composition and processing parameters

In this mode, the input parameters of the program are the optimisation criteria under any conditions. Loops are for alloy composition, heat treatment and temperature (Fig. 15.11). For each combination of inputs (alloy composition, heat treatment and temperature), the output values are predicted from the neural network and compared with the input criteria. As a result of computation, the best solution in respect of alloy composition and/or heat treatment corresponding to the desired properties is obtained at the output. In the following, one example simulated from the program is demonstrated:

Find: Alloy composition with maximal tensile strength (R_m) at 420 °C.

Fix: Heat treatment = $\alpha + \beta$ annealing; $T = 420$ °C; zero amount of Sn, Cr, Fe, Si, Nb, Mn; O = 0.12;

Vary: Al, Mo, Zr, V;



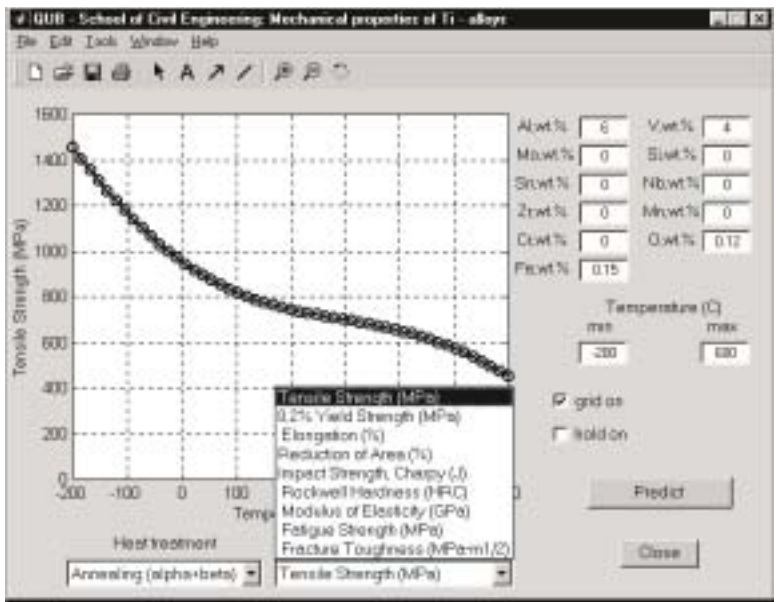
15.11 Block diagram of computer program for optimisation of the alloy composition and heat treatment conditions as functions of the desired properties and working temperature.

Solution: The optimal composition is Al = 5.8 wt.%, Mo = 7.3 wt.%, Zr = 5.2 wt.%, V = 0 wt.%. This composition gives tensile strength at 420 °C $R_m = 932$ MPa. The other mechanical properties at 420 °C are: $R_p = 665$ MPa; $E = 10\%$; $ME = 94$ GPa; $R_{-1} = 448$ MPa; $K_{IC} = 101$ MPa m^{1/2}.

The above program can be used to find a solution for the best alloy composition and processing parameters for arbitrary optimisation criteria or combination of optimisation criteria.

15.1.7 Graphical user interface

On input of the chemical composition of the titanium alloy, temperature interval and the heat treatment, the chosen mechanical property is simulated and plotted (Fig. 15.12). In this way, the user can very easily obtain the temperature dependence of any from the nine mechanical properties involved in the model, for any heat treatment conditions and arbitrary alloy composition. An option is incorporated, where the mechanical properties can be calculated and plotted versus the amount of a chosen alloying element at any fixed temperature. The GUI also allows easy switch between the different heat treatments and mechanical properties. In this way, the user can analyse the



15.12 Graphical user interface for prediction of mechanical properties of titanium alloys as functions of alloy composition, heat treatment and operating temperature.

influence of the different factors (heat treatment and alloy composition) on the various mechanical properties, at different operating temperatures. It should be noted here that the program will work with appropriate accuracy within the range of the data set used for training of the neural network.

15.1.8 Summary

An artificial neural network model has been developed for the prediction of the mechanical properties of titanium alloys, as functions of the alloy composition, heat treatment condition and working temperature. The model has been used to study the influence of different factors on the mechanical properties in titanium alloys.

A graphical user interface for the use of the model has been created.

The model is a convenient and powerful tool for practical optimisation of the alloy composition and processing parameters of titanium alloys in order to obtain the desired combination of properties at different working temperatures.

15.2 Fatigue stress life (S-N) diagrams

Jet aircraft manufacturers are the principal consumers of Ti-6Al-4V, which is often specified for critical parts, the failure of which could result in the loss of an entire system.

Fatigue stress life is one of the most important properties for Ti-6Al-4V alloys. Several metallurgical and environmental variables have been identified during years of research that influence the fatigue behaviour of Ti-6Al-4V. These variables or conditions can alter and influence the fatigue stress life of Ti-6Al-4V in beneficial or adverse manners. The main factors and conditions which influence fatigue stress life S-N curves are microstructure, texture, environment, temperature, surface treatment, and stress ratio. Experimental investigation of fatigue stress curves has been carried out extensively, but computer modelling of fatigue stress life using neural networks has not yet been widely used for titanium alloys.

This section will demonstrate a model of an artificial neural network for the prediction and simulation of fatigue stress life S-N diagrams for Ti-6Al-4V.

15.2.1 Model description

The general scheme of the model is given in Fig. 13.1c. The input parameters of the neural network are microstructure, texture, environment, temperature, surface treatment and stress ratio. The microstructure includes the most common structures, namely bimodal, fine and coarse equiaxed, fine and

coarse lamellar. The test environments are air, vacuum or an aqueous solution of 3.5% NaCl. The two major types of texture of Ti-6Al-4V are basal and transverse, and the test direction is also noted as either the rolling or the transverse test direction. The surface treatment comprises electrolytically polished, shot peened, stress relieved, and mechanically polished conditions. The stress ratio, R , is the ratio of the stress cycles ($R = S_{\min}/S_{\max}$) and ranges from -1 to 0.54 . Table 15.4 shows the complete list of inputs.

The output of the artificial neural network model is the S-N fatigue diagram, which is plotted for the corresponding conditions inputted into it.

Data set and output parameters

The database was constructed by collecting available fatigue stress life S-N diagrams for Ti-6Al-4V. In total, 58 available S-N diagrams for Ti-6Al-4V alloy at different conditions were collected and used in the training procedure. The stress (S) corresponding to 10^5 , 10^6 , 10^7 and 10^8 cycles to failure (N) was recorded and used as the output data set.

This model includes six neurons in the input layer, four neurons in the hidden layer and four neurons in the output layer.

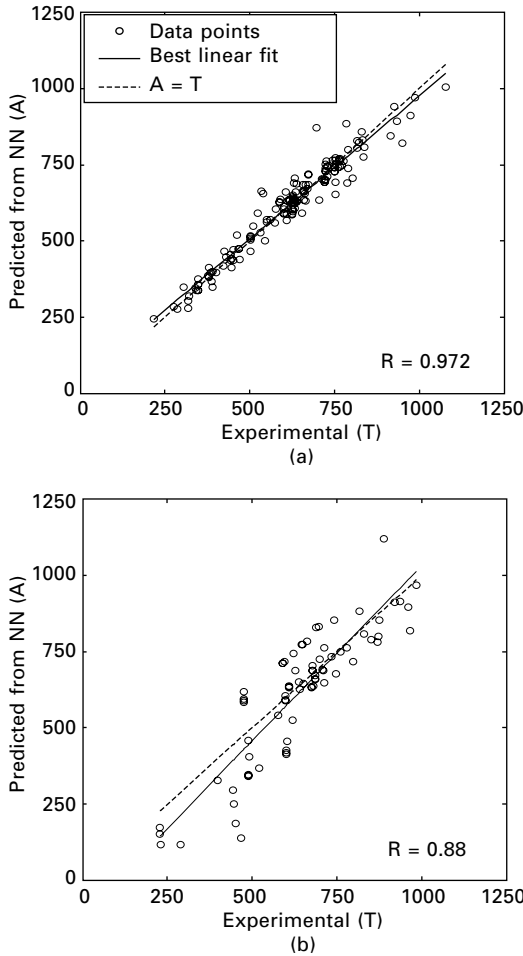
Table 15.4 List of inputs used for training of the neural network for fatigue stress life

Input	Values
Microstructure	Bimodal; Fine equiaxed; Fine lamellar; Coarse equiaxed; Coarse lamellar
Environment	Vacuum; Air; 3.5% NaCl
Texture	No texture; B/T-TD = basal-transverse texture, transverse test direction; B = basal texture; B/T-RD = basal-transverse texture, rolling test direction; T-TD = transverse texture, transverse test direction; T-RD = transverse texture, rolling test direction
Temperature	20 °C; 200 °C; 500 °C
Surface treatment	SP = shot peened; EP = electrolytically polished; SP+EP; SP+SR = shot peened + stress relieved; SP+SR+EP; MP = Mechanically polished with 7, 80 and 180 μm particle size
Stress ratio (R)	-1 ; -0.3 ; 0 ; 0.05 ; 0.1 ; 0.3 ; 0.5 ; 0.54

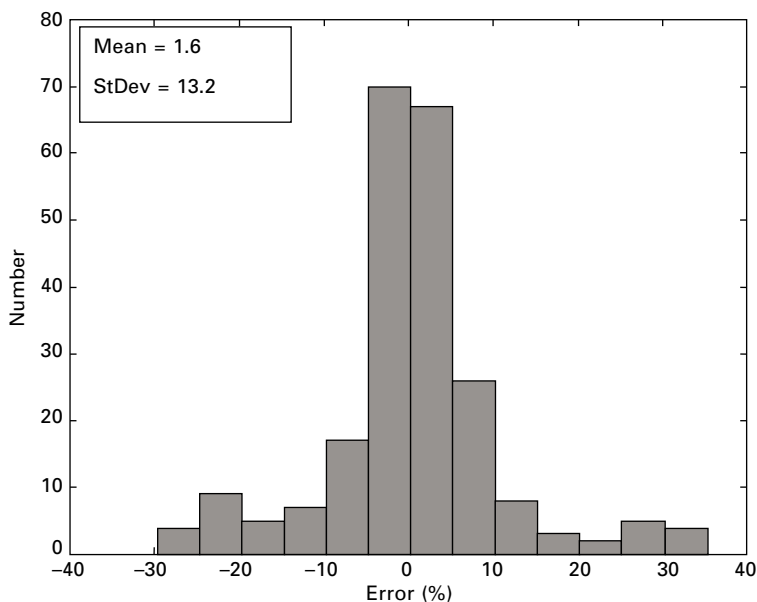
15.2.2 Neural network test and performance

The performance is demonstrated in Fig. 15.13.

Further analysis of the performance accuracy can be carried out (Fig. 15.14). For the test data set, neural network predictions are compared with the corresponding experimental values. For more than 80% of the test data set, the error of prediction is within $\pm 10\%$.



15.13 Performance of the neural network for simulation of fatigue stress life S-N curves, plotting the neural network versus experimental values for (a) the training and (b) the test sets. T is the experimental stress amplitude, in MPa. A is the predicted stress amplitude from the NN, in MPa.



15.14 Statistical analysis of the error of the neural network predictions for fatigue stress life.

15.2.3 Calculations and comparison with experimental data

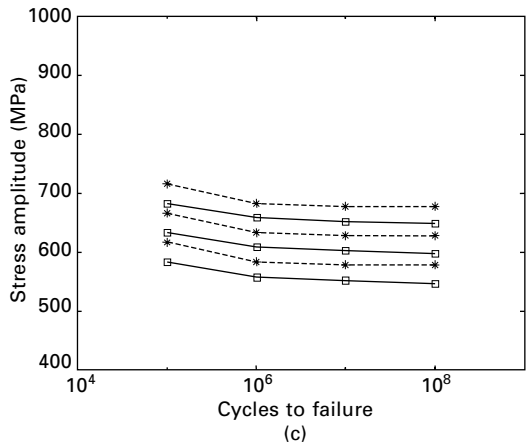
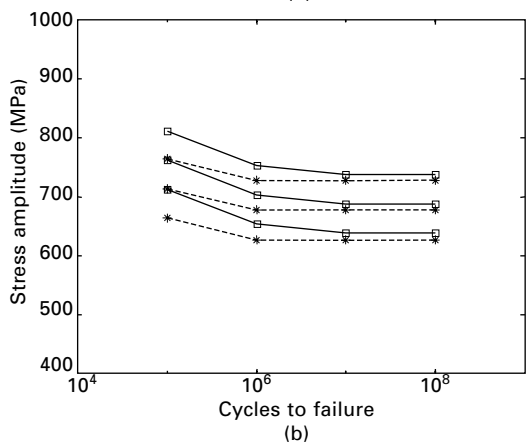
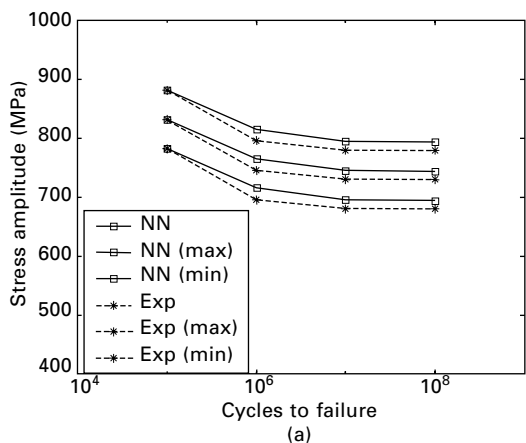
Using the trained neural network, a model for simulation of the fatigue stress life of Ti-6Al-4V was created. This model can be used to predict fatigue curve diagrams.

Firstly, some fatigue stress diagrams for Ti-6Al-4V are calculated, to examine how effective the prediction can be (Fig. 15.15). Both the predicted NN and experimental curves are plotted within a maximum and minimum stress amplitude range of ± 50 MPa, in order to visualise how exact the fatigue stress curve predictions are. The figure of ± 50 MPa is chosen as the average deviation from the fatigue curve based on the experimental results.

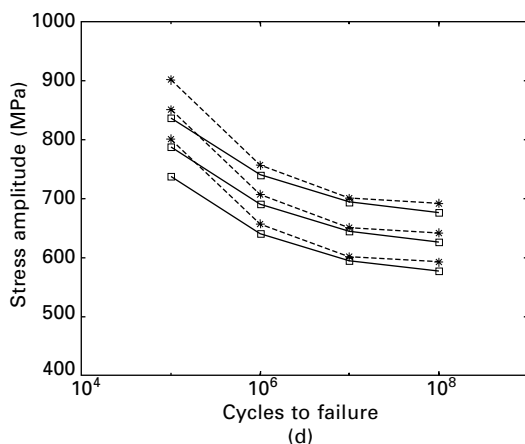
Generally, for the predicted curves, a good agreement is seen when compared with the experimental data. The accuracy of the neural network predictions is higher for certain cases compared with others, because more experimental data are available for some conditions. However, the accuracy of the neural network predictions is within an acceptable error range in all cases.

To further show the effectiveness of the neural network at predicting fatigue stress curves for Ti-6Al-4V, different input values are used, modelled and thereafter analysed.

The influence of microstructure as an input on the fatigue stress curves of Ti-6Al-4V is modelled (Fig. 15.16a). Fatigue stress diagrams are computed



15.15 Comparison of experimental S-N diagrams with neural network predictions for different conditions: (a) fine equiaxed, air, B, 20 °C, SP, $R = -1$; (b) bimodal, air, B, 200 °C, EP, $R = -1$; (c) fine lamellar, 3.5% NaCl, T-RD, 20 °C, EP, $R = -1$; (d) coarse equiaxed, vacuum, B, 20 °C, EP, $R = -1$.



15.15 Continued

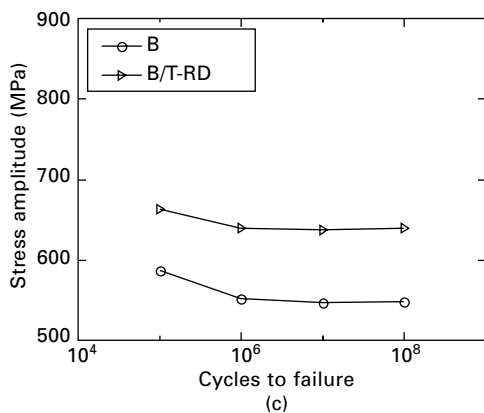
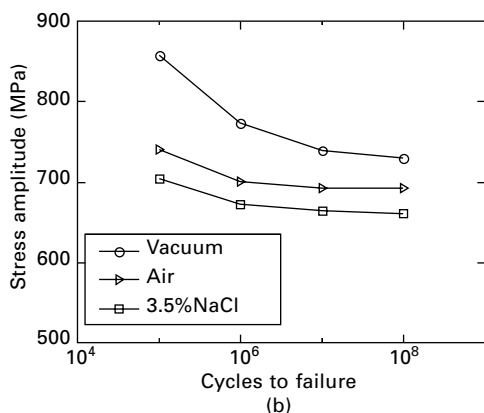
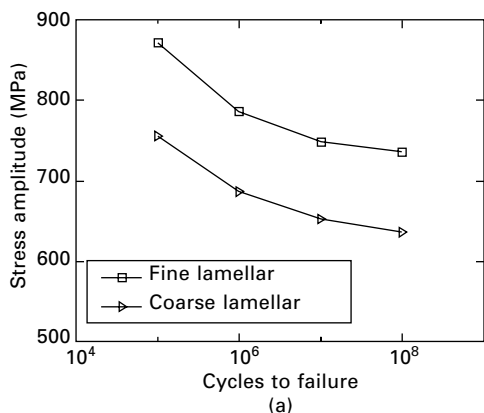
for fine lamellar and coarse lamellar structures, while the other inputs remain constant. The diagram shows that fine lamellar has the greater fatigue stress level. From a metallurgical perspective, it is of no surprise that good fatigue strength involves structures which have finer grain sizes, e.g. fine lamellar. Incidentally, the result for fine lamellar should be more accurate compared with the results for coarse lamellar, as more data are available for this microstructure.

For Ti-6Al-4V alloy, the influence of the environment is also modelled (Fig. 15.16b). All other inputs remain constant throughout. Comparing the three environments (vacuum, air, and 3.5%NaCl), it is evident that the fatigue strength is the greatest for the vacuum input. Laboratory air and NaCl solution are aggressive environments, which can harbour impurities. From the metallurgical viewpoint, the vacuum environment is the purest of the three environments, and therefore should give higher fatigue strength as shown by the neural network results.

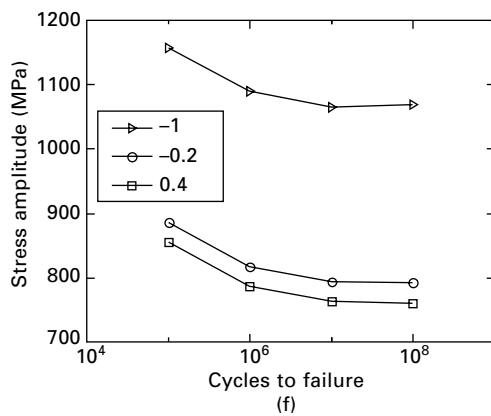
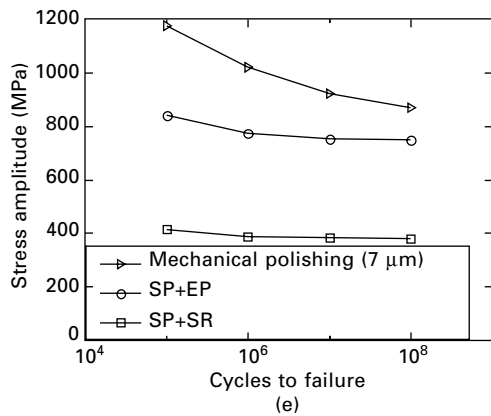
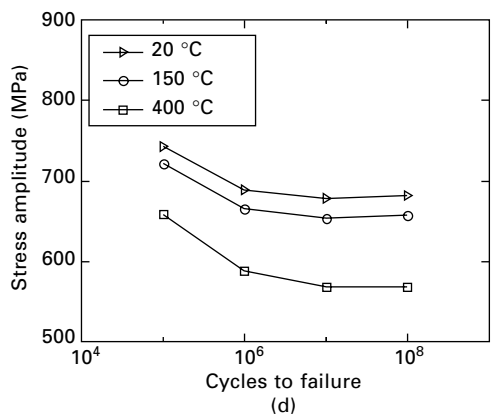
The influence of texture is shown in Fig. 15.16c for two cases, basal texture and basal transverse texture tested in a rolling direction. Texture is an important parameter for fatigue stress curves.

Temperature influence is very important. The diagram in Fig. 15.16d shows that, at 20 °C (room temperature), the alloy has the greatest fatigue stress life. The other two temperatures of 150 and 400 °C are not included in the training data set, but the neural network is capable of estimating the fatigue curves for these inputs.

The influence of surface treatment appears to be the most significant on the fatigue curves (Fig. 15.16e), and it seems to be more complicated than other factors. However, the neural network is able to predict the curves using the known data set.



15.16 Simulation of S-N diagrams modelling the effect of input parameters: (a) microstructure (vacuum, B/T-RD, 20 °C, EP, $R = -1$); (b) environment (fine equiaxed, B/T-RD, 20 °C, EP, $R = -1$); (c) texture (fine lamellar, air, 20 °C, EP, $R = -1$); (d) temperature (fine equiaxed, air, no texture, EP, $R = -1$); (e) surface treatment (fine equiaxed, air, B, 20 °C, $R = -1$); (f) stress ratio (fine equiaxed, air, T-RD, 20 °C, SP).



The stress ratio (R) influence is modelled for increasing stress ratios within the data set range of -1 to 0.54 (Fig. 15.16f). The model confirms that, with increasing stress ratio, the fatigue S-N curve moves downwards. It shows that, under a stress ratio of -1 , the alloy has the greatest fatigue stress life. It may be noted that most data in the data set have this stress ratio. The other two curves for stress ratios of -0.2 and 0.4 are not used in the data set. These two curves are close to each other, much below the curve for $R = -1$. A clear tendency of decreasing S-N curve with increasing stress ratio is shown.

The model can also be used to simulate fatigue stress life diagrams for new conditions for which S-N diagrams are not available in the literature. Here, we use the model to simulate S-N diagrams for Ti 6-4 alloy at different microstructure conditions and temperatures (Fig. 15.17). The neural network model predicts that the coarser microstructure and the higher temperature lead to lower fatigue strength. In a similar way, the model can be used to quantitatively simulate the S-N diagrams at various combinations of microstructure, surface, temperature and environment conditions.

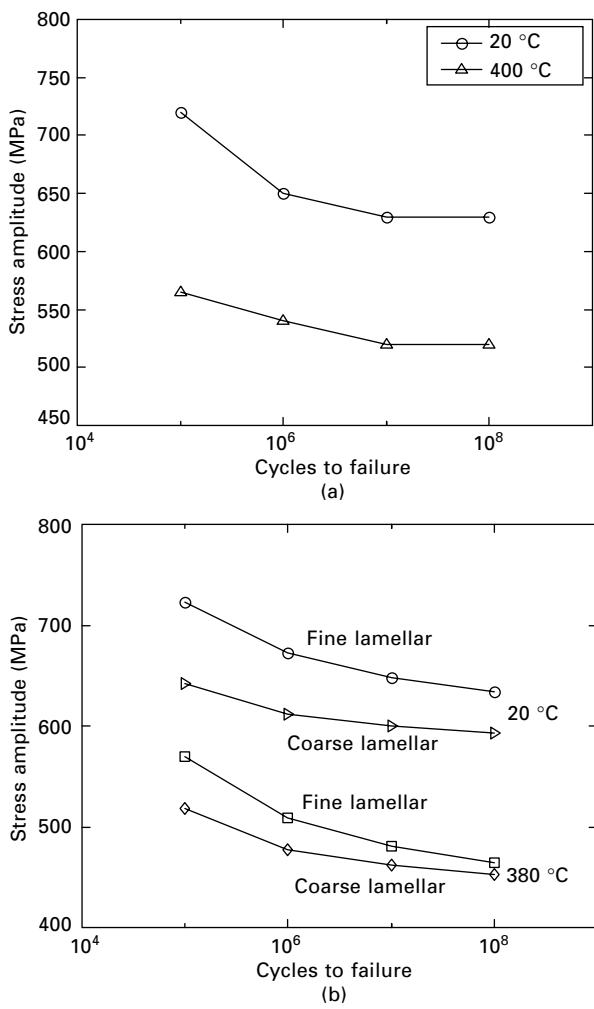
15.2.4 Graphical user interface

Based on the designed model of the artificial neural network, a graphical user interface (GUI) is created for easy use of the model (Fig. 13.2c). On input of the six parameters, the S-N diagram is simulated and plotted. In this way, the user can easily obtain a fatigue stress life diagram for Ti-6Al-4V. The GUI also allows comparison of two or more diagrams by plotting them together.

15.2.5 Summary

An artificial neural network has been created to predict the fatigue stress S-N diagrams for the Ti-6Al-4V alloy. The model has been used to study six conditions which influence the S-N curves, viz. microstructure, environment, texture, test/work temperature, surface treatment, and stress ratio. A graphical user interface has been created for use with the model. The program and the model can be used for:

- simulating S-N curves for the Ti-6Al-4V alloy as a function of the input conditions;
- investigating the influence of different factors affecting the fatigue of Ti-6Al-4V;
- reducing the amount of experimental work for measuring Ti-6Al-4V S-N fatigue strength.



15.17 Neural network simulations of fatigue stress life S-N diagrams for Ti-6Al-4V alloy. (a) Different temperatures. Microstructure: bimodal without texture; surface treatment: electrolytically polished; environment: 3.5% NaCl; stress ratio: -1. (b) Different temperatures and microstructures. Environment: 3.5% NaCl; surface treatment: mechanically polished (7 μ m); stress ratio: -1; texture: basal-transverse texture; transverse test direction.

15.3 Mechanical properties of gamma-based titanium aluminides

The objective of this section is to demonstrate a computer program to accurately predict the tensile properties of gamma-based titanium aluminides at various working temperatures as functions of alloy composition and strain rate. Since

experimental data has shown there to be no simple relationship between the tensile properties, alloy composition and microstructure, an artificial neural network (ANN) model is used to accurately predict these properties.

A successful and user-friendly system should reduce the need for room- and elevated temperature testing, thus reducing the cost of employing these materials. This could lead to an increased use of the materials within industry, although the challenge brought by the alloy ductility will remain the governing factor in their future application. This will have to be addressed by metallurgists if the alloy is to achieve the widespread use currently monopolised by conventional superalloys.

15.3.1 Model generation and description

Model overview

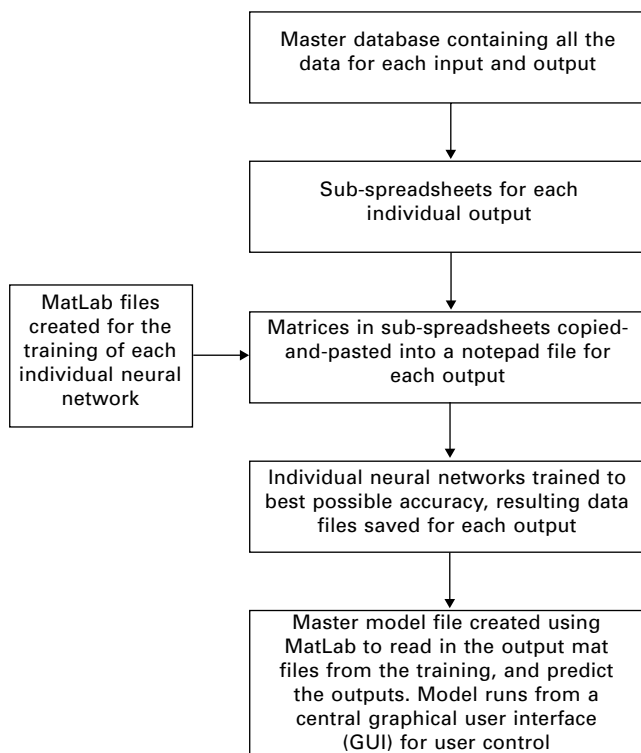
The input parameters of the model are alloy composition, microstructure and work (test) temperature. The composition includes the most commonly used alloying elements in γ titanium aluminide alloys: Al, Cr, Nb, V, Mn and C, and is presented by the amounts of the alloying elements. The microstructure of the alloy is taken into account, and is related to its thermomechanical processing (TMP) conditions. The test temperature is included since gamma-based titanium alloys will be used in elevated temperature environments. The outputs of the neural network model are the most important tensile mechanical properties: ultimate strength, elongation, reduction of area, and elastic modulus. A further input of strain rate (in s^{-1}) is required for the outputs of reduction of area. A most general schematic diagram of the network model is shown in Fig. 13.1d.

Principles of the model

The process of neural network modelling starts with the collection of data from external sources. These data are stored on a database, and used to decide the number and type of the input and output parameters. The data may need to be pre-processed in order to obtain a usable form for the network to read. A program to set up the neural network is then created, which then is trained using the stored database. The training process has many sub-processes. These are based on the availability of data and the reliability of output. This process is summarised in Fig. 15.18.

Input parameters

In order to train the network sufficiently, large arrays of input and output data pairs are used for each output parameter. These input and output arrays



15.18 Steps in creating the gamma-based titanium aluminides' mechanical properties model.

were taken from a master database, which was developed using available literature on the alloy types (Winstone, 2001). Table 15.5 gives the number of input/output data pairs for different gamma titanium aluminides collated from various sources. The selection of the input parameters is based on the planned model structure, with all relevant parameters represented as input data of the network. In order to reduce the training times, it is good practice to remove any input parameters from the training input layer that are constant throughout the data set. The following input parameters are used.

Alloy composition

Analysis of initial data led to the selection of six alloying elements: Al, Cr, V, Mn, Nb and C. The Rolls Royce XD type alloys were not used due to their specialist application. The use of carbon is widely documented in sources, and so was included in the model. The oxygen level in the alloys was mostly unknown and so was not included.

Table 15.5 Analysis of input and output data for the titanium aluminides model

Output	Number of data	Minimum value	Maximum value	Mean	Standard deviation	Alloying elements	Microstructure (for codes refer to Table 15.6)	Temperature range (°C)	Strain rate range (s ⁻¹)
Elastic modulus (GPa)	73	91	177	151	17	Al, V, C	All 0 (unknown)	25–1000	N/A
Ultimate strength (MPa)	185	37	1287	335	192	All	No 5	18–1200	N/A
Elongation (%)	142	0	99	17	25	All	All	15–1012	N/A
Reduction in area (%)	81	0	73	34	22	Al, Cr, Nb	Only 9 and 10	977–1200	0.0005–0.01

Microstructure

The morphology of the alloy is governed by its TMP conditions. In this model, 12 different microstructure types are described. Since the microstructure of an alloy is a qualitative measure, and since neural networks operate with numeric entries only, the microstructure types need to be represented numerically. This is achieved by assigning each microstructure a reference number, which will be used for the model input (Table 15.6).

A considerable amount of the available data does not describe the microstructure (about 40% of total data entries). However the remaining data (about 60% of total data entries) cover a wide variety of attainable microstructures, and are useful. The overlap in microstructure types is due to the different terminology used in different sources. For example, ‘fully transformed’ microstructure is similar to ‘fully lamellar’. These different terminologies are preserved in modelling however, to avoid possible distortion from original literature data. It should be noted that the difference in the numerical value, e.g. 5 for ‘fully transformed’ and 9 for ‘fully lamellar’ is not proportional to the difference in the nature of the corresponding microstructures.

Temperature

A wide range of temperature entries is used in the model, ranging from 15 to 1200 °C. Room temperature is assumed to be 25 °C. In the cases where the tensile test temperature is unknown, it is assumed that a room temperature (RT) tensile test is used. Most (about three quarters of total data entered) data range from 500 to 1200 °C, so the model will work with sufficient accuracy within these limits. It must also be noted that to form the sub-

Table 15.6 Microstructures used in the titanium aluminides neural network and their numerical equivalents

Alloy microstructure	Reference number
Unknown	0
Duplex	1
Single-phase	2
Equiaxed bimodal	3
Fully transformed	5
Fine lamellar grains	6
Coarse lamellar grains	7
Fully lamellar	9
Nearly lamellar	10
Primary gamma grains: fine grains	11
Primary gamma grains: coarse grains	12
Equiaxed gamma grains	13

models to predict the tensile properties, not all the temperature data entries were used, and only those that were relevant to the particular output were included. This means whilst overall the model functions with sufficient accuracy for a range of 500–1200 °C, for each individual output the working temperature range differs from the overall working range (Table 15.5).

Output parameters

The tensile properties predicted by the model are elastic modulus, ultimate stress, elongation and reduction in area. There are four models, one for each tensile property. However, in the text, sometimes the word ‘model’ is used to refer to the four models collectively.

Training of the artificial neural network

An important factor in the successful training of a network is the optimisation technique. Recent advances have led to much improved methods of numerical optimisation. There are non-linear relationships in alloys between their processing parameters and their mechanical properties.

Before the network was trained, the input and output variables were normalized within the range -1 to 1 . For the various models, the number of neurons in the hidden layer varied from 2 to 9 neurons. A Bayesian regularisation technique was used to improve the generalisation of the models.

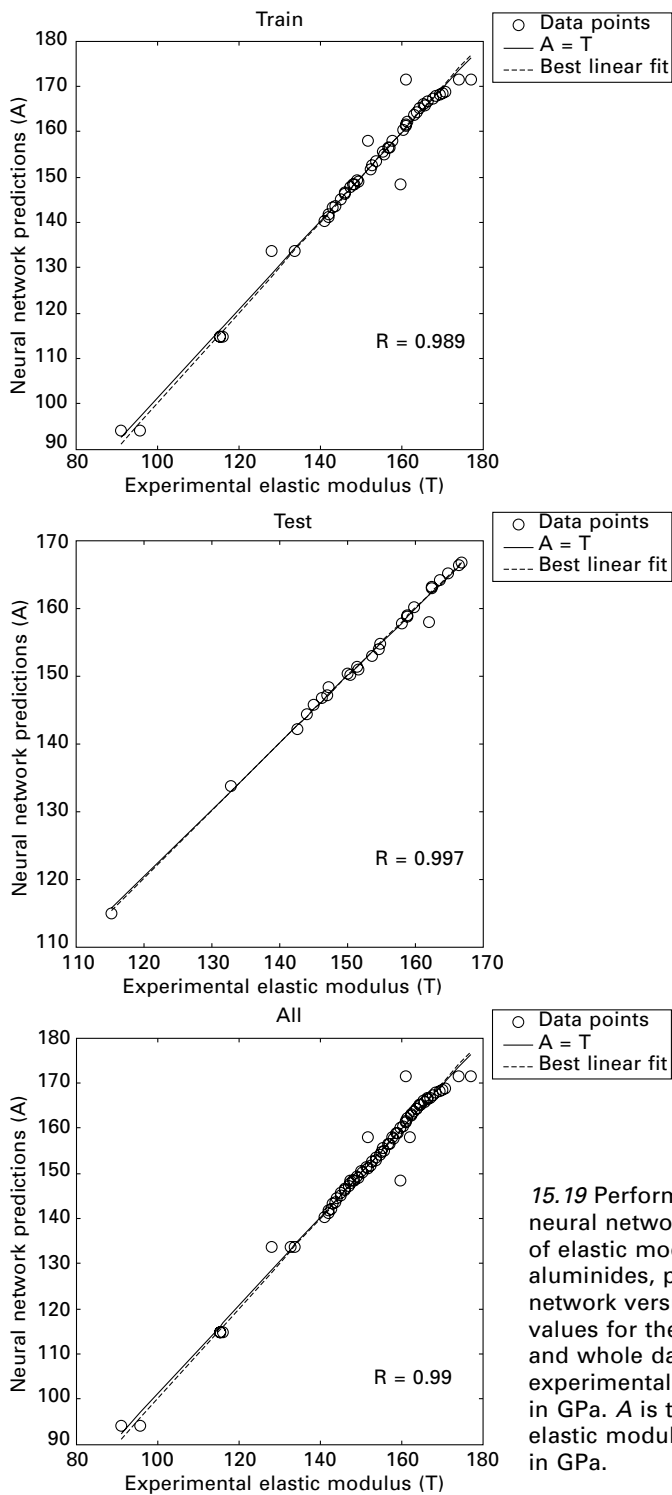
Performance of the neural network

The performance of the neural network was checked after training (Fig. 15.19). The analysis of the network response is plotted in the form of linear regression analysis between the network output (predictions) and the corresponding targets (experimental data). The neural network predicts the values to a high degree of accuracy. Similar graphs are obtained for other tensile properties.

The correlation coefficient (R) values for the test data sets only, for all outputs, are shown in Table 15.7. Five model training runs were made for each output, with the same neural network architecture but different division of training and testing data sets. The model with the highest R value (as given in Table 15.7) was chosen as the final model.

Further analysis of the performance accuracy was carried out using statistical analysis of the error of neural network predictions. Neural network predictions were compared to the corresponding experimental values. The relative errors were then calculated, using a relationship similar to Eq. [15.1].

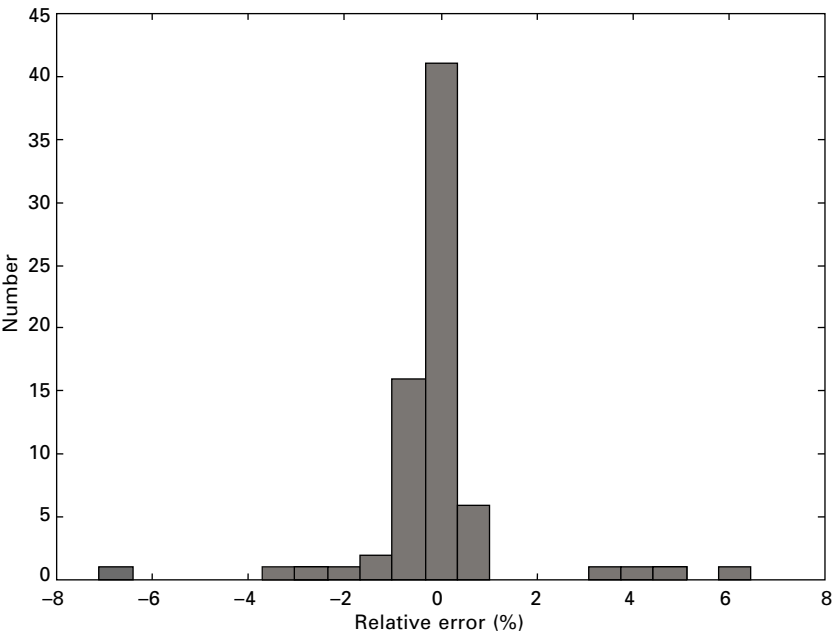
The results are displayed graphically, in a number versus error plot, using, as an example, the elastic modulus (Fig. 15.20). For most of the data set, the



15.19 Performance of the neural network for simulation of elastic modulus of titanium aluminides, plotting the neural network versus experimental values for the training, test, and whole data sets. T is the experimental elastic modulus, in GPa. A is the predicted elastic modulus from the NN, in GPa.

Table 15.7 Regression coefficients for each titanium aluminide tensile property model

Property	Test accuracy (<i>R</i>)	Number of neurons in hidden layer
Elastic modulus	0.997	2
Ultimate strength	0.957	9
Elongation	0.943	7
Reduction in area	0.971	3



15.20 Statistical analysis of the error of the neural network predictions for elastic modulus of titanium aluminides.

error of prediction is within $\pm 2\%$, which is a high degree of accuracy, of this particular model.

The other models exhibit reasonable degrees of error. The models give an overall satisfactory performance, and their output predictions are of an acceptable accuracy.

15.3.2 Comparison of the prediction and the experimental data

Using trained artificial neural networks, a model for the prediction of the tensile properties of titanium aluminides was created. It can be used to

predict, with sufficient accuracy, each of the four properties within the ranges given in Table 15.5.

In the following, tensile properties for different gamma titanium aluminides, with different microstructures and test temperatures, are predicted by the model and then analysed. All the results are compared with experimental data from the relevant literature, with positive outcomes.

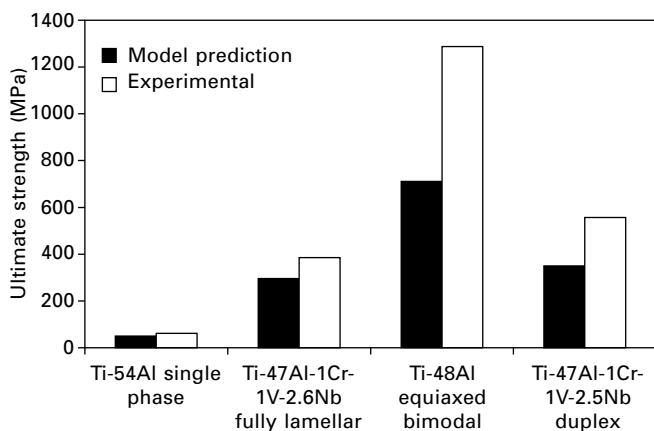
Room temperature properties

Room temperature tensile strength is selected for comparison purposes (Fig. 15.21). The accuracy of the other models is reasonably similar.

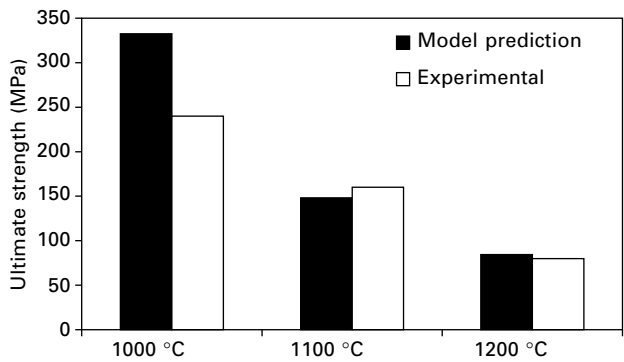
There is good agreement between the predicted values from the model and the experimental data for most of the outputs. Note that the reduction in area could not be compared in this case since the database for this property contained no data from room temperature tests. Some poor correlation is due to a lack of data, causing insufficient NN accuracy. This accuracy cannot be improved through training if no data are available.

Properties at elevated temperatures

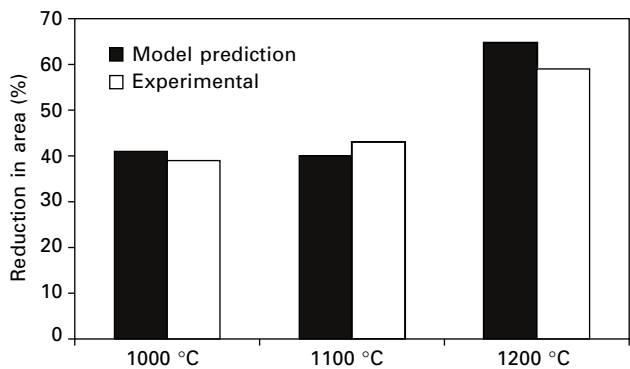
It is also required that the model predict, to within a sufficient degree of accuracy, the tensile properties at elevated temperatures, e.g. 200–1200 °C. This is important for the use of the alloys in aerospace applications. The tensile properties of various alloys are calculated across temperature ranges from 20 to 1200 °C, and compared with experimental data available for these temperatures in Figs. 15.22–15.24.



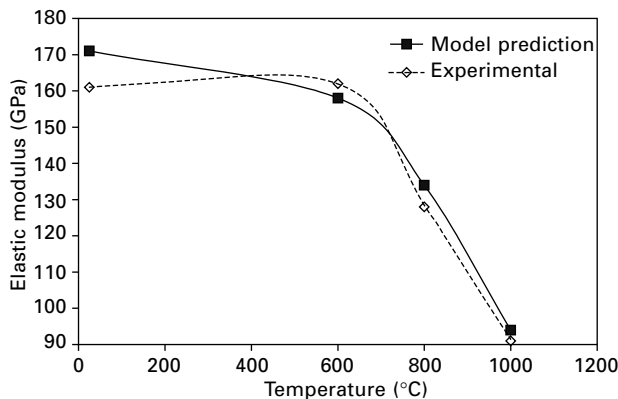
15.21 Accuracy of the model prediction for ultimate strength of titanium aluminides, at room temperature, when compared with experimental data.



15.22 Comparison between predicted and experimental tensile strength for Ti-46.5Al-5Nb alloy with a nearly lamellar microstructure, at different temperatures.



15.23 Comparison between predicted and experimental reduction in area for Ti-47Al-2Cr alloy with a nearly lamellar microstructure, at different temperatures.



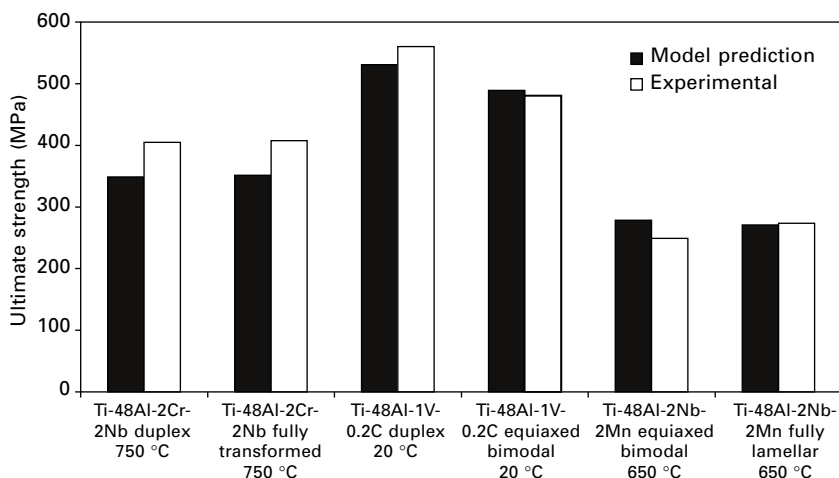
15.24 Correlation between predicted and experimental elastic modulus for Ti-40Al with increasing temperatures (20–1000 °C).

As can be seen, there is a good correlation between the predicted and the experimental values. This was also found with most of the other tests. It is useful to note that the strength properties (ultimate strength and elastic modulus) obtained from the model reduce as the temperature increases. The plasticity properties (elongation and reduction in area) obtained from the model increase as the temperature increases. Therefore the effect of the temperature on the model prediction of the tensile properties is consistent with what is expected from a metallurgical point of view. It is confirmed further by the experimental data. The output of the model allows us to obtain the safe working ranges of the alloys. For example, we can see from the predicted elastic modulus for Ti-40Al (Fig. 15.24) that no serious reduction in this parameter is apparent from 0 to 600 °C, after which it reduces rapidly. This is confirmed by the curve obtained from experimental data. Therefore we can say, in this instance, that the alloy has a safe working range of 0–600 °C for structural applications requiring a high elastic modulus. This is vitally important for the use of such an alloy in an aircraft.

Overall, the model performs well at elevated temperatures, giving sufficiently accurate predictions.

Effect of the microstructure conditions

The microstructure of the alloy is of considerable importance to its mechanical properties. The type of heat treatment can determine the microstructure of the alloy, and hence its ductility or strength. In order to understand the effect of microstructure types, the model is used for three alloys to predict the ultimate strength achieved with different microstructures (Fig. 15.25).



15.25 Correlation between predicted and experimental ultimate strength for three titanium aluminide alloys with various microstructures.

The model is in good agreement with the experimental data. However microstructures are described qualitatively, and have no quantitative information. The particular thermomechanical processing (TMP) conditions which produce the various microstructures, e.g. heating temperature, time, heating and cooling rates and environments are not taken into account in the model. Thus the model assumes that all alloys have received the optimal TMP conditions required to obtain the corresponding microstructures. The model would be more accurate, and of greater use to metallurgists, if it included the various degrees of TMP as well as the resulting microstructure. It would allow the user to estimate the TMP conditions needed to obtain the desired microstructure, and hence the desired properties. However, there are insufficient data sources available in the literature to do this.

Effect of alloy composition

The composition of the alloy has a major influence on its mechanical properties. Compositions for a wide range of alloys were used in the model. Attempts to simulate the correlation between the proportion of alloying elements and the alloy tensile properties showed that the experimental data were sufficiently accurate to allow the model to correctly simulate the effect of these alloying elements on the properties. The influence of oxygen was not considered in this model. This was assumed to be a constant value throughout for developmental purposes. However, the oxygen content in alloys may be desirable for certain applications, and would give a more accurate result if included. It would allow the user to obtain the optimum oxygen content within the alloy for certain properties, and enable them to decide the appropriate heat treatment procedure necessary to achieve it.

15.3.3 Graphical user interface

A graphical user interface (GUI) such as the ones shown in Chapter 13 and Section 15.1.7 was created for easy user interface with the model. When alloy composition, test temperature range and microstructure are entered, the model will plot a graph depicting the specified property variance over the temperature range. This allows the user to easily see the temperature dependence of any of the four tensile properties involved in the model for a selection of microstructures and any alloy composition. This allows various combinations of the inputs to be examined.

15.3.4 Summary

An artificial neural network has been created for the prediction of the tensile properties of gamma-based titanium aluminides using existing experimental

data from available literature. The model has been used to study the influence of the three most important input conditions, viz. alloy composition, microstructure and temperature, on four tensile properties. These properties are ultimate stress, elastic modulus, elongation, and reduction in area. Further input of strain rate is used in the modelling of reduction in area. Most of the models created are of acceptable accuracy within the experimental data range. A GUI has been created for use with the model. The program and the model can be used for:

- prediction of tensile properties for gamma titanium aluminide alloys as functions of their chemical composition, microstructure and working temperature;
- investigation of the interaction of these factors on the properties;
- reducing the amount of sample testing needed to obtain these properties.

Although the model produced for the tensile properties of gamma-based titanium aluminides has met with some success, there are several future additions that could be included to further improve the accuracy of prediction. Most importantly, new inputs could be added to the model. The actual TMP conditions used to achieve the described microstructures has been omitted from this model, and would provide benefit for users wishing to find the optimum TMP inputs to achieve their desired properties. Also the oxygen content within the alloys, an aspect affected by TMP conditions, could be included. More up-to-date experimental data could be included which would improve the less successful models. By increasing the amount of input data, there should be an improved training accuracy.

Alternative work relating to this topic would be the formation of corrosion models for similar alloys. The benefit of gamma-based titanium aluminides is their improved oxidation resistance, so it would be of great benefit to researchers and engineers if such a model was attempted. Then all available data on gamma titanium aluminides, including mechanical properties and corrosion resistance, could be collected on one master database and simulated on a master model. This may lead to an improved use of these materials within industry by reducing the cost of research and development into them, offering them as a viable alternative to conventional superalloys.

15.4 Reference

Winstone M R (ed) (2001), *Titanium Alloys at Elevated Temperature: Structural Development and Service Behaviour*, London; IoM Communications.

15.5 Appendix

A list of the alloys used for training and test of artificial neural network for prediction of mechanical properties of titanium alloys:

Ti-6Al-2Sn-1.5Zr-1Mo-0.35Bi-0.1Si, Ti-6Al-2Nb-1Ta-0.8Mo, Ti-6Al-2Nb-1Ta-1Mo, Ti-6Al-1Mo-2Nb-1Ta, Ti-3Al-2.5V, Ti-5Al-2.5Sn, Ti-5Al-2Zr-2Mo-0.25Si, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-2Sn-4Zr-2Mo-0.1Si, Ti-1Sn-5Zr-2.25Al-1Mo-0.25Si, Ti-8Al-1Mo-1V, IMI 834, IMI 417, Titanium 1100, Ti-10V-2Fe-3Al, Ti-11.5Mo-Zr-4.5Sn, Ti-3Al-8V-6Cr-4Mo-4Zr, Ti-12V-2.5Al-2Sn-6Zr, Ti-15Mo-5Zr, β -21S, Ti-11.5V-2Al-2Sn-11Zr, Ti-13V-11Cr-3Al, Ti-13V-2.7Al-7Sn-2Zr, Ti-15V-3Cr-3Al-3Sn, Ti-15Mo-5Zr-3Al, Ti-8Mo-8V-2Fe-3Al, β -CEZ, Ti-4.5Al-5Mo-1.5Cr (Corona 5), Ti-8Mn, Ti-5Al-2Sn-2Zr-4Mo-4Cr (Ti-17), Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si, Ti-4Al-4Mo-2Sn-0.5Si (IMI 550), Ti-6Al-2Sn-4Zr-6Mo, Ti-6Al-4V, Ti-6Al-6V-2Sn, Ti-7Al-4Mo, Ti-5Al-5Sn-2Zr-2Mo-0.25Si, Ti-5Al-3.5Sn-3Zr-1Nb-0.3Si, Ti-5Al-6Sn-2Zr-1Mo-0.25Si, Ti-6Al-1.7Fe-0.1Si, Ti-4.5Al-3V-2Mo-2Fe, Ti-6Al-7Nb, Ti-4Al-4Mo-4Sn-0.5Si, Ti-4Al-3Mo-1V, Ti-5Al-1.5Fe-1.4Cr-1.2Mo, Ti-5Al-2.5Fe, Ti-6.4Al-1.2Fe, Ti-2Fe-2Cr-2Mo, Ti-8V-5Fe-1Al, Ti-16V-2.5Al, Ti-3Al-1.5Cr-1.5Fe, Ti-6Al-2Fe, Ti-6Al-2Fe-0.1Si, Ti-6Al-1Fe-1Cr, Ti-8Al-2Fe, VT14, VT15, VT16, VT18, VT20, VT22, OT4, VT1-00, VT3-1, VT5, VT5-1, VT-6, VT-6C, VT-8, VT-9.

Surface gas nitriding: phase composition and microstructure

Abstract: This chapter is about experimental research using differential scanning calorimeter while nitriding titanium alloys at various temperatures and for various periods. X-ray diffraction technique reveals the phase transformations that occur during gas nitriding. Because of the nitrogen interaction, a nitrided layer is formed that consists of titanium nitrides, followed by an interstitial solution of nitrogen in titanium. The microstructural changes in relation to the alloy composition and processing parameters are detailed. The microstructure of alloys nitrided at temperatures below their β -transus temperatures is uniform and homogeneous. With an increase of temperature above their β -transus temperatures, the microstructure changes to irregular.

Key words: nitriding, microstructure, metallography, X-ray diffraction, scanning electron microscopy (SEM).

16.1 Introduction

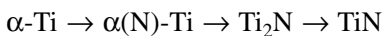
Though they have excellent corrosion resistance, titanium and titanium alloys have had rather little use in mechanical engineering applications because of their poor fretting fatigue resistance, low surface hardness and wear resistance, high coefficient of friction and susceptibility to fatigue and fracture (Guleryuz and Cimenoglu, 2005; Škorić *et al.*, 2004). From theoretical calculations, metals with low theoretical tensile and shear strengths have higher coefficients of friction than higher-strength materials. Within the class of hexagonal close-packed (hcp) structures, titanium has relatively low values for tensile & shear strengths. It is therefore expected that titanium would exhibit high frictional values, which has been demonstrated for titanium sliding against itself in air.

The low surface hardness and wear resistance limit the application of titanium alloys for structures working in conditions of friction and contact loading. To achieve the full benefit of titanium alloys in friction and wear applications, surface modification treatments are required to effectively increase the surface hardness and the near surface strength, thereby reducing the coefficient of friction. There are many ways to improve the wear performance of titanium alloys, including physical vapour deposition, thermal spray, and thermo-chemical conversion treatments. Different technologies for surface treatment aiming at improving the tribological properties of titanium alloys are being attempted. Some of these treatments aim mainly to change the microstructure of the surface layers (without change of the chemistry), using

thermal influence with extraordinarily high heating and cooling rates. The second group of methods can be classified as the formation of coatings on top of the base material. Finally, the third and probably the largest group consists of technologies for thermo-chemical surface treatments of titanium alloys – nitriding, carburising and oxidation. Recently, duplex surface engineering (combining two or more of the above groups) of titanium alloys is also developed.

One of the most widely used technologies for thermo-chemical treatments of titanium alloys is nitriding, by which nitrogen is incorporated into Ti-based alloys at elevated temperature via the surface. This process can achieve various combinations of improved material performances. In principle, surface hardness, wear performance and fatigue performance, as well as aesthetic appeal, can be improved. Different technologies of nitriding of titanium alloys have been developed, including plasma nitriding, laser nitriding, ion nitriding and gas nitriding. Compared to the other technologies, gas nitriding is a promising method for many applications because of its simplicity in terms of equipment, and independency in terms of geometry and dimensions of the work pieces to be treated. Gas nitriding is one of the thermo-chemical surface conversion treatments whereby nitrogen is applied forming a nitride layer such as titanium nitride. The mechanical properties of titanium alloys through the application of nitrogen to the surface reflect the characteristics of the microstructures. The change of phase composition and morphology of the surface layers is the main reason for the surface hardening after gas nitriding. This method of nitriding promises to improve the surface hardness, corrosion resistance, wear performance, friction coefficient and fatigue and fracture performance. It is shown to easily form a harder layer on the surface of the material, but it requires a high temperature of about 650–1000 °C, and a long period of nitriding time of 1–100 hours.

The development of the nitrided layer in the surface region of titanium alloys is through a complicated diffusion process. The phases of the transition on the surface of titanium under nitriding can be written as (Zhecheva *et al.*, 2005):



where $\alpha(\text{N})\text{-Ti}$ denotes $\alpha\text{-Ti}$ with N in solid solution.

The structure of nitrided layers described above is evolved assuming the diffusion of nitrogen in pure titanium, and it can be derived by using the rules of the reaction diffusion to the binary Ti–N phase diagram. The thickness of the nitrided layer is due to the diffusion process. The coefficient of diffusion can be determined by:

$$D = A \exp\left(-\frac{A}{RT}\right) \quad [16.1]$$

where D is the diffusivity, A is the pre-exponential frequency factor, Q is the activation energy, R is the molar gas constant and T is absolute temperature in Kelvin.

The growth of the nitrided layer depends on two parameters: nitriding time and temperature. As reported by Paransky *et al.* (2000), the reaction phase development at the AlN–Ti and AlN–TiAl interface showed that the increase in growth of Ti_3AlN and TiN grains blocked the path of the diffusion flow. The progressive increase of nitrided layer thickness can be described by the parabolic time law, i.e. the thickness of the layer with the square root of nitriding time.

Nitriding can improve the tribological properties of Ti–Al based alloys. Research has found that the thin layer of titanium nitride (TiN) on such alloys is effective in increasing their wear resistance. TiN is more thermodynamically stable than aluminium nitride (AlN); therefore a TiN layer can be formed on Ti–Al alloys by direct gas nitriding.

16.1.1 Research objectives

Because gas nitriding is a complicated diffusion process, it is important to quantify the influences of different processing parameters and alloy composition on the phase composition, microstructure and properties of the surface layers after gas nitriding of titanium alloys. Various experimental work in this direction was motivated by the desire to optimise processing parameters for gas nitriding of different titanium alloys.

The nitriding behaviour of titanium alloys in relation to the effects of alloy composition and processing conditions can normally be analysed using the physical and statistical approaches. However, it would be useful to create computer-based models for simulation and prediction of characteristics and properties of titanium alloys after the thermo-chemical treatment of gas nitriding. They would allow an optimisation of the nitriding processing parameters for various applications. This would have advantages for the experimental work in terms of reducing cost and time consumption.

Therefore, for the nitriding chapters in this book, the following objectives were considered:

- (i) To investigate the phase transformations and the microstructural changes of titanium alloys after nitriding at different temperatures and for different periods of time.
- (ii) To study and analyse the surface hardness behaviour and the surface morphology in relation to the alloy composition and the nitriding processing parameters.
- (iii) To analyse the corrosion behaviour of titanium alloys before and after nitriding in relation to the alloy composition and corrosive conditions.

- (iv) To develop a computer-based statistical model for simulation and prediction of the influence of the type of nitriding, temperature and time of nitriding, gas mixtures and alloy composition on the microhardness profile behaviour of titanium alloys.
- (v) To model the evolution of the surface layers during gas nitriding of titanium alloys.

16.1.2 Structure of the nitriding chapters

This and the next two chapters describe the experimental study and modelling of the process of surface gas nitriding of titanium alloys. The scope of investigation for titanium alloys covers the experimental studies of the phase transformations, microstructural changes, the evolution of the hardness and the surface morphology in relation to the alloy composition and nitriding processing parameters such as temperature and time. The corrosion behaviour of nitrided titanium alloys under various corrosive conditions will be discussed. Neural network modelling for simulations and predictions of microhardness profiles of nitrided titanium alloys as well as modelling of the evolution of surface nitrided layers will be also described. The structure of the three chapters is as follows.

Chapter 16 discusses the experimental study of the phase modifications and microstructural changes of various titanium alloys after surface gas nitriding in relation to alloy type and processing parameters. X-ray diffraction (XRD) analyses and microscopy observations are discussed.

Chapter 17 presents the analyses of the mechanical properties, including microhardness, tensile, and fatigue, for the nitrided titanium alloys in relation to the effects of the alloy composition and nitriding processing parameters. The chapter then shows the surface morphology of titanium alloy after nitriding. The influence of the initial surface roughness on the surface characteristics of one titanium alloy will be examined. The influence of the processing parameters of gas nitriding on the surface roughness, phase modifications and the microstructure of the nitrided layers will be analysed. The chapter finally examines the corrosion behaviour of titanium alloys before and after gas nitriding in relation to the different alloy composition and corrosive conditions, using a weight loss corrosion test method.

Chapter 18 is on modelling, and starts with the artificial neural network (ANN) modelling of microhardness profiles of nitrided titanium alloys. The computer models have been developed using data from the literature and the experimental data given in Chapter 17. The models are used for simulation and prediction of microhardness profiles in relation to the type of nitriding, temperature and time of nitriding, gas mixtures and alloy composition. The chapter then details the modelling of the nitrogen distribution, the thickness of the nitrided layers and the incubation time for the formation of the layers

for titanium alloys. Models for simulation and monitoring of the evolution of surface layers during gas nitriding of titanium alloys are developed, based on analytical and numerical solutions of the diffusion equation.

16.1.3 The nitriding experimental process

The objective of this chapter is to examine the effect of surface gas nitriding at different temperatures and for different periods of time on the phase transformation behaviour and the microstructure of several titanium alloys with different chemical compositions. All samples were surface gas nitrided in a pure nitrogen atmosphere using different processing parameters. Their phase modifications and microstructure are studied using X-ray diffractometer, optical microscope and scanning electron microscope. The main aim is to reveal the influence of the gas nitriding processing parameters on the microstructure and properties for different titanium alloys.

The nitriding experiments will be divided into two parts. The first part starts with surface gas nitriding at two temperatures, 950 and 1050 °C. These temperatures are purposely chosen because they are closely below and above the β -transus temperatures for three of the alloys (Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V). This means that when the nitriding is performed at 1050 °C, these alloys will be in a homogeneous β -phase state whereas when the nitriding is performed at 950 °C, these alloys will be in an $\alpha + \beta$ mixture phase state. Hence, one can expect different kinetics as well as microstructure morphologies and properties for nitriding under these different phase composition conditions. For the Ti-10V-2Fe-3Al alloy, both temperatures are above its β -transus temperature, implying that at both temperatures of nitriding, this alloy would be in β -phase state.

The second part of the nitriding experiments is at a lower temperature of 850 °C, which is at the same time just above the β -transus temperature of the Ti-10V-2Fe-3Al alloy. For this alloy, experiments at 750 °C, which is below its β -transus are performed. The purpose is to demonstrate the influence of the processing temperature and time of nitriding on the phase modifications, microstructural changes and properties. The choice of nitriding temperatures for other alloys is based on similar consideration around their β -transus.

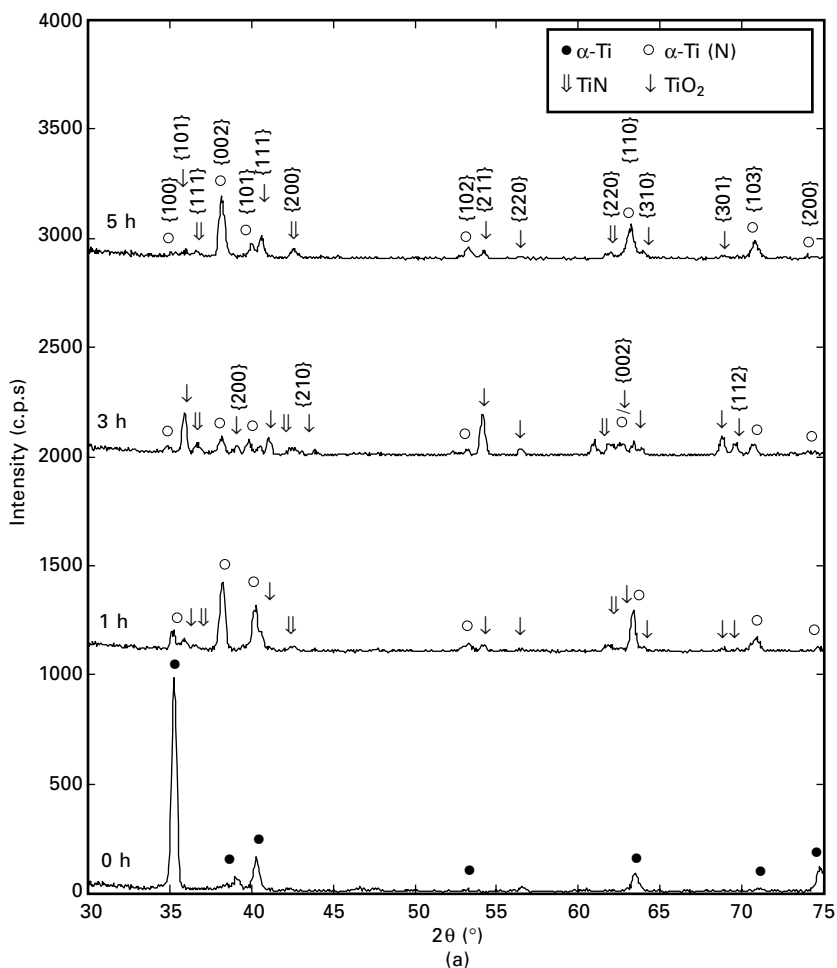
16.2 Near- α Ti-8Al-1Mo-1V

16.2.1 Phase composition

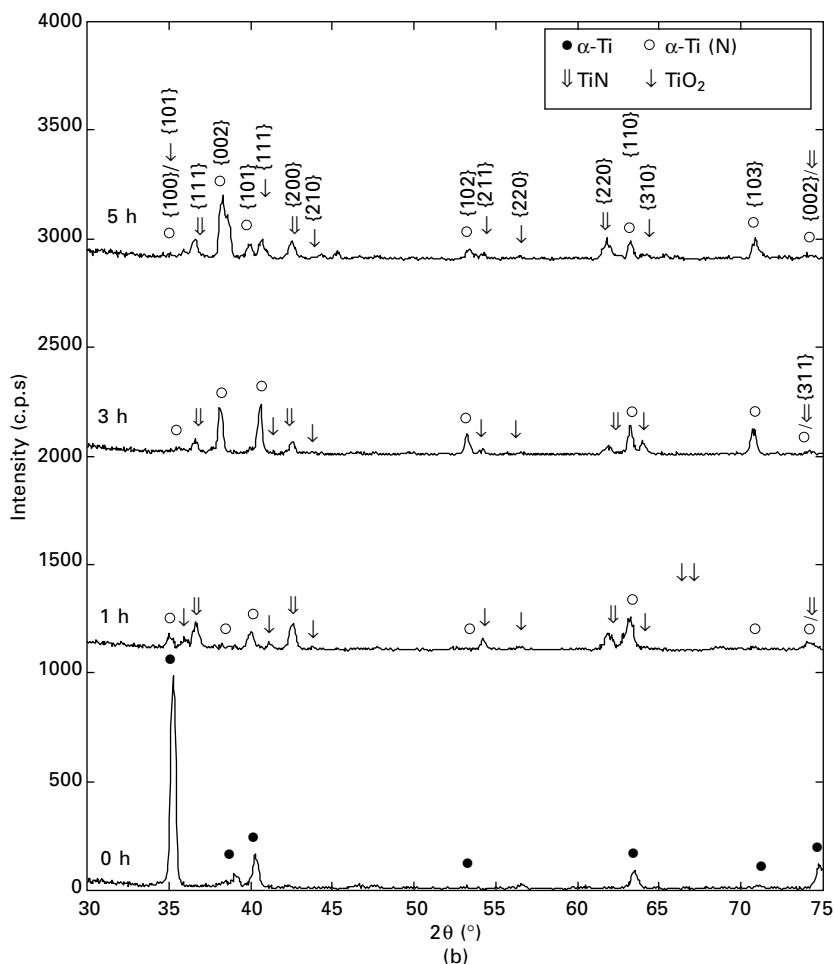
When titanium is in an active nitrogen atmosphere at high temperature, the nitrogen absorbed at the surface diffuses into the material. As a result of the nitrogen interaction, a nitrided layer is formed that consists of a compound layer on the surface of the material, which is mainly composed of the titanium nitrides Ti_2N and TiN in the general case, followed by a diffusion zone

which is composed of an interstitial solution of nitrogen in the hcp α titanium phase.

The coloration of the surface changes after nitriding, due to the new compound phase formation. The colour of the alloy surface is grey after gas nitriding at 950 and 1050 °C for 1 hour. It turns red after nitriding for 3 and 5 hours, again at both temperature regimes. The new phases are confirmed by X-ray analyses. The initial sample of Ti-8Al-1Mo-1V consists of hcp α -Ti (Fig. 16.1a,b bottom). The initial α phase has a crystallographic texture. During nitriding and subsequent cooling, α -Ti transforms to α -Ti(N) that has a hexagonal crystal structure, face centred cubic TiN and tetragonal



16.1 X-ray diffraction patterns of Ti-8Al-1Mo-1V after gas nitriding at (a) 950 and (b) 1050 °C for 1, 3 and 5 hours. New phases of titanium nitride and titanium oxide are formed.



16.1 Continued

TiO_2 . The α -Ti(N) phase is distinguished from the α -Ti because the peaks belonging to the hcp structure are shifted to lower 2θ angles, due to the increased lattice parameter caused by interstitial nitrogen. The presence of oxygen is also possible, but it is expected to be in a small amount compared to the nitrogen. The phase transformations taking place on the surface during the nitriding can be expressed as: $\alpha\text{-Ti} \rightarrow \alpha\text{-Ti(N,O)} + \text{TiN} + \text{TiO}_2$. For simplicity, in this book, only α -Ti(N) will be used, instead of α -Ti(N,O).

Tetragonal Ti_2N phase is not detected in the X-ray diffraction patterns, in contradiction of some results from the early Russian literature (Boriskina *et al.*, 1981; Fedirko *et al.*, 1993). Despite the high purity of the nitrogen gas (99.998%), for all the cases, tetragonal TiO_2 phase is detected in the compound layer together with TiN. This oxide film formation can be explained as follows, taking into account that oxygen is very active at temperatures above

800 °C. The first reason can be that, even using a high purity nitrogen, there is still a possibility for a small amount of O₂ to remain in the nitriding system. The second reason can be that there are always small leaks.

After nitriding at the lower temperature of 850 °C for 1, 3, 5 and 10 hours, as well as at 950 °C for 10 hours, mainly titanium oxide and small amounts of titanium nitride and α titanium enriched with nitrogen are detected. The same results are observed for the rest of the samples from the second part of the experiments (see the last paragraph of Section 16.1). These results may be caused by some problems with the equipment, such as the ones mentioned above. That is the reason why some additional X-ray analyses after removing layers were performed, to reveal the phase composition beneath these oxide films (Section 16.3).

Ti-8Al-1Mo-1V alloy contains a relatively high amount of aluminium, but no nitrides of aluminium are formed on the surface during high temperature nitriding. The precipitation of these phases in the diffusion zone underneath the compound layer, if it happened, is probably not detectable by X-ray measurements from the surface of the specimens.

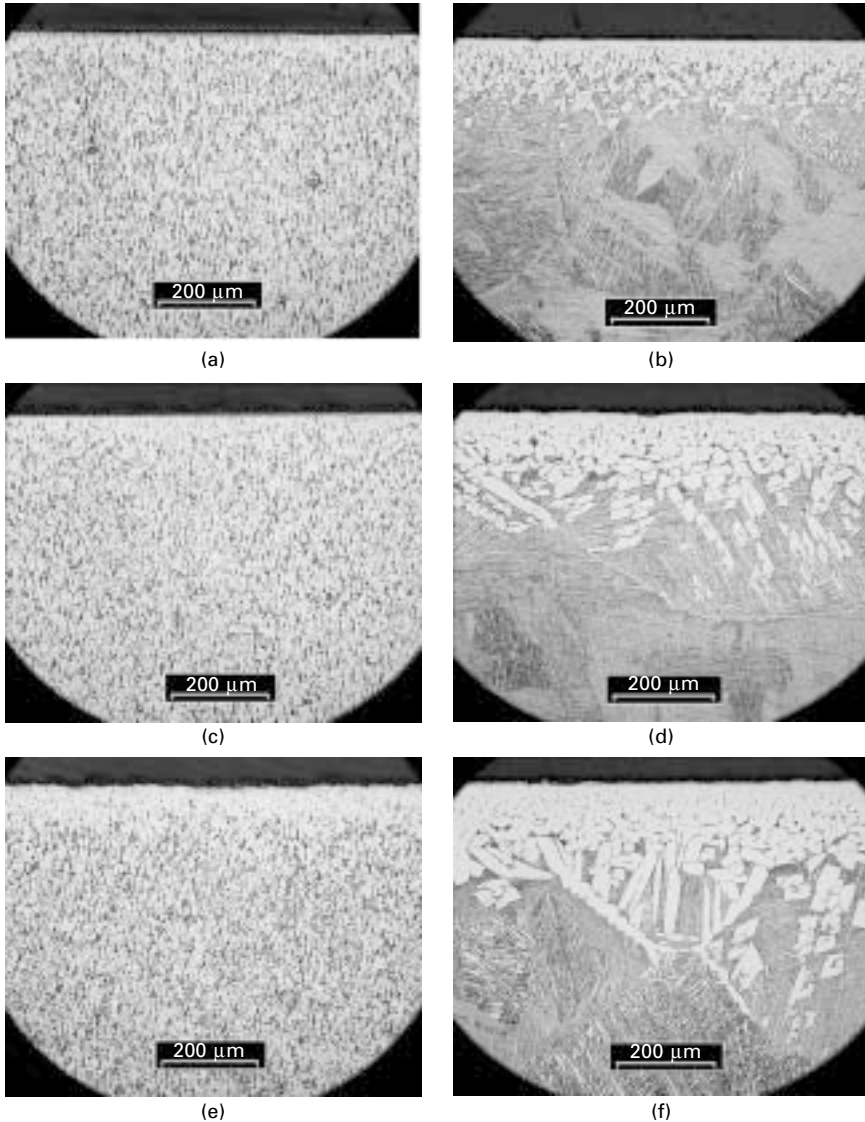
The lattice parameters a and c of the α phase are calculated for the nitrided alloy, by fitting the entire diffraction patterns. There is no clear tendency for variation of the lattice parameters after nitriding for different periods of time.

Residual stress may be expected in the nitrided layer induced by the process of nitriding. These internal stresses can be either tensile or compressive. More than 95% of the reflected X-ray beam for the α -Ti {213} diffraction peak is from within the depth of penetration at 15.5 μm . Since the thickness of the compound layer formed on the surface of these titanium alloys during gas nitriding is estimated at 5–10 μm , the entire compound layer is subjected to the penetrated X-ray beam and α -Ti(N) reflections are observed in the diffraction pattern.

The angles of 2θ from α -Ti {213} obtained at different tilted angles during XRD analysis do not show significant shift. Therefore, nitrided Ti-8Al-1Mo-1V has insignificant amount of residual surface stress in the α -Ti(N) phase.

16.2.2 Microstructure

The microstructure of the cross-section is shown in Fig. 16.2. The shape of all optical micrographs is due to the circular configuration of the microscopy imaging unit and not the shape of the specimens. The microstructure shows the three zones formed during the nitriding: compound layer, diffusion zone and unaffected substrate. There is a clear boundary between the compound layer and the diffusion zone for most of the samples. The compound layer covers the entire surface. It is very hard, thin and brittle. Its thickness for



16.2 Microstructure of Ti-8Al-1Mo-1V after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours. (a) 950 °C, 1 h; (b) 1050 °C, 1 h; (c) 950 °C, 3 h; (d) 1050 °C, 3 h; (e) 950 °C, 5 h; (f) 1050 °C, 5 h.

the samples nitrided at both temperatures for 3 and 5 hours varies between 2 and 10 μm , depending on the time and the temperature of nitriding. Time prolongation and temperature increase result in an increase of its thickness.

Below the compound layer is the diffusion zone. With an increase of the temperature from 950 to 1050 °C and the time from 1 to 5 hours, the thickness

of this zone increases. There is a difference between the microstructures after gas nitriding at temperatures below and above the β -transus for this alloy. The microstructure is homogenous for Ti-8Al-1Mo-1V nitrided at 950 °C, and inhomogeneous for the alloy nitrided at the higher temperature (Fig. 16.2). This difference is due to the phase transformations between α and β that appear at the higher temperature of nitriding.

After nitriding at a higher temperature than the β -transus, the diffusion layer consists of two sub layers. The first one is immediately below the compound layer, which is continuous α solid solution enriched with nitrogen. There might also be some precipitates of titanium nitrides. In most of the cases, this is a uniform white layer formed during the process of gas nitriding and further cooling. The solubility of nitrogen in α -Ti is very high, according to the Ti-N phase diagram, and it can reach 20 at.%. The thickness of this layer can increase with the increase of the time of nitriding. The second layer below the first one and above the inner unaffected substrate is composed of white coarse column-like grains and a finer structure, the latter appearing the same as the substrate layer. These coarse grains have grown in depth, albeit usually inclined, and in some places along the grain boundaries in the substrate. This layer was probably formed during cooling as a result of β -(N) to α -(N) phase transformation. It was probably β phase enriched with nitrogen, which during cooling was transformed to α -Ti(N,O) phase. In turn, on further cooling, the α -Ti(N,O) phase could precipitate titanium nitrides. The solubility of nitrogen is much smaller in β than in α phase. As a result of this, the values of the microhardness in the second zone are much lower than in the first zone (see Chapter 17) (Shashkov, 2001).

With an increase of the temperature from 950 to 1050 °C, the thickness of the nitrided layer increases. This is because the diffusion coefficient increases with an increase of temperature. Naturally, the increase of the diffusion time from 1 to 5 hours results in an increase of the layer thickness. The maximal thickness of the nitrided layer varies between 100 and 350 μm , which can be seen from the microhardness profiles in Chapter 17. It is difficult to determine the thickness of the nitrided layer from the microstructure images of the cross-sections, because there is no clear boundary between the diffusion zone and the substrate.

The microstructure after nitriding at the lower temperature of 850 °C is similar to the microstructure after nitriding at 950 °C, because they both are below the β -transus temperature of Ti-8Al-1Mo-1V.

16.3 Near- α Ti-6Al-2Sn-4Zr-2Mo

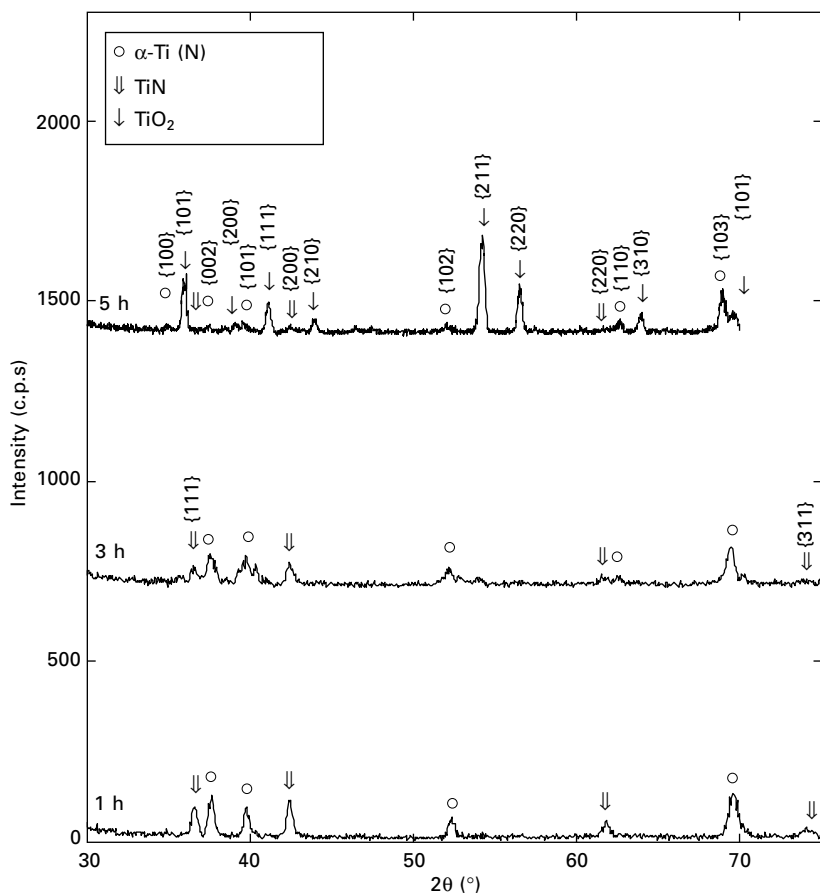
16.3.1 Phase Composition

As a result of the nitrogen and oxygen interaction with the alloy surface, α -Ti(N), TiN and TiO₂ lie at the outmost surface of nitrided Ti-6Al-2Sn-4Zr-

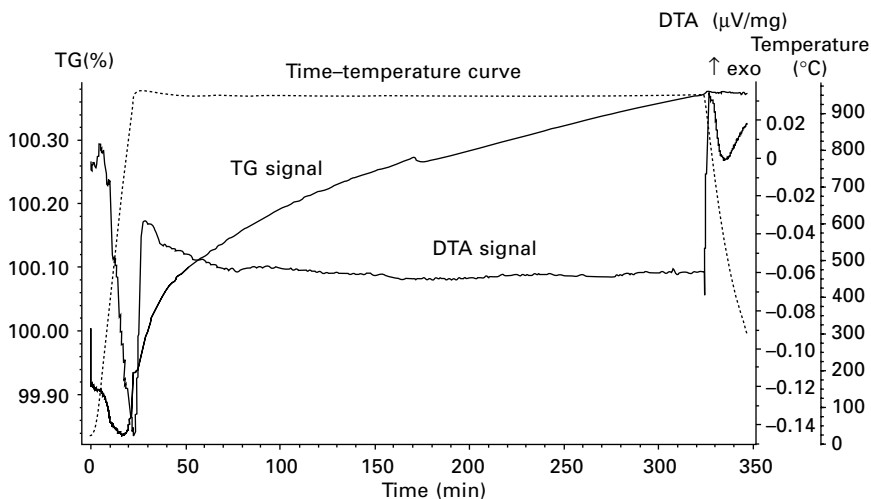
2Mo (Fig. 16.3). α -Ti(N) has a similar diffraction pattern to $\text{TiN}_{0.3}$. $\text{TiN}_{0.3}$ has the lowest nitrogen content among all titanium nitrides and a similar structure to α -Ti, and it was detected on the surface of titanium alloys nitrided under similar processing conditions, as reported in the literature. It is difficult to distinguish which of these phases is present, due to the similarity of their diffraction patterns.

Ti-6Al-2Sn-4Zr-2Mo alloy, as well as Ti-8Al-1Mo-1V alloy, has a high aluminium content and because of that it is supposed that the aluminium-rich phases Ti_3Al or Ti_2AlN may exist under certain processing conditions. XRD analyses (Fig. 16.3), however, do not show Ti_3Al or Ti_2AlN phases.

The formation of new phases is also evident in the differential scanning calorimetry and thermo-gravimetry (DSC/TG) curves in Fig. 16.4. It can be seen that phase transformations took place during heating and cooling for



16.3 X-ray diffraction patterns of Ti-6Al-2Sn-4Zr-2Mo after gas nitriding at 1050 °C for 1, 3 and 5 hours.



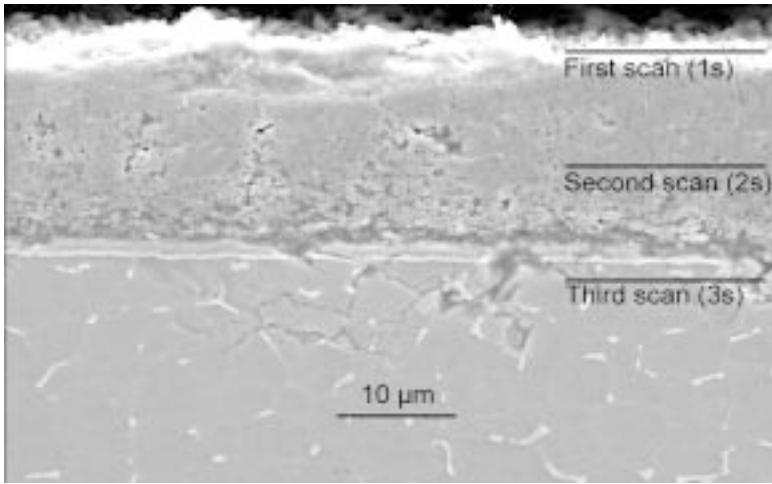
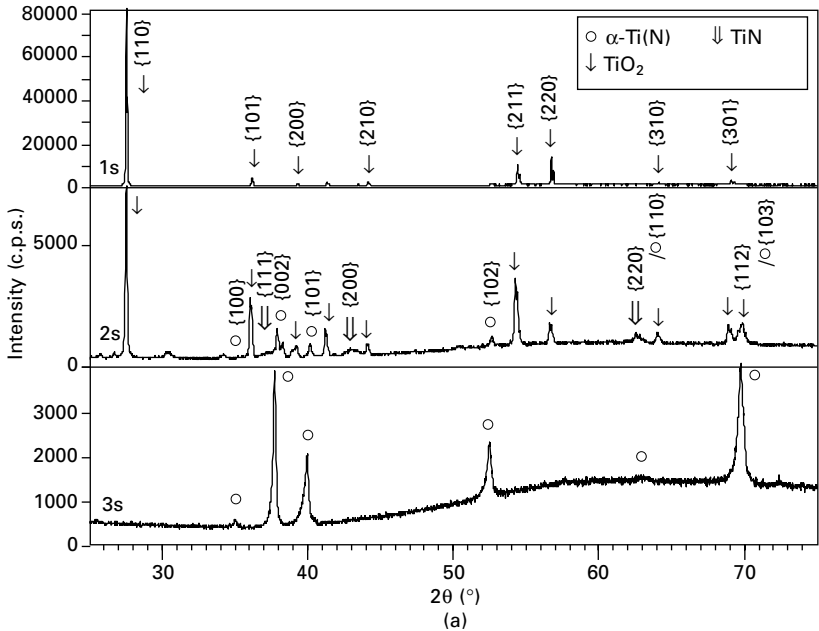
16.4 DSC and TG curves of Ti-6Al-2Sn-4Zr-2Mo nitrided at 950 °C for 5 hours.

the sample nitrided at 950 °C for 5 hours. These curves are from the DSC with TG, so the increase of the sample mass could also be recorded during the process of nitriding. An increase of about 0.5% is obtained for the sample nitrided at 950 °C for 5 hours.

Titanium oxide TiO_2 is detected for all alloys. Further experiments were carried out, removing the surface layers of a nitrided sample in steps of approximately 10 μm , performing X-ray analyses after each removing step. These experiments were carried out in order to see how the phase composition changes with depth (Fig. 16.5). From the first scan, it can be seen that the top layer consists of mainly TiO_2 . Underneath, TiN and $\alpha\text{-Ti(N)}$ are also detected. The third scan shows the existence of only $\alpha\text{-Ti(N)}$. These results prove that the oxide is present on the surface of the materials and does not penetrate the sample.

16.3.2 Microstructure

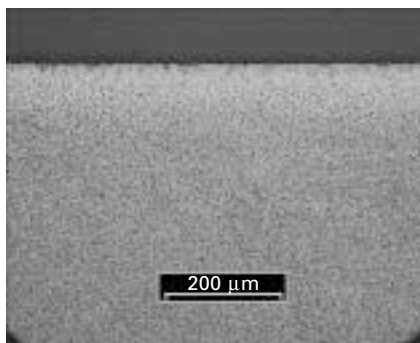
There are differences in the microstructure of the alloy nitrided at different temperatures and for different times (Fig. 16.6). The nitrided layer after 950 °C is uniform and homogeneous, and the layer thickness can be measured. The layer thickness is 60, 120, and 180 μm after 1, 3, and 5 hours, respectively, with an error of $\pm 10 \mu\text{m}$. By increasing the nitriding temperature to 1050 °C, an irregular needle structure is formed under the surface. In this case, it is difficult to define the layer thickness from the microstructure. The grain growth at the higher nitriding temperature is because 1050 °C is above the β -transus temperature for this alloy (995 ± 15 °C). The grain size increases to



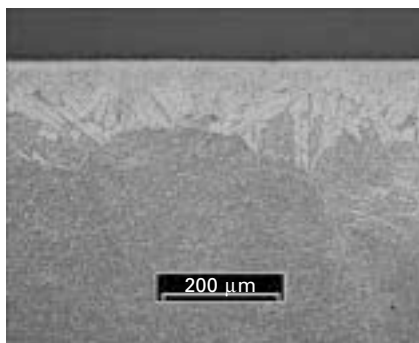
(b)

16.5 (a) X-ray diffraction patterns of Ti-6Al-2Sn-4Zr-2Mo after gas nitriding at 950 °C for 5 hours and removing the surface layers in steps of 10 μm; and (b) SEM micrograph of the microstructure and the positions of the scans.

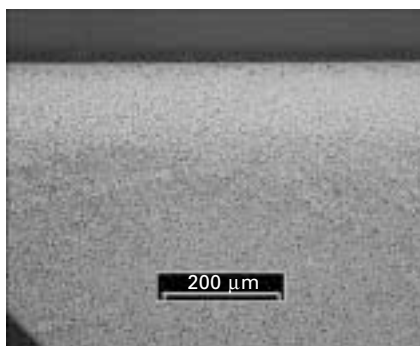
the order of 400 μm in length and 50 μm in width, after 5 hours nitriding time, similar to the results for Ti-8Al-1Mo-1V. The alloys are in different phase conditions during nitriding at 950 and 1050 °C. At 950 °C, the diffusion zone is mainly in the α phase state, while at 1050 °C, the β phase is the only



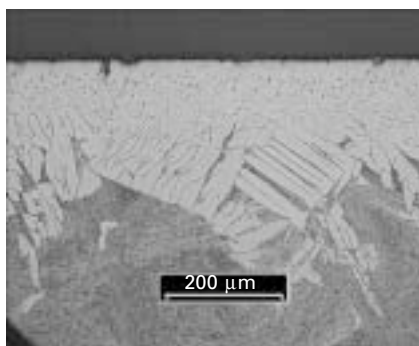
(a)



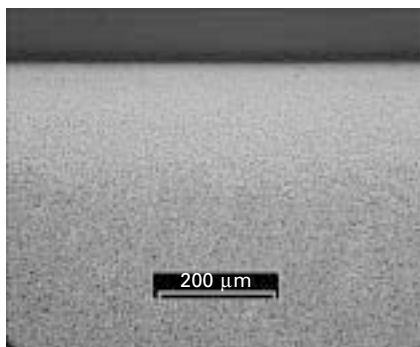
(b)



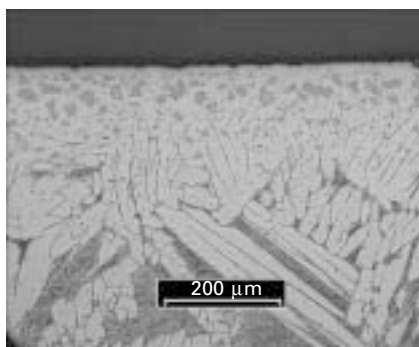
(c)



(d)



(e)



(f)

16.6 Microstructure of Ti-6Al-2Sn-4Zr-2Mo after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours. (a) 950 °C, 1 h; (b) 1050 °C, 1 h; (c) 950 °C, 3 h; (d) 1050 °C, 3 h; (e) 950 °C, 5 h; (f) 1050 °C, 5 h. The dark particles near the surface, most clearly seen in (f), are stains after etching possibly due to residual etchant near the metal/resin interface.

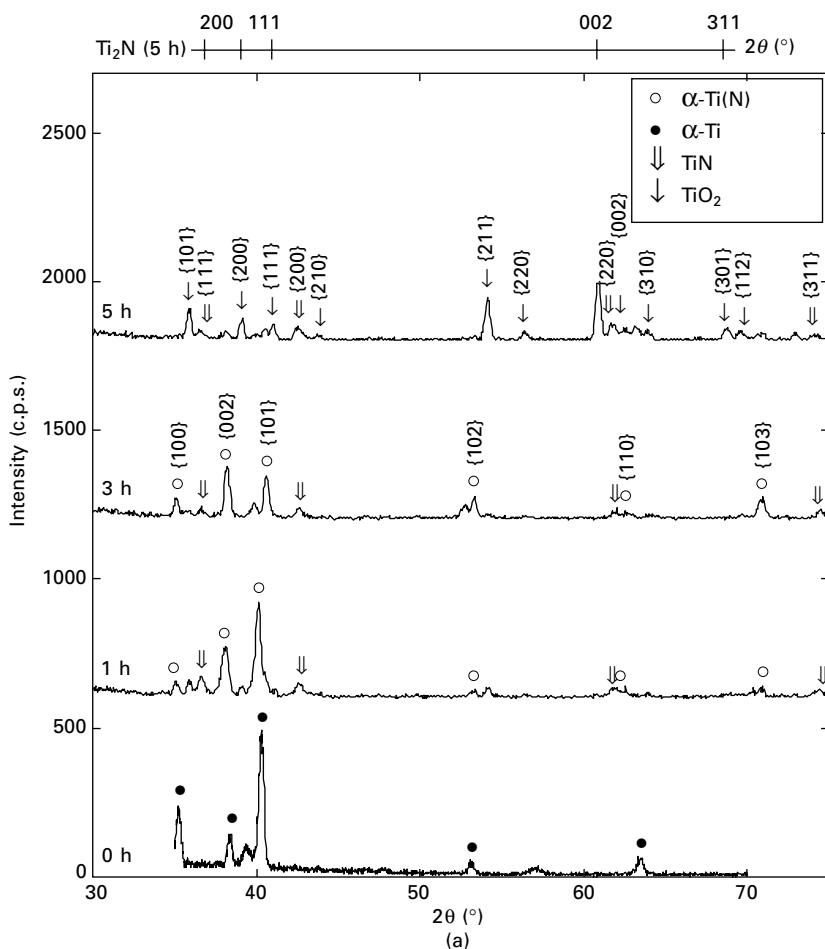
phase. The mechanisms and kinetics of diffusion would be different, which would result in the difference in the microstructure morphology.

The microstructure after nitriding at a lower temperature of 850 °C is similar to the 950 °C microstructure. Both temperatures are below the β -transus temperature for this alloy.

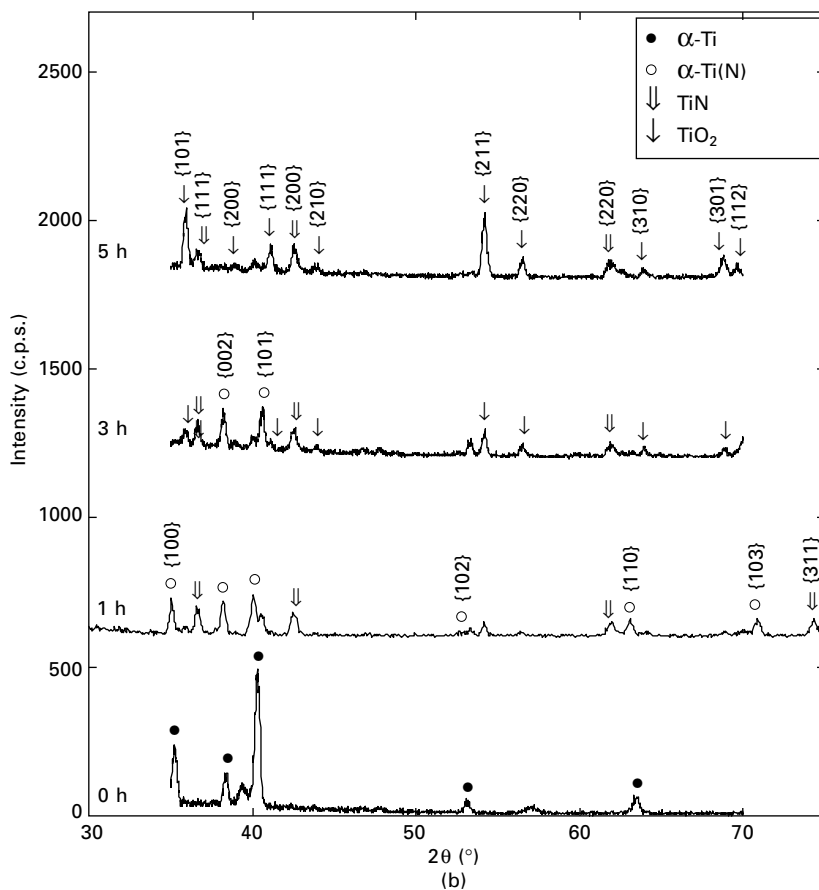
16.4 $\alpha + \beta$ Ti-6Al-4V

16.4.1 Phase composition

As discussed in the previous sections about Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo, as a result of the diffusion process of gas nitriding, α -Ti(N),



16.7 X-ray diffraction patterns of Ti-6Al-4V after gas nitriding at (a) 950 and (b) 1050 °C for 1, 3 and 5 hours.



16.7 Continued

cubic titanium nitride TiN and TiO_2 phases are formed on the surface of Ti-6Al-4V alloy (Fig. 16.7). With the increase of the time to 10 hours and for the alloy nitrided at 850 °C, the nitrided surface layer has the same phase composition.

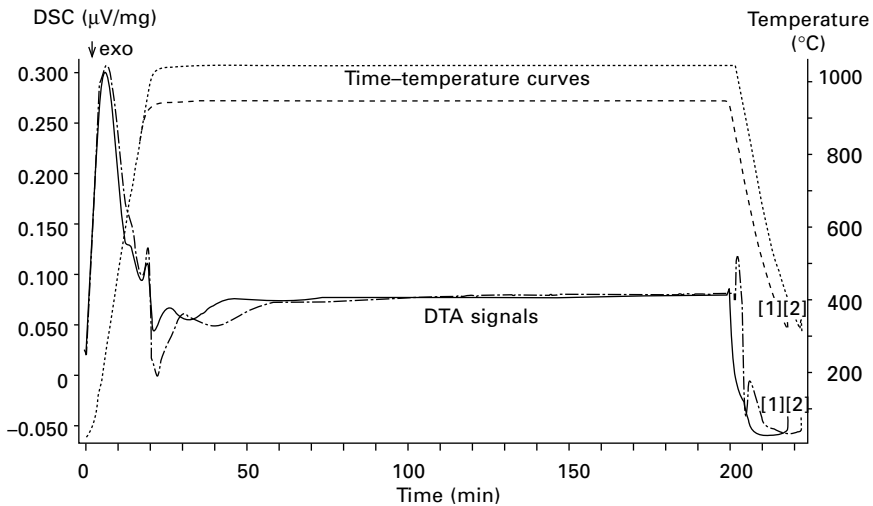
The coloration of the compound layer is different after nitriding at 950 and 1050 °C for different periods of time. After 1 hour of nitriding Ti-6Al-4V has a golden colour, corresponding to the TiN compound. The red colour of Ti-6Al-4V nitrided for 3 hours indicates the simultaneous formation of titanium nitrides. Compounds identified by XRD are TiN and possibly Ti_2N at 950 °C, and TiN with a small amount of TiO_2 at 1050 °C. After 5 hours, the metal colour is white, and the compounds are TiO_2 and TiN . The coloration depends on the process parameters and the appearance of the new phases, and is, by and large, consistent with the X-ray diffraction data.

As mentioned in the previous section about Ti-6Al-2Sn-4Zr-2Mo, the

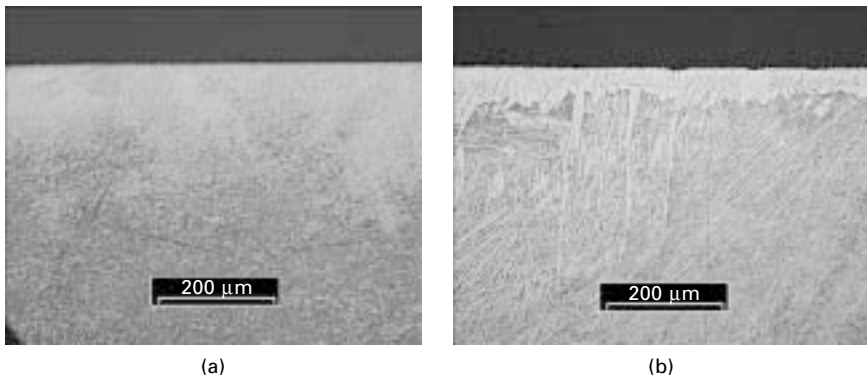
phase transformations are also evident in the DSC curves obtained during nitriding (Fig. 16.8). The peaks that appear during heating and cooling are probably caused by the new phase formation.

16.4.2 Microstructure

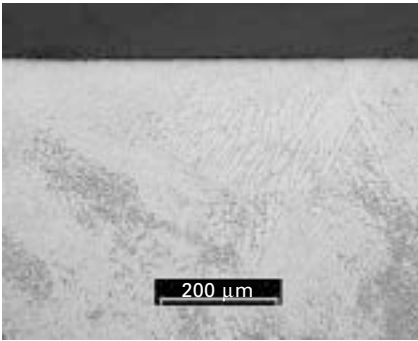
The microstructure of Ti-6Al-4V, being an $\alpha + \beta$ alloy, is different from the microstructure of the near- α alloys (Fig. 16.9, the microstructure of the alloy nitrided for 10 hours, is similar).



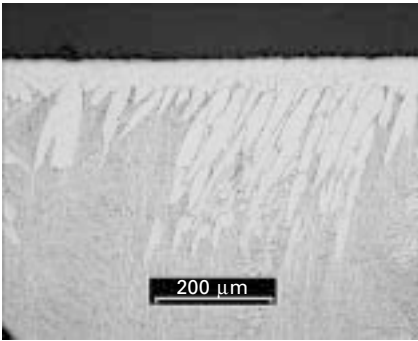
16.8 DSC curves of Ti-6Al-4V nitrided at 950 (curve 1) and 1050 (curve 2) °C for 3 hours



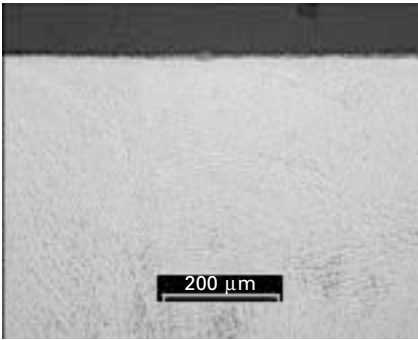
16.9 Microstructure of Ti-6Al-4V after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours. (a) 950 °C, 1 h; (b) 1050 °C, 1 h; (c) 950 °C, 3 h; (d) 1050 °C, 3 h; (e) 950 °C, 5 h; (f) 1050 °C, 5 h.



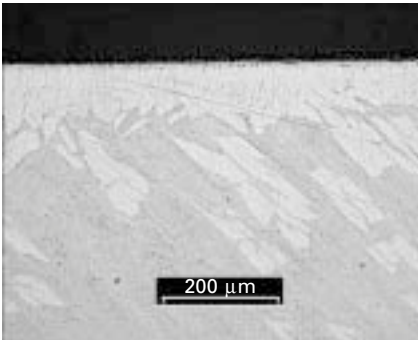
(c)



(d)

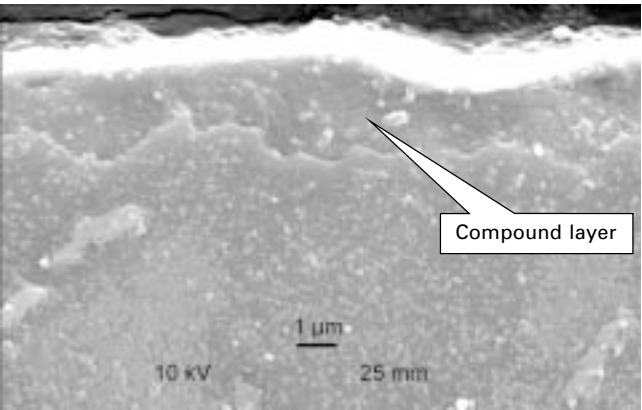


(e)



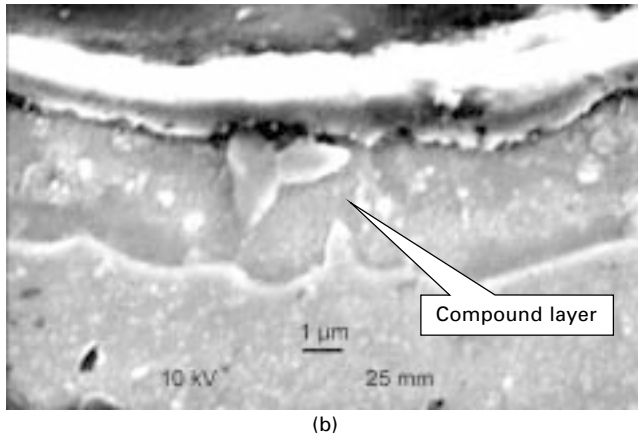
(f)

16.9 Continued



(a)

16.10 SEM images of compound layer of Ti-6Al-4V after gas nitriding at (a) 950 and (b) 1050 °C for 3 hours.



16.10 Continued

The thickness of the compound layer increases with the increase of temperature (Fig. 16.10).

16.5 Near- β Ti-10V-2Fe-3Al

16.5.1 Phase composition

Ti-10V-2Fe-3Al forms the same phases as the titanium alloys in the previous sections during nitriding at the same processing parameters (Fig. 16.11). The initial alloy condition consists of α -Ti and β -Ti, and the reaction during the process of nitriding is as follows: $\alpha\text{-Ti} + \beta\text{-Ti} \rightarrow \alpha\text{-Ti(N)} + \text{TiN} + \text{TiO}_2$. The same phase constitution is observed after nitriding at the lower temperatures of 750 and 850 °C.

The coloration of the compound layer is different after nitriding, grey after 1 hour of at 950 and 1050 °C, turning red after 3 and 5 hours at same temperature regimes.

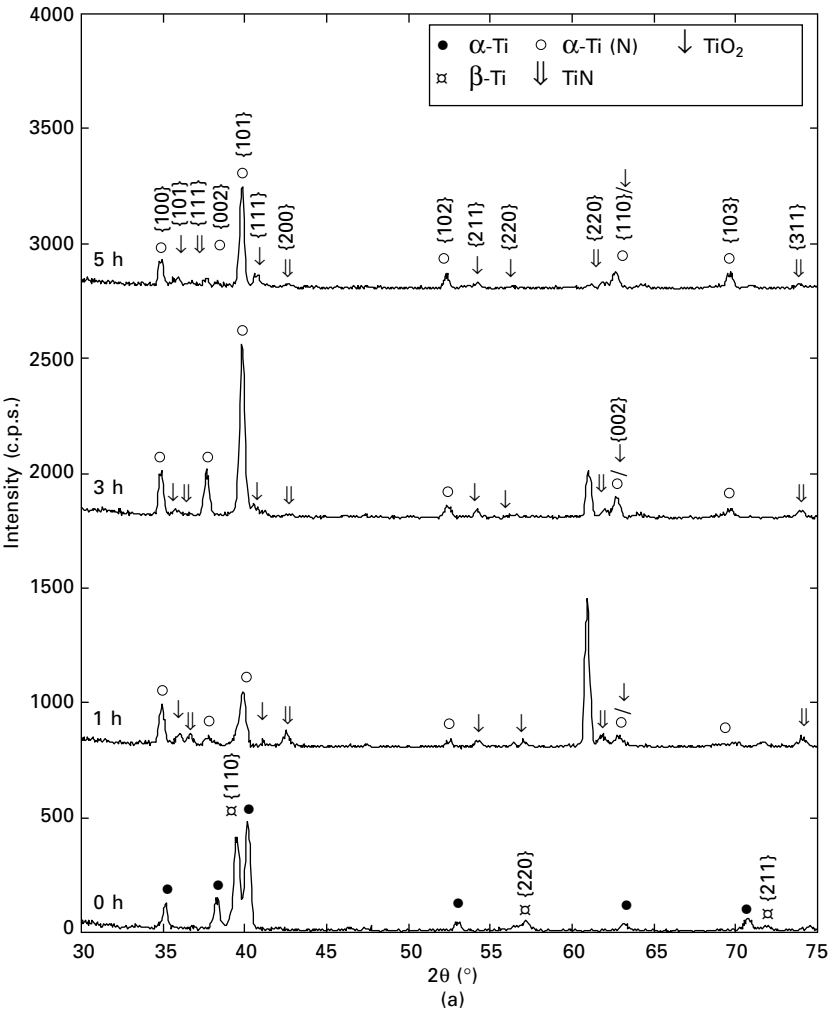
Ti-10V-2Fe-3Al contains 10% vanadium, but no nitrides of vanadium are detected on the surface of the metal after the nitriding.

The lattice parameters a and c of the α phase increase after nitriding for 1 hour at 950 and 1050 °C. There is no significant change of both a and c with further increase of the nitriding time to 3 and 5 hours at the temperature of nitriding of 950 °C. There is no clear tendency for the lattice parameter a after nitriding for different periods of time at 1050 °C. The values of the lattice parameters a and c of the α phase are higher for Ti-10V-2Fe-3Al after nitriding at the same processing parameters, though lower for the initial samples as compared to these for Ti-8Al-1Mo-1V, possibly related with the difference in the chemical composition of these two titanium alloys.

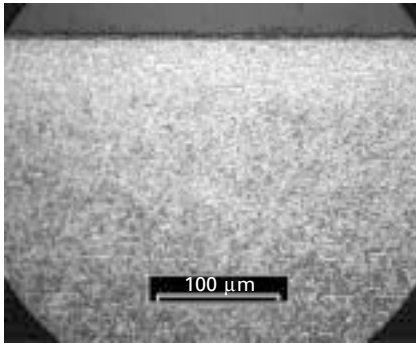
16.5.2 Microstructure

The compound layer in most cases is continuous and its thickness for the alloy nitrided at 950 and 1050 °C for 3 and 5 hours varies between 5 and 10 μm , as seen from the cross-section.

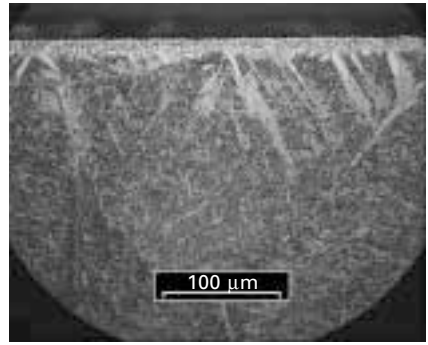
The microstructure of the alloy nitrided at 750 °C is homogeneous, because this temperature is below the β -transus temperature for this alloy (see Fig. 16.12a,c,e). Similar results are obtained for the other three alloys above. The



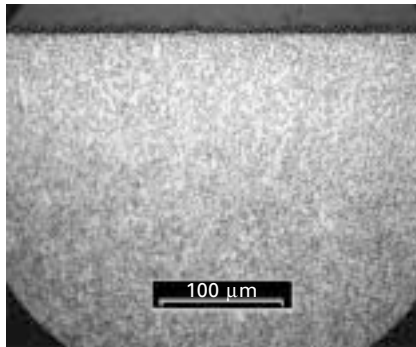
16.11 X-ray diffraction patterns of Ti-10V-2Fe-3Al after gas nitriding at (a) 950 and (b) 1050 °C for 1, 3 and 5 hours.



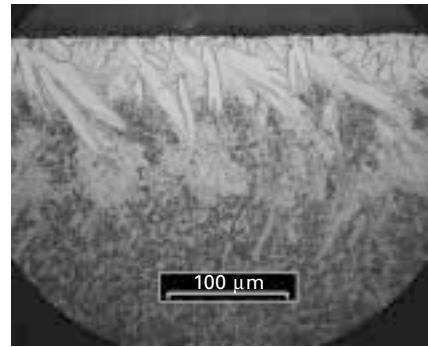
(a)



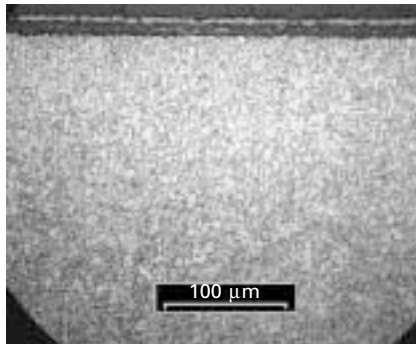
(b)



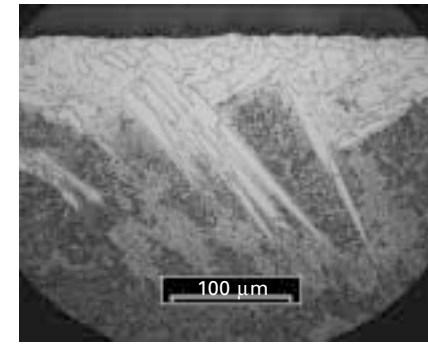
(c)



(d)



(e)



(f)

16.12 Microstructure of Ti-10V-2Fe-3Al after gas nitriding at 750 and 950 °C for 1, 3 and 5 hours. (a) 750 °C, 1 h; (b) 950 °C, 1 h; (c) 750 °C, 3 h; (d) 950 °C, 3 h; (e) 750 °C, 5 h; (f) 950 °C, 5 h.

16.6 β 21s

16.6.1 Physical appearance change

Before nitriding, the colour of the β 21s alloy is silver-grey. After nitriding at 850 °C, it turns grey. After nitriding at 950 °C for 1 and 3 hours, the alloy appears white. After 5 hours at 950 °C, the alloy is grey. From the X-ray analyses (the following section), TiN is formed on the nitrated surface and hence a golden colour should appear. However, the surface of the nitrated layer is white or grey in colour. The colour of the nitrated alloy may be due to the contribution of other phases appearing on the surface layer.

16.6.2 X-ray diffraction analysis

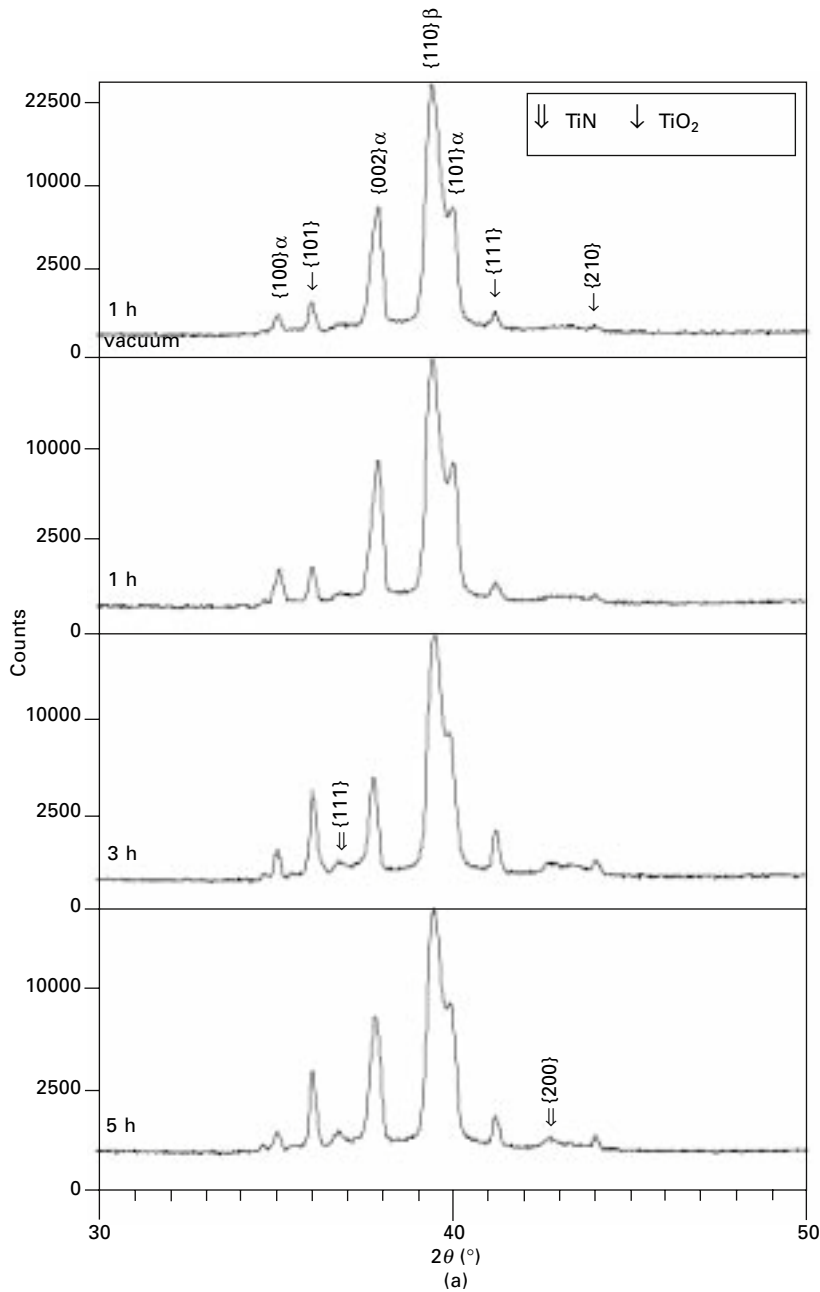
Diffraction patterns for this alloy without nitriding are shown in Figs. 3.3, 6.6 and 6.7, and in Malinov *et al.* (2002). Though not quantitative, the changes of relative proportions of the different phases present in the surface can be seen from the changes in the relative intensities of the various peaks (Fig. 16.13). For example, comparing the three diffraction patterns from the alloy nitrated at 950 °C (Fig. 16.13b), there is little TiN in the alloy nitrated for 1 hour. The amount of TiO₂, however, appears to be the highest after 1 hour nitriding, decreasing at 3 hours but increasing again after 5 hours. In addition, the amount of the NbN_{0.9} phase appears to decrease with increasing nitriding time. In the binary alloy phase diagram of the N–Nb system, above 500 °C, NbN (cubic structure) should be present. From the diffraction results, the NbN_{0.9} phase is present instead of NbN, but the NbN_{0.9} phase in the X-ray analysis software database may refer to the same phase as the NbN phase in the phase diagram.

Between 1 hour with evacuation and 1 hour without evacuation (850 °C), the phases present are similar, so nitrogen purging appears to have the same effect regardless of pre-evacuation.

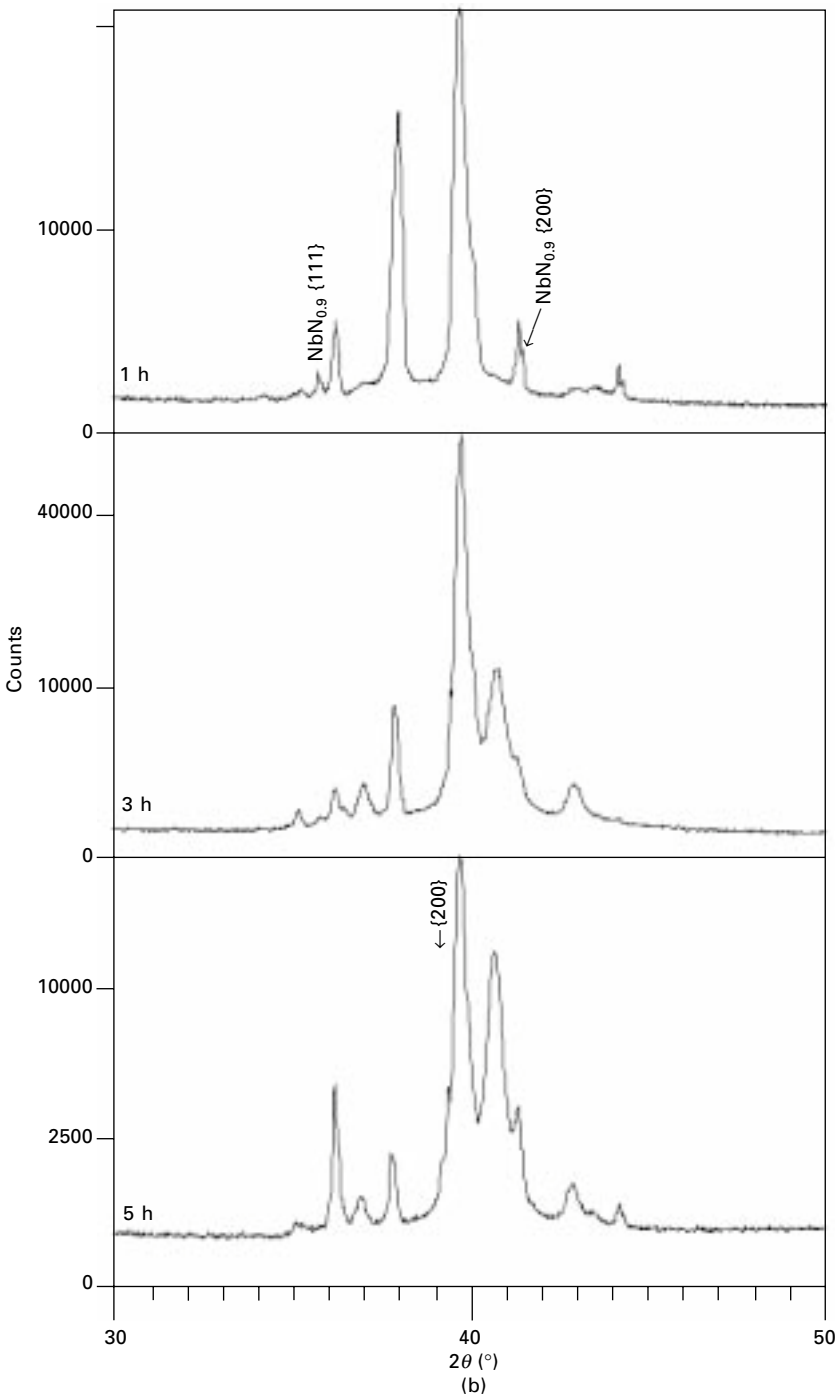
At 950 °C, higher amounts of the oxide and the nitride are formed than at 850 °C. Despite the high nitrogen concentration in the nitriding process, rutile (TiO₂) and possibly Ti₆O were detected. Ti₆O has the same diffraction lines as α -Ti.

16.6.3 Microstructure using optical microscopy

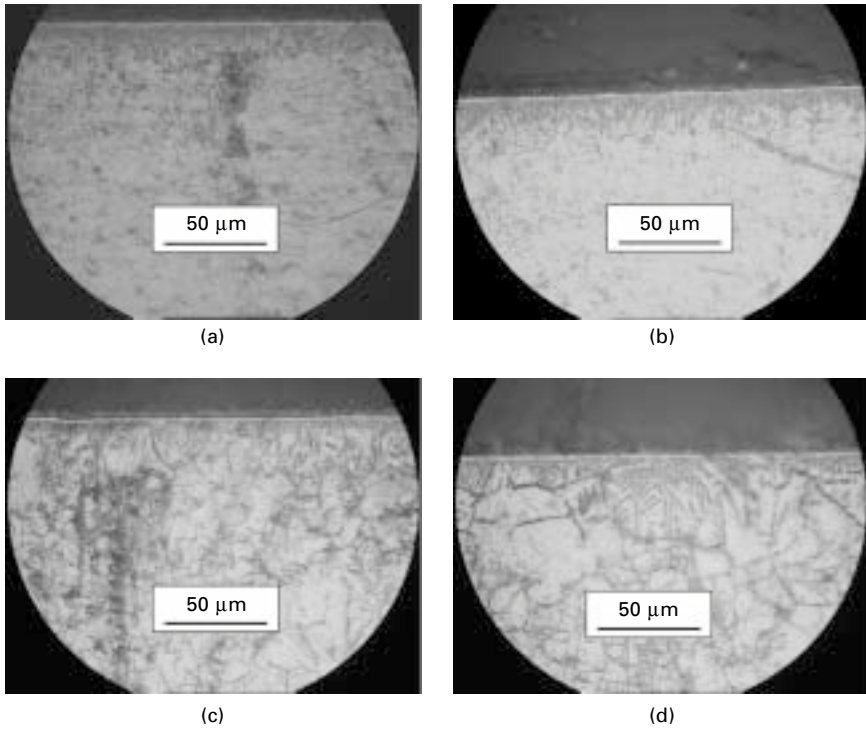
Needle-like microstructure forms at the exposed top surface (Fig. 16.14). The needles are acicular α phase formed from the high temperature β phase upon cooling. Grain size increases with increase in the nitriding time, as shown in the micrographs.



16.13 X-ray diffraction patterns of $\beta 21s$ after gas nitriding at (a) 850 °C, where 'vacuum' refers to evacuation of the nitriding chamber before the start of nitriding, and (b) 950 °C, where, for clarity, only the peaks additional to those appearing in (a) are indexed.



16.13 Continued



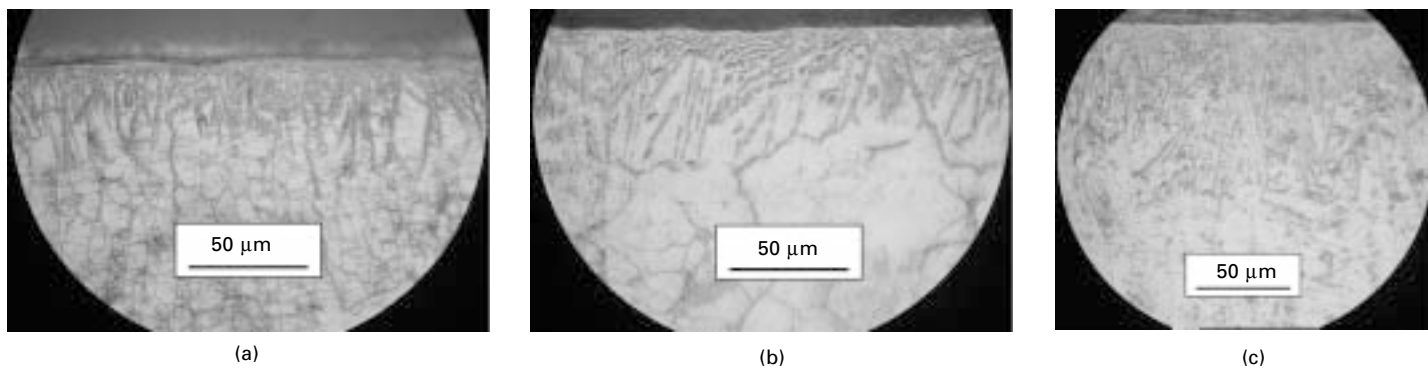
16.14 Optical micrographs of $\beta 21s$ after gas nitriding at 850 °C. (a) 1 h with evacuation; (b) 1 h without evacuation; (c) 3 h; (d) 5 h.

Similar to the microstructures of the alloy nitrided at 850 °C, a needle-like structure forms at 950 °C (Fig. 16.15). Comparing with the alloy nitrided at 850 °C, the grain sizes are larger after nitriding at 950 °C, due to faster grain growth at the higher temperature.

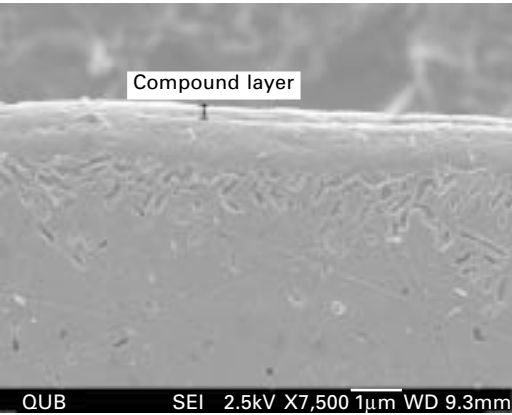
16.6.4 Microstructure using scanning electron microscopy

At high magnification, using a low acceleration voltage (2.5 kV) gives much better image quality (Fig. 16.16) compared with using the more traditional ~15 kV, a feature of the field emission gun (FEG) SEM. The compound layer is clearly shown.

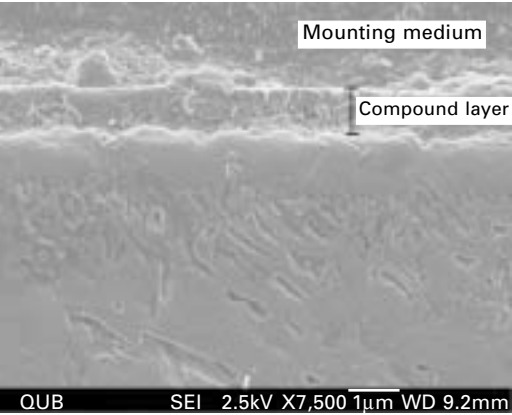
There is some difference in morphology and appearance of the compound layer between this alloy (Fig. 16.17) and the Ti-6Al-2Sn-4Zr-2Mo alloy studied before (Section 16.3). The compound layer in the $\beta 21s$ alloy appears better adhered to the substrate (compare Fig. 16.17c and Fig. 16.5b).



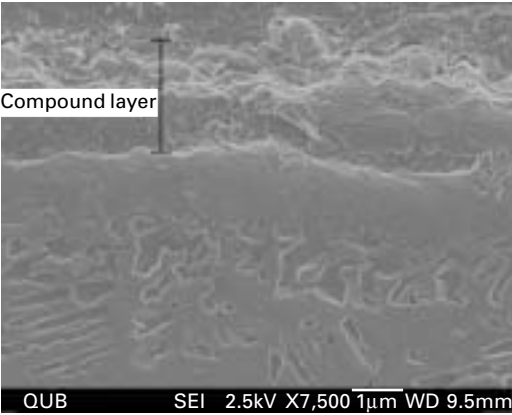
16.15 Optical micrographs of $\beta 21s$ after gas nitriding at 950 °C. (a) 1 h; (b) 3 h; (c) 5 h.



(a)

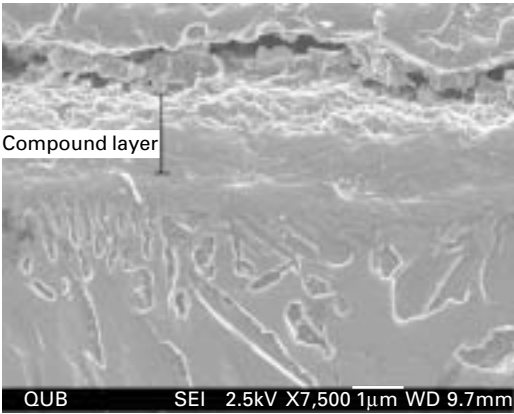


(b)

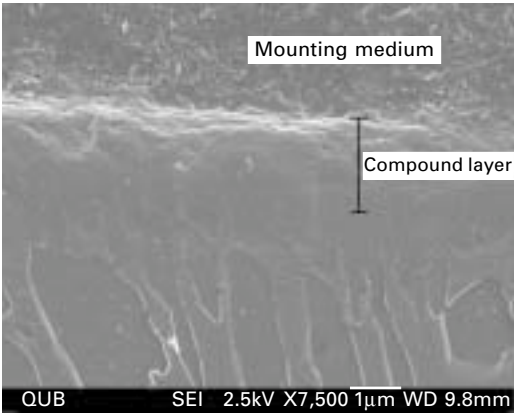


(c)

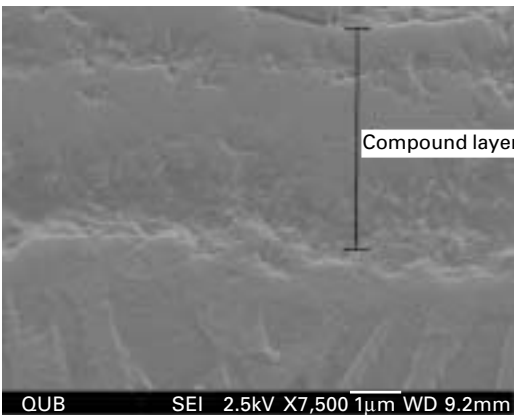
16.16 High magnification scanning electron micrographs of $\beta 21s$ after gas nitriding at 850 °C. (a) 1 h; (b) 3 h; (c) 5 h.



(a)



(b)



(c)

16.17 High magnification scanning electron micrographs of $\beta 21s$ after gas nitriding at 950 °C. (a) 1 h; (b) 3 h; (c) 5 h.

The surface compound layer shown in these images contains TiN and TiO₂ phases identified in X-ray diffraction. A detailed profiling work is shown earlier in this chapter.

The depth of nitrogen penetration in the diffusion layer in β and TiAl alloys is smaller than in α or $\alpha + \beta$ alloys, indicating a less strong hardening effect. This is demonstrated in Chapter 17.

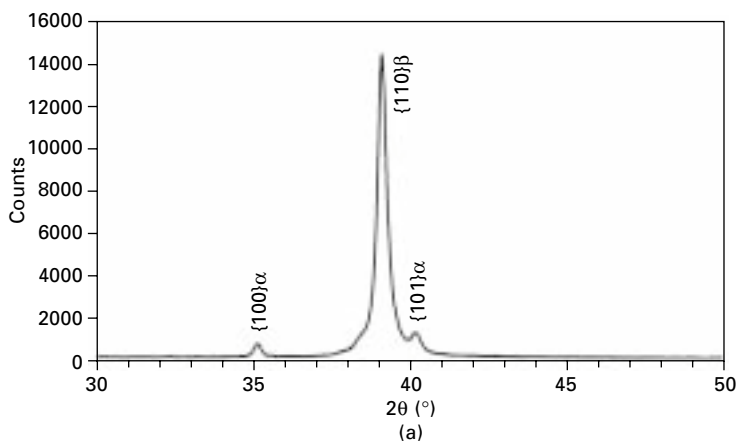
16.7 Timetal 205

16.7.1 X-ray diffraction analysis

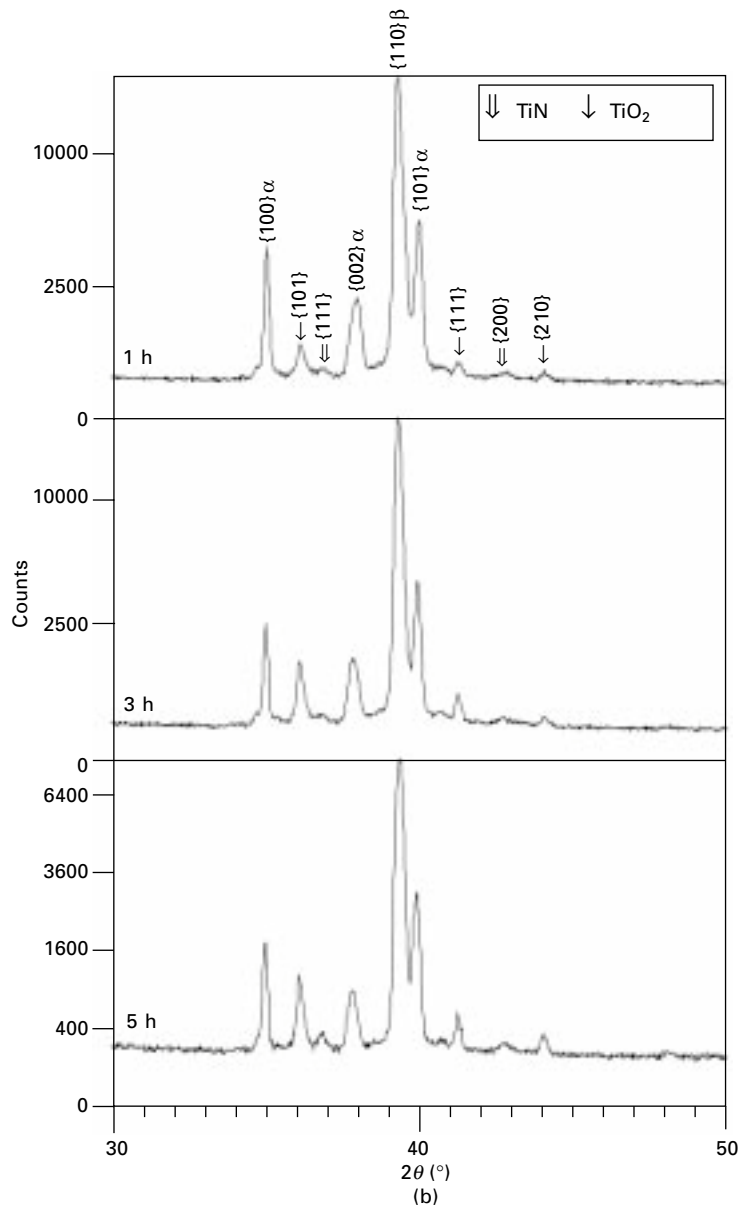
The main phases on the surface after nitriding are TiN and TiO₂ (Fig. 16.18b compared with Fig. 16.18a), in addition to the titanium α and β phases. The presence of oxygen in the nitriding system is revealed by the formation of TiO₂ phase. Comparing 730 °C (Fig. 16.18b) and 830 °C (Fig. 16.18c), the higher nitriding temperature causes increases in TiN and TiO₂ intensities.

16.7.2 Microstructure using optical microscopy

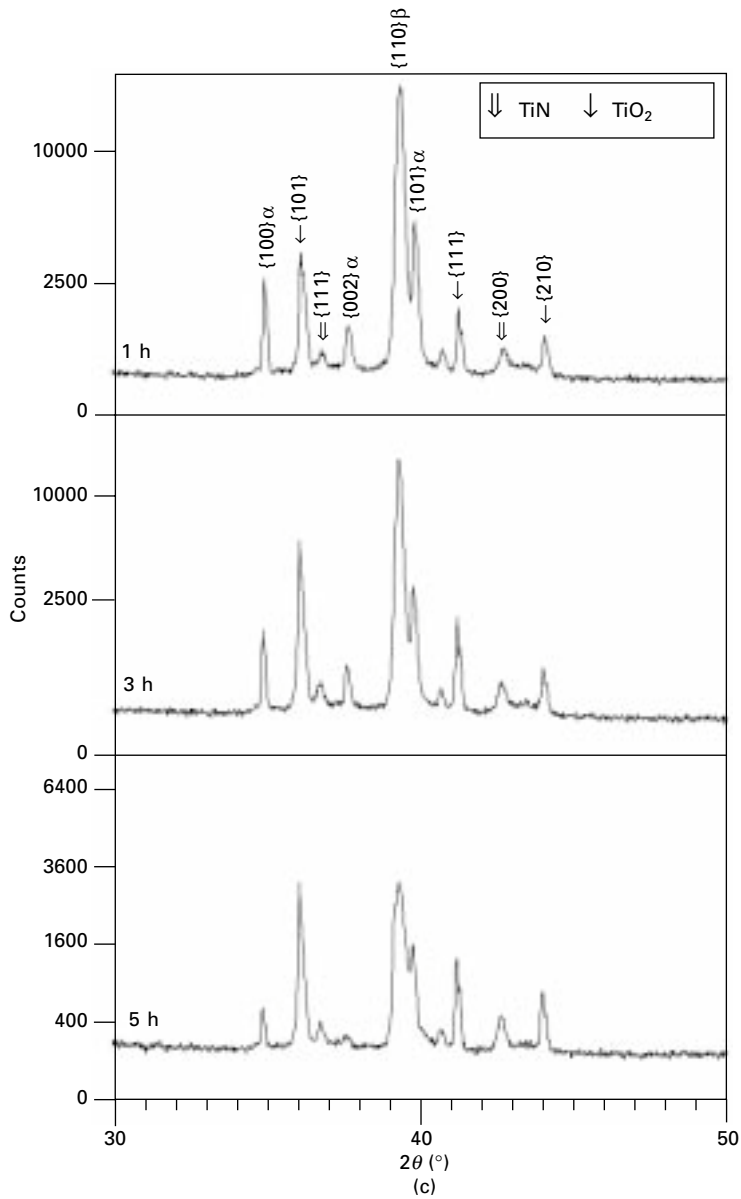
In the cross-sectional optical micrographs, the effect of nitriding at first sight appears as streaks or patches of dark areas as shown in Fig. 16.19a–c, its extent and depth increasing with increasing nitriding time. Such dark areas occupy the entire surface, but extend to the depth of the samples only along certain paths, indicating a type of diffusion-channel functioning. This diffusion argument is substantiated by the very visible increasing dark areas and the frequency of the strips with increasing nitriding time.



16.18 X-ray diffraction patterns of Timetal 205 alloy. (a) Untreated; (b) nitrided at 730 °C; (c) nitrided at 830 °C.

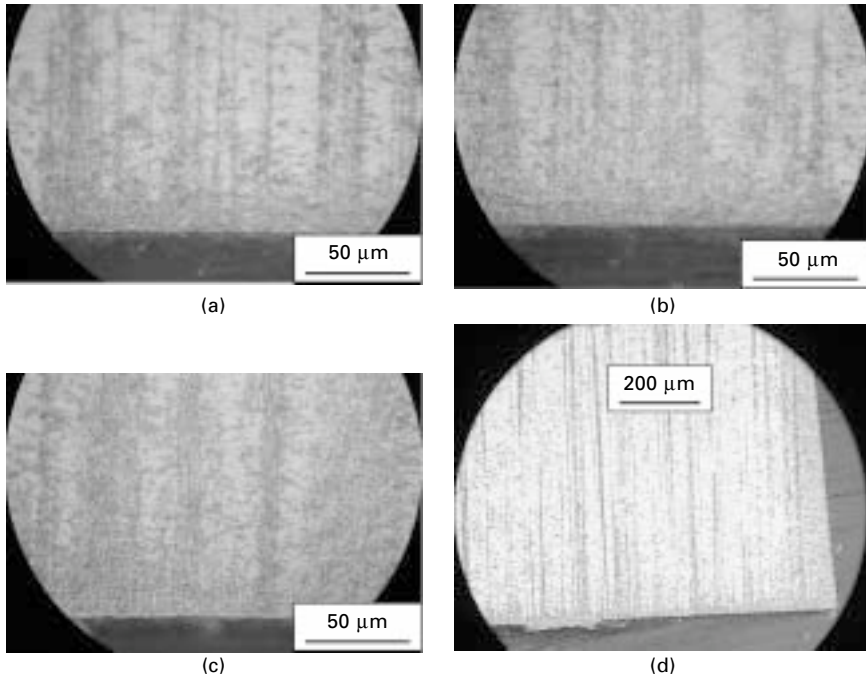


16.18 Continued



16.18 Continued

However, Fig. 16.19d reveals the unidirectional nature of such patches. Note that nitriding was made on both sides (perpendicular to each other) of the sample. So, the direction of the patches is not determined by the nitriding process, i.e. not always perpendicular to the nitriding surface as Fig. 16.19a–c would suggest. These are possibly related with the extrusion of the Timetal 205 rod

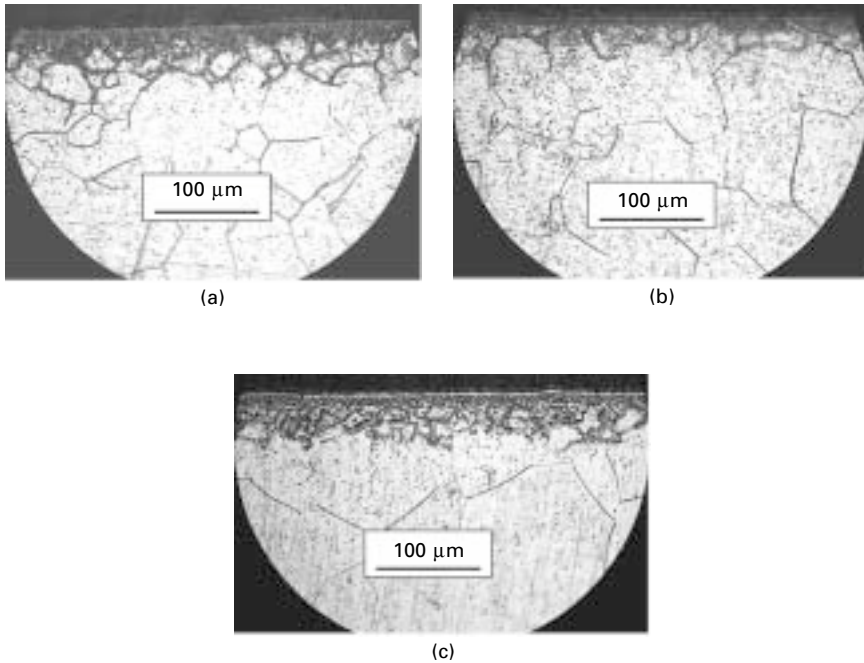


16.19 Optical micrographs of dark layer and patches forming near the surface of Timetal 205 after gas nitriding at 730 °C. (a) and (d) 1 h; (b) 3 h; (c) 5 h.

from which the samples were prepared. There seems to be an interaction of the nitriding process with this feature. This feature is erased after nitriding at 830 °C, a temperature above the β -transus of the alloy.

The origin of the ‘banding’ in Fig. 16.19 is most likely due to the presence of chemistry differences in the Timetal 205, which are both aligned parallel to the extrusion direction. Since they extend deep into the sample, it is possibly just a difference in the etching response. Alternatively, the variation in chemistry promotes a different response to the ingress of nitrogen during treatment.

After nitriding at 830 °C, the grain structure is completely different (Fig. 16.20), confirming that the samples were at the β region during nitriding at this higher temperature. After nitriding for 1 hour, an acicular or irregular needle structure on the nitrided surface is formed (Fig. 16.20a), extending approximately 50 μm into the depth from the surface. A homogeneous layer is present beneath this depth. No significant change in the depth of this nitrogen-effected reaction layer is observed after nitriding for 3 hours (Fig. 16.20b) or 5 hours (Fig. 16.20c) at 830 °C.



16.20 Optical micrographs of dark layer forming near the surface of Timetal 205 after gas nitriding at 830 °C. (a) 1 h; (b) 3 h; (c) 5 h.

16.8 Ti–Al

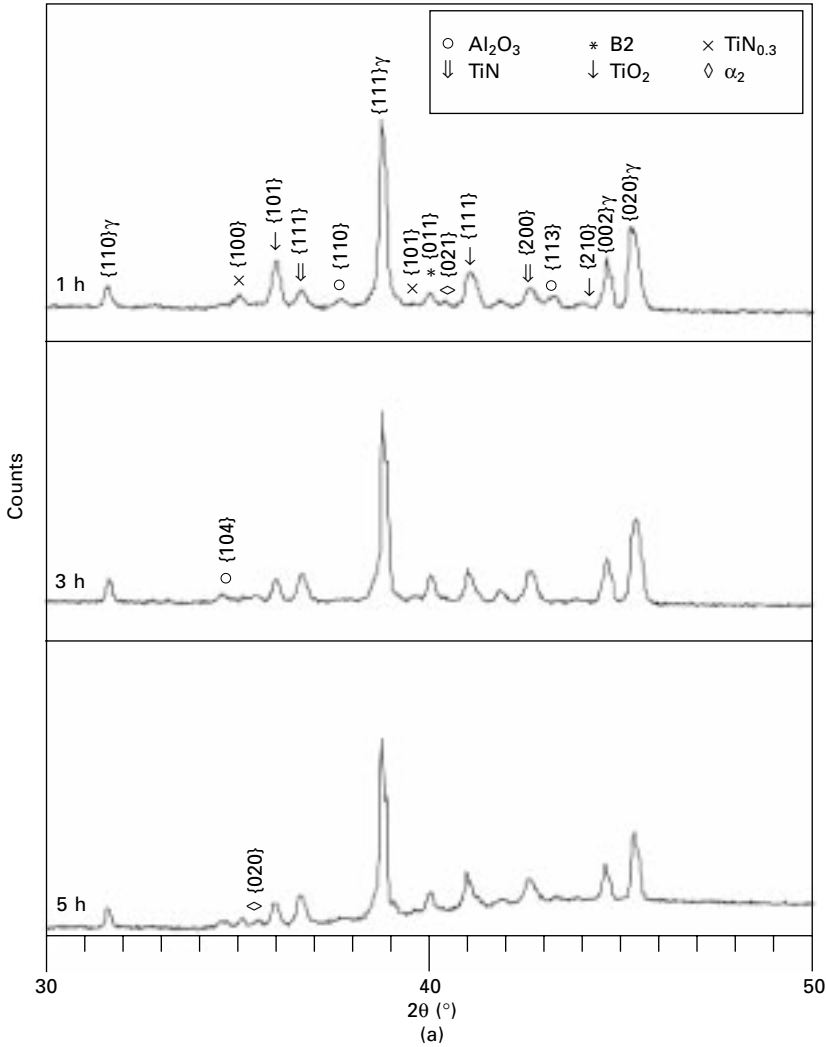
In the case of the Ti–Al alloy (Ti-46Al-1.9Cr-3Nb, at. %), colouration is also observed after nitriding. A silver to golden colour change happens for the alloy nitrided at 1050 °C.

16.8.1 X-ray diffraction analysis

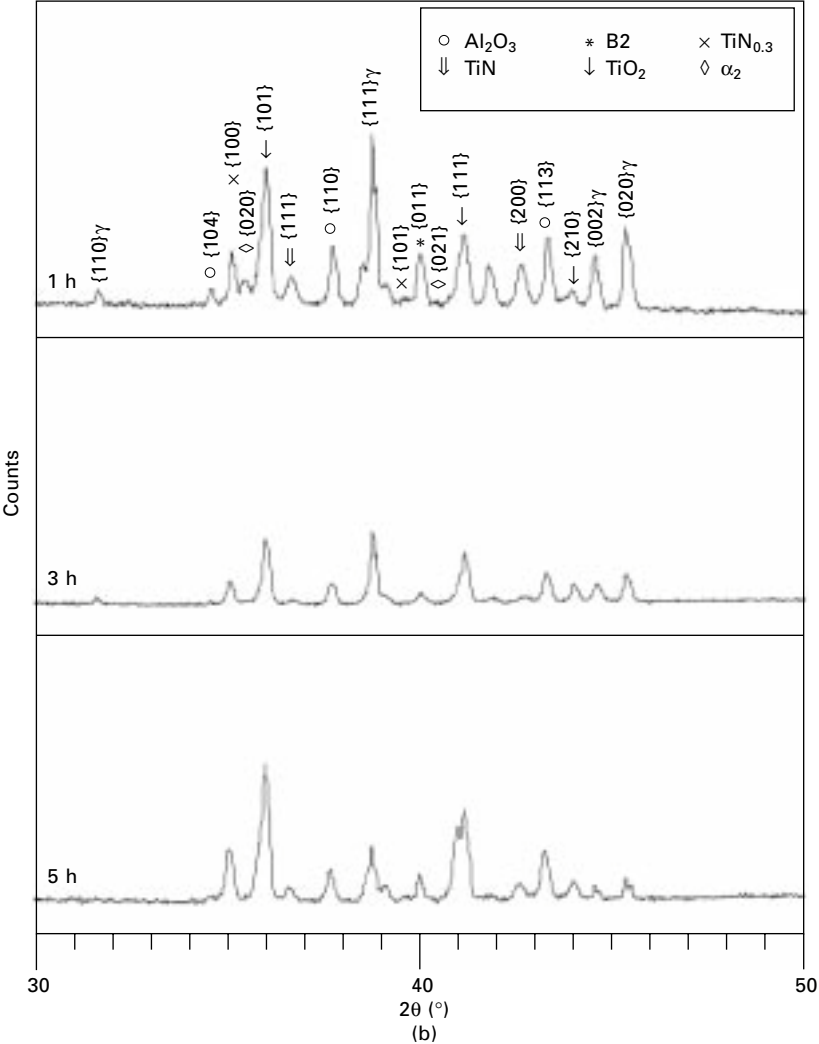
Phase transformation involves the formation of new compounds after treatment under N_2 , which are observed in the diffraction peaks in Fig. 16.21. Nitrogen-containing compounds are formed during the surface nitriding. The phases formed on the Ti–Al alloy are strongly influenced by the nitriding process. For example, Al_2O_3 is present on the surface after nitriding at 950 °C for 1 hour, but little after 3 or 5 hours (Fig. 16.21a). Also, $TiN_{0.3}$ has appeared in higher abundance after nitriding at the higher temperature of 1050 °C. The compounds found are TiN, $TiN_{0.3}$, TiO_2 , and Al_2O_3 , among which TiN and TiO_2 are more dominant.

16.8.2 Microstructure using optical microscopy

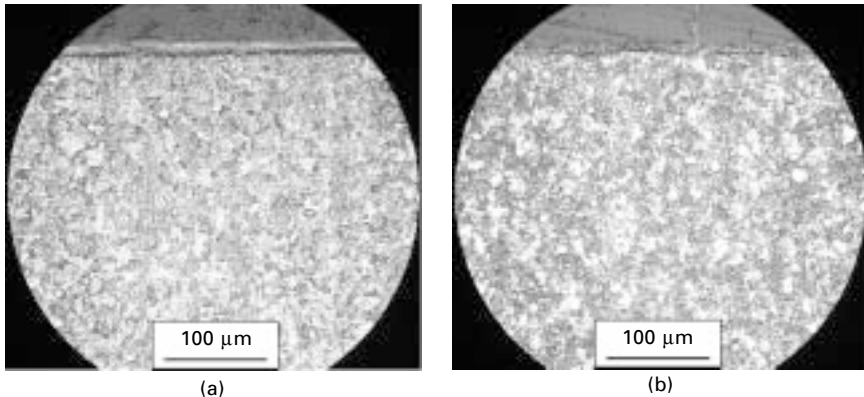
Examining the microstructure provides some information towards the formation of TiN in enhancing the strength of the Ti–Al alloy. There is not a great difference in grain size and distribution, or changes in the thickness of the compound layer at the very top of the nitrided surface, after nitriding for different lengths of time (Fig. 16.22).



16.21 X-ray diffraction patterns of the Ti–Al alloy after gas nitriding at (a) 950 and (b) 1050 °C.



16.21 Continued



16.22 Optical micrographs of the Ti-Al alloy after gas nitriding at 1050 °C. (a) 1 h; (b) 5 h

16.9 Summary of the effect of the parameters of gas nitriding on the microstructure

The microstructure of nitrided titanium alloys depends on the chemical composition of the alloy and the processing parameters of gas nitriding. Temperature and time are the most important parameters of gas nitriding. There is a tendency of grain growth with increase of the temperature and the time, as well as new phase formation on the surface of these materials. The nitrogen diffuses into the metal substrate, forming a compound layer on the surface of the material which is composed mainly of titanium nitrides Ti_2N and TiN in the general case, followed by a diffusion zone that consists of an interstitial solution of nitrogen in the α or β titanium phases. After nitriding at temperatures below the β -transus temperatures of the titanium alloys, they have a uniform and homogeneous microstructure, which changes to irregular and inhomogeneous with increase of the nitriding temperature above their β -transus temperature. The difference in the microstructure is due to the phase transformations between α and β that occur during the higher temperature nitriding or during the heating and cooling stages to and from the nitriding temperature. The microstructure and thickness of the nitrided layer depend also on the nitriding time.

The phase composition at the outmost surface layer after surface gas nitriding is α -Ti (N,O), TiN and TiO_2 (rutile), the amount of the nitride and the oxide increasing with nitriding time. Oxidation could not be eliminated during the nitriding process, though the titanium oxide is formed only on the surface top. There is not any significant amount of residual surface stress in the α -Ti(N) phase. The compound layer, in most of the cases, is continuous, with a thickness varying between 2 and 10 μm , depending on the time and the temperature of nitriding.

16.10 References

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Surface gas nitriding: mechanical properties, morphology, corrosion

Abstract: Microindentation hardness testing using both Vickers and Knoop indenters is used to analyse the hardness evolution of nitrided titanium alloys in relation to the nitriding processing parameters and alloy composition. The microhardness increases with increase of the temperature and time of nitriding. This is followed by discussions on tensile properties and fatigue performance after nitriding, and the surface morphology of the alloys in relation to the initial surface roughness and nitriding processing parameters. The corrosion behaviour of the titanium alloys before and after gas nitriding in response to the corrosive conditions and alloy composition is examined in the final part of the chapter.

Key words: nitriding, mechanical properties, microhardness, roughness, corrosion.

17.1 Hardness evolution

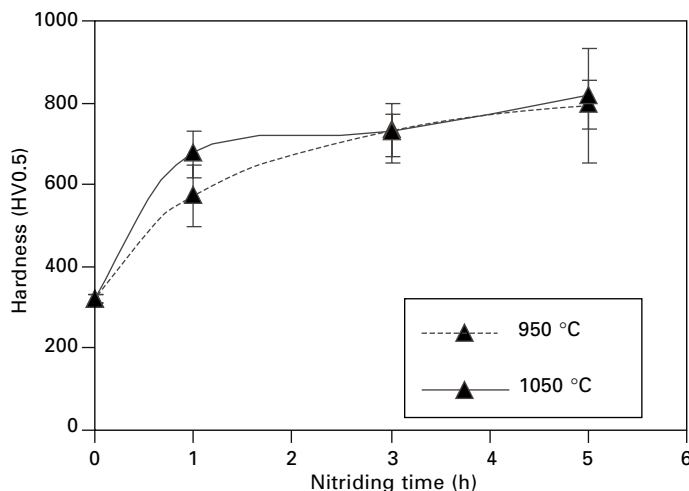
This section examines the hardness evolution of titanium alloys in relation to the processing temperature, time and the alloy composition. The Vickers indenter is suitable for measuring the hardness from the surface, whereas the Knoop indenter is for investigating the change of the microhardness across the depth (distance from the surface towards the substrate core) of the cross-sections. Optical microscopy assists the study of the difference in the microhardness of different phases.

The temperature and time of nitriding are the most important processing parameters of gas nitriding and it is essential to understand their influence on the hardness behaviour of the titanium alloys.

17.1.1 Near- α Ti-8Al-1Mo-1V

The surface hardness of the alloy nitrided at 950 and 1050 °C increases with the time prolongation (Fig. 17.1), in agreement with the established effect of the time of nitriding (Shashkov, 2001). The increase of the hardness is probably due to the new phases formed on the surface of the materials during the process of nitriding, such as TiN and TiO₂. There is no significant change of the surface hardness with the increase of the temperature.

The time prolongation and the temperature increase result in increase of the nitrided layer thickness, which can be estimated from microhardness profiles because it can be supposed that the nitrided layer ends where the microhardness value approaches the core microhardness.



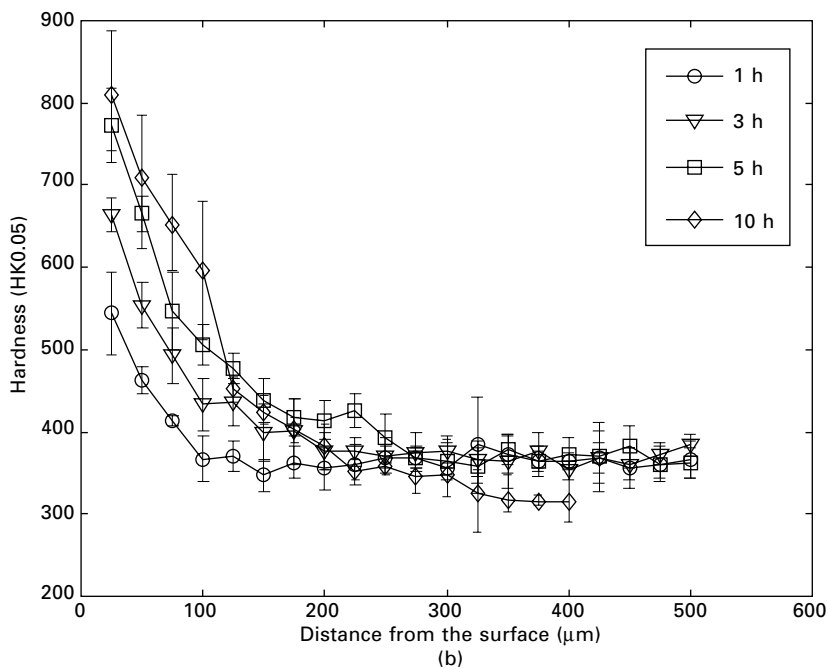
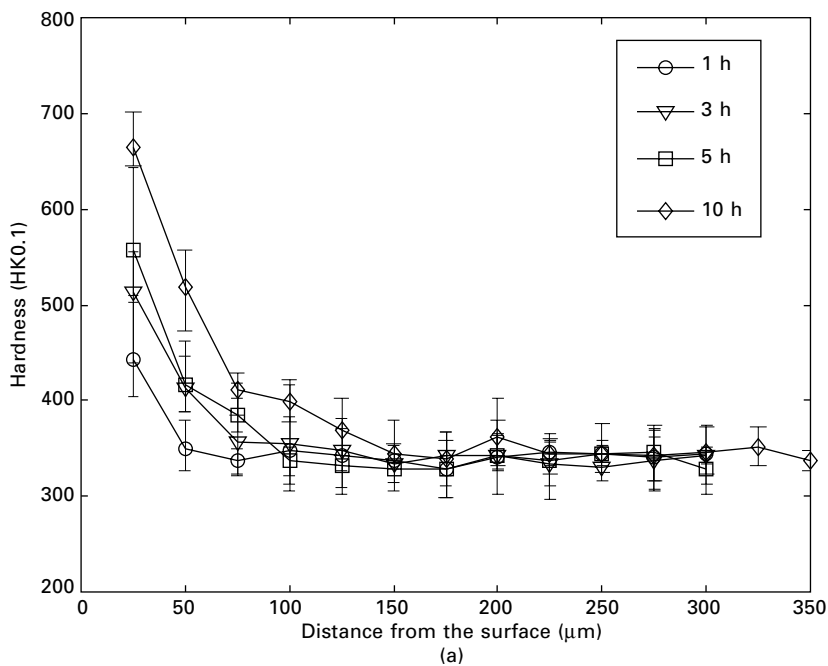
17.1 Surface hardness of Ti-8Al-1Mo-1V after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours.

With the increase of the temperature from 850 to 1050 °C, the thickness of the nitrided layer increases (Fig. 17.2). For this alloy it varies between 50 and 350 μm , depending on the temperature and time of nitriding. It is difficult to determine the thickness of the nitrided layer from the microstructure images of the cross-sections because there is no clear boundary between the diffusion zone and the substrate core.

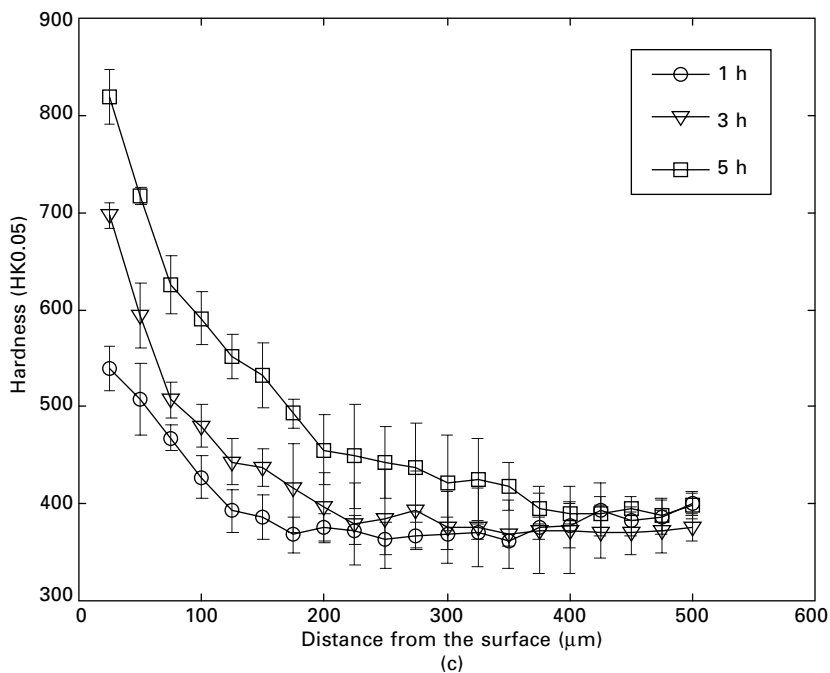
The hardness values of the surface layer are very high and they decrease with the depth of the materials through the diffusion zones to approach the base microhardness of the matrix in the unsaturated core. There is a tendency of increase in the microhardness values with the time prolongation and the temperature of nitriding for this alloy. The increase of the microhardness values and the thickness of the nitrided layer after nitriding at higher temperatures is due to the increase of the diffusion coefficient. The influence of the temperature on the microhardness behaviour has been studied by Galliano *et al.* (2001).

The maximal value of the microhardness for Ti-8Al-1Mo-1V is 820 HK0.05 for the sample nitrided at 1050 °C for 5 hours. Figure 17.3 presents an optical micrograph showing the microhardness values from the surface to the core, associated with the decrease of the nitrogen content.

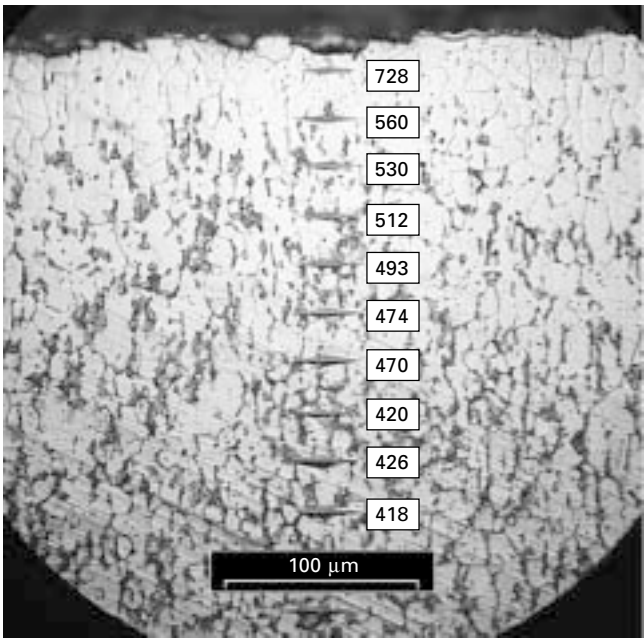
The variation in the microhardness values for the alloy nitrided at temperatures higher than its β -transus is due to local differences in the irregular microstructure (see Fig. 17.4). The microhardness values of the white grains are higher, possibly because of the different nitrogen content. Nitriding at temperatures above the β -transus for titanium alloys is not recommended for



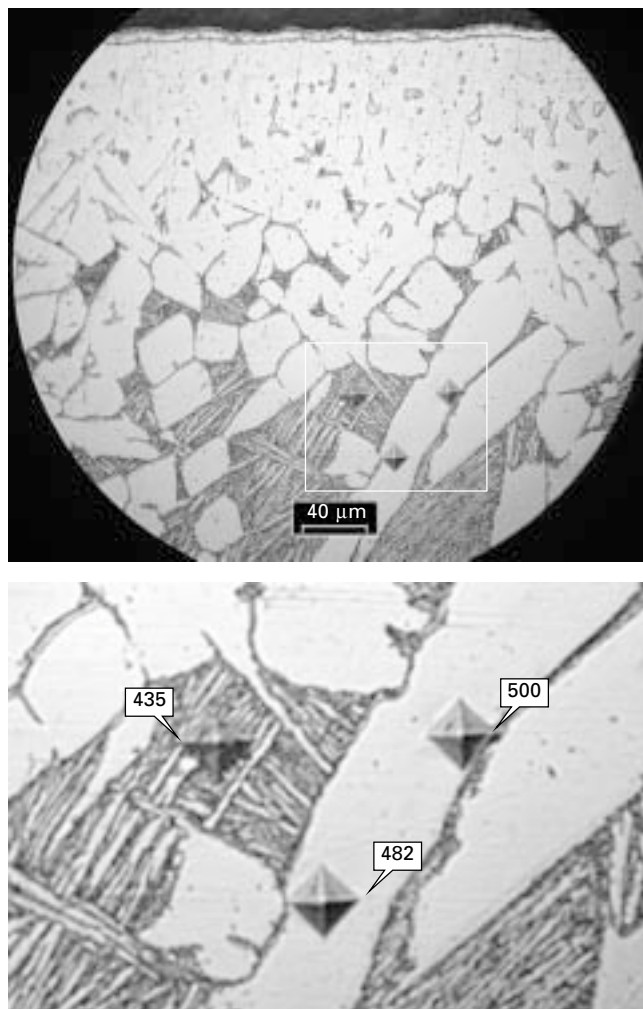
17.2 Microhardness profiles of Ti-8Al-1Mo-1V after gas nitriding at (a) 850, (b) 950 and (c) 1050 °C for different periods of time.



17.2 Continued



17.3 Microhardness values (HK0.05) of Ti-8Al-1Mo-1V nitrided at 950 °C for 5 hours showing the decrease of the microhardness with increasing depth.

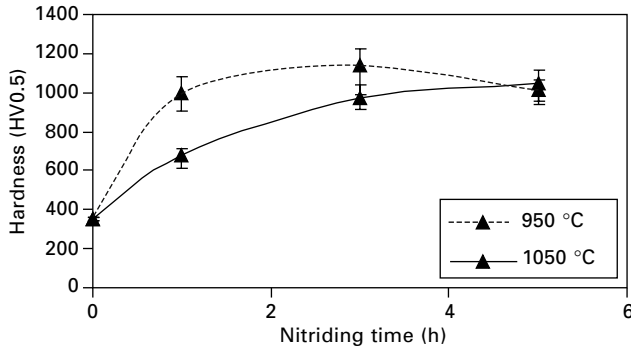


17.4 Microhardness values (HV0.1) measured at different places in Ti-8Al-1Mo-1V nitrided at 1050 °C for 5 hours.

practical applications because of the high hardness and brittleness of the surface layer.

17.1.2 Near- α Ti-6Al-2Sn-4Zr-2Mo

The surface hardness increases with the time prolongation, except for at 950 °C from 3 to 5 hours (Fig. 17.5). The hardness decreases with the increase of the temperature from 950 to 1050 °C after nitriding for 1 and 3 hours. The higher hardness values at the lower temperature is because the compound



17.5 Surface hardness of Ti-6Al-2Sn-4Zr-2Mo alloy after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours.

layer was very hard and brittle after nitriding at the higher temperature and it was destroyed during the hardness measurements.

The microhardness profiles (HK0.05) in the cross-sections are shown in Fig. 17.6. Maximal values of the microhardness are obtained for this alloy nitrided at 1050 °C for 5 hours, reaching 1027 HK0.05. The microhardness increases with time, and with increase of temperature.

From the microhardness profiles, the thickness of the nitrided layer can be estimated after nitriding at different processing parameters. For Ti-6Al-2Sn-4Zr-2Mo nitrided at 950 and 1050 °C, the thickness varies between 75 and 200, and 100 and 350 μm , respectively, depending on the length of nitriding time. The parabolic law of growth may be applied to the variation of the nitrided layer thickness (Malinova *et al.*, 2001).

17.1.3 $\alpha + \beta$ Ti-6Al-4V

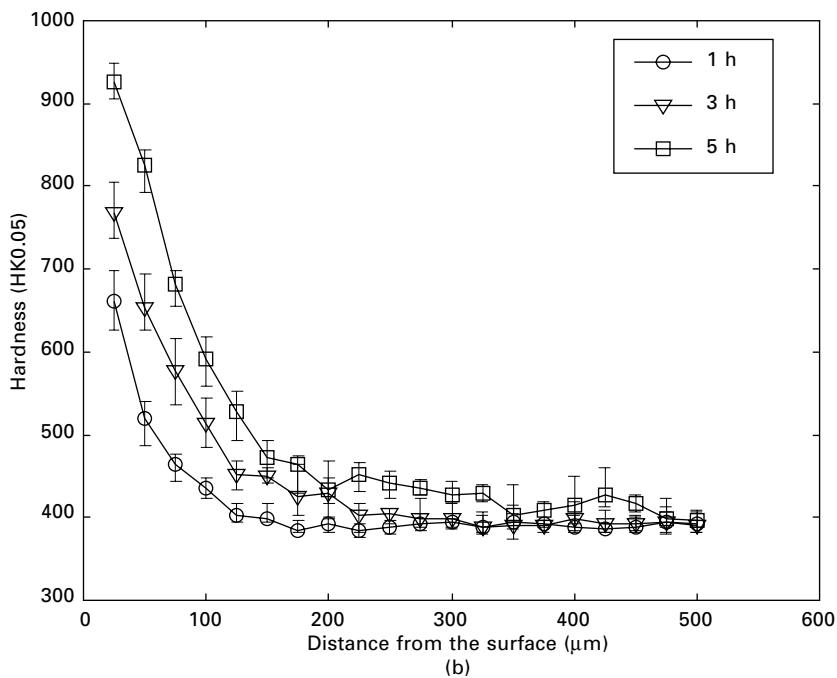
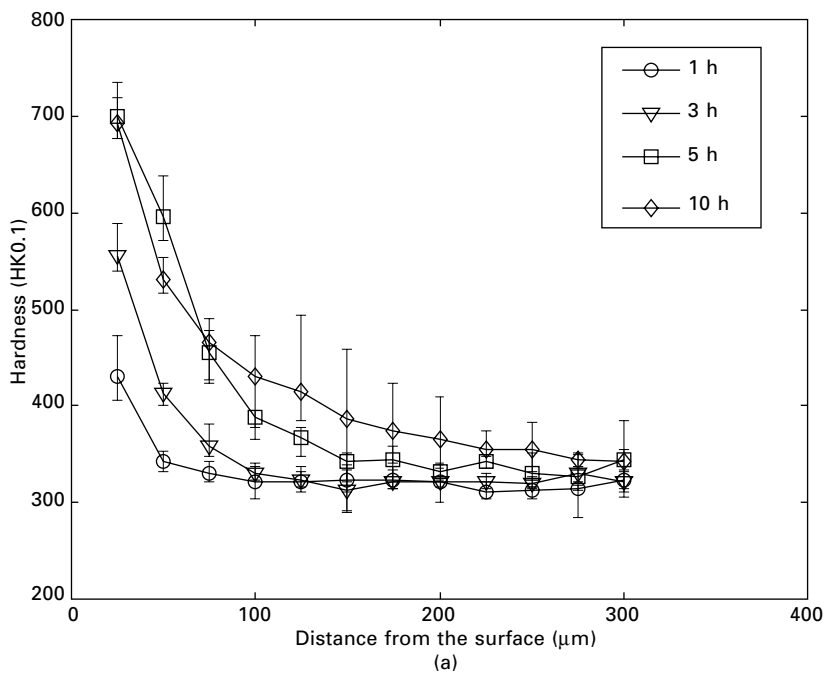
The surface hardness increases with the time prolongation and increase of the temperature from 950 to 1050 °C (Fig. 17.7).

For most of the cases, the microhardness increases with the increase of the time (Fig. 17.8). A maximal value of 770 HK0.05 is recorded for the alloy nitrided at 1050 °C for 5 hours. The microhardness increases also with the increase of temperature. Similar results were obtained by Kessler *et al.* (2002).

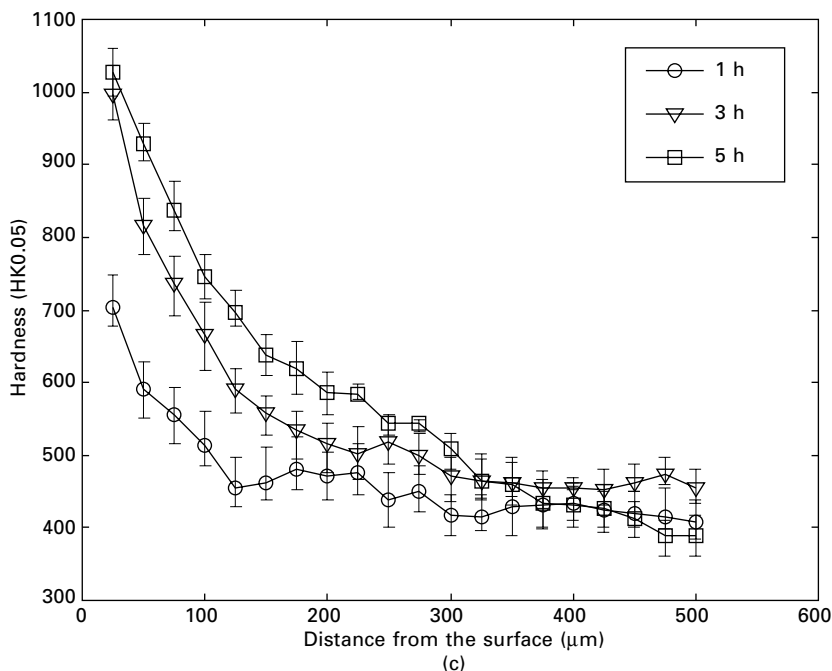
The thickness of the nitrided layer of Ti-6Al-4V increases with the increase of temperature and time.

17.1.4 Near- β Ti-10V-2Fe-3Al

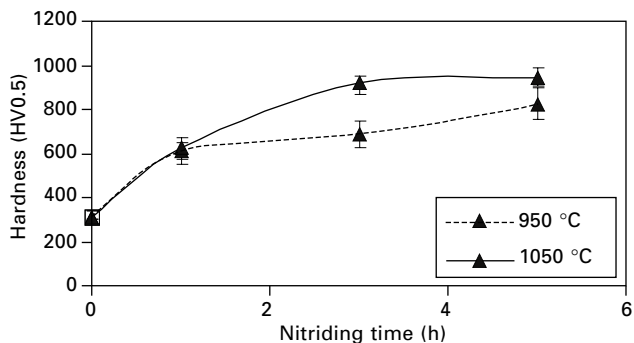
The surface hardness increases with the time prolongation and with the increase of the temperature after nitriding for 1 and 3 hours (Fig. 17.9),



17.6 Microhardness profiles of Ti-6Al-2Sn-4Zr-2Mo after gas nitriding at (a) 850, (b) 950 and (c) 1050 °C for different periods of time.



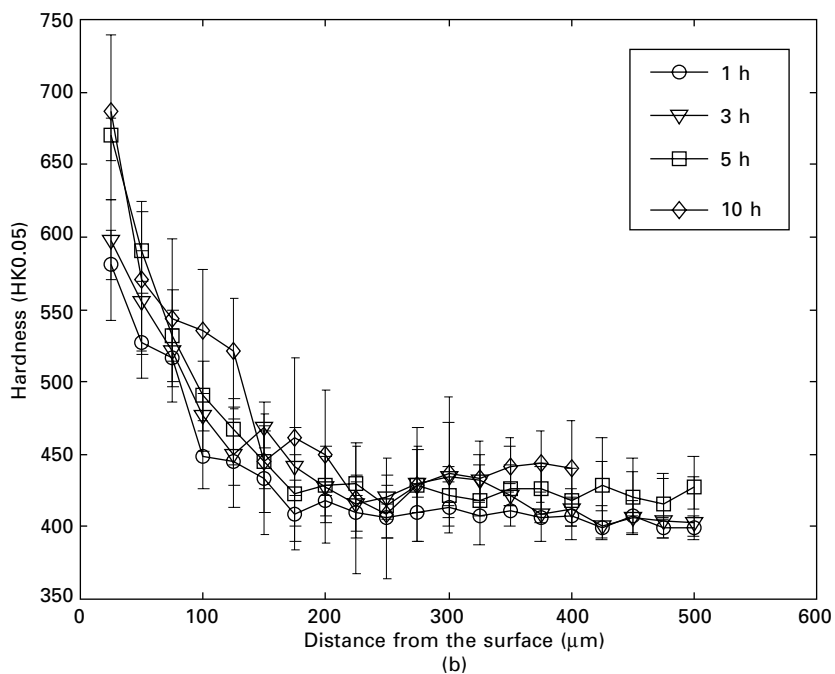
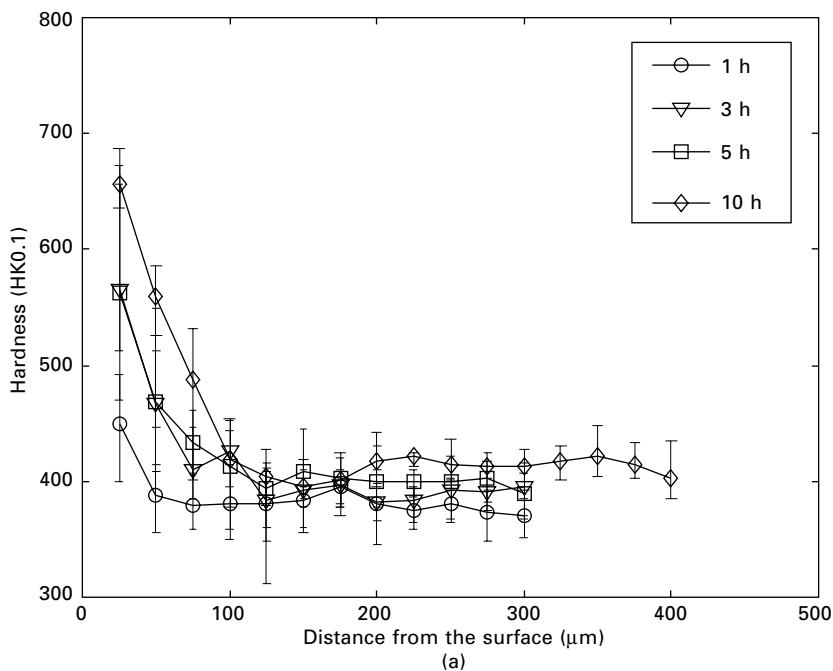
17.6 Continued



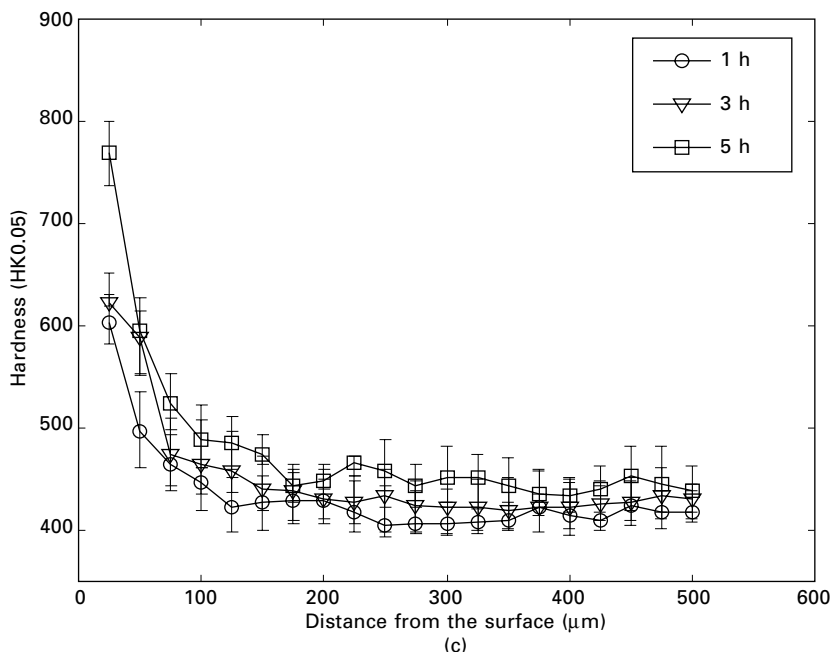
17.7 Surface hardness of Ti-6Al-4V after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours.

albeit with no significant change of the hardness with the time prolongation after nitriding at 1050 °C.

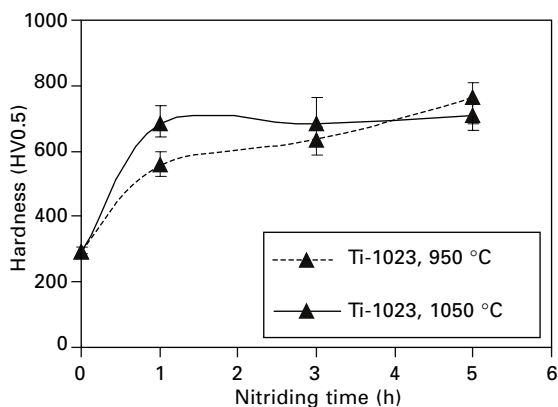
As discussed for the previous alloys, the microhardness and the thickness of the nitrided layer increase with the time prolongation for most of the cases (Fig. 17.10). They also increase with increase of the nitriding temperature. The thickness of the nitrided layer for this alloy varies between 25 and 200 μm.



17.8 Microhardness profiles of Ti-6Al-4V after gas nitriding at (a) 850, (b) 950 and (c) 1050 °C for different periods of time.

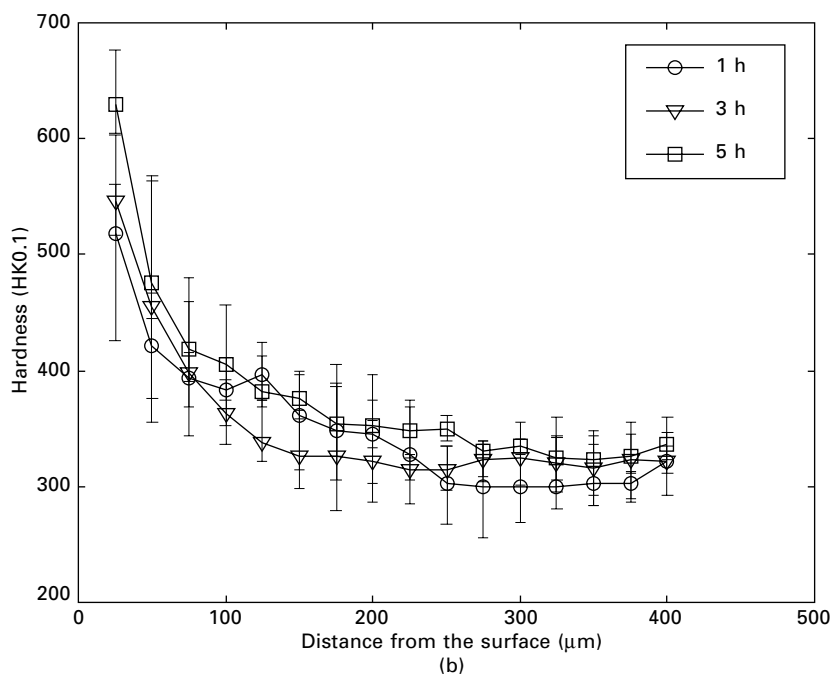
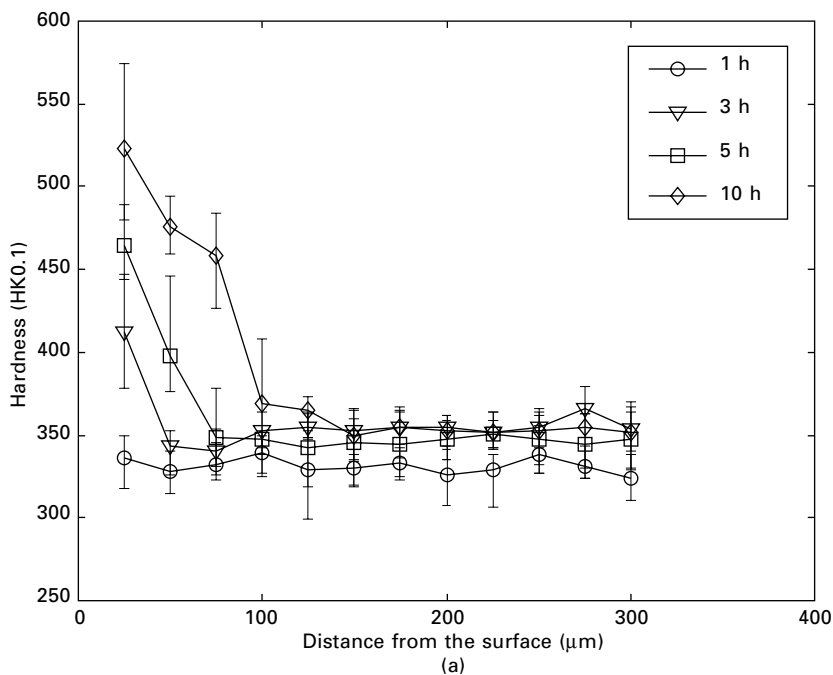


17.8 Continued

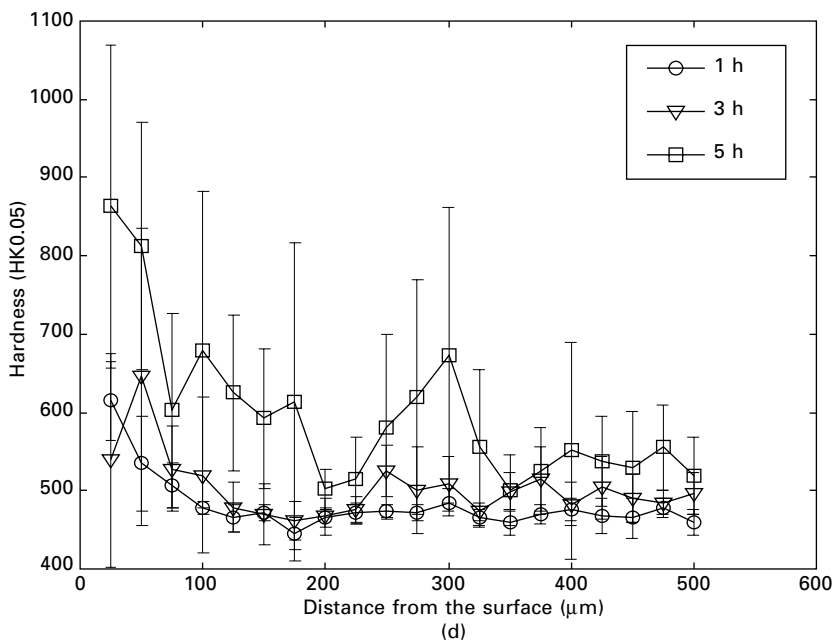
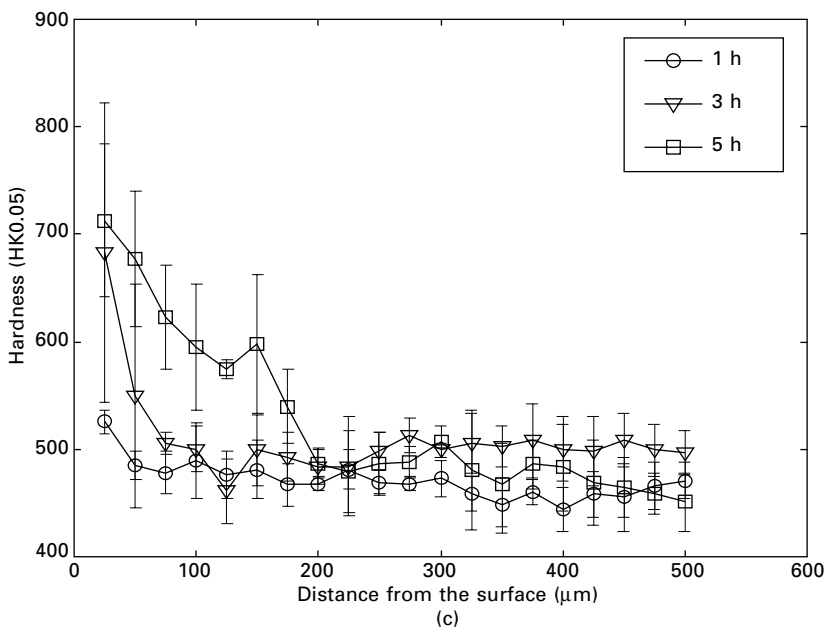


17.9 Surface hardness of Ti-10V-2Fe-3Al after gas nitriding at 950 and 1050 °C for 1, 3 and 5 hours.

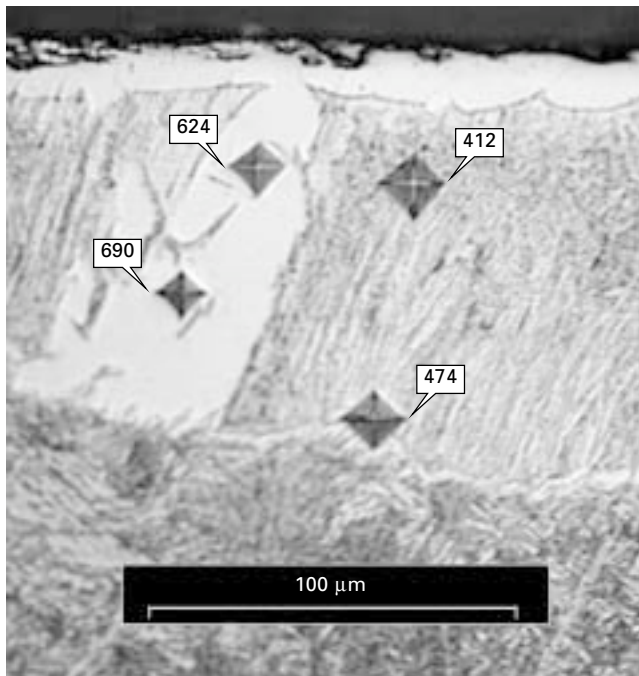
The big variation in the microhardness values for the alloy nitrided at temperatures higher than the β -transus for Ti-10V-2Fe-3Al is due to the difference in the irregular microstructure (see Fig. 17.11). That difference causes the large error bars for Ti-10V-2Fe-3Al nitrided at 850, 950 and 1050 °C (see Fig. 17.10). The values of the microhardness of the white grains are



17.10 Microhardness profiles of Ti-10V-2Fe-3Al after gas nitriding at (a) 750, (b) 850, (c) 950 and (d) 1050 °C for different periods of time.



17.10 Continued



17.11 Microhardness values (HV0.1) of different phases in Ti-10V-2Fe-3Al nitrided at 1050 °C for 5 hours.

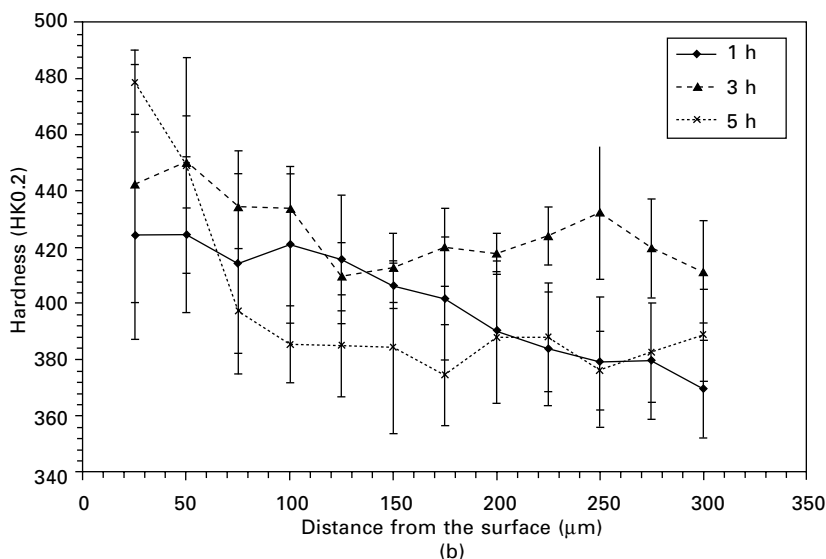
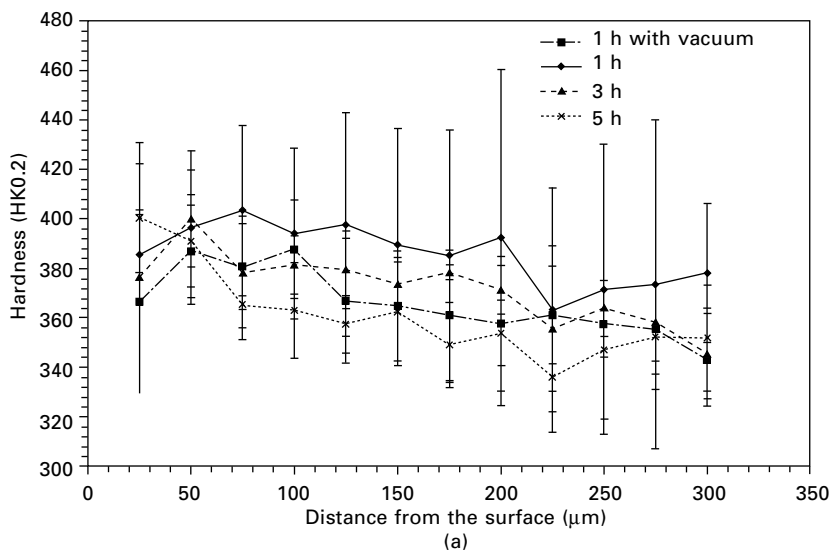
higher than those of the substrate because of the possible different nitrogen content, as was discussed earlier in this chapter.

17.1.5 $\beta 21s$

In the case of nitriding at 850 °C (Fig. 17.12a), the microhardness is not significantly different for each nitriding time and with the variation of depth. Gas nitriding at 850 °C is not effective in increasing the hardness near the surfaces. After gas nitriding at 950 °C (Fig. 17.12b), the microhardness increases compared to 850 °C. There is evidence of a limited increase in hardness near the outer surface.

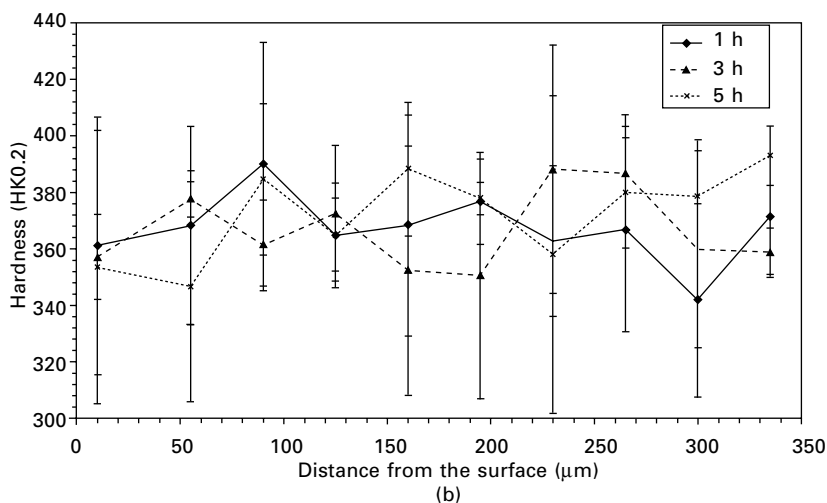
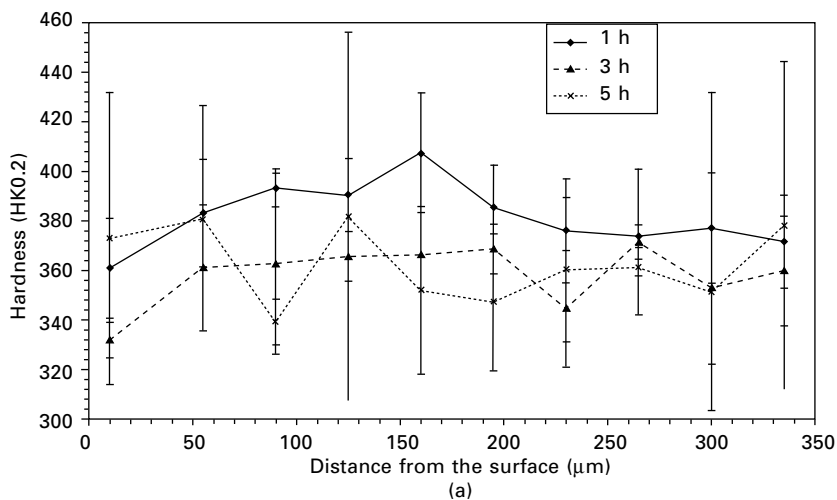
17.1.6 Timetal 205

Somewhat surprisingly, there is no significant difference in the hardness values through the cross-sections of this alloy (Fig. 17.13). This is contrary to previous sections on other titanium alloys. The hardness next to the surface after 1, 3 and 5 hours nitriding is similar to the hardness 335 μm into the substrate. There is also no significant difference in the hardness between the



17.12 Microhardness profiles of $\beta 21s$ after gas nitriding at (a) 850 and (b) 950 °C for different periods of time. 'With vacuum' refers to evacuation of the nitriding chamber prior to nitriding commencement.

different nitriding temperatures and lengths of time. The microstructure images in Section 16.7.2 show that the depth of the nitriding-affected layer is approximately 50 μm . Therefore, the apparent uniformity of the hardness through the cross-sections might be explained by the majority of the indents

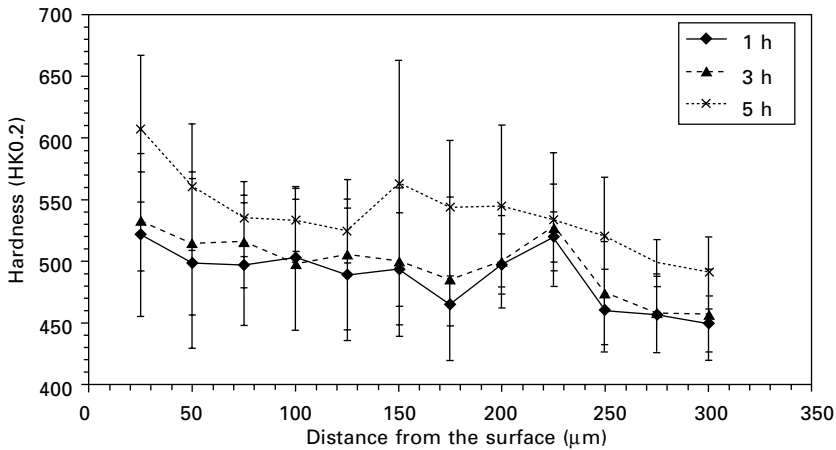


17.13 Microhardness profiles of Timetal 205 after gas nitriding at (a) 730 and (b) 830 °C for different periods of time.

being situated at depths larger than 50 μm from the very surface. However, the first indents of each sample are situated within 50 μm , but the hardness values for the first indents are not higher than the hardness values in the rest of the samples.

17.1.7 Ti–Al

The hardness of the nitrided Ti–Al samples increases near the surface of the alloy (Fig. 17.14). The maximum and minimum hardness values of 1050 °C nitrided Ti–Al alloy are 608 HK0.2 and 449 HK0.2, respectively.



17.14 Microhardness profiles of the Ti-Al alloy after gas nitriding at 1050 °C for different periods of time.

All the hardness increases shown in cross-sectional microhardness profiles are due to the sub-surface solid solution strengthening, because the first indent below the surface is already beyond the thickness of the compound layer. The error bars are standard deviations of three to five measurements. They are large relative to the hardness increases because of the possible sample inhomogeneity, limited equipment accuracy with the small load, and the small number of measurements in the cases of averaging from three data only.

17.1.8 Influence of the alloy type

Literature sources revealed that in more than 80% of reported surface hardening of titanium alloys by means of nitriding, the Ti-6Al-4V alloy was used. This is not surprising because this is the most widely used titanium alloy. However, over recent years, Ti-6Al-4V has been ‘force fitted’ in many applications, and there might be better alloy compositions for different particular applications.

Following this thought, the nitriding response of different types and classes of titanium alloys is compared, in order to reveal the influence of the nitriding on the microhardness evolution with respect to their alloy composition. Microhardness profiles of these alloys after nitriding at 850, 950 and 1050 °C for 5 hours show that the maximal microhardness values are obtained for Ti-6Al-2Sn-4Zr-2Mo, after nitriding for 5 hours at various temperatures. They also show that Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V have stronger nitriding response in terms of hardness and thickness of the hardened nitrided layer as compared with the other alloys. The conclusion is that the near- α

alloys give better results than the $\alpha + \beta$ (Ti-6Al-4V), near- β (Ti-10V-2Fe-3Al) and β (β 21s and Timetal 205) alloys. Two reasons are suggested for this:

- (i) The ratio between the α and β phases at the same temperature (e.g. 950 °C) is different in the different alloys. There is more α phase in Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V as compared to the other alloys. This difference in the phase composition probably results in differences in the diffusion conditions.
- (ii) Some alloying elements that are β -stabilisers (e.g. vanadium) may have a negative effect on the diffusion of nitrogen in titanium. One evidence for this is a comparison between the nitriding response of Ti 6-2-4-2 and Ti 8-1-1 alloys. The Ti 6-2-4-2 alloy (without vanadium) gives a better result than the Ti 8-1-1 alloy (with vanadium).

On the basis of the above, for practical applications, near- α titanium alloys such as Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V are recommended to be used for nitriding.

17.1.9 Summary of the influence of gas nitriding on the hardness of titanium alloys

Surface gas nitriding significantly increases the hardness of titanium alloys, due to the new phase formation on the surface of these materials during nitriding, such as TiN and TiO₂. The titanium nitride formed on the surface of the alloys has a very high hardness that can reach values above 2000 HV. The evolution of the surface hardness of the near- α , $\alpha + \beta$ and near- β titanium alloys in response to the nitriding temperature and time is similar.

The microhardness increases with the increase of temperature and time of nitriding. A maximal value of 1027 HK0.05 is recorded for Ti-6Al-2Sn-4Zr-2Mo after nitriding at 1050 °C for 5 hours. One of the main purposes of the nitriding is to increase the surface hardness of the materials in order to improve their tribological properties. The increase of the surface hardness does not necessarily improve significantly the wear properties of titanium alloys, which is one of the main problems of titanium alloys for mechanical applications.

The microhardness profiles of the titanium alloys after nitriding, prepared on cross-sections, give information not only about the microhardness behaviour of the materials but also about the thickness of the nitrified layer, because it can be assumed that the nitrified layer ends where the microhardness values reach the microhardness of the unsaturated core of the sample. The thickness of the nitrified layer varies between 25 and 350 μm , depending on the processing parameters of nitriding and the chemical composition of the alloy.

Nitriding at temperatures below the β -transus for titanium alloys is recommended for practical applications. However, with gas nitriding, β 21s shows marginal success in achieving higher value of hardness along the cross-section of the near surface layer. Nitriding Timetal 205 below and above the β -transus temperature of 780 °C does not cause any significant increase in hardness at all. The gas nitriding technique is not effective in increasing the hardness of near surface regions in β -titanium alloys because of the low β -transus temperatures. Normally, it is most effective to nitride titanium alloys at temperatures just below their β -transus temperatures, but for β alloys, this necessitates a very low nitriding temperature. Because of the lower nitriding temperatures required compared with α or $\alpha + \beta$ alloys, the diffusion activity of nitrogen during the process is much lower, resulting in less nitrogen entering the substrate, thus the low hardness increase. It is also possible that nitrogen solid solution in the bcc β -phase is not so effective in increasing its strength compared to that in the hcp α -phase.

Gas nitriding is not overly effective in increasing the hardness of Ti–Al alloy. However, the explanation for this is not clear, because there is no α to β transformation occurring at around the nitriding temperatures.

17.2 Tensile properties and fatigue performance after nitriding

Gas nitriding is seen to be a promising method to improve the surface hardness, wear resistance and, in general, the tribological properties of titanium alloys. However, it is still not quite clear in what direction and to what extent the nitriding can influence the bulk mechanical properties of these materials. This section examines the effect of nitriding on the tensile properties and fatigue performance of titanium alloys.

17.2.1 Nitriding and testing conditions

Two materials are used for this purpose, commercially pure titanium (CP-Ti) and the widely used Ti-6Al-4V alloy. Tensile and fatigue samples are surface gas nitrided in a pure nitrogen atmosphere for periods of 1 and 5 hours, at 830 °C for CP-Ti and at 950 °C for Ti-6Al-4V alloy. The temperatures are chosen to be 50 °C below the β -transus for each material. Reference samples are also prepared by heat treatment in vacuum, at the same temperatures for 5 hours. Thus, the reference samples and the samples after nitriding for 5 hours will have the same bulk microstructure and properties, and only the effect of the surface layer on the tensile and fatigue performance will be extracted.

17.2.2 Properties and micro- and nano-structure of the nitrided layer

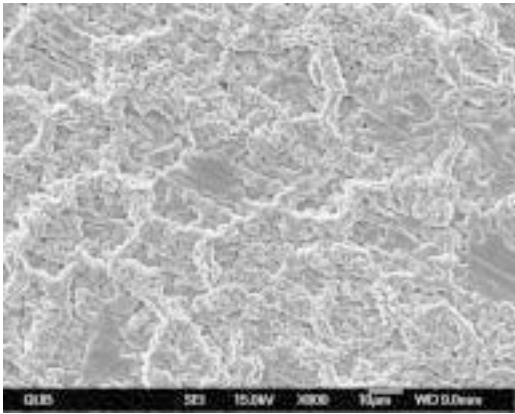
The surface hardness of the tensile and fatigue samples after nitriding is 780 and 870 HV, for CP-Ti and Ti-6Al-4V, respectively. The thickness of the hardened surface layer is about 75 μm for CP-Ti and about 200 μm for Ti-6Al-4V. The difference in the thickness is due to the difference in the temperature of nitriding for the two materials.

The surface of the nitrided CP-Ti is a light gold colour. The surface of the nitrided Ti-6Al-4V is a deeper golden colour. Colonies of grown titanium nitride are observed on the surface of Ti-6Al-4V alloy nitrided for 5 hours (Fig. 17.15). These colonies result in a rougher surface, which will be discussed in Section 17.3. Between the colonies, there are microcracks. The image at the highest magnification (Fig. 17.15c) reveals the presence of fine lamella crystals with widths in the nano-scale.

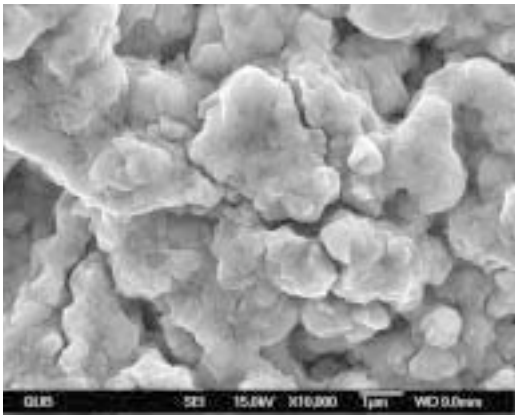
17.2.3 Tensile strength and elongation

Nitriding influences the tensile behaviour. Fig. 17.16 compares the average values of the tensile strength of four types of samples, where ET refers to tensile testing at 230 °C. The tensile strength at room temperature is not affected very much by nitriding. For Ti-6Al-4V alloy, there is a small decrease of 2% after nitriding for 1 hour, and 4% after nitriding for 5 hours. The tensile strength of CP-Ti is decreased by 6% after nitriding for 5 hours. The elongation is significantly affected by the formation of the nitrided surface layer. The elongation of Ti-6Al-4V alloy decreases after nitriding for 1 hour, and further after nitriding for 5 hours. The fracture type also changes (Fig. 17.17). The reference sample breaks after necking and reduction of the cross-section (Fig. 17.17a). The nitrided samples break along a 45° angle across the section of the specimens, with a very small reduction of the cross-section (Fig. 17.17c). The reduction of the elongation after nitriding of Ti-6Al-4V alloy can be explained by the formation of a surface hard layer with very low ductility. The trend in the elongation change of CP-Ti after nitriding is the opposite. The elongation after nitriding is slightly higher as compared to the reference sample. Indeed, for CP-Ti, the nitrided surface layer is very thin and should not have much influence on the bulk properties as is the case for Ti-6Al-4V alloy.

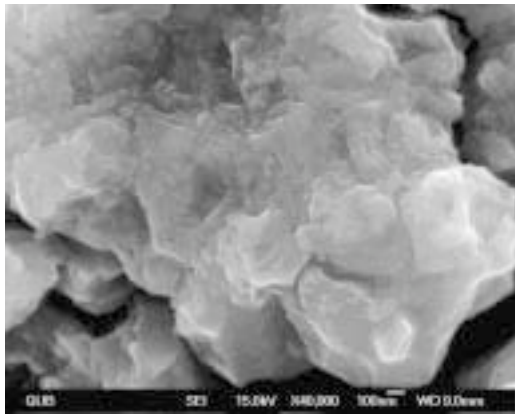
Naturally, nitrided samples have lower tensile strength and higher elongation when tested at elevated temperature, as compared to the same samples tested at room temperature. The tensile strength is decreased by 26% for Ti-6Al-4V and by 55% for CP-Ti. A neural network model for the prediction of mechanical properties (see Chapter 15) can calculate the change of the tensile properties from RT to 230 °C of titanium alloys without nitriding, which gives similar



(a)

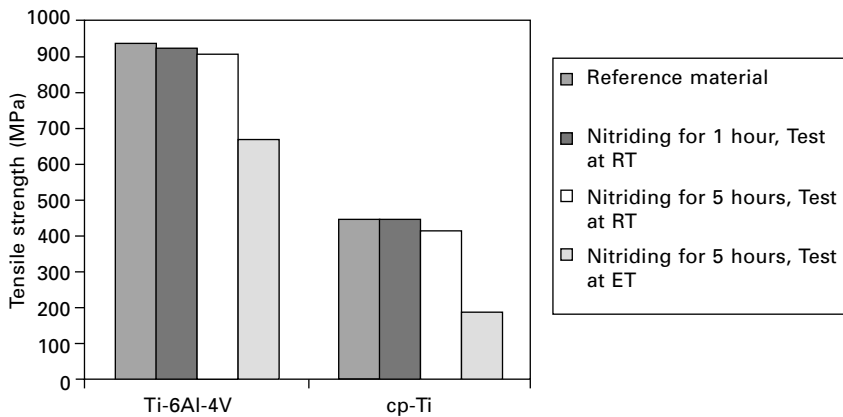


(b)



(c)

17.15 Scanning electron microscopy images, at different magnifications, of the surface of Ti-6Al-4V alloy after nitriding.



17.16 Influence of nitriding on the tensile strength of titanium alloys.

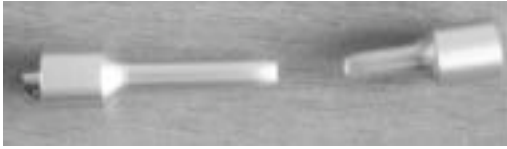
values to the percentage decrease of the tensile strength and increase of the elongation. Hence, formation of a surface nitrided layer does not have any influence on the degree of change of tensile properties with temperature increase.

17.2.4 Fatigue strength

Nitriding decreases the low cycle fatigue (Fig. 17.18). The reason for this is the formation of a rougher surface after nitriding, consisting of titanium nitride colonies and microcracks (see Fig. 17.15). The microcracks serve as ready nucleation sites for the formation of macrocracks. There is some indication for improvement of the fatigue performance in the high cycle region after nitriding. Probably, at lower stress, the stresses acting on the sample surface are not high enough for formation of macrocracks. On the other hand, the formation of the nitrided surface layer creates residual stresses in the surface, which could result in an increase of the fatigue life in the high cycle region.

17.3 Surface morphology and roughness of Ti-6Al-2Sn-4Zr-2Mo after nitriding

Ti-6Al-2Sn-4Zr-2Mo has shown a good nitriding performance in comparison with the other alloys, especially after nitriding at 950 °C for 5 hours. This section studies how the surface morphology of this alloy changes after the thermo-chemical treatment of gas nitriding and how this change influences its surface properties. The influence of the processing parameters of nitriding on the surface roughness, phase modifications and the microstructure of the nitrided layer will be shown.



(a) Ti-6Al-4V, reference condition



(b) CP-Ti, reference condition



(c) Ti-6Al-4V, nitrided and tested at room temperature



(d) CP-Ti, nitrided and tested at room temperature



(e) Ti-6Al-4V, nitrided and tested at elevated temperature



(f) CP-Ti, nitrided and tested at elevated temperature

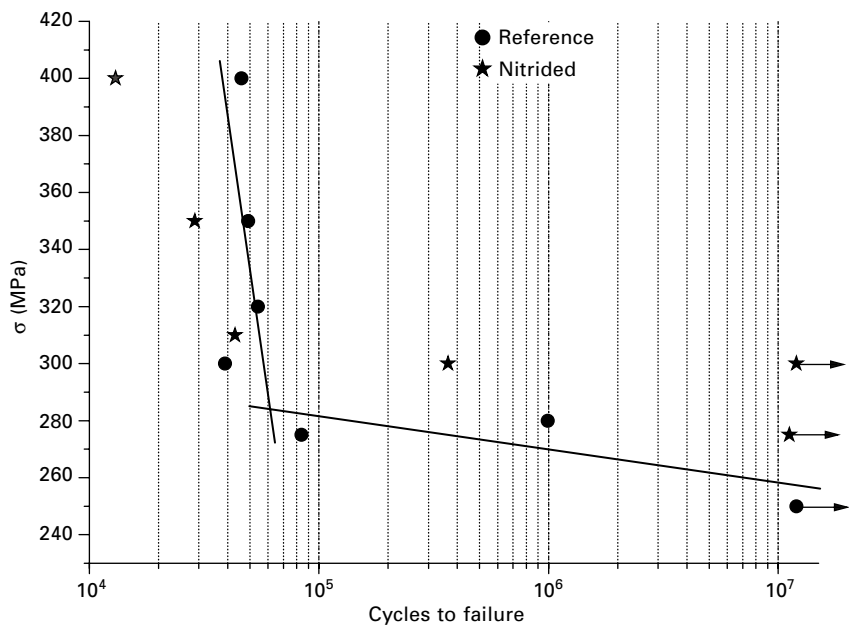
17.17 Samples after tensile tests under different conditions.

17.3.1 Surface morphology

For quantifying the surface roughness, the most frequently used parameter is R_a . This value is the arithmetic mean of the deviations of the height from the image mean value. R_a can be written as:

$$R_a = \frac{1}{N} \sum_{i=1}^N |Z_i - \bar{Z}| \quad [17.1]$$

where the image mean value ($\bar{Z}$) is defined as the sum of all the height values (Z) divided by the number of data points (N) in the image:



17.18 Fatigue data for CP-Ti in reference condition and after nitriding.

Table 17.1 Roughness of Ti-6Al-2Sn-4Zr-2Mo under different initial surface conditions before and after nitriding at 950 °C for 5 hours

Initial surface preparation	R_a before nitriding (μm)	R_a after nitriding (μm)
Abrasive paper #220	$0.402^{+0.126}_{-0.115}$	$0.449^{+0.270}_{-0.097}$
Abrasive paper #2400	$0.070^{+0.025}_{-0.023}$	$0.266^{+0.021}_{-0.017}$
Polished $\frac{1}{4} \mu\text{m}$	$0.036^{+0.007}_{-0.007}$	$0.290^{+0.074}_{-0.087}$

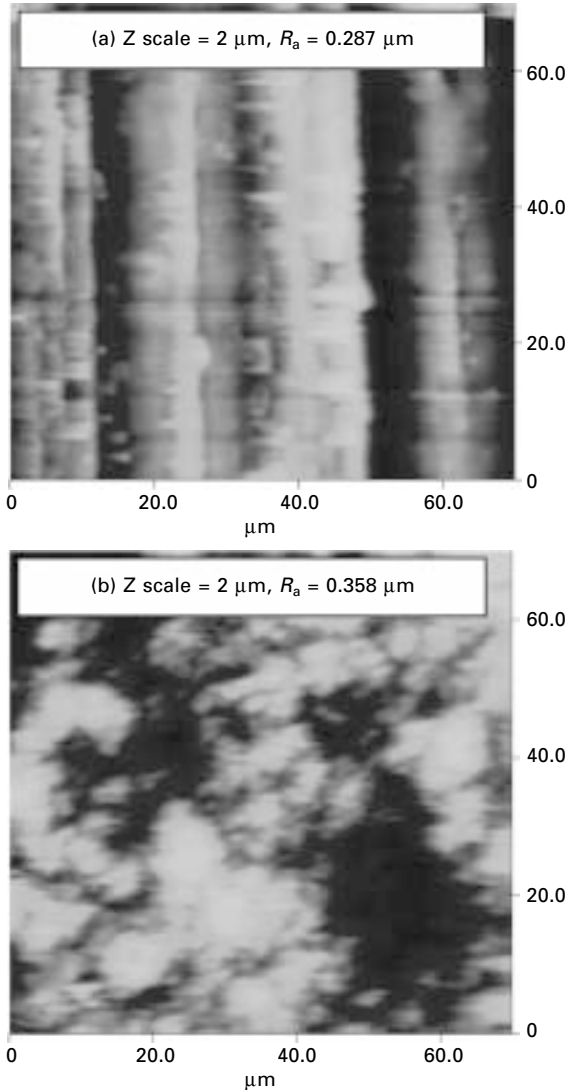
$$\bar{Z} = \frac{1}{N} \sum_{i=1}^N Z_i$$

[17.2]

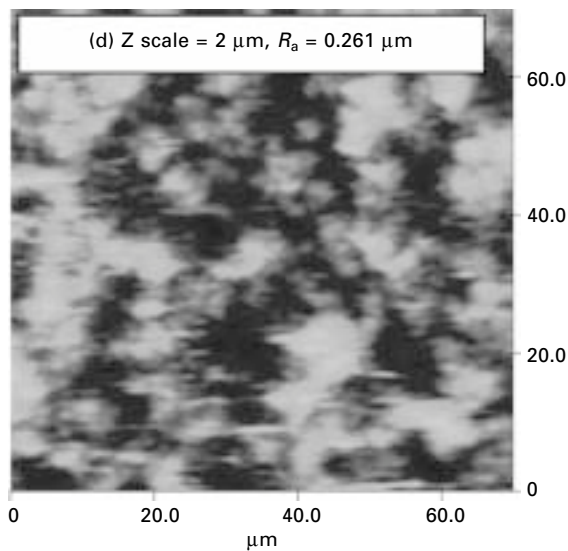
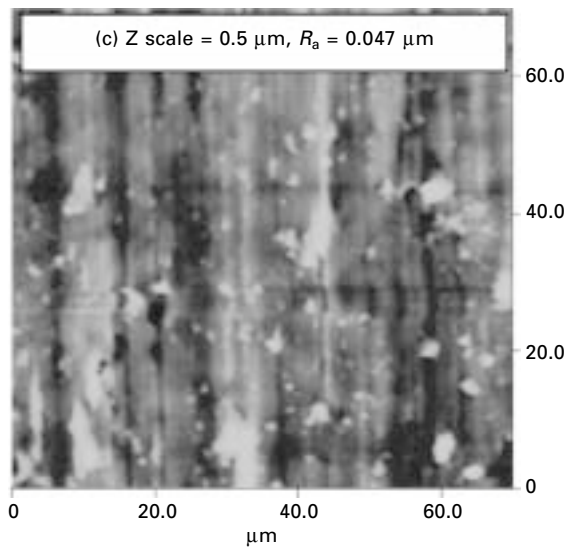
After nitriding, there are compound layers formed on the surface, mainly consisting of titanium nitride, discussed in the next section. On the top of that layer, a thin oxide film is formed. These films have a very high surface roughness, >1 μm , that it is impossible to measure by atomic force microscopy (AFM). That is the reason why they have to be removed in order to perform the roughness measurements. The data for R_a are given in Table 17.1.

There is an increase in surface roughness after gas nitriding at 950 °C for 5 hours. For the roughest sample, ground with abrasive paper #220, the increase of R_a is not significant whereas for smoother samples ground with abrasive paper #2400 or polished, which have lower initial roughness, R_a

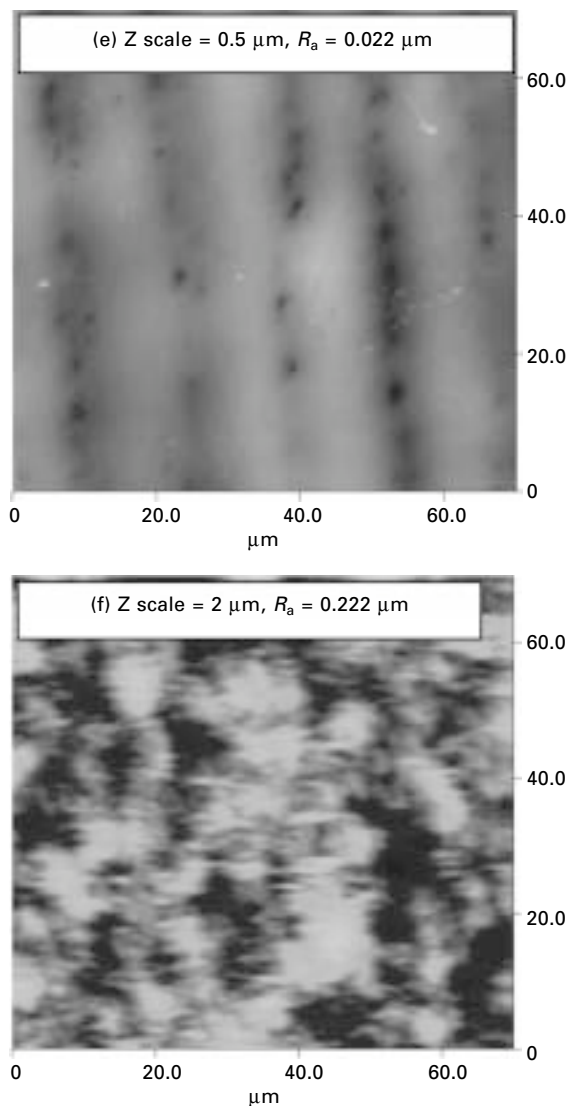
increases up to eleven times. After nitriding the smoother samples, they show similar values of R_a , whereas the roughest sample has much higher roughness, obviously due to the difference in the initial roughness. The surface morphology is presented by 2D and 3D images in Figs. 17.19 and 17.20.



17.19 Surface morphology of Ti-6Al-2Sn-4Zr-2Mo (a, c and e) before and (b, d and f) after gas nitriding at 950 °C for 5 hours. (a) and (b) Abrasive paper #220; (c) and (d) abrasive paper #2400; (e) and (f) polished. The lightest area corresponds to the highest points in the alloy surface, but there is no quantitative calibration of the brightness scheme.

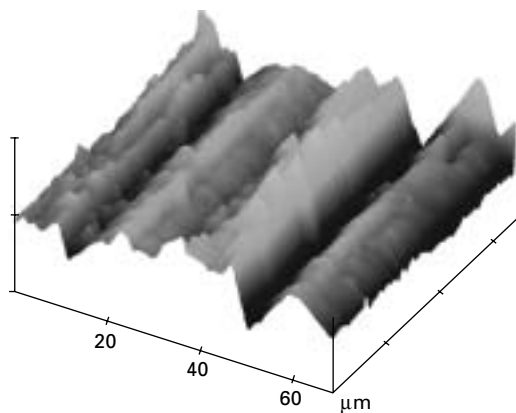


17.19 Continued

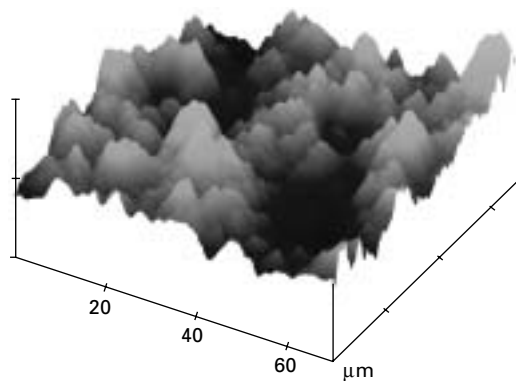


17.19 Continued

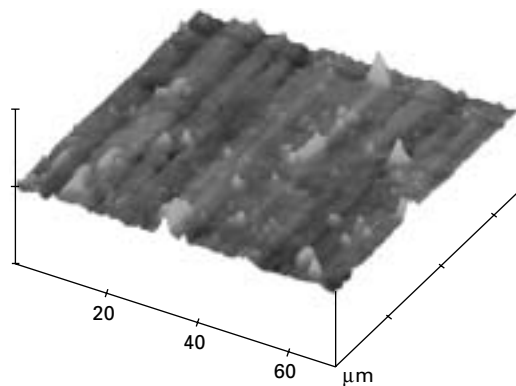
Table 17.2 shows the influence of the processing parameters on the surface roughness after gas nitriding. The surface roughness increases with the time prolongation from 3 to 5 hours at 950 °C, but there is no significant change of the surface roughness with the increase of temperature from 950 to 1050 °C. At the same time, there is a huge increase of R_a (25 times) after treatment at 950 °C for 1 hour. This is because the surface oxide layer and the layer underneath have a good adhesion so it is difficult to remove the very top



(a)



(b)



(c)

17.20 3D images of the surface morphology of Ti-6Al-2Sn-4Zr-2Mo (a, c and e) before and (b, d and f) after gas nitriding at 950 °C for 5 hours. (a) and (b) Abrasive paper #220; (c) and (d) abrasive paper #2400; (e) and (f) polished. The Z scale for all images is 2 μm /division.

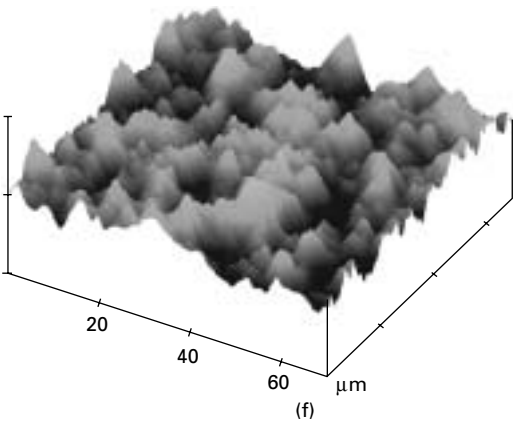
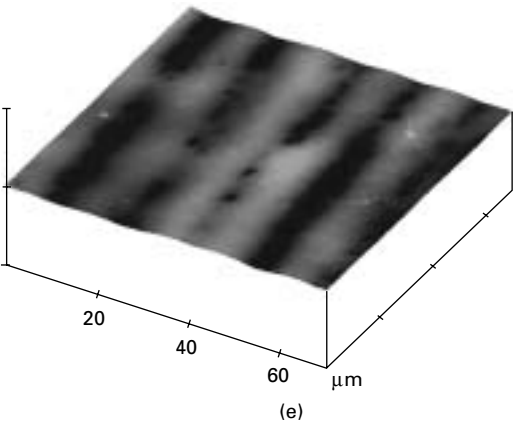
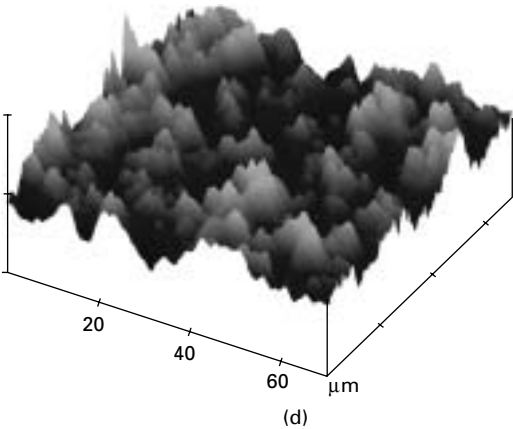


Table 17.2 Roughness of polished Ti-6Al-2Sn-4Zr-2Mo under different nitriding conditions

Nitriding condition	R_a after nitriding (μm)*
950 °C, 1 hour	0.894 ^{+0.081} _{-0.091}
950 °C, 3 hours	0.167 ^{+0.015} _{-0.019}
950 °C, 5 hours	0.290 ^{+0.074} _{-0.087}
1050 °C, 5 hours	0.282 ^{+0.032} _{-0.017}

*The roughness before nitriding is 0.036^{+0.007}_{-0.007} μm

layer. The surface oxide layer has much higher surface roughness. The surface morphology is presented by 2D and 3D images in Figs. 17.21 and 17.22.

17.3.2 Phase modifications and microstructure

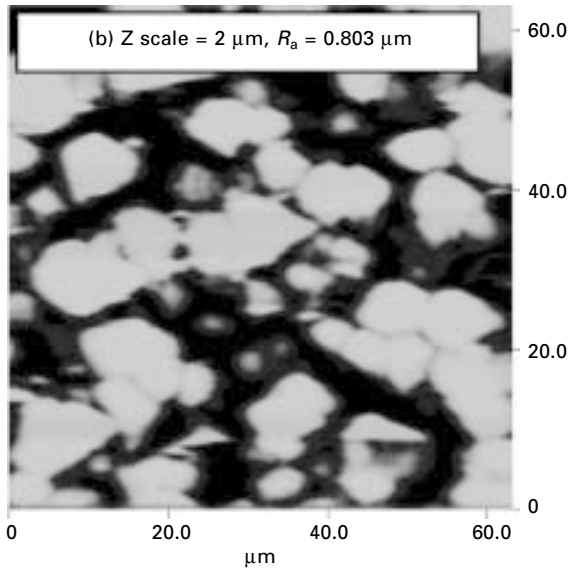
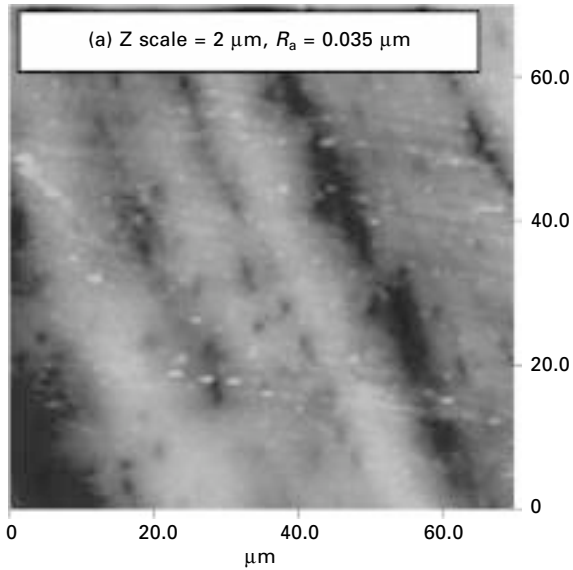
As discussed in Chapter 16, when the alloys were in an active nitrogen atmosphere at high temperature, the nitrogen absorbed at the surface diffused into the material, forming different nitrogen compounds. As a result of the nitriding process, a nitrided layer is formed that consists of a compound layer on the surface of the material, which is mainly composed of titanium nitride, followed by a diffusion zone which is composed of an interstitial solution of nitrogen in the hcp α titanium phase, α -Ti(N). More details are given in Chapter 16.

The change of the surface roughness is related to the phase transformations that took place during gas nitriding, as revealed in diffraction patterns (Fig. 17.23).

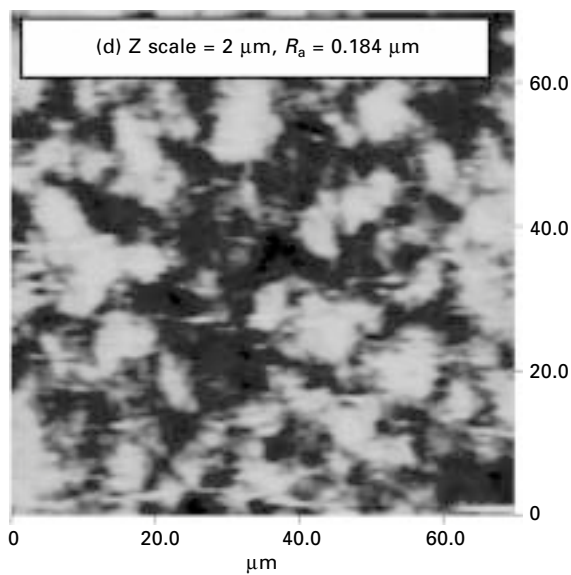
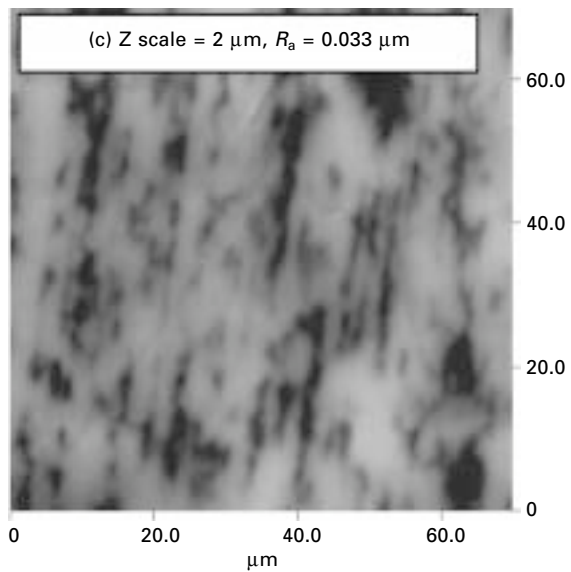
After gas nitriding at 950 °C for 3 and 5 hours and at 1050 °C for 5 hours, the compound layer consists of titanium nitride and a small amount of titanium oxide. After gas nitriding at 950 °C for 1 hour, the surface layer consists mainly of TiO_2 , because, as mentioned above, the top oxide film was not removed. There are two possible reasons for this oxide film formation and they are discussed in Chapter 16.

Optical images reveal the difference in the microstructure of the alloy nitrided at different temperatures and for different times (Fig. 17.24).

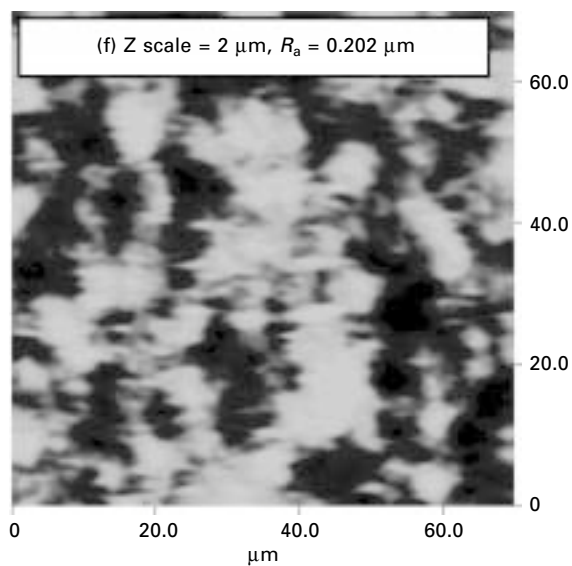
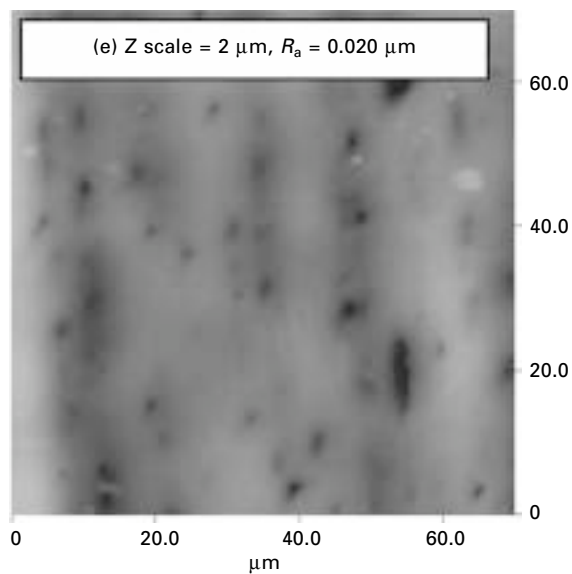
As discussed in Chapter 16, after gas nitriding of the alloy at 950 °C, the nitrided layer has a homogeneous microstructure, and its thickness increases with increase of the nitriding time. This can be seen from the micrographs in Fig. 17.24a–c. By increasing the nitriding temperature to 1050 °C, an irregular needle structure is formed. In this case, it is difficult to define the layer thickness from the microstructure. The grain growth at the higher nitriding temperature is because 1050 °C is above the β -transus temperature for this alloy (see Chapter 16).



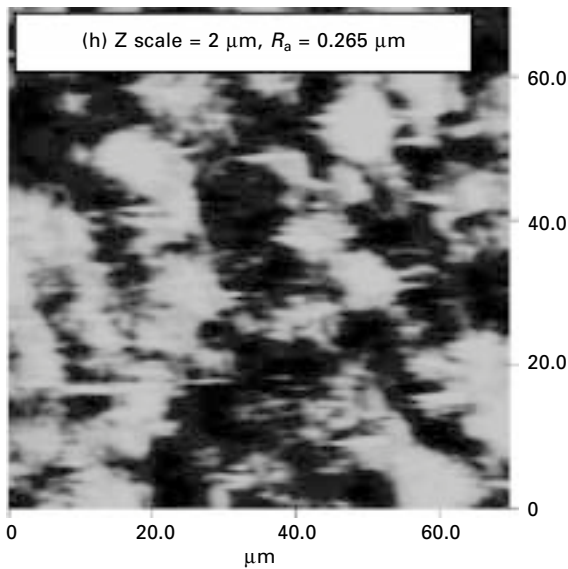
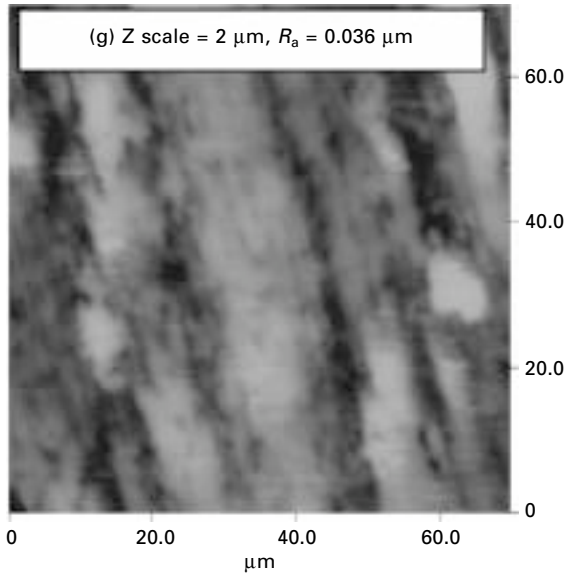
17.21 Surface morphology of polished Ti-6Al-2Sn-4Zr-2Mo (a, c, e and g) before and (b, d, f and h) after gas nitriding at different temperatures and for different periods of time. (a) and (b) 950 °C, 1 hour; (c) and (d) 950 °C, 3 hours; (e) and (f) 950 °C, 5 hours; (g) and (h) 1050 °C, 5 hours.



17.21 Continued



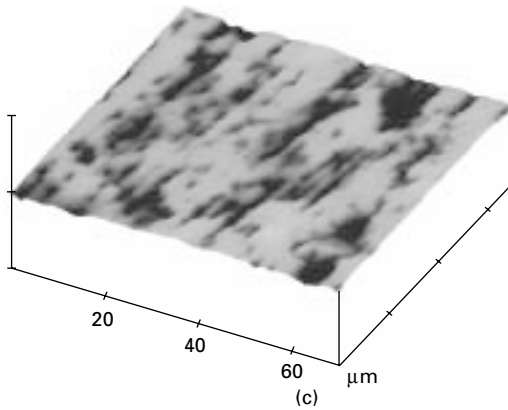
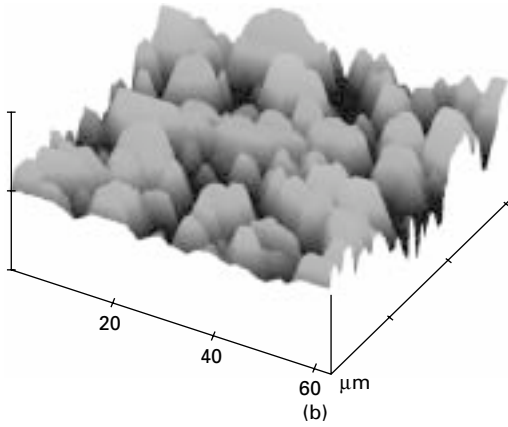
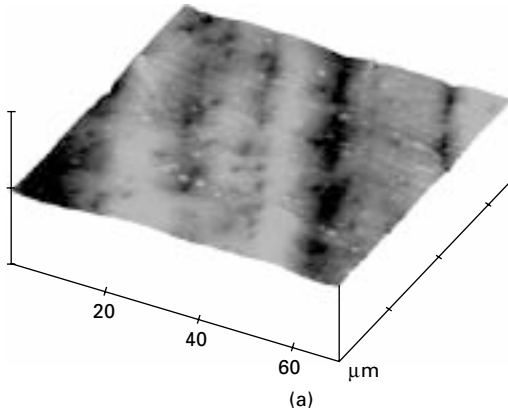
17.21 Continued



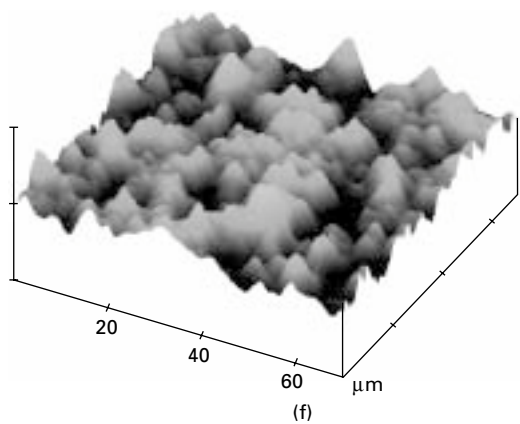
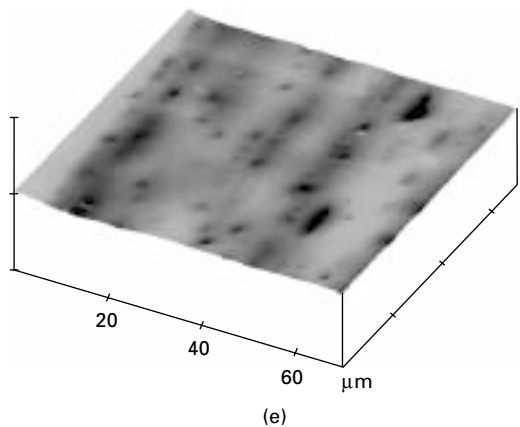
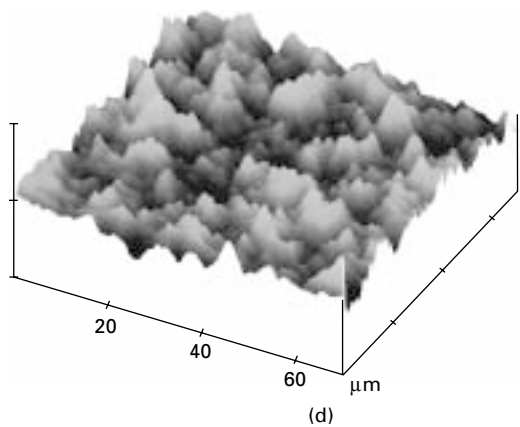
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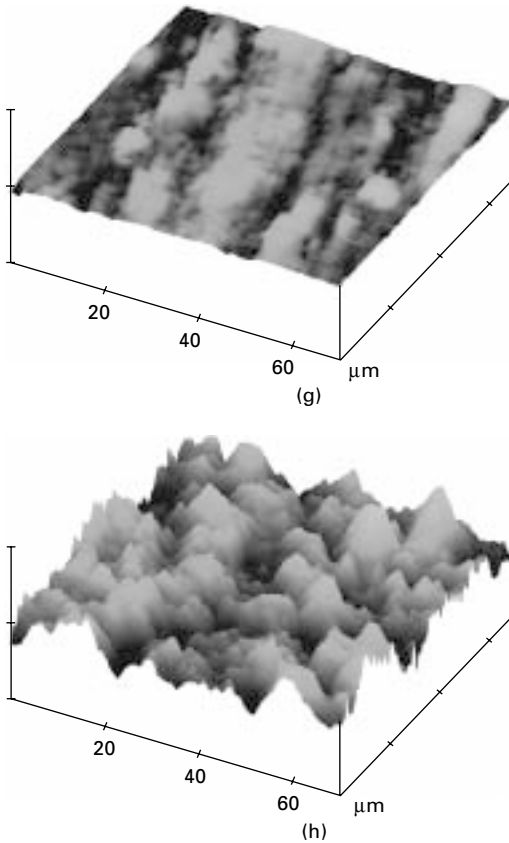
17.3.3 Microhardness profiles

The microhardness is very high near the surface and falls gradually with the distance from the surface. There is no significant difference in the microhardness values for different initial roughness.



17.22 3D images of the surface morphology of polished Ti-6Al-2Sn-4Zr-2Mo (a, c, e and g) before and (b, d, f and h) after gas nitriding at different temperatures and for different periods of time. (a) and (b) 950 °C, 1 hour; (c) and (d) 950 °C, 3 hours; (e) and (f) 950 °C, 5 hours; (g) and (h) 1050 °C, 5 hours. The Z scale for (b) is 4 μm /division and for all the rest is 2 μm /division.



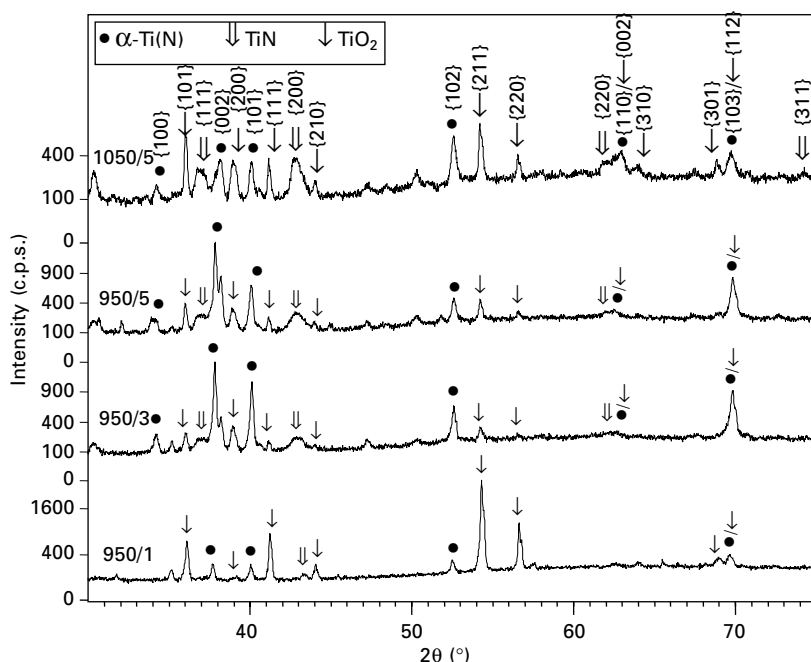


17.22 Continued

The thickness of the nitrided layer can be estimated from the microhardness profiles (see Section 17.1). As was discussed in that section, it can be supposed that the nitrided layer ends where the microhardness value approaches the core microhardness. For Ti-6Al-2Sn-4Zr-2Mo, gas nitrided at 950 °C for 5 hours, nitrided layers of about 200 μm have been obtained.

17.3.4 Summary

Gas nitriding significantly increases the surface roughness of Ti-6Al-2Sn-4Zr-2Mo titanium alloy, up to the order of 25 times, except for the substrate with high initial roughness already. The surface roughness after nitriding depends on the initial surface roughness of the material. It increases with increase of the initial roughness. The surface roughness increases with increase of the nitriding time, but there is no significant change of the surface roughness with increase of the temperature from 950 to 1050 °C. The increase of the

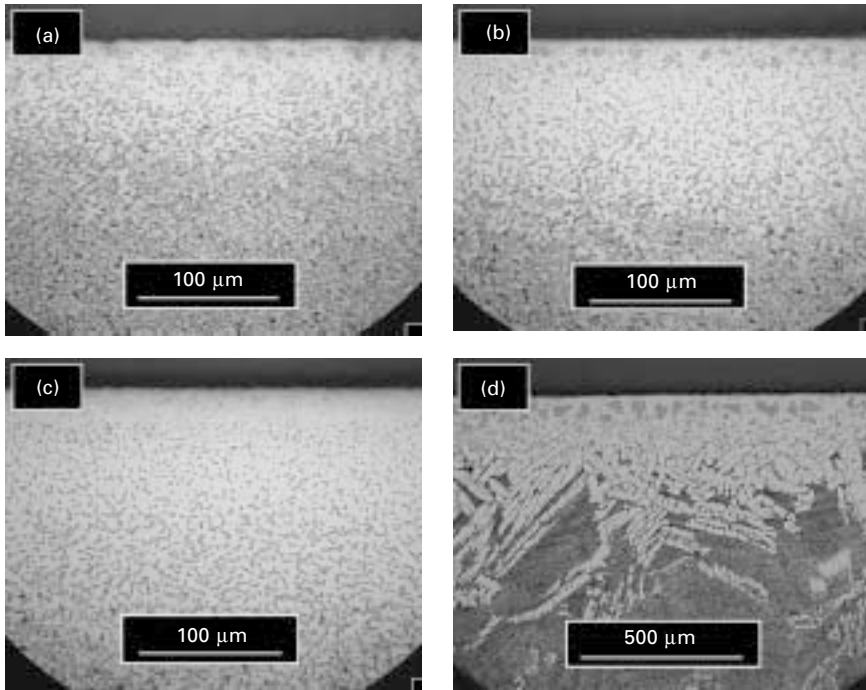


17.23 X-ray diffraction patterns of Ti-6Al-2Sn-4Zr-2Mo after gas nitriding at 950 °C for 1, 3 and 5 hours and at 1050 °C for 5 hours.

surface roughness after gas nitriding is caused by the formation of titanium nitride and titanium oxide on the surface of the materials. There is no significant influence of the different initial surface roughness on the microhardness and the thickness of the nitrided layer after nitriding.

17.4 Corrosion behaviour

One of the biggest advantages of titanium alloys is their good corrosion resistance. Much research and testing have been carried out to assess the corrosive behaviour of titanium alloys in different environments before and after different types of thermo-chemical surface treatments, which can either improve or worsen their corrosion resistance properties. The data in the literature is quite diverse and inconsistent in this area. This section will quantify the effect of the corrosive media and test temperature on the corrosion behaviour of Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V before and after the surface thermo-chemical treatment of gas nitriding.



17.24 Microstructure of Ti-6Al-2Sn-4Zr-2Mo. (a) 950 °C, 1 hour; (b) 950 °C, 3 hours; (c) 950 °C, 5 hours; (d) 1050 °C, 5 hours.

17.4.1 Basic principles of titanium alloys corrosion

General corrosion of titanium alloys

Titanium, like any other metal, is subject to corrosion in certain environments. The types of corrosion that have been observed on titanium may be classified under the following general headings: general corrosion, crevice corrosion, stress corrosion cracking, anodic breakdown pitting, and galvanic corrosion.

This section (Section 17.4) is aimed specifically at the general corrosion resistance of titanium alloys before and after surface gas nitriding. General corrosion is characterised by a uniform attack over the entire exposed surface of the metal. The severity of this type of attack can be expressed by the corrosion rate. General corrosion in aqueous media may take the form of mottled or severely roughened metal surfaces. When titanium is fully passive, corrosion rates are typically around 0.04 mm/yr, much lower than 0.13 mm/yr maximum rate accepted by engineers. This very low corrosion rate is attributed to a titanium oxide film on the surface. The exact process will be explained next in this section. As a result, titanium is often designed with a zero corrosion allowance in passive environments. However, in some environments,

titanium may experience an oxide growth, characterised by a coloured surface and slight weight gain.

General corrosion really becomes a concern in reducing acid environments, especially if the acidity and temperatures begin to rise. In strong or hot reducing acids, the oxide film on the surface will deteriorate and break down, so leaving the metal surface susceptible to corrosion.

Mechanism of corrosion resistance

The excellent corrosion resistance of titanium alloys is due to the formation of a very stable, continuous, highly adherent, and protective oxide film on the metal surfaces. Because titanium metal itself is highly reactive and has an extremely high affinity for oxygen, these beneficial surface oxide films form spontaneously and instantly, when fresh metal surfaces are exposed to air, or moisture. In fact, a damaged oxide film can generally heal itself instantaneously if at least traces (that is, parts per million) of oxygen or water (moisture) are present in the environment.

The composition of this film varies from TiO_2 at the surface to Ti_2O_3 and TiO at the metal interface. Oxidising conditions promote the formation of TiO_2 , so that in such environments the film is primarily TiO_2 . This film is transparent in its normal thin configuration, and not detectable by visual means. A study of the corrosion resistance of titanium is basically a study of the properties of the oxide film, which is attacked only by certain substances, under, for example, anhydrous conditions in the absence of a source of oxygen.

Therefore, the successful non-corrosive properties of titanium and its alloys can be expected in mildly reducing to highly oxidising environments, in which protective oxide films spontaneously form and remain stable. Titanium exhibits excellent resistance to atmospheric corrosion in both marine and industrial environments.

The following is some background information on the effects of some corrosive media.

Salt solutions

Titanium alloys are very resistant to almost all salt solutions over the pH range of 3 to 11, and to temperatures that exceed their boiling point. Titanium can withstand exposure to solutions of chlorides, bromides, iodides, sulfites, sulfates, borates, phosphates, cyanides, carbonates, bicarbonates, and ammonium compounds. The corrosion rate values for titanium alloys in this variety of salt solutions are generally less than 0.03 mm/yr. Titanium alloys are frequently used in many process streams, brines, and seawater, because of their good resistance to the chlorides typically found in them.

Reducing acids

This category includes hydrochloric, sulfuric, hydrobromic, hydriodic, hydrofluoric, phosphoric, sulfamic, oxalic, and trichloroacetic acids. The corrosion resistance of titanium alloys in reducing acid solutions is very sensitive to the acid concentration, solution temperature and purity of the acid solution, as well as to the alloy composition. With increase of the temperature, or the concentration of the reducing acid solution, the protective oxide film on the surface of the material may break down, which would result in severe general corrosion. Various oxidising species can effectively inhibit the corrosion of titanium in reducing acid environments, when present in small concentrations. These inhibiting species often occur as natural process stream constituents or contaminants, and do not need to be intentionally introduced to achieve passivation.

Enhancing the corrosion resistance of titanium alloys

Basically, the only methods of increasing the corrosion resistance of titanium in reducing environments are:

- (i) increasing the surface oxide film thickness by anodising or thermal oxidation
- (ii) anodically polarising the alloy with a more noble metal, in order to maintain the surface oxide film
- (iii) applying precious metal surface coatings
- (iv) alloying titanium with certain elements
- (v) adding oxidising species to the reducing environment to permit oxide film stabilisation.

Of these five methods, the last two are the most practical, and are widely used in service.

Thermo-chemical nitriding of titanium alloys may also improve their corrosion resistance. The problem after these types of treatments is that if the nitrided surface has become pitted, the corrosion is higher for the nitrided material, because of the potential difference between core and case. Many researchers have studied the corrosion behaviour of titanium alloys before and after nitriding (Gokul Lakshmi *et al.*, 2002; Meletis, 2002; Takahashi and Kimura, 2001).

Considering phase transformations taking place during the thermo-chemical treatment of gas nitriding, one can expect that these newly-formed surface layers would affect the corrosion properties.

17.4.2 Influence of the alloy composition and surface gas nitriding

The two alloys discussed in this section are the near- α titanium alloys Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo. Normally, the additions of molybdenum and vanadium improve the corrosion resistance of titanium alloys, and aluminium content worsens it. These two alloys have different alloy composition, and they would have different corrosion behaviour in various media.

0.5M NaCl

In 40 °C solution, Ti-8Al-1Mo-1V shows better corrosion resistance in comparison with Ti-6Al-2Sn-4Zr-2Mo. At the higher medium temperature of 80 °C, the relative corrosion resistance between the two alloys is the opposite, and the weight loss increases under each condition except for Ti-6Al-2Sn-4Zr-2Mo nitrided at 950 °C for 5 hours. Gas nitriding worsens the corrosion resistance of Ti-6Al-2Sn-4Zr-2Mo at both medium temperatures, but improves the corrosion resistance of Ti-8Al-1Mo-1V.

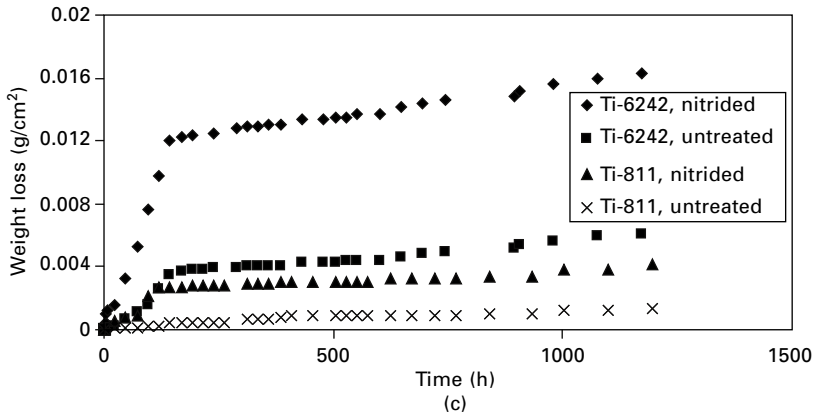
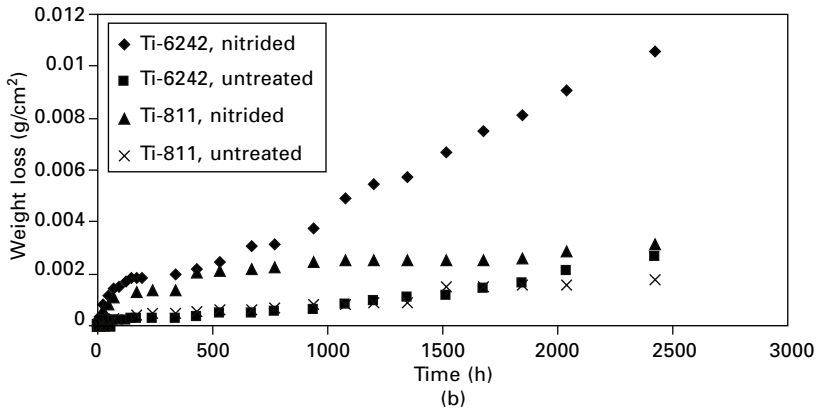
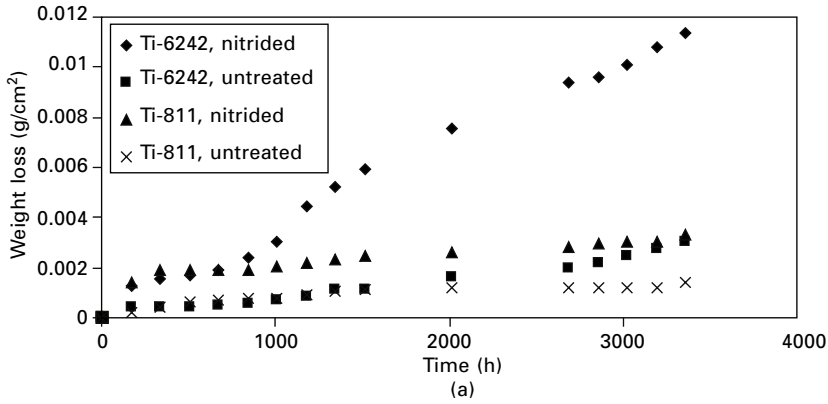
Despite the above differences, the corrosion resistance of these alloys in 0.5M NaCl at both solution temperatures may be concluded as excellent, with or without the nitriding, considering that the average weight loss values never reach 0.0005 g/cm² after 1500 hours of corrosion test. The level of weight loss in this salt solution is insignificant in comparison to the weight loss in acidic media. These results are partly in contradiction to the results given by Fleszar *et al.* (2000), where it was reported that plasma nitriding significantly increased the corrosion resistance of Ti-6Al-3Mo-2Cr.

4.9M HCl

The weight loss increases for all conditions with the time prolongation and the increase of the temperature, except that there is no significant influence of the temperature on the corrosion behaviour of the untreated Ti-8Al-1Mo-1V alloy (Fig. 17.25).

The nitrided Ti-8Al-1Mo-1V shows, in general, better performance than the nitrided Ti-6Al-2Sn-4Zr-2Mo. The weight loss values of the untreated condition are similar for the two alloys at 20 and 40 °C. At 80 °C, Ti-8Al-1Mo-1V shows a better performance in 4.9M HCl in comparison to Ti-6Al-2Sn-4Zr-2Mo, probably due to the advantageous combination of the alloying elements in the former. These data are in contradiction with the results obtained for Ti-6Al-4V by Galvanetto *et al.* (2002).

Gas nitriding worsens the corrosion resistance of these alloys and especially of Ti-6Al-2Sn-4Zr-2Mo. The reducing acid solution is very aggressive and



17.25 Weight loss versus time of Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V, untreated and nitrided (950 °C for 5 hours), after holding them in 4.9M HCl at (a) room temperature, (b) 40 and (c) 80 °C.

breaks the oxide film and the nitrided compound layers, leading to a significant increase of weight loss.

1.8M H₂SO₄

Surface gas nitriding worsens the corrosion resistance of Ti-6Al-2Sn-4Zr-2Mo in 1.8M H₂SO₄ at 20 and 80 °C solutions (Fig. 17.26). At a solution temperature of 40 °C, the untreated and nitrided alloys are quite similar.

Surface gas nitriding worsens the corrosion resistance of Ti-8Al-1Mo-1V in 1.8M H₂SO₄ at room temperature. After holding the same alloy at higher medium temperatures of 40 and 80 °C, the alloy in the nitrided condition has better corrosion resistance than that in the untreated condition. The weight loss of the nitrided Ti-8Al-1Mo-1V increases with the time prolongation, and with the increase of the temperature from 40 to 80 °C. There is no clear tendency in the corrosion behaviour of Ti-8Al-1Mo-1V in 1.8M H₂SO₄.

At 40 °C, the untreated Ti-6Al-2Sn-4Zr-2Mo has better corrosion resistance in comparison with the untreated Ti-8Al-1Mo-1V.

At 80 °C, the nitrided Ti-8Al-1Mo-1V shows better performance than Ti-6Al-2Sn-4Zr-2Mo and the opposite tendency can be seen for the untreated alloys.

17.4.3 Influence of the corrosive medium

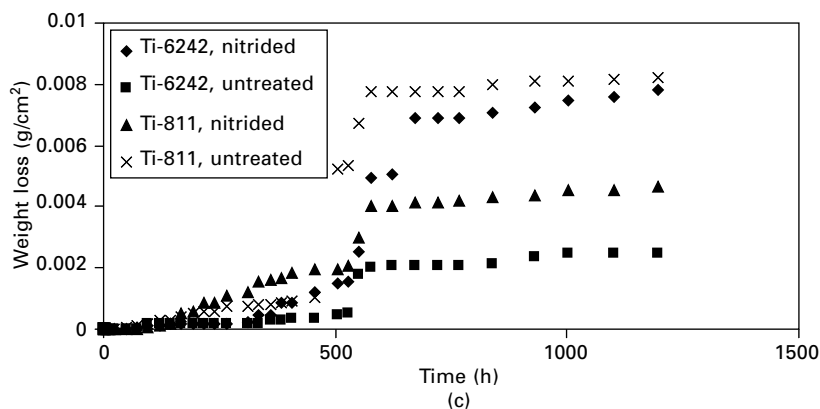
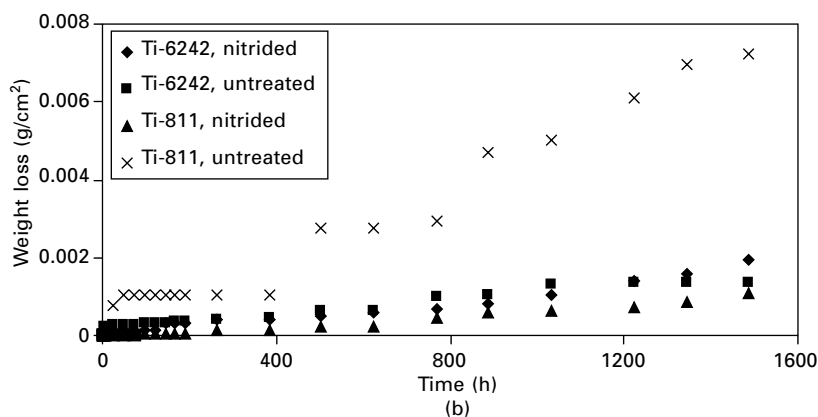
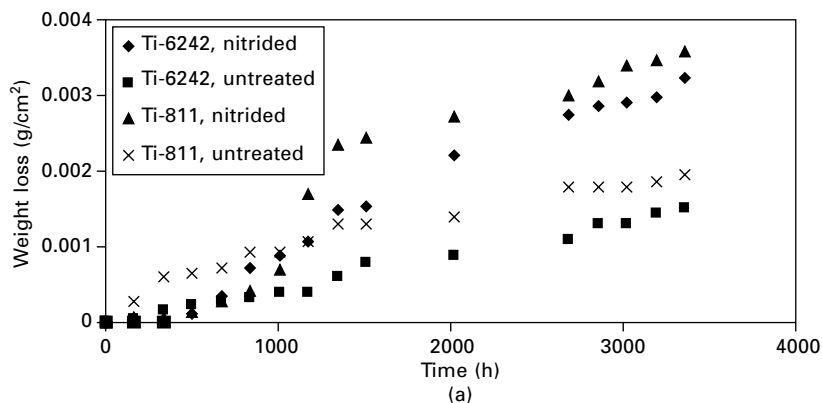
The corrosive medium is an important parameter determining the corrosion behaviour of the materials. The corrosion behaviour of nitrided Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V in three different corrosive media at three different temperatures is compared.

At room temperature, the Ti-6Al-2Sn-4Zr-2Mo alloy nitrided at 950 °C for 5 hours has better corrosion resistance in sulfuric acid solution than in hydrochloric acid solution. At 40 °C, the alloy shows a very good corrosion resistance in 0.5M NaCl. The corrosion resistance worsens in 1.8M H₂SO₄ and the weight loss dramatically increases in 4.9M HCl. A similar tendency exists at the higher solution temperature of 80 °C.

The Ti-8Al-1Mo-1V alloy nitrided at 950 °C for 5 hours is very resistant to 0.5M NaCl at 40 and 80 °C. The overall corrosion response is different from the nitrided Ti-6Al-2Sn-4Zr-2Mo alloy.

17.4.4 Influence of the media temperature

In 0.5M NaCl solution, as mentioned earlier, the weight loss values of Ti-6Al-2Sn-4Zr-2Mo after nitriding at 950 °C for 5 hours are very small. In 4.9M HCl solution, the weight loss values are quite similar at 20 and 40 °C, and they increase with the increase of the temperature to 80 °C. The same



17.26 Weight loss versus time of Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V, untreated and nitrided (950 °C for 5 hours), after holding them in 1.8M H₂SO₄ at (a) room temperature, (b) 40 and (c) 80 °C.

tendency exists in 1.8M H_2SO_4 solution. The sudden jumps in the weight loss values in both reducing acid solutions at 80 °C are probably due to the breaking of the surface oxide and nitride layer.

As described by Galvanetto *et al.* (2002), the failure of the compound layer is probably due to local dissolution of the layer, which leads to penetration by the solution and then the fast corrosion of the inner titanium matrix, eventually causing cracking and removal of the fragile compound layer.

There is a difference between the surface morphology of the untreated and nitrided Ti-6Al-2Sn-4Zr-2Mo before and after the corrosion test, probably due to an increase of surface roughness caused by the aggressive attack of the corrosive medium.

Nitrided Ti-8Al-1Mo-1V has a similar tendency to the one for Ti-6Al-2Sn-4Zr-2Mo. Ti-8Al-1Mo-1V has better corrosion resistance in all cases.

For untreated and nitrided Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V alloys, the corrosion rate increases with the increase of the temperature. For Ti-6Al-2Sn-4Zr-2Mo, the corrosion rate in 0.5M NaCl is up to 0.002 mm/yr and for Ti-8Al-1Mo-1V is up to 0.006 mm/yr. In 4.9M HCl, for Ti-6Al-2Sn-4Zr-2Mo, the corrosion rate varies from 0.013 to 0.26 mm/yr, and for Ti-8Al-1Mo-1V, it varies from 0.015 to 0.067 mm/yr. In 1.8M H_2SO_4 , for Ti-6Al-2Sn-4Zr-2Mo, it varies from 0.007 to 0.13 mm/yr, and for Ti-8Al-1Mo-1V, it varies from 0.017 to 0.13 mm/yr.

For most of the cases, the corrosion rate is below 0.13 mm/yr, which is the maximum corrosion rate accepted by designers. The only exception is nitrided Ti-6Al-2Sn-4Zr-2Mo in 4.9M HCl at 80 °C, for which the corrosion rate is 0.26 mm/yr. The cases for which we have a corrosion rate below 0.04% can be considered as fully passive conditions.

17.4.5 Summary of the corrosion resistance of titanium alloys after gas nitriding

The correlation between the corrosion behaviour of titanium alloys and nitriding processing parameters, the corrosive conditions and alloy composition is important for many industrial applications.

The corrosion weight loss tests show that surface gas nitriding does not change significantly the corrosion resistance properties of titanium alloys. These properties depend on the corrosive environment and conditions. Titanium alloys show excellent corrosion resistance in salt solutions. In aggressive reducing acid solutions, gas nitriding either worsens or improves the corrosion resistance, depending on the alloy composition, corrosive environment and the corrosive solution temperature.

Ti-8Al-1Mo-1V has better corrosion resistance in comparison with Ti-6Al-2Sn-4Zr-2Mo in most of the cases. The weight loss values increase in most cases with increase of the solution temperatures from 20 to 80 °C and

time prolongation. The corrosion rate of Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V is below 0.13 mm/yr, with the only exception of nitrided Ti-6Al-2Sn-4Zr-2Mo in 4.9M HCl at 80 °C (0.26 mm/yr).

17.5 References

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Nitriding: modelling of hardness profiles and the kinetics

Abstract: The first half of the chapter shows the reader how results from microhardness testing can be used to develop artificial neural network models for the simulation and prediction of microhardness profiles after nitriding in relation to the type of nitriding, temperature, length of time of nitriding, gas mixtures and alloy composition. The second half switches to physical modelling of the evolution of surface layers during gas nitriding. These models are based on analytical and numerical solutions of the diffusion equation and calculate the nitrogen distribution, the thickness of the nitrided layers and the incubation time for the formation of layers on the surface.

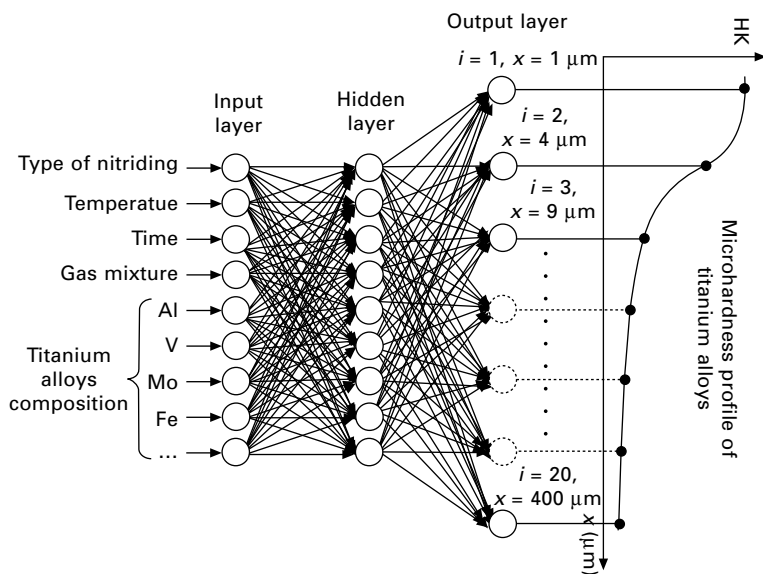
Key words: neural network, microhardness, diffusion, kinetics, numerical simulations.

18.1 Artificial neural network modelling of microhardness profiles

Gas and plasma nitriding are among the most widely used thermo-chemical treatments for improving the surface properties of titanium alloys. There have been many studies on these types of treatments, especially of titanium alloys (Galliano *et al.*, 2001; Shashkov, 2001). They are diffusion methods that can easily increase the hardness of these alloys. Understanding the correlation between the processing parameters of nitriding and the hardness of the materials is important, because this would allow an optimisation of the processing parameters and alloy selection in order to achieve properties desired for various applications. Artificial neural network (ANN, Chapters 13–15) (Keong *et al.*, 2004; Li and Xiong, 2002; Li *et al.*, 2002a,b; Öhl *et al.*, 2003) models can be developed and used to help achieve this purpose.

This section will describe artificial neural network modelling for simulation and prediction of microhardness profiles of titanium and titanium alloys after gas and plasma nitriding. The basic principles of this modelling technique are described in Chapter 13. Apart from modelling, ANNs can be applied for classification, transformation, association and process control (Chapters 13 and 15) (Malinova *et al.*, 2001).

There are two different types of neural networks – hierarchical networks and auto associators. The choice of the type of neural network depends on the nature of the problem to be solved. In this section, feed-forward hierarchical networks are used. The model is shown schematically in Fig. 18.1.



18.1 A schematic model of ANN for simulation and prediction of microhardness profiles of titanium alloys after gas and plasma nitriding.

18.1.1 Model description

Input parameters

The training of an ANN requires a large number of input/output pairs. This leads to more precise work but also an increase of the training time. The most important parameters of gas and plasma nitriding used to obtain desirable surface properties are temperature of the process, time for saturation and gas atmosphere.

As input parameters for the model, type of nitriding, temperature and time of nitriding, gas mixtures and the chemistry of the titanium alloys presented by the following most commonly used alloying elements and impurities: Al, V, C, Fe, N, O, Sn, H, Ni, Mo, Si, Zr, Cr, B are used. For the design of the ANN, input/output pairs from the published literature, including data by Galliano *et al.* (2001) and Shashkov (2001), as well as the experimental data in Chapter 17 on gas nitriding, are collected, pre-processed and used.

For the input parameter 'type of nitriding', the following notations are adapted:

- plasma nitriding '1'
- gas nitriding '2'.

For the input parameter 'gas mixture', the following notations are adapted:

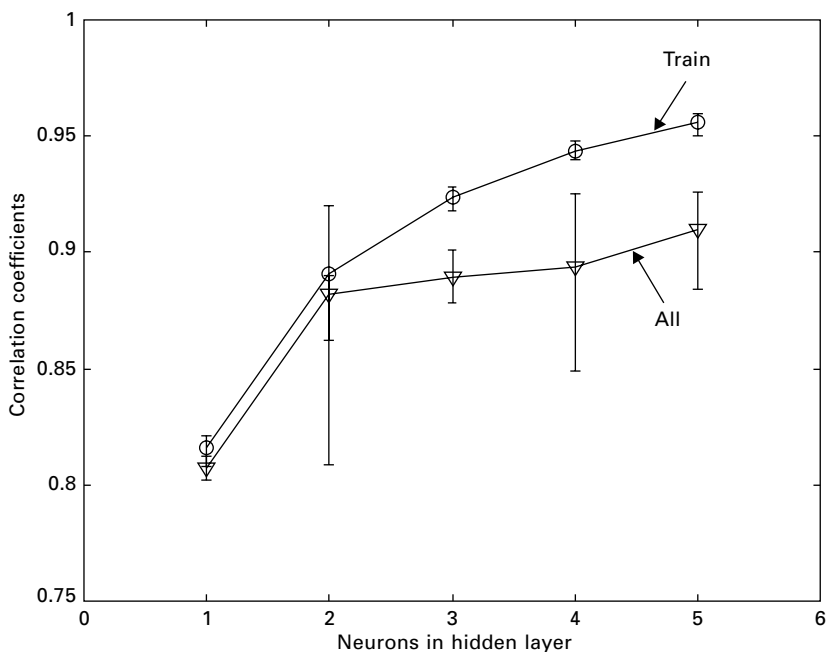
- pure N₂ ‘1’
- 80%N₂-20%H₂ ‘2’
- 77%N₂-22%H₂-1%C ‘3’
- 70%N₂-24%H₂-6%C ‘4’
- NH₃ ‘5’
- 95%N₂-5%H₂ ‘6’
- 80%N₂-20%Ar ‘7’.

The output parameter, which in this case is a graph, also has to be converted to a numerical format. Following this aim, all graphics are scanned, put in electronic format and rescaled to the same scale. All the values are transformed to Knoop hardness using the conversion tables. After these procedures, each microhardness profile is described by a set of numbers giving the hardness values at distance x from the surface (where $x = i^2$ and $i = 1, 2, 3, 4, \dots, 20$). In this way, the output, given schematically in Fig. 18.1 as a graph, is actually presented by a set of 20 output neurons. All the data that are not consistent are excluded from the dataset, such as methods of nitriding with processing parameters not covered above or experimental cases not fitting well to the general database.

Training

Descriptions of the ANN transfer functions, Levenberg–Marquardt training method and Bayesian regularisation are given in Chapter 13. In order to determine the optimal architecture, several steps are required. The alloying elements that are present in a small number of cases are ignored, as well as the impurities. Only seven alloying elements remain as input parameters and they are Al, V, Fe, Sn, Mo, Zr and Cr. Training with the dataset of 112 data was performed. The influence of the number of neurons in the hidden layer on the NN response, shown by the correlation coefficient (R) for the training and the whole datasets, is given in Fig. 18.2. For each case, the values for the R coefficient are the average from five separate training runs under the same conditions and using a different random distribution of the dataset. When the number of neurons in the hidden layer is increased from one to three, the R coefficient for both training and whole datasets increases. A further increase of the neurons to five makes a further slight improvement of the NN, although the correlation coefficients remain stable and do not change dramatically.

The best NN architecture is when there are five neurons in the hidden layer. For this case, 50 runs with different database distributions were performed, and the best case for the NN architecture and data distribution was found. The performance for this case is demonstrated in Fig. 18.3. The figures show a linear regression analysis between the network outputs (predictions) and the corresponding targets (experimental data) for the different datasets. The correlation coefficient R values for all cases of training, test and whole

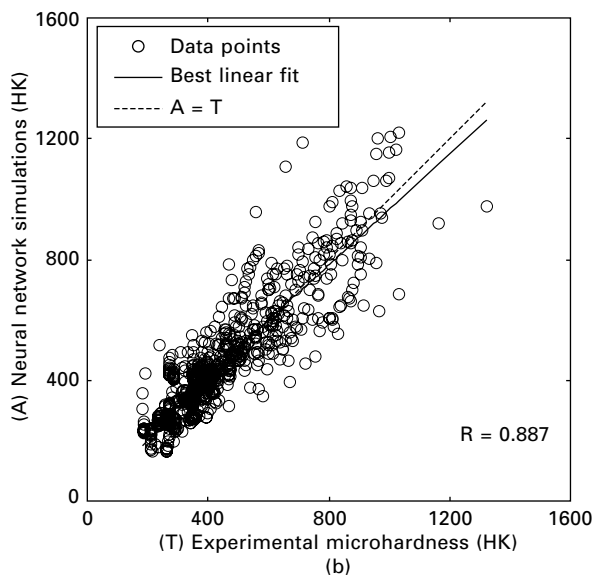
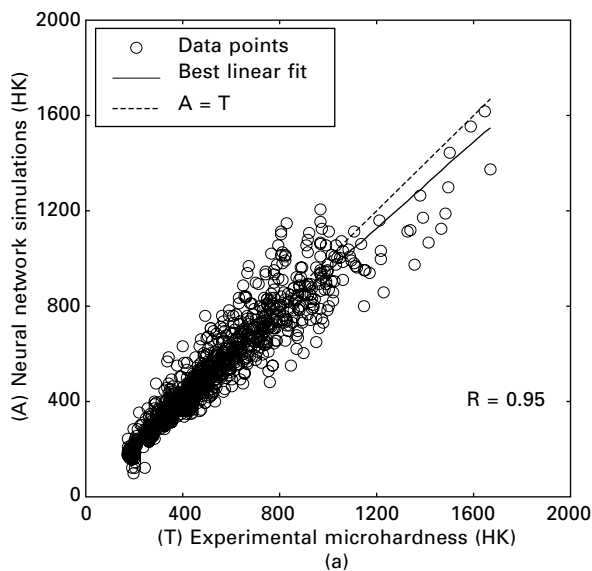


18.2 Influence of the number of neurons in the hidden layer on the neural network performance.

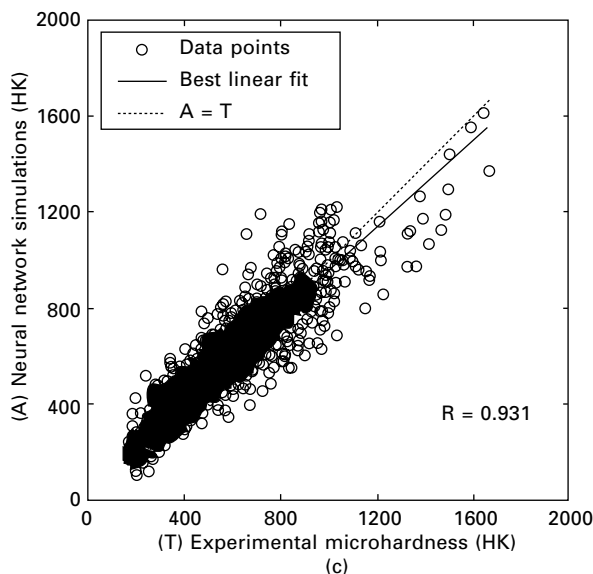
datasets are above 0.88. This means that a good performance of the neural network is achieved and the network can be used for further simulations and predictions. The optimum performance of this model has eleven neurons in the input layer, five neurons in the hidden layer and twenty neurons in the output layer.

The data for plasma nitriding and the data for nitriding in nitrogen atmospheres different from pure N_2 are quite limited. Will including these data as inputs in the model make it possible for it to predict efficiently microhardness profiles for new situations for plasma nitriding and nitriding using different gas mixtures? A second model, excluding all the data for plasma nitriding and all the data using gas mixtures different from pure N_2 , is created in order to see the influence of these two parameters on the performance of the NNs. This leads to a decrease of the input parameters from 11 to 9. The whole dataset is for gas nitriding performed in a pure nitrogen atmosphere. The training is performed with 9 inputs, 20 outputs and 84 data pairs, with 56 in the training dataset and 28 data for test. The number of neurons in the hidden layer varies from 1 to 5. Then, the best correlation coefficients for Bayesian regularisation are selected and these are for 5 neurons. 50 runs were again performed for this case with different database distributions, and the best case for the new NN architecture and data distribution is given in Fig. 18.4. The correlation coefficient R values for all cases of training, test

and whole datasets are above 0.91 which means a good performance of the neural network, slightly better compared with the first model. The optimum performance of this second model has nine neurons in the input layer, five neurons in the hidden layer and twenty neurons in the output layer.



18.3 Microhardness values predicted from the first neural network model versus experimental microhardness for (a) the training, (b) test and (c) the whole dataset.



18.3 Continued

At the end of the NN training, there are two trained models that can be used for simulation of microhardness profiles of nitrided titanium alloys. The first model can predict microhardness profiles after gas and plasma nitriding using different gas mixture. The second model can predict microhardness profiles after gas nitriding only in a pure nitrogen atmosphere. These models are compared in the following sections.

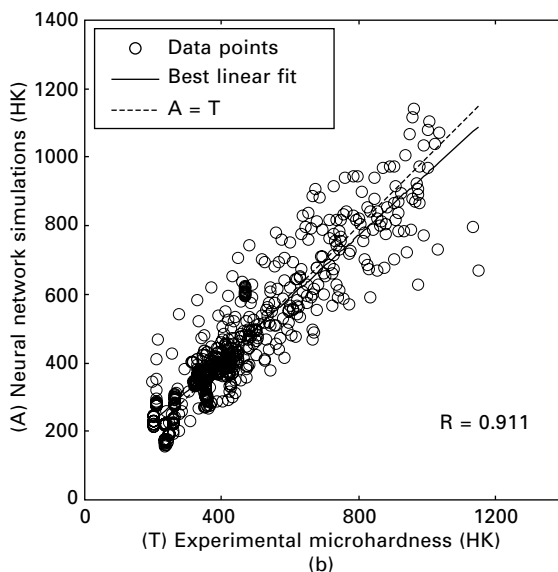
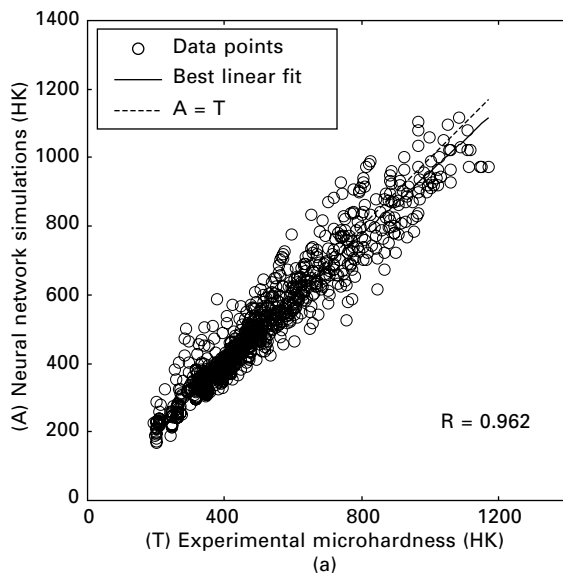
Performance and test

The neural networks performance is checked after the training, using the test dataset and the whole set of the two models. The linear regression presented in Figs. 18.3b,c and 18.4b,c is a kind of neural network test. Furthermore, the experimental microhardness profiles and those predicted from the trained neural networks are compared in Fig. 18.5, where there is no significant difference between the predictions from the two models. A good agreement between the experimental microhardness profiles and prediction from the NNs is shown.

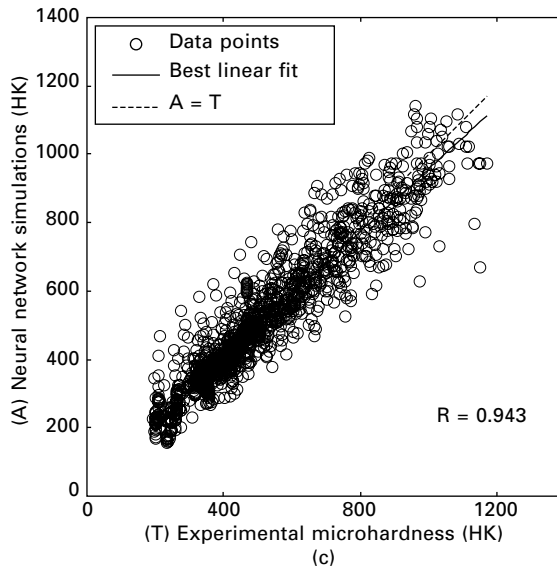
18.1.2 Use of the neural networks for simulations and predictions

NN modelling gives the correlations between the model inputs (which in this case are the processing parameters and the alloy compositions) and the model

outputs (which in this case are the microhardness profiles), but it does not model directly and does not involve and explain the metallurgical changes and formations in the surface layers during nitriding causing the increase in microhardness.



18.4 Microhardness values predicted from the second neural network model versus experimental microhardness for (a) the training, (b) test and (c) the whole dataset.

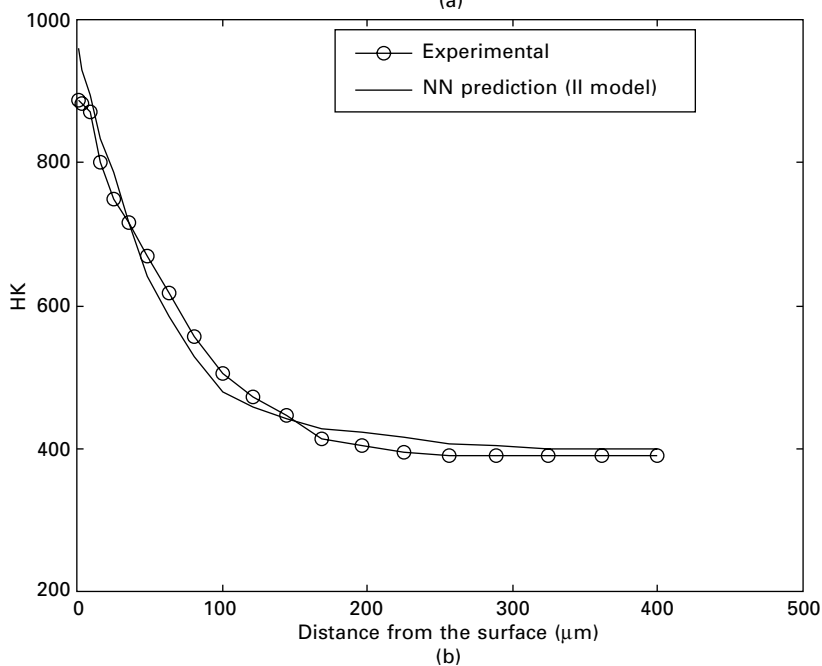
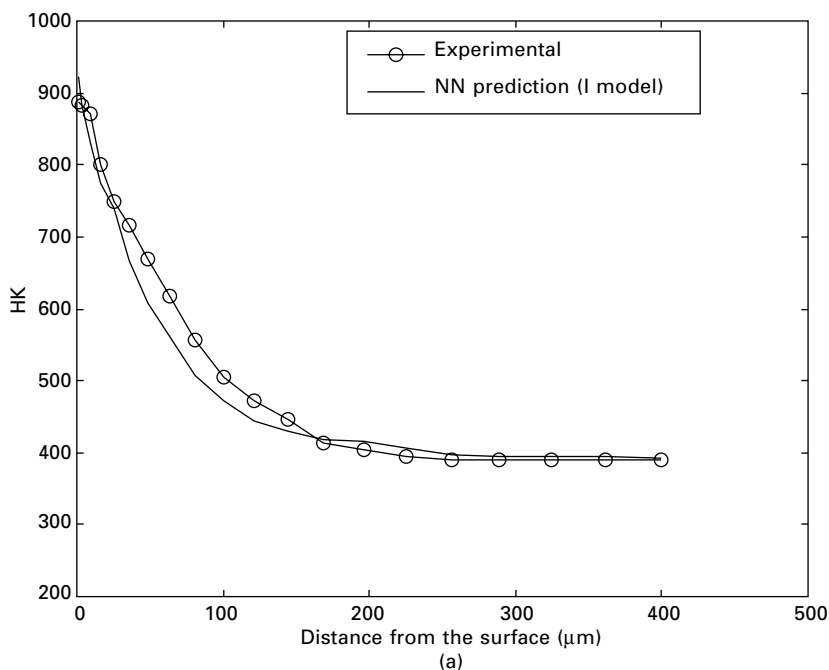


18.4 Continued

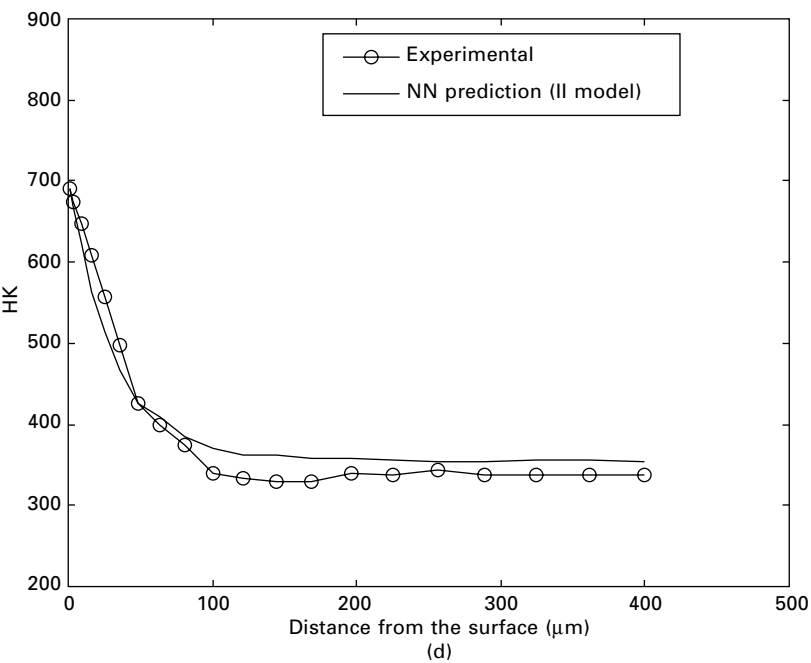
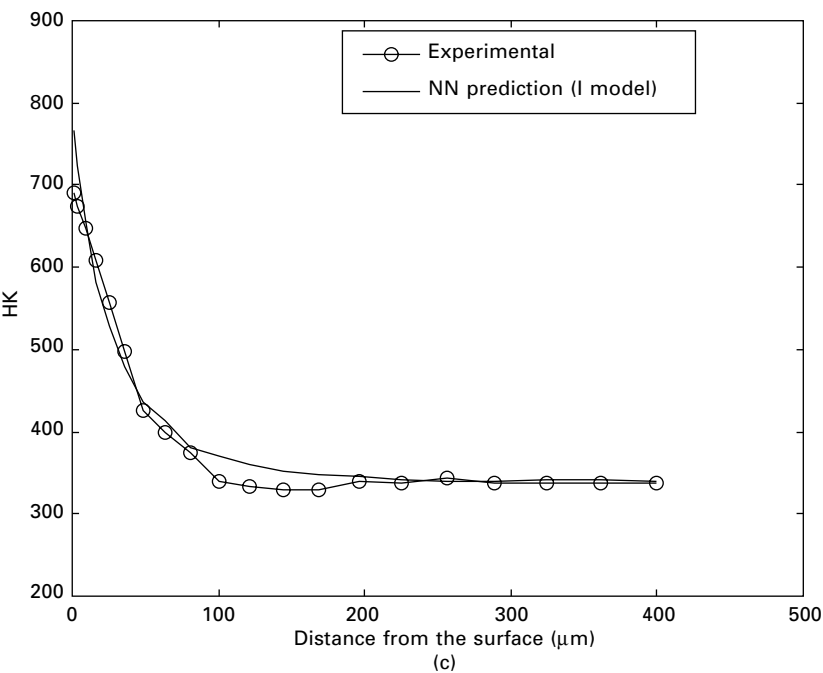
The two models can be used to predict microhardness profiles of titanium alloys with sufficient accuracy after gas or plasma nitriding at temperatures between 700 and 1100 °C for periods of time in the range of 1–100 hours. Data within these ranges are used to train the models. Some microhardness profiles after gas and plasma nitriding under different conditions are predicted by the two models in this section. The influence of the basic processing parameters and the alloy compositions is discussed and analysed.

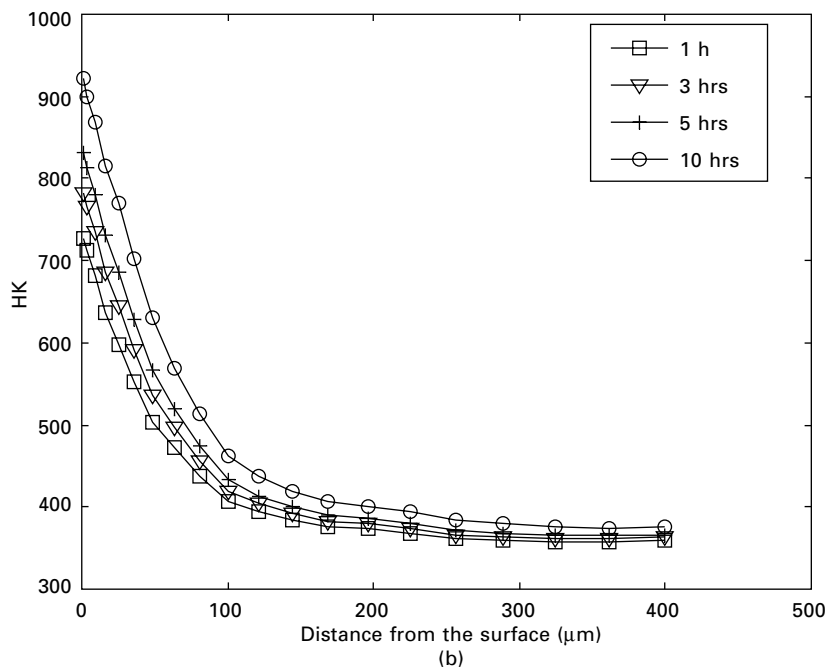
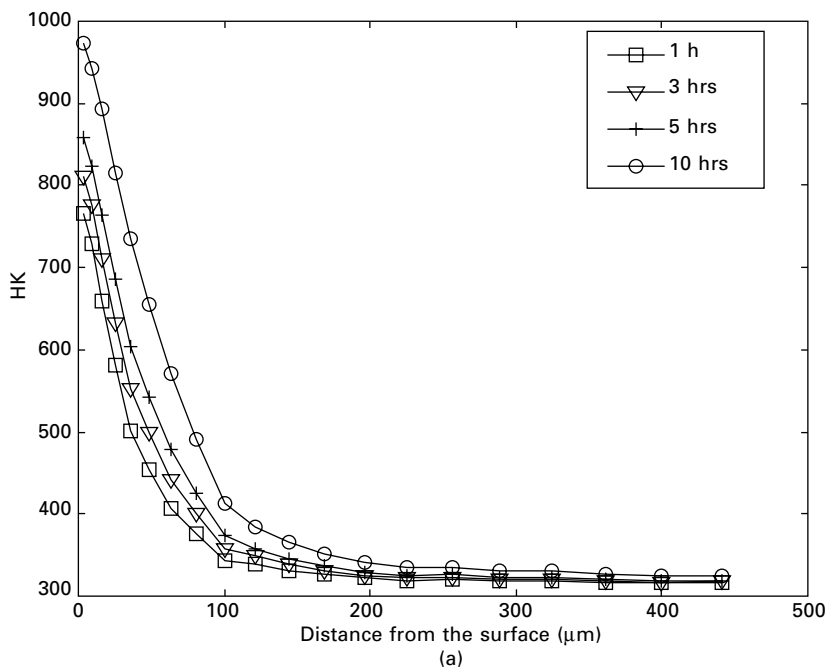
The time of nitriding is an important processing parameter so its effect is shown in Fig. 18.6. The outcome from the models is quite similar. With the increase of the time, there is an increase of the microhardness near the surface and at the same time an increase of the thickness of the nitrided layer. These predictions of the NNs are in agreement with what is expected from the fundamental diffusion theory. The formation of the nitrided layers is a diffusion process in which the nitrogen diffuses into the substrate. Hence, there is a deeper penetration of nitrogen as well as a higher concentration of nitrogen in the nitrided layer after a longer saturation time. This leads to an effective production of thicker nitrided layers with higher values of microhardness.

The effect of the temperature on the microhardness and the depth of the nitrided layers can also be revealed from the trained NNs. Some predictions of microhardness profiles are shown in Fig. 18.7. The higher temperature of nitriding causes, in general, an increase in the thickness of the nitrided layer and an increase in the microhardness of the surface compound layer that is

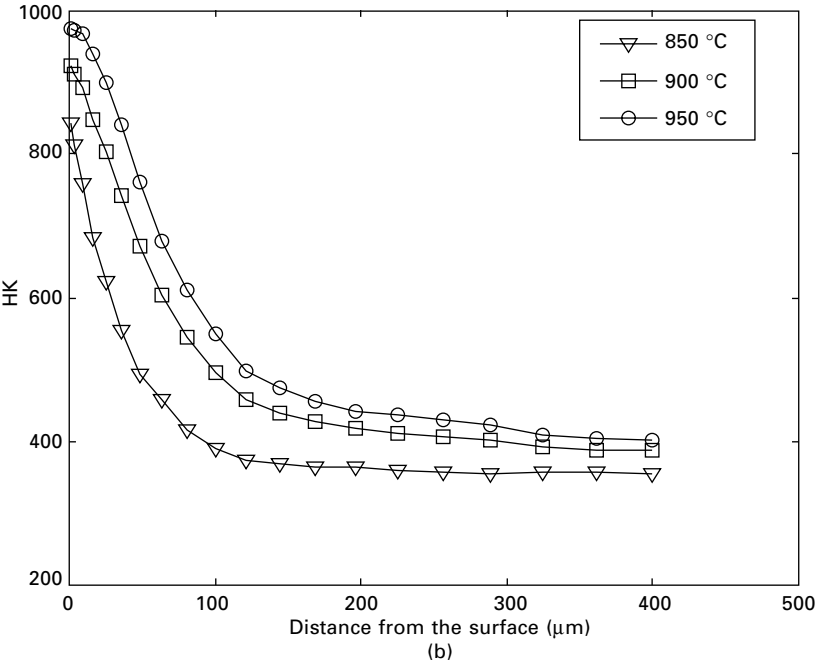
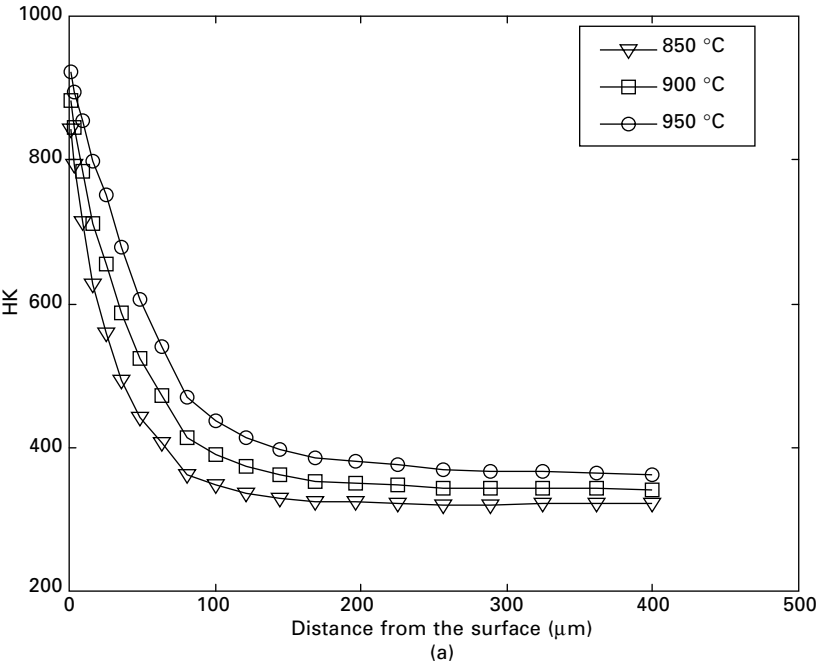


18.5 Comparison between experimental microhardness profiles and those predicted from the neural network models for: (a) and (b) Ti-15Mo-5Zr-3Al, gas nitrided in pure N₂ at 750 °C for 60 hours and (c) and (d) Ti-8Al-1Mo-1V gas nitrided in pure N₂ at 850 °C for 5 hours. The predictions in (a) and (c) are made by the first model and in (b) and (d) by the second model.





18.6 Neural network predictions of microhardness profiles for Ti-6Al-2Sn-4Zr-2Mo, gas nitrided at 900 °C for different periods of time. Predictions with (a) the first and (b) the second model.

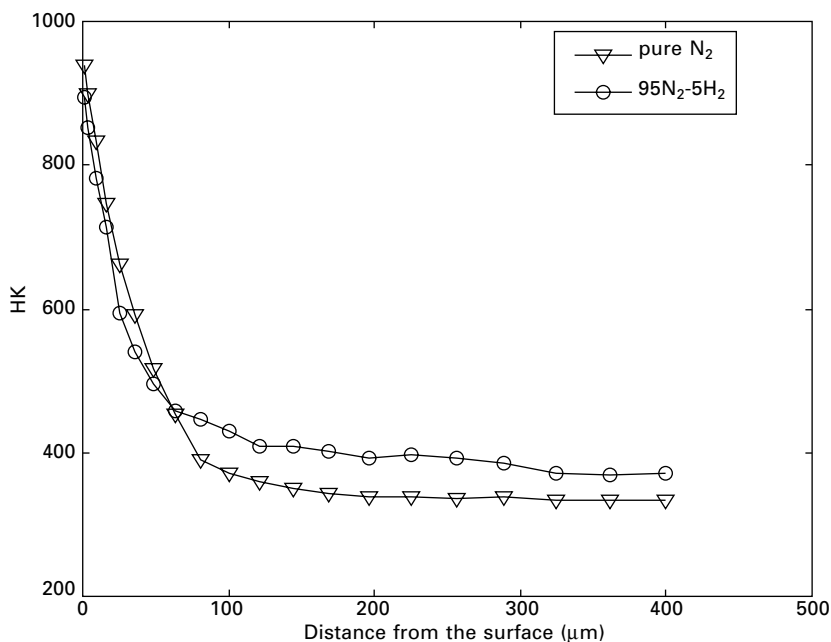


18.7 Neural network predictions of microhardness profiles of Ti-8Al-1Mo-1V, gas nitrided for 10 hours at different temperatures. Predictions with (a) the first and (b) the second model.

in agreement with the results predicted from the NN models. The influence of the nitriding temperature has been studied in Chapters 16 and 17 and by Galliano *et al.* (2001). The effect of the layer thickness increases with the increase of temperature due to the higher diffusion coefficient at higher temperatures of nitriding. Figures 18.6 and 18.7 also show that the inclusion of plasma nitriding and gas mixture as inputs (Model 1), although limited data are available for these, does not worsen the predictions for the influence of the temperature and the time of nitriding using the model (Model 1) where these are not used for inputs.

The gas mixture is another processing parameter in nitriding for determining the characteristics of the nitrided layers. The experimental data for the influence of the gas mixtures on the surface properties during plasma and gas nitriding of titanium alloys in the literature are quite limited, so the results from the NNs such as those shown in Fig. 18.8, need to be proved with further experimental work.

Another significant process parameter is the alloy composition. The optimisation of the alloy composition in order to achieve the desirable microhardness profiles after nitriding is another possibility for using the model. The effect of the most commonly used alloying elements for titanium



18.8 Neural network predictions of microhardness profiles of Ti-6Al-2Sn-4Zr-2Mo, plasma nitrided at 850 °C for 8 hours using pure N₂ and a gas mixture of 95N₂-5H₂.

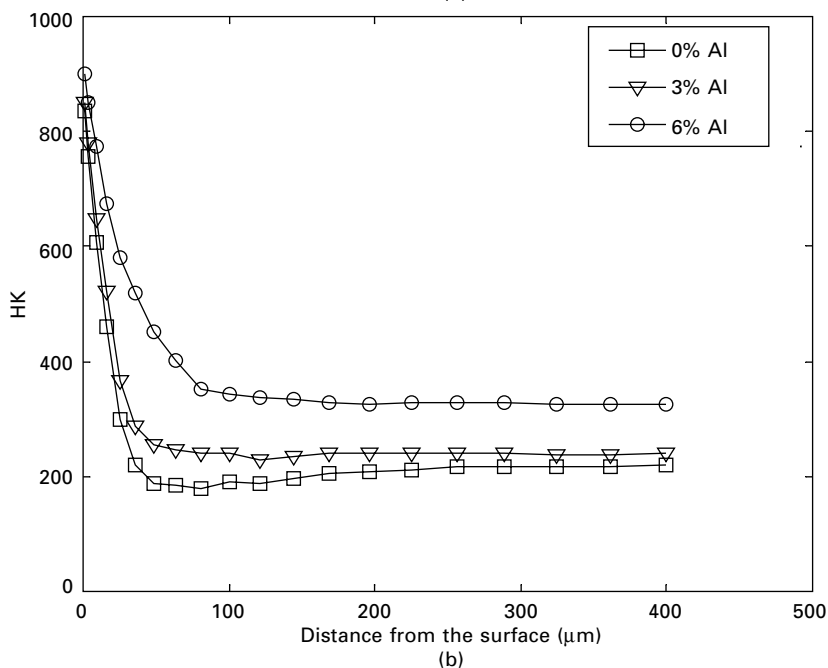
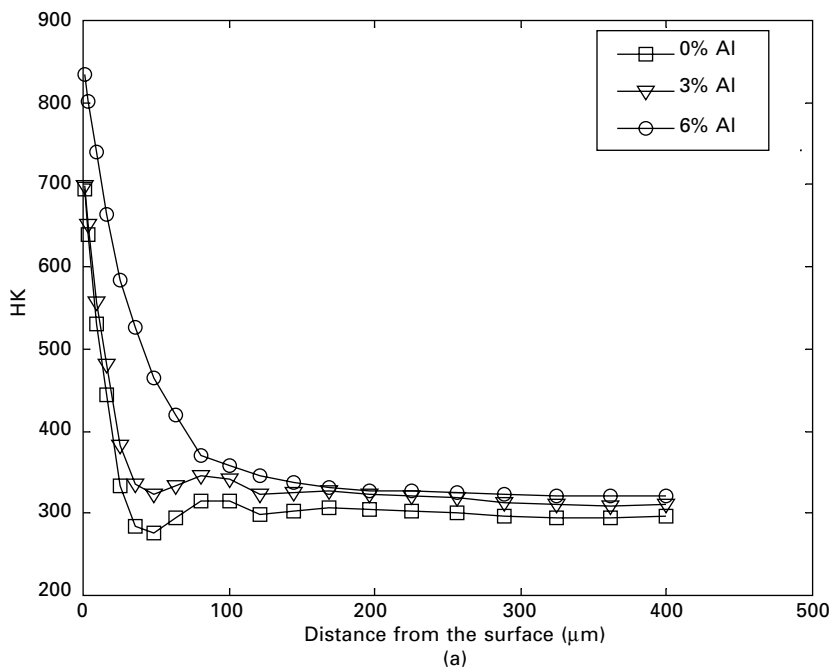
alloys can be studied, but there is not enough information in the literature in this direction. Nevertheless, an example can be given for the influence of the alloying elements on the microhardness profiles as their concentration is varied. Aluminium is probably the most widely used alloying element in titanium alloys and it exists in the vast majority of the cases in the dataset. Using the first model, microhardness profiles are obtained after gas and plasma nitriding changing the aluminium concentration (Fig. 18.9). There is increase of the microhardness with the increase of the element concentration after gas nitriding. The tendency for plasma nitriding is similar. Next, we check the influence of a less common (compared to aluminium) alloying element such as molybdenum on the microhardness profiles.

There are only four molybdenum-containing alloys in the entire dataset and all the cases are for gas nitriding in pure N_2 . Therefore, the results for plasma nitriding of these alloys might not be accurate but anyhow we plot microhardness profiles predicted from the first model for gas and plasma nitriding to compare them (Fig. 18.10). From the cases containing molybdenum (all for gas nitriding in pure N_2), the model has learned to predict that the increase of molybdenum would result in an increase of hardness and thickness of the nitrided layer after gas nitriding (Fig. 18.10a). The same tendency has been directly transferred to the process of plasma nitriding (Fig. 18.10b), although such data do not exist in the dataset. Although reasonable, this tendency needs further experimental verification.

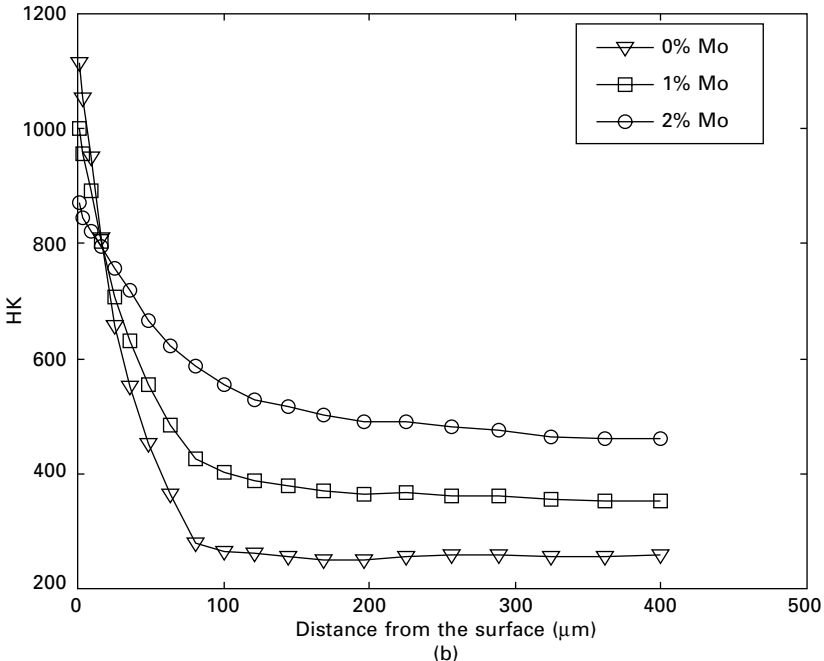
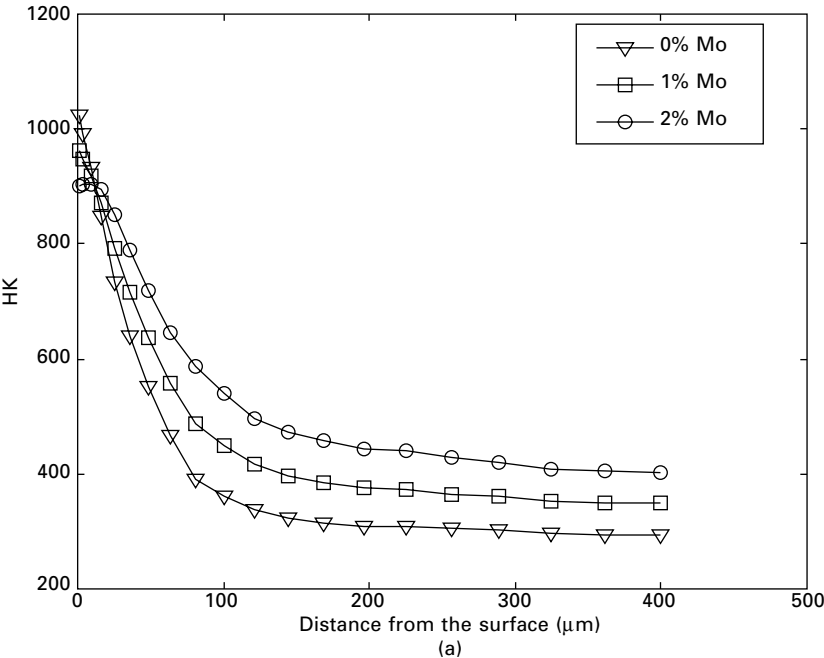
18.1.3 Summary

The correlation between the processing parameters of nitriding and the hardness of titanium alloys is important. Neural network modelling is a very powerful and useful modelling technique for modelling of the materials properties and characteristics. Two neural network models for the simulation and prediction of microhardness profiles of titanium alloys after gas and plasma nitriding are developed and described in this section. After training the models, they show a very good performance, using type, or method, of nitriding, temperature and time of nitriding, gas atmosphere mixtures and alloy chemical composition as input parameters for the first model. The second one has a smaller scale, using temperature and time of nitriding and alloy composition as input parameters. The NN models, created using experimental data in Chapter 17 as well as those collected from the published literature, can simulate and predict microhardness profiles after gas and plasma nitriding. Using MatLab, a microhardness profile can be easily obtained for any combination of input parameters.

The neural network models are used for the prediction of microhardness profiles for some real cases of gas and plasma nitrided titanium alloys, which are in good agreement with the experimental results. The models can be used



18.9 Neural network predictions of microhardness profiles for titanium alloy with composition Sn = 1.93 wt.%, Zr = 3.97 wt.%, Mo = 1.95wt.%, Fe = 0.07 wt.%, Si = 0.11 wt.% and different Al contents after (a) gas nitriding and (b) plasma nitriding at 900 °C for 4 hours.



18.10 Neural network predictions of microhardness profiles for titanium alloy with composition Al = 6.13 wt.%, Sn = 1.93 wt.%, Zr = 3.97 wt.%, Fe = 0.07 wt.%, Si = 0.11 wt.% and different Mo contents after (a) gas nitriding and (b) plasma nitriding at 950 °C for 5 hours.

for the prediction of microhardness profiles with high accuracy within the range of the data used for the models.

The influence of the nitriding processing parameters on the microhardness profiles, calculated using both models, is explained from a metallurgical point of view, showing good agreement with the fundamental diffusion theory and the data from the literature.

The results obtained with the models are quite similar so it can be assumed that they both may be used for simulations of microhardness profiles with sufficient accuracy. The first model can potentially be used effectively for optimisation of the processes of gas and plasma nitriding and it can predict microhardness profiles of titanium alloys, nitrided at temperatures between 700 and 1100 °C for periods of time in the range of 1–100 hours. The second model can be used for the same purpose but only for gas nitriding in the same temperature and time ranges.

These models can be used by titanium users, saving them both experimental time and cost. Similar models can be created for the simulation and prediction of different materials' properties and characteristics.

18.2 Kinetics of gas nitriding

In this section, the objective is to model the kinetics of formation and growth of nitrided layers in commercial titanium alloys under different thermodynamic conditions. The modelling can help in optimisation of the processing parameters in order to achieve a desirable combination of microstructure and properties. The gas nitriding of titanium and titanium alloys is a diffusion process. Hence, the kinetics of formation and growth of the surface nitrided layer can be modelled by appropriate application of the fundamental diffusion theory. For this purpose, analytical and numerical solutions are introduced, based on the physical model discussed below.

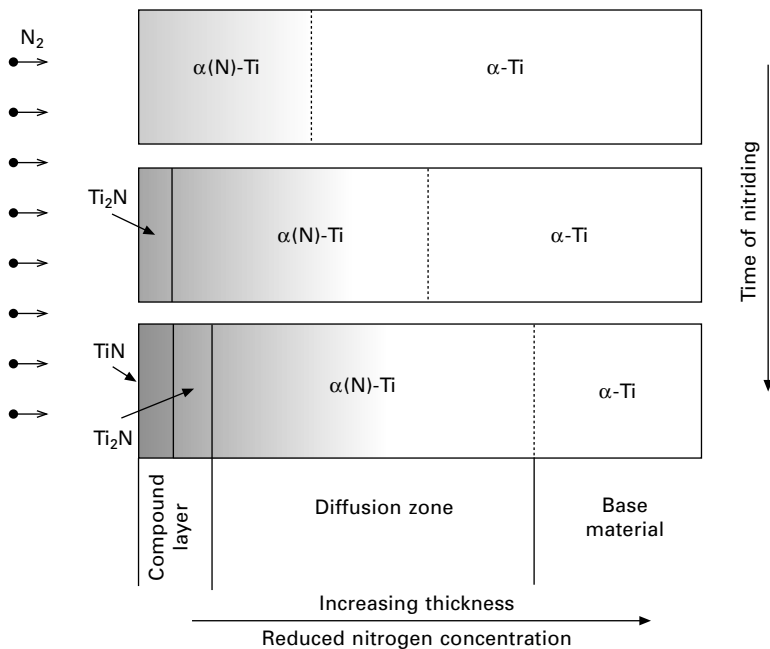
18.2.1 Phase transformations during the process of nitriding

The formation of nitrided layers in titanium alloys is a complicated process and involves several reactions taking place simultaneously at the boundary between the gas atmosphere and the metal and within the substrate. The kinetics of the diffusion process of nitriding have been studied in the past. A simplified physical model for the formation and growth of nitrided layers during gas nitriding in titanium is suggested and described by Malinov *et al.* (2003). The model is based on reaction diffusion rules and is applicable for nitriding temperatures below the β -transus. If the titanium material is in an active nitrogen containing environment at high temperature, a nitrogen mass transfer from the medium to the solid occurs. The nitrogen absorbed at the

surface diffuses into the titanium, forming an interstitial solution of nitrogen in the hcp α titanium phase (Fig. 18.11 top). The surface layer formed is called the diffusion zone, $\alpha(N)$. This process can continue as long as the α titanium matrix can dissolve nitrogen at the nitrogen medium–solid interface, where the nitrogen concentration is the highest. If the concentration of nitrogen at the interface becomes higher than the α phase is able to retain in interstitial solution, a reaction at the interface occurs leading to the formation of a new phase – Ti_2N (Fig. 18.11 middle). There is a concentration jump of nitrogen at the surface and, as a result, the total nitrified layer consists of a compound layer (Ti_2N) on the top and a diffusion zone underneath. Following the same rules, when the concentration of nitrogen at the interface becomes higher than the one acceptable in Ti_2N , there is a phase transformation at the surface and the Ti_2N transforms to TiN (Fig. 18.11 bottom). The sub-layer with titanium nitrides only (TiN and Ti_2N) forms the compound layer, while $\alpha(N)$ is the diffusion zone.

For real cases of nitriding of titanium alloys, the alloying elements present can cause different deviations and modifications. The presence of alloying elements in the general case might result in:

- simultaneous formation of two or more titanium nitrides;



18.11 A schematic presentation of the kinetics of formation and growth of surface layers during gas nitriding of titanium.

- formation of complex stable or metastable nitrides of the alloying elements;
- change of the composition ranges of existence of the different phases.

Despite these possible influences, the alloying additions in the classical titanium alloys are small in quantity and usually are dissolved in the hcp α -titanium matrix by forming a substitutional solid solution. Hence, dramatic changes to the kinetics of formation and the phase compositions of nitrided layers in titanium alloys are not very likely. This has been confirmed by experimental studies of the microstructure and the phase compositions of nitrided layers in different titanium alloys (Lakshmi *et al.*, 2002).

18.2.2 Physical model

In most of the cases, the main phases observed on the surface after nitriding of different titanium alloys at different thermodynamic conditions are TiN and Ti₂N (Chapter 16) (Shashkov, 2001; Song *et al.*, 2002; Spies *et al.*, 2001). Hence, the model suggested in Section 18.2.1 can be adopted with sufficient accuracy to model the formation of nitrided layers in titanium alloys. The development of the mathematical model based on this physical model for solving the diffusion equation in appropriate conditions will allow quantitative simulations of the kinetics of nitride layer formation under various processing conditions. The mathematical models are discussed in the following sections.

It should be admitted that the presence of TiO₂ is not taken into account in the models. The oxygen may have significant influence on the kinetics of formation and growth of nitrided layers and should be a subject for further studies. At present, it is difficult to model simultaneous formation of titanium nitrides and titanium oxides. The models will work with better accuracy when there is no formation of oxides or the oxygen is a very small amount.

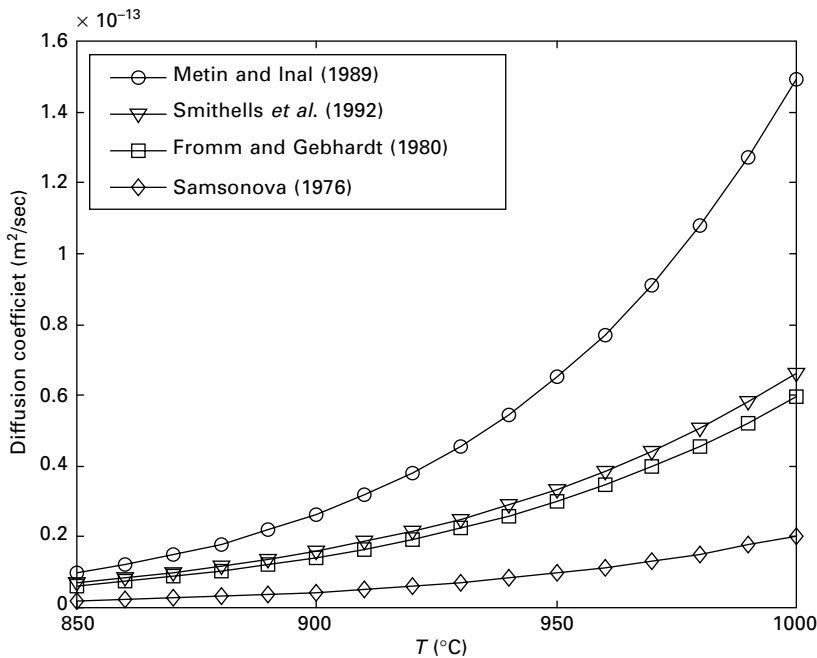
18.2.3 Diffusion coefficients

Precise data on the diffusion coefficients are necessary for accurate mathematical modelling of any diffusion process. A literature survey on the diffusion coefficients of nitrogen in α titanium, however, reveals some discrepancies between diffusion coefficients given by different authors. Various values of A and Q have been given, based on the general form of the equation, Eq. [16.1].

Samsonova (1976) gave parameters for the diffusion coefficient for nitrogen in α -Ti in the temperature range 900–1400 °C as follows: $A = 1.2 \times 10^{-6}$ m²/sec and $Q = 189.45$ kJ/mole. Similar values were given by Fromm and Gebhardt (1980) ($A = 1.2 \times 10^{-6}$ m²/sec and $Q = 178$ kJ/mole) for the same temperature interval and by Smithells *et al.* (1992) ($A = 1.2 \times 10^{-6}$ m²/sec

and $Q = 176.9$ kJ/mole) for the temperature range 900–1570 °C. Different data for the diffusion parameters were suggested by Metin and Inal (1989), $A = 9.6 \times 10^{-5}$ m²/sec and $Q = 214.7$ kJ/mole. The diffusivity of nitrogen in α -Ti is calculated using Eq. [16.1] and the parameters reported in various sources (Fig. 18.12).

The calculations are carried out for a temperature range of 850–1000 °C, the usual temperature interval for nitriding of titanium alloys. Some of the results are in agreement, but there are also significant differences between the diffusion coefficients suggested by the various authors. For further comparison, the diffusivity of nitrogen in α -Ti is calculated for a temperature of 950 °C using the data from various authors and the results are compared



18.12 Diffusion coefficients of nitrogen in α -Ti according to various authors.

Table 18.1 Diffusion coefficients of nitrogen in α -Ti at 950 °C according to different authors

Source	D , m ² /s ($\times 10^{-14}$)
Samsonova (1976)	0.973
Fromm and Gebhardt (1980)	2.999
Smithells <i>et al.</i> (1992)	3.341
Metin and Inal (1989)	6.496

in Table 18.1.

There is up to six times difference between calculated diffusion coefficients based on different sources. The modelling results will be different depending on which one of the diffusion coefficients is used in the calculations. In the models here, experimental data are compared with modelling results using different diffusion coefficients.

18.2.4 Analytical solutions

Mathematical modelling of the diffusion processes in materials is carried out by solving the fundamental differential equation of diffusion for the appropriate initial and boundary conditions. If the diffusion is one-dimensional, i.e. there is a gradient of concentration only along one axis (the case in nitriding of titanium) and if the diffusion coefficient is constant, the general diffusion equation can be simplified to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad [18.1]$$

where C is the concentration of the diffusing element (nitrogen), t is time and x is the space coordinate.

Both analytical and numerical approaches are used, depending on the nature of the problem. Analytical solutions are simpler but are applicable only for ideal initial and boundary conditions. In spite of this, they can be applied to model different phenomena in materials science. One significant disadvantage is that analytical solutions are difficult to find for moving boundary problems, and where there is a point of interruption. Here, analytical solutions are used for the first and approximate calculation of the nitrogen gradient in the diffusion zone and the layer thickness under different thermodynamic conditions. In order to apply a simple analytical solution, it is assumed that there is no compound layer formed. This assumption is quite reasonable for approximate calculations, and has experimental justification. Experimental results with nitrided layers in titanium show that the thickness of the compound layer is within a range of 1–20 μm , while the diffusion zone is in the range of hundreds of micrometers, depending on the temperature and time of nitriding. Thus, the diffusion zone contributes to more than 95% of the entire layer. Hence, if the concentration profile and the thickness of the diffusion zone are modelled, the results can be used for estimation of the layer thickness. The first simple solution can be obtained assuming simple initial and boundary conditions from first order:

$$C(x, 0) = C_0 \quad [18.2a]$$

$$C(0, t) = C_s \quad [18.2b]$$

The first condition, Eq. [18.2a], means that the initial concentration of nitrogen in the alloy is C_0 . This value can be obtained from the alloy bulk composition analysis. The second condition, Eq. [18.2b], implies that the concentration of nitrogen at the surface accepts value C_s from the very beginning of the nitriding and is maintained at this constant value throughout the process. The immediate jump of the concentration of nitrogen is not justified because, in reality, the concentration of nitrogen on the surface gradually increases from C_0 to C_s during the early period of the process. However, the condition of maintaining the concentration at the surface at constant value C_s (after it has been reached) is correct. It should be reiterated here that the above analytical solution concerns only the diffusion zone. The concentration of nitrogen at the top of the diffusion zone (at the interface between the compound layer and the diffusion zone) is kept constant and is equal to the maximum solubility of nitrogen in α -Ti. This value can be taken from the Ti-N phase diagram.

Solving Eq. [18.1] in initial and boundary conditions Eq. [18.2], one can obtain:

$$C(x, t) = C_0 + (C_s - C_0)(1 - \text{erf}(\eta)) \quad [18.3a]$$

where

$$\eta = \frac{x}{2\sqrt{Dt}} \quad [18.3b]$$

Using these equations, the nitrogen profile in the diffusion zone is calculated after nitriding at 950 °C for 1, 3 and 5 hours. For C_s , a value of 6 wt.% is used, which is taken from the Ti-N phase diagram. Nitrogen concentration profiles are calculated for diffusion coefficients suggested by different authors (see Section 18.2.3) and the results are compared with experimental results for the thickness of the nitrided layer after nitriding at the same temperature and time (Fig. 18.13). The experimental values are obtained from microhardness profiles.

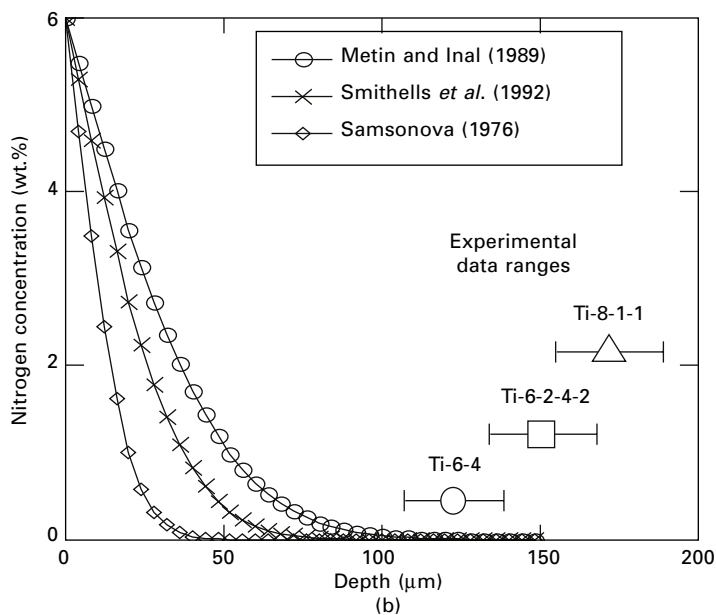
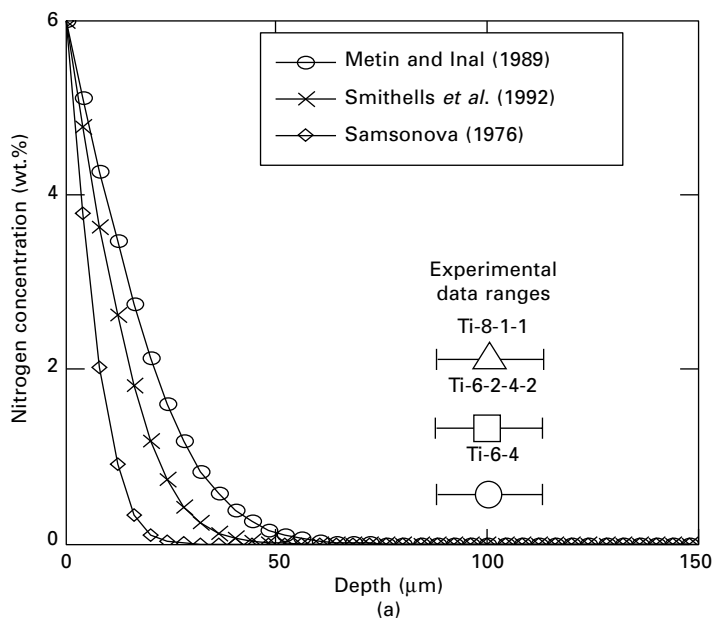
The best correspondence between experimental and calculated values for the layer thicknesses is after using the diffusion coefficient given by Metin and Inal (1989). This coefficient is therefore used in the further simulations.

A more realistic analytical solution can be derived by applying boundary conditions from third order. If the flux of nitrogen atoms across the boundary interface (J_N) is proportional to the difference between the equilibrium (C_s) and the current ($C(0, t)$) concentration of nitrogen at the boundary, the boundary condition can be written as:

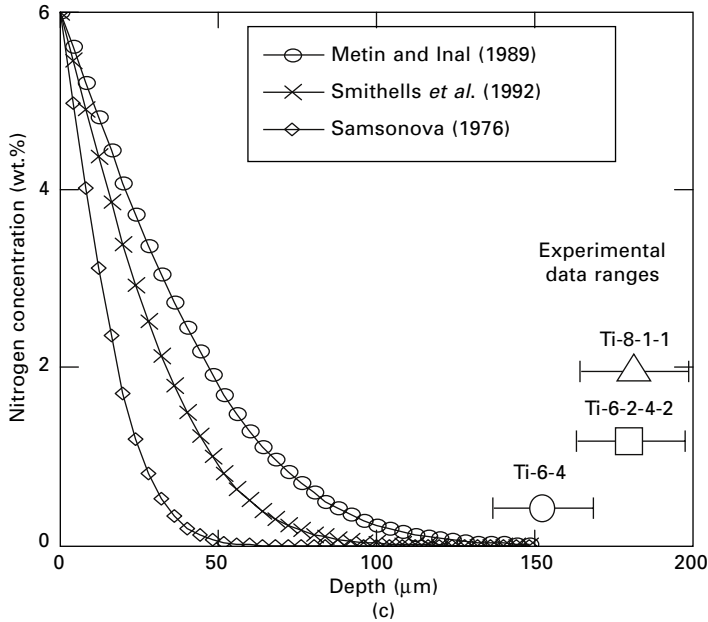
$$J_N = -D \frac{\partial C(0, t)}{\partial x} = \alpha(C_s - C(0, t)) \quad [18.4]$$

where α is a coefficient in m/s.

This condition traces the realistic evolution of the nitrogen profile in the



18.13 Calculated profiles for nitrogen concentration in the diffusion layer using different diffusion coefficients compared with experimental data, for layer thickness. Nitriding temperature 950 °C. Nitriding time: (a) 1 h; (b) 3 h; (c) 5 h.



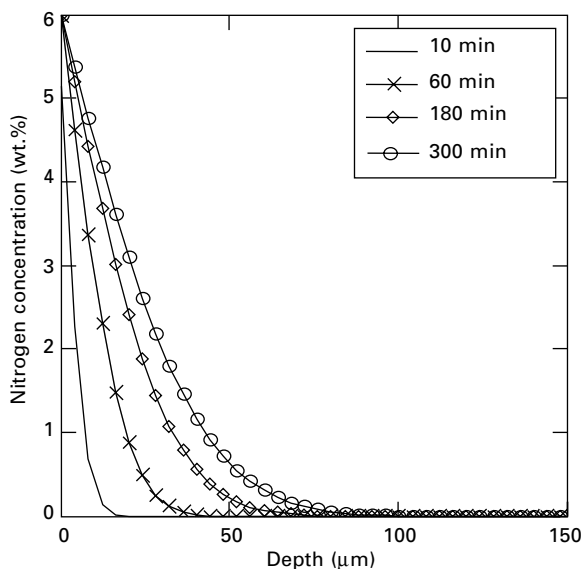
18.13 Continued

diffusion zone. The nitrogen concentration at the boundary increases gradually from zero (or any other value) to the equilibrium concentration (C_s), and is kept at this value afterwards. These are the real conditions for the evolution of the diffusion zone during nitriding of titanium alloys. One disadvantage of this boundary condition is that the coefficient α is unknown. It depends on many factors and varies significantly for different conditions. To obtain the α coefficient, experimental data are necessary.

The analytical solution of Eq. [18.1] at boundary condition Eq. [18.4] is:

$$C(x, t) = C_s \left(\operatorname{erfc}(\eta) - \exp\left(\frac{\alpha^2 t}{D} + \frac{2\alpha\sqrt{t}\eta}{\sqrt{D}}\right) \operatorname{erfc}\left(\eta + \frac{\alpha\sqrt{t}}{\sqrt{D}}\right) \right) \quad [18.5]$$

This solution is used to model the evolution of nitrogen in the diffusion zone during nitriding of Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V alloys. The value of α is obtained by fitting the modelling results to experimentally observed nitrided layers. The best correspondence between modelling and experimental results is obtained for $\alpha = 2.55 \times 10^{-8}$ m/sec. The simulation results after nitriding at 900 and 950 °C for different periods of time are shown in Figs. 18.14 and 18.15, respectively. The concentration of the nitrogen at the surface gradually increases as the concentration gradient develops.



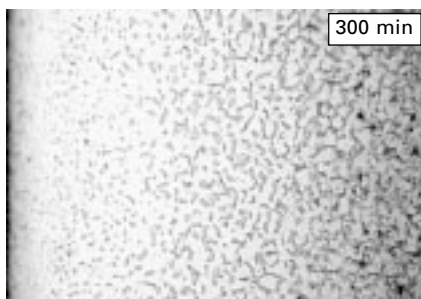
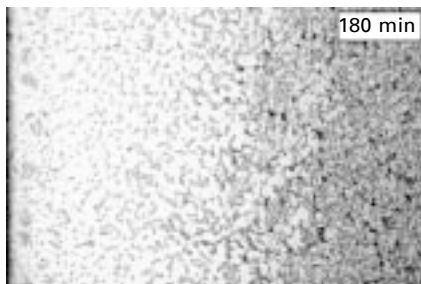
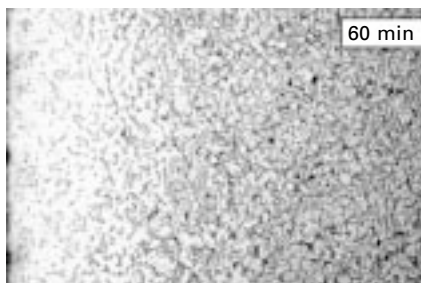
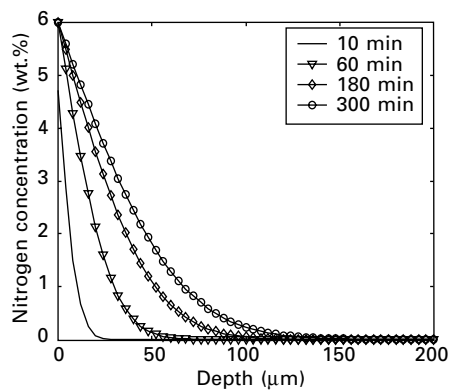
18.14 Calculated profiles for nitrogen concentration in the diffusion layer for different times of nitriding at 900 °C.

The concentration of nitrogen at the surface reaches a value of 4.5 wt.% after nitriding for 10 min at both temperatures, but is still not in equilibrium. After nitriding for one hour, again at both temperatures, the nitrogen concentration in the α phase at the surface already reaches the equilibrium value of 6 wt.%. This means that titanium nitride should be formed already. These simulation results are in agreement with the experimental observations from the X-ray analysis. The diffraction patterns show the presence of titanium nitride after nitriding at 950 °C for one hour. Good correspondence between modelling and experimental results regarding the layer thickness evolution is observed.

Finally, it should be stated once again that the analytical solutions described above can be used to describe the evolution of the diffusion zone only. It is possible to apply some analytical solutions to model the reaction diffusion and formation of the entire (including compounds) layers in certain conditions. However, it is preferable to use numerical simulation for modelling the entire physical model.

18.2.5 Numerical simulations

In addition to the analytical solutions, a mathematical model and program package for numerical simulation of the nitriding process in titanium alloys have been developed. The mathematical model, based on the physical model



18.15 Profiles for nitrogen concentration in the diffusion layer for different times of nitriding at 950 °C, compared with experimental micrographs, of Ti-6Al-2Sn-4Zr-2Mo nitrided at the same conditions.

described in Section 18.2.2, solves the moving-boundary diffusion problem (Schuh, 2000) and considers the simultaneous diffusion of nitrogen in α -Ti and development of a compound layer consisting of TiN and Ti₂N.

Boundary conditions from third order (see above) are used to model the nitrogen mass transfer from the nitrogen containing medium to the solid. The intrinsic diffusion coefficient is assumed to be independent of the nitrogen concentration. The growth is described in terms of mass balance between phases in thermodynamic equilibrium. The model is capable of predicting the nitrogen distribution, layer thickness and incubation times for the formation of layers.

The finite element method is used for solving the diffusion equation on the domains occupied by different phases. The elements chosen have dimensions in both space and time. This allows easy determination of the position of the interface between different phases. The method is essentially an implicit time stepping technique and is therefore stable even for a relatively large time step.

The problem to be solved involves diffusion through two adjacent single phases 'a' and 'b', which are separated by a moving boundary. In general, the diffusivities in each phase D_a and D_b are not equal, and the concentration has a discontinuity across the boundary. A local equilibrium is assumed at the interface, and the interfacial compositions of both phases are calculated from the equilibrium phase diagrams. The interface may move in either direction normal to it as the reaction proceeds. The moving velocity of the interface is calculated from flux balance equations.

Mass transfer from the diffusant-containing media to the solid occurs as a result of the reactions at the diffusant–solid interface. The mass transfer reactions determine the surface boundary conditions of the process. For conventional gaseous nitriding, the surface boundary conditions from third order must be applied:

$$-D \frac{\partial C(x,t)}{\partial x} \bigg|_{x=0} = K(a - C(x,t)) \big|_{x=0} \quad [18.6]$$

where $C(x, t)$ is the concentration at depth x and time t , D is the diffusion coefficient, K is the reaction rate coefficient and a is the diffusant potential in the atmosphere.

In the single-phase region, the usual diffusion model is used. Fick's first law, relating flux and concentration gradient in the case of isothermal, isobaric diffusion, is expressed as:

$$J = -D \frac{\partial C}{\partial x} \quad [18.7]$$

The conservation of solute in the solid then requires:

$$\frac{\partial C}{\partial x} = \frac{\partial}{\partial x}(-J) \quad [18.8]$$

A mass balance must be maintained at the interface, which is determined by the relation of the inward and outward flux through the interface:

$$D_a \left. \frac{\partial C_a}{\partial x} \right|_{x=\xi} - D_b \left. \frac{\partial C_b}{\partial x} \right|_{x=\xi} = (C_b - C_a) \frac{\partial \xi}{\partial t} \quad [18.9]$$

where D_a , D_b , C_a and C_b are the diffusion coefficients and interface concentrations in the corresponding phases, ξ is the interface position, and $\frac{\partial \xi}{\partial t}$ indicates the layer's growth rate. The speed of the displacement of the discontinuity $\frac{\partial \xi}{\partial t}$ is determined by Eq. [18.9]. There will be one flux balance equation for each interface and the solution of the second Fick's equation is necessary.

Input parameters

The model based on the numerical simulations is used to develop user-friendly software for monitoring the process of surface nitriding in titanium and titanium alloys under various processing conditions. On input of the processing temperature, parameters for the diffusion coefficient (activation energy and pre-exponential term) and concentration limits of the different phases, the nitriding process can be monitored. In this way, the model can be used for simulation of surface nitriding not only in pure titanium but in titanium alloys, if the diffusion coefficients of nitrogen are known.

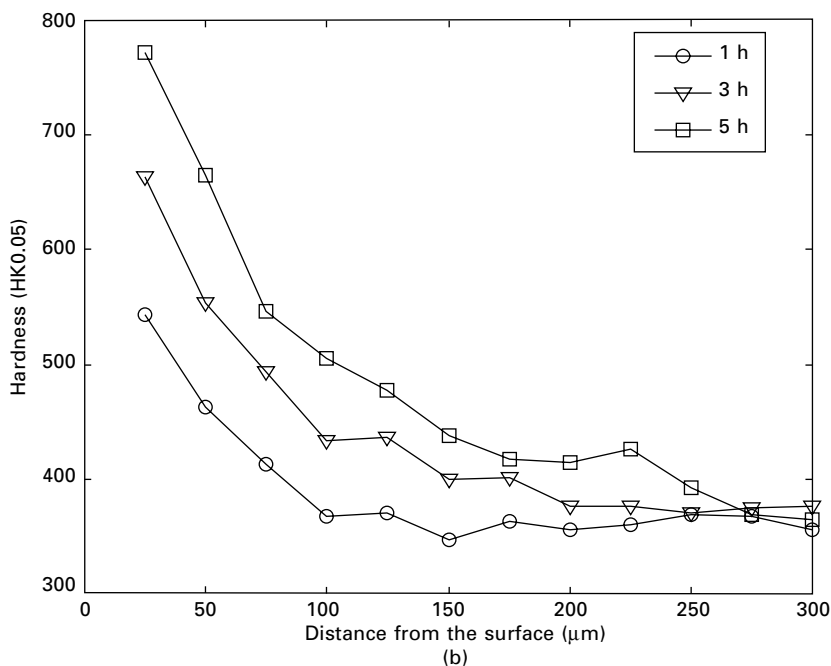
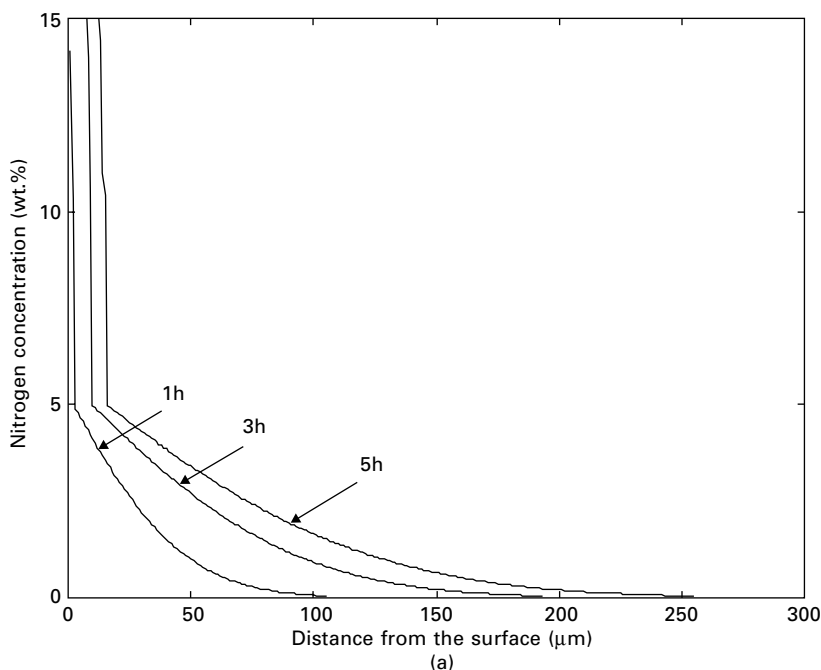
The frequency factor A and the activation energy Q are changed for each alloy, to obtain results close to the experimental results in terms of thickness of the compound and the diffusion layers. Then, for each alloy the best-fit diffusion data are found (see Table 18.2).

Finite element modelling test and performance

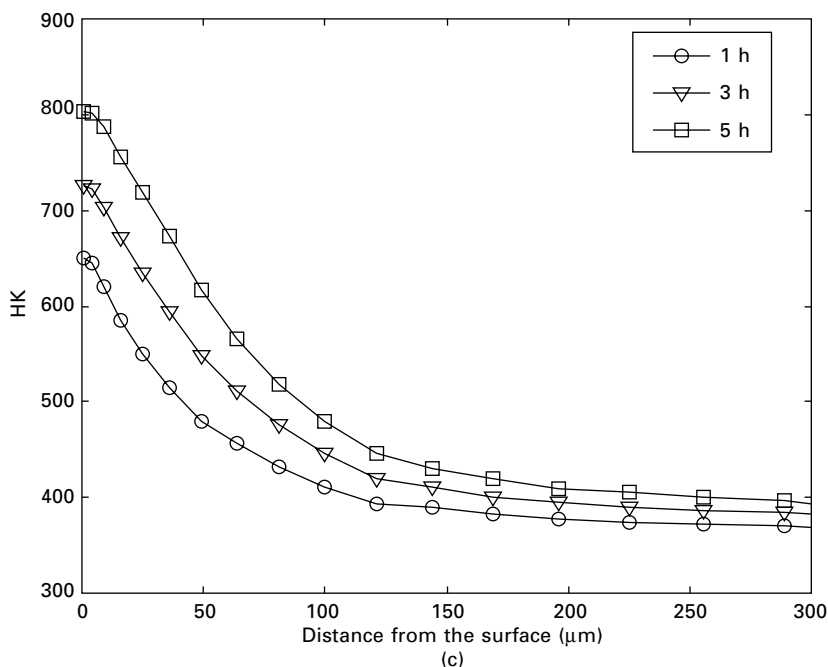
The model performance is tested comparing simulation results with experimental data. Figure 18.16 illustrates one example of the numerical model simulations. The calculated results are compared with experimental data on microhardness in Ti-8Al-1Mo-1V after nitriding for the same temperature and time. These results can also be compared with the neural network predictions of microhardness profiles made by the models described in Section 18.1 and, in particular, Model 2 (see Fig. 18.16c). A good correspondence between the numerical simulations, experimental results and

Table 18.2 Diffusion data obtained from the modelling of Ti–Ti₂N–TiN system

Alloy	α -Ti		Ti ₂ N		TiN	
	A , m ² /s	Q , kJ/mole	A , m ² /s	Q , kJ/mole	A , m ² /s	Q , kJ/mole
Ti (Metin and Inal, 1989)	9.6×10^{-5}	215	2.7×10^{-7}	150	4.4×10^{-9}	153
Ti-8Al-1Mo-1V	1.1×10^{-3}	225	2.0×10^{-7}	160	1.0×10^{-7}	160
Ti-6Al-2Sn-4Zr-2Mo	0.5×10^{-3}	225	1.0×10^{-7}	165	6.0×10^{-7}	163
Ti-6Al-4V	0.5×10^{-3}	225	1.0×10^{-7}	165	6.0×10^{-7}	163
Ti-10V-2Fe-3Al	1.0×10^{-3}	210	2.0×10^{-7}	155	5.0×10^{-8}	145



18.16 (a) Numerical simulations for the evolution of the surface layer after nitriding of Ti-8Al-1Mo-1V at 950 °C for 1, 3 and 5 hours, compared with (b) experimental microhardness profiles of the same alloy after nitriding at the same conditions and (c) neural network predictions of microhardness profiles for the same alloy.



18.16 Continued

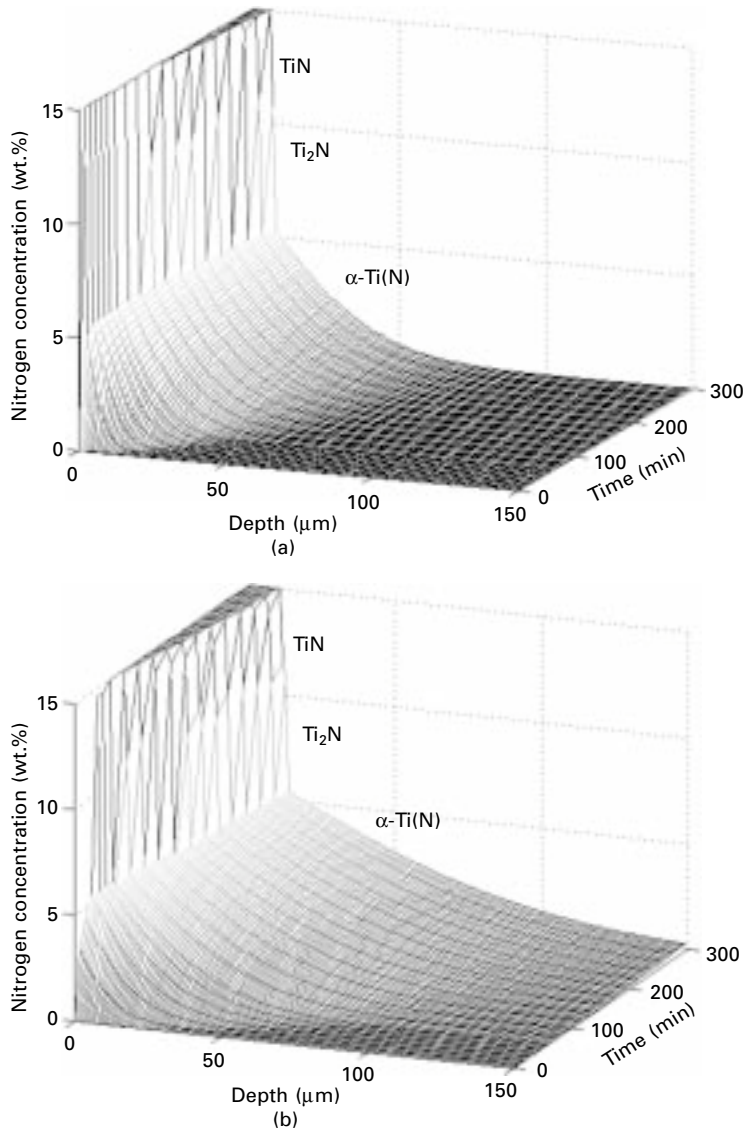
the NN results is found. The use of the best-fit diffusion parameters for each alloy makes it possible for the model to predict nitrogen concentration profiles and the thickness of the layers for new situations within the used experimental time and temperature range.

Furthermore, the model can be used to optimise the processing parameters (temperature and time) of nitriding in order to achieve a desirable surface layer thickness. Figure 18.17 demonstrates an example of model simulations and monitoring of the evolution of nitrided layers. The simulations are for Ti-8Al-1Mo-1V, temperature of nitriding 840 and 920 °C and using the diffusion data of nitrogen in different phases from Table 18.2.

The layer's thickness increases with increase of the time and the temperature of nitriding, in agreement with the diffusion theory and the experimental results.

There is a higher concentration of nitrogen in the nitrided layer after longer saturation time, leading to an effective production of thicker nitrided layers with higher values of the microhardness.

From Figs. 18.16a and 18.17, the thickness of the sub-compound layer that consists of Ti_2N is very small. This is because the concentration profile in this phase is very steep, which leads to a very short incubation time for the formation of the Ti_2N phase. This thickness is achieved by verifying the

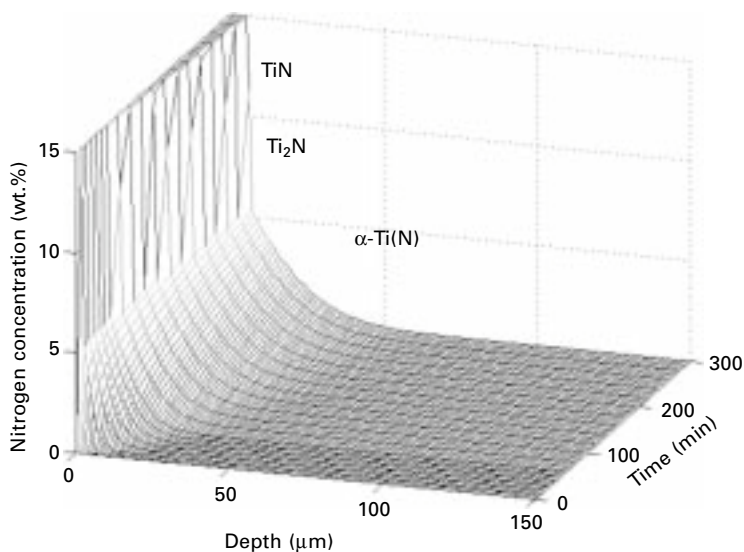


18.17 Numerical model simulations for the evolution of the surface layer during nitriding at (a) 840 and (b) 920 °C for Ti-8Al-1Mo-1V.

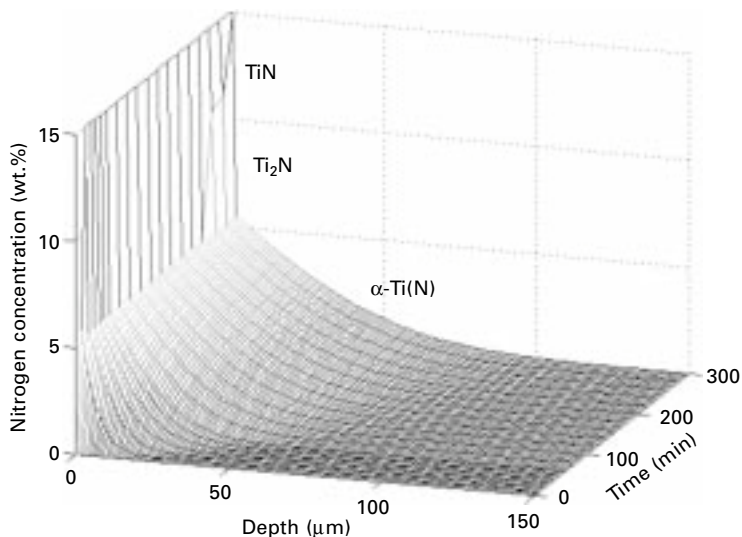
diffusion data used for the simulation by the time an insignificant thickness of this phase is obtained. It is desirable to obtain such a small thickness of this phase because, from the experimental results (Chapter 16), no Ti₂N phase is observed on the surface after nitriding under different thermodynamic conditions.

Another example can be given for Ti-6Al-2Sn-4Zr-2Mo nitrided at 840 °C using the diffusion data from Table 18.2 (see Fig. 18.18).

The simulation of Ti-10V-2Fe-3Al during nitriding at 790 °C is shown in Fig. 18.19. Using the diffusion data from Table 18.2, a good agreement



18.18 Numerical model simulations for the evolution of the surface layer during nitriding at 840 °C for Ti-6Al-2Sn-4Zr-2Mo.



18.19 Numerical model simulations for the evolution of the surface layer during nitriding at 790 °C for Ti-10V-2Fe-3Al.

between the fundamental diffusion theory and the experimental results can be seen.

18.2.6 Summary of numerical modelling of the nitrided layer growth

Models for simulation and monitoring of the evolution of the surface layers during gas nitriding of titanium alloys are based on analytical and numerical solutions of the diffusion equation. The temperature and time of gas nitriding can be varied for each of the titanium alloys. The growth of the nitrided layers can be observed and monitored.

These numerical models, together with the NN models, are able to give a complete picture of the nitrided layers of titanium alloys after thermo-chemical treatment of nitriding and can be useful tools for titanium users and the titanium industry in general for optimising the processing parameters of nitriding to obtain the desirable surface properties and characteristics of the titanium alloys for various applications.

The best-fit diffusion data for each of the Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V and Ti-10V-2Fe-3Al titanium alloys are shown. Using these data, numerical simulations and predictions of the nitrogen distribution, the thickness of the nitrided layers and the incubation time for the formation of the layers can be made for new thermodynamic conditions.

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Aluminising: fabrication of Al and Ti–Al coatings by mechanical alloying

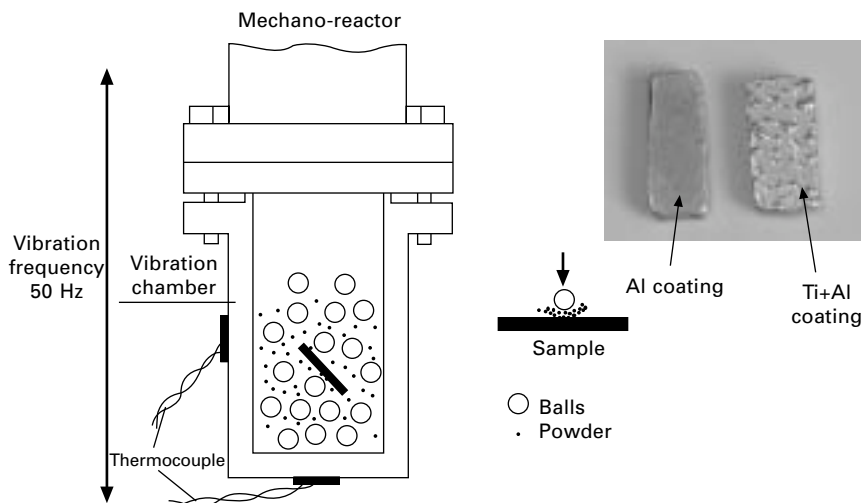
Abstract: During mechanical alloying (MA) processing, aluminium is better deposited on the surface in the presence of titanium particles. MA technique produces titanium/aluminium coatings with thickness of ca. 200 μm and aluminium coatings with thickness of ca. 50 μm after two hours at room temperature. As-synthesized coatings show a structure with high apparent density and no porosity. Annealing at temperatures ranging between 600 and 1100 $^{\circ}\text{C}$ gives different aluminide phases on the samples. In the case of the aluminium coating, Al_3Ti and Ti_3Al compounds are observed upon heating. In the case of the titanium/aluminium coating, Al_3Ti , Al_2Ti , TiAl and Ti_3Al are formed on the surface.

Key words: coating, mechanical alloying, titanium aluminides, phase transformation, microstructure.

19.1 Introduction

A surface mechanical attrition treatment technique has been developed for obtaining nanostructured surface layers of various metals (Tao *et al.*, 2003; Wang *et al.*, 2003). The surface layer of the metal substrate is subject to repeated ball collisions in the absence or presence of a second metal in the form of a powder and as a result the structure at the surface becomes refined into a nanometre scale. In the absence of a metal powder, a nanostructured surface layer with a thickness of 10–50 μm is obtained. In the presence of an Al or Al/Ti powder, coatings on Ti or Ti–Al substrates can be obtained by this mechanical alloying (MA) method. The structural formation of aluminised layer during subsequent annealing is described.

By the MA method, coatings of aluminium or titanium and aluminium can be deposited on the substrates (Fig. 19.1). The metal substrate piece(s) and the powder along with the steel balls are placed into the chamber and are vibrated by the mechano-reactor for two hours. The milling process can be carried out in air, though the chamber should be sealed to limit the amount of available oxygen and nitrogen. The temperature of the chamber walls during MA processing does not exceed 100 $^{\circ}\text{C}$. During mechano-activation processing, the metal surface is impacted by a large number of flying balls along with particles of powder. The repeated ball collisions with the metal result in deposition of powder on the surface.

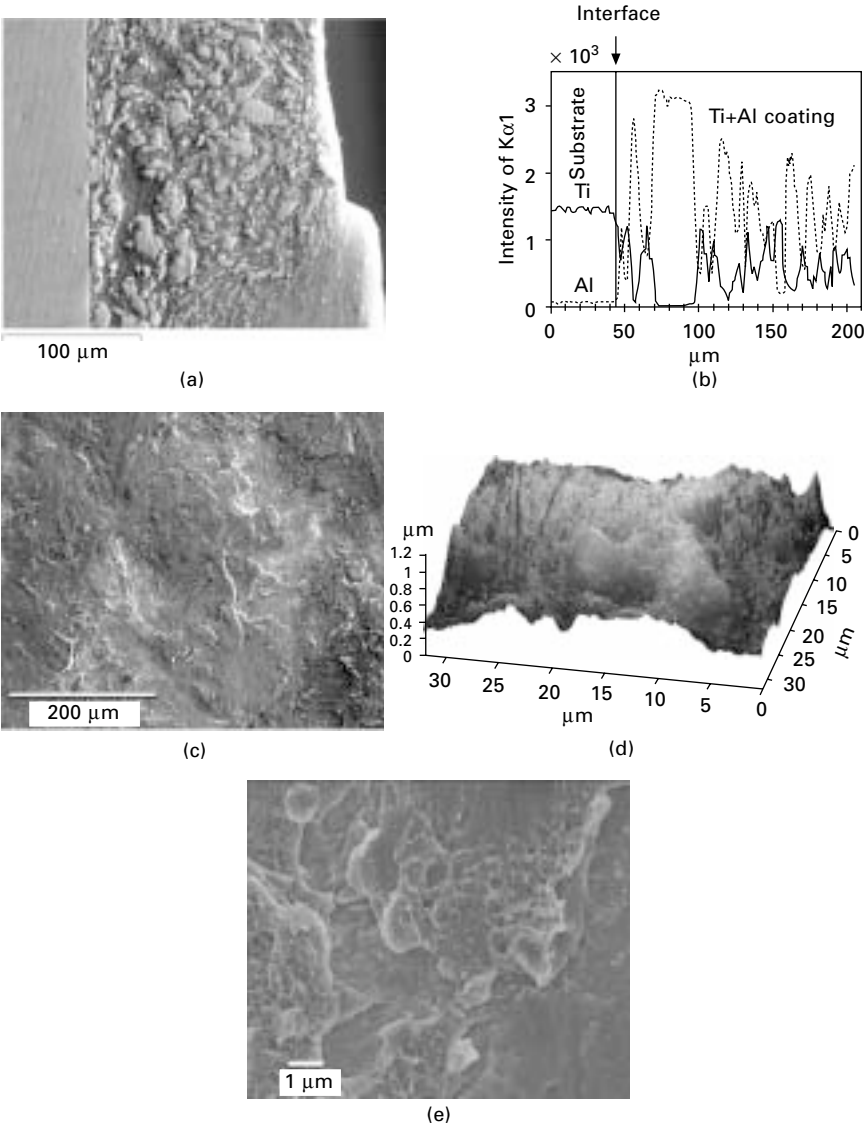


19.1 Schematic illustration of the mechanical alloying method.

19.2 As-synthesised state

The thickness of the *titanium/aluminium* MA-coating is about 200 μm ; it has a high apparent density and is free of porosity and cracks (Fig. 19.2a,b). The coating consists of titanium particles, with non-uniform sizes, in an aluminium matrix. The maximum iron content in the titanium/aluminium coating is about 0.3 at.% near the coating/substrate interface. It decreases in the direction of the coating surface. The reason for such low content of iron is that the balls and the chamber inner walls are being coated by titanium/aluminium layer in the early stages of MA processing, preventing the release of iron into the coating. There are no traces of nitrogen and oxygen in the titanium/aluminium coating. The magnitude of contamination during MA depends on the time and intensity of milling, nature of the powder, ball-to-powder weight ratio, and seal integrity (Suryanarayana, 2001). If the container is not properly sealed, the atmosphere surrounding the container leaks into the container and contaminates the powder. Thus, when reactive metals such as titanium are milled in improperly sealed containers, the powders are contaminated with nitrogen and oxygen. By careful control and improvements of the seal quality, the interstitial contaminants in the titanium alloy can be reduced to as low as 100 ppm of oxygen and 15 ppm of nitrogen (Suryanarayana, 2001).

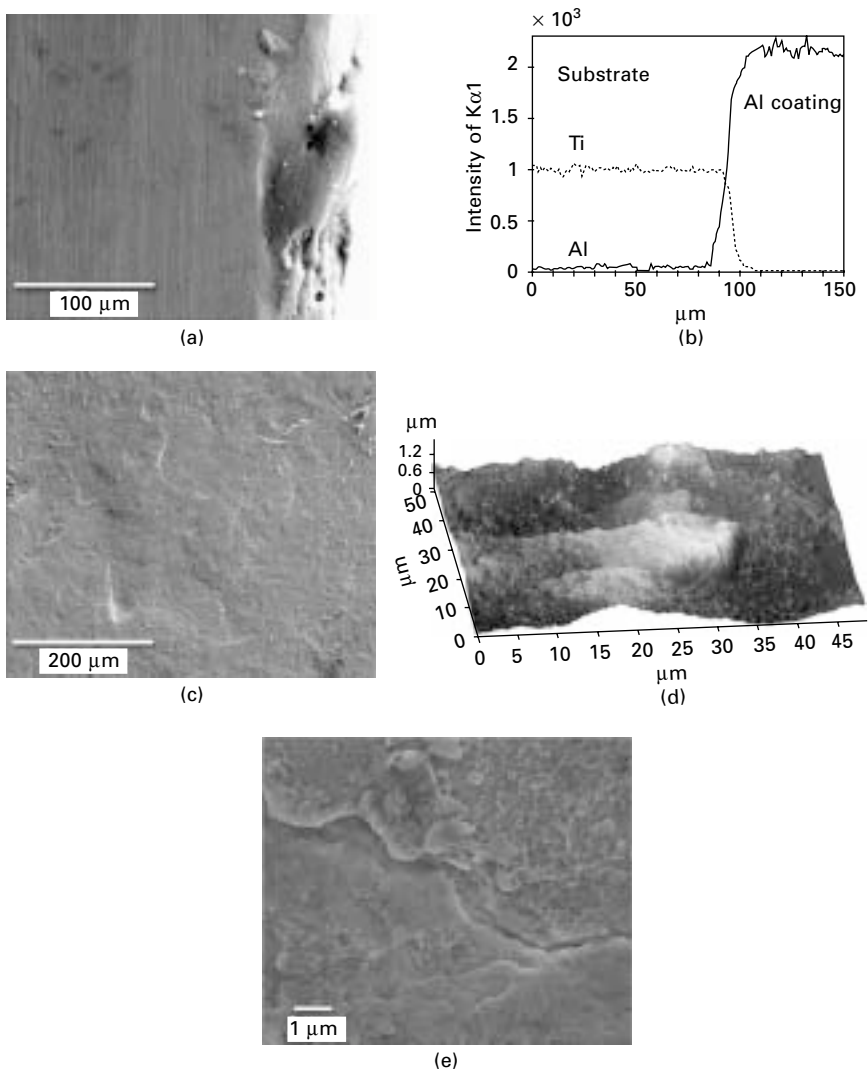
The microstructure is rough, with no clear grain structure on the coating surface (Fig. 19.2c). The typical surface morphology obtained by atomic force microscopy (AFM) appears similar to a ductile fractured surface, the nodules in the image showing flow of material at fracture (Fig. 19.2d). Furthermore, the dimple structure in some areas of the titanium/aluminium



19.2 As-synthesised titanium and aluminium coating produced by MA method: (a) secondary electron image of cross-section microstructure; (b) concentration profile; (c) surface microstructure; (d) morphology; (e) dimple structure.

coating at high magnification may provide evidence of the ductile behaviour of the material during MA processing (Fig. 19.2e).

The thickness of the *aluminium* coating is about 50 μm, without a clear interface between the substrate and aluminium layer (Fig. 19.3a,b). The



19.3 As-synthesised aluminium coating produced by MA method: (a) secondary electron image of cross-section microstructure; (b) concentration profile; (c) surface microstructure; (d) morphology; (e) dimple structure.

coating is continuous and very dense (Fig. 19.3c). The surface of the aluminium coating is flatter and more homogenous than that of the titanium/aluminium coating (Fig. 19.2). The morphology is again similar to a fracture surface (Fig. 19.3d). The dimple structure and microcracks in some areas of the aluminium coating at high magnification are observed (Fig. 19.3e). The

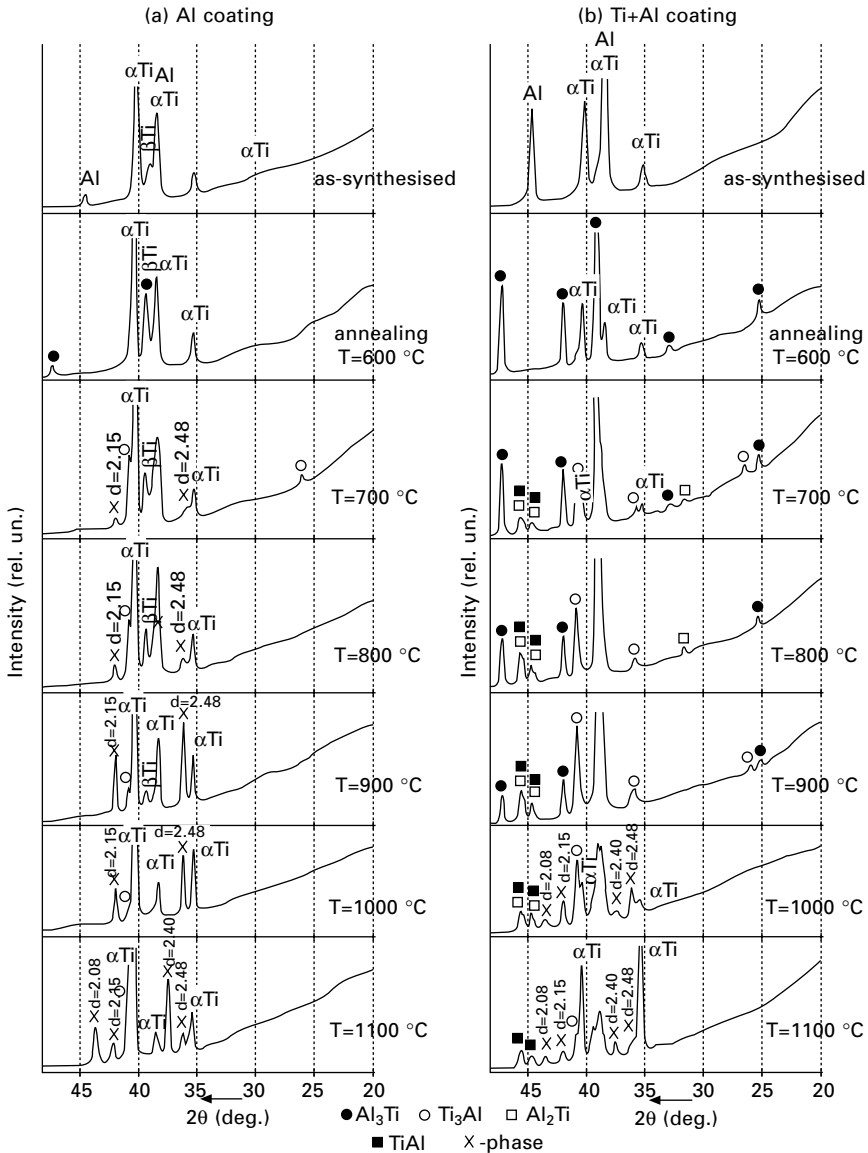
absolute amount of aluminium in the titanium/aluminium coating is more than that in the aluminium coating because the former is thicker.

During MA processing, aluminium is better deposited on the surface in the presence of titanium particles. The microstructure of the coating surface provides evidence of ductile behaviour of the material during MA (Figs. 19.2 and 19.3). This behaviour would indicate that the local temperature under the ball impacts is higher than the temperature of the chamber walls. The stress generated during MA may be rather high as well (Suryanarayana, 2001). The titanium particles are in the aluminium matrix (Fig. 19.2a). Titanium appears as a dispersive material and aluminium serves as a bonding one. Cold welding between particles and substrate under repeated ball collisions leads to the formation of a composite coating. Aluminium flows into the pores between the titanium particles under the impact of the balls. As a result, a dense titanium and aluminium coating grows. Cold welding occurs non-uniformly. Therefore, a very rough surface on the titanium/aluminium coating is formed (Figs. 19.1 and 19.2c). In the case of using the powder of pure aluminium, an aluminium layer with some thickness is coated, but extensive cold welding between aluminium particles and the aluminium layer cannot happen. Cold welding may occur in the early stages of MA, when the aluminium particles are soft, and their tendency to weld is high. Under deformation, the particles and the aluminium layer become harder and more brittle (Suryanarayana, 2001). This is confirmed by the microcrack in Fig. 19.3d. With increase of MA-time, cold welding is restrained. Under the ball collisions, the aluminium coating starts flaking and becomes smoother in comparison with the titanium/aluminium one (Figs. 19.1, 19.2 and 19.3). In the case of the titanium/aluminium coating, alloying may occur rapidly in the presence of titanium particles. There is no time for the coating to become brittle.

19.3 Annealing treatment of aluminium coating

Table 19.1 summarises the phase composition, without including the phases of the substrate, α -Ti and β -Ti. During annealing, on the surface of the sample different aluminide phases are formed as the result of interdiffusion and reaction between titanium and aluminium. Aluminium reacts with titanium on heating up to 600 °C, and forms Al_3Ti . No diffraction peaks of pure aluminium are in the X-ray pattern (Fig. 19.4a), but it completely reacts on the formation of Al_3Ti .

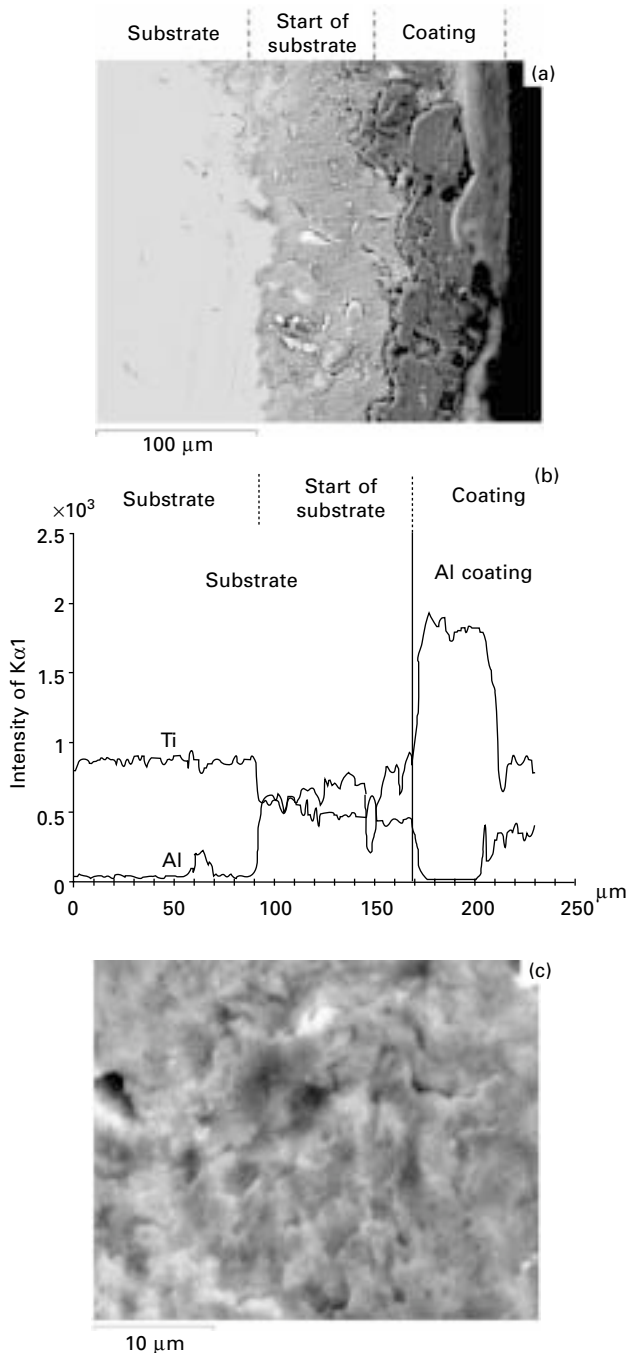
The contrast difference in Fig. 19.5a, a back-scattered electron image, reflects different compositions. On heating up to 600 °C, aluminium diffuses into the substrate. The grey dark layer from the start of the substrate is enriched by aluminium (Fig. 19.5b). The thickness of the diffusion layer is about 80 μm . The coating itself becomes porous after annealing treatment at



19.4 X-ray diffraction patterns ($\text{CuK}\alpha$) of MA-coatings after annealing at temperatures ranging between 600 and 1100 °C: (a) aluminium coating; (b) titanium/aluminium coating.

600 °C, with microcracks between substrate and coating (Fig. 19.5a). The coating surface is porous and rough as well. Upon heating up to 600 °C, pits are formed on the surface (Fig. 19.5c).

A second anneal at 700 °C after annealing treatment at 600 °C leads to the formation of Ti_3Al on the surface (Table 19.1 and Fig. 19.4a). In addition,



19.5 Aluminium coating after annealing at 600 °C: (a) back-scattered electron image showing cross-section microstructure; (b) concentration profile; (c) surface microstructure.

new diffraction lines with $d = 2.48$ and $2.15 \text{ \AA}$ are in the X-ray pattern (Fig. 19.4a). In Table 19.1 and Fig. 19.4, this phase is denoted as X-phase. After subsequent increase of the annealing temperature from 700 to 1000 °C, the intensity of the X-phase diffraction lines increases while the intensity of the Ti_3Al ones decreases. Increase of annealing temperature increases the volume fraction of X-phase at the expense of Ti_3Al . After annealing treatment at 1100 °C, only slight asymmetry of the $\alpha\text{-Ti}$ diffraction peaks at the high-angle side may indicate the presence of the Ti_3Al phase (Fig. 19.4a). The intensity of the X-phase lines with $d = 2.48$ and $2.15 \text{ \AA}$ considerably decreases after annealing at 1100 °C, in comparison with treatment at 1000 °C, while the other strong peaks with $d = 2.40$ and $2.08 \text{ \AA}$ appear in the X-ray diffraction pattern (Fig. 19.4a).

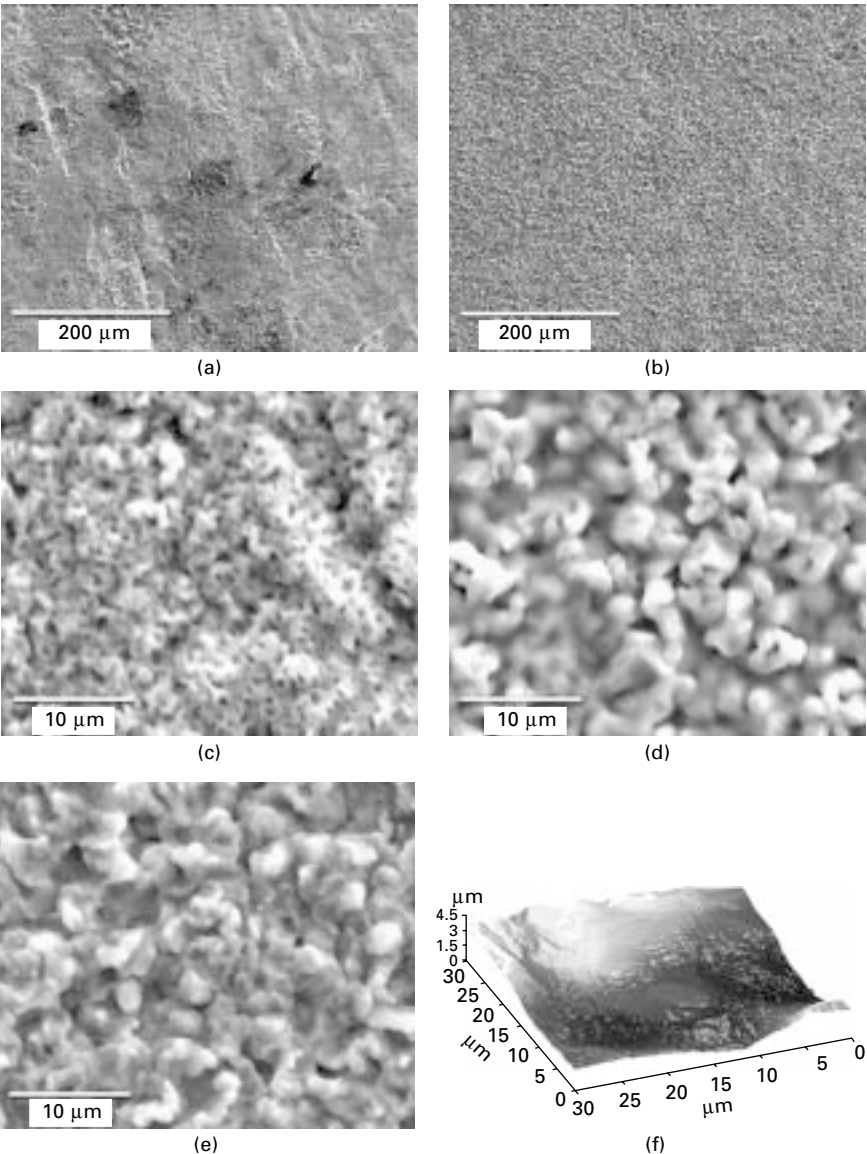
The lines with $d = 2.48$ and $2.15 \text{ \AA}$ could be attributed to TiC , and the ones with $d = 2.40$ and $2.08 \text{ \AA}$ could be attributed to Ti_3AlC . The above sequence of peaks appearing means that Ti_3AlC could be formed from TiC (Zhou *et al.*, 2003). Formation of carbide phases during annealing treatments can be due to carbon contamination of the coating during MA. The X-phase completely disappears after the elimination of the aluminised layer.

Moreover, formation of Al_2Ti and TiAl compounds on the titanium surface coated by the aluminium film precedes formation of Ti_3Al (Romankov *et al.*, 2006, 2007). In the case of the aluminium coating produced by MA, Al_2Ti and TiAl phases are not present. This can be a result of the stress and structural features of MA-coating. During MA processing, the substrate surface and coating are plastically deformed, leading to grain refinement into the nanometre scale and an extremely high density of dislocations (Wang *et al.*, 2003). The large amount of grain boundaries and defects may provide rapid atomic diffusion in the surface layers. As a result, diffusion transformation on the substrate with the aluminium coating produced by MA can occur very fast, and Al_2Ti and TiAl phases will not remain after 2 hours annealing. These phases may be skipped altogether. Defect structure formed during MA processing can have a great effect on the thermodynamics of the interdiffusion process.

Table 19.1 The principal temperature ranges of the aluminide phase formation and the phase composition on Ti-4%Al-3%Mo-1%V alloy of the mechanical alloying deposited coatings

Temperature (°C)	Aluminium coating	Titanium/aluminium coating
600	Al_3Ti	Al_3Ti
700–900	Ti_3Al , X-phase	Al_3Ti , Al_2Ti , TiAl , Ti_3Al
1000	Ti_3Al , X-phase	Al_2Ti , TiAl , Ti_3Al , X-phase
1100	Ti_3Al (trace), X-phase	TiAl , Ti_3Al , X-phase

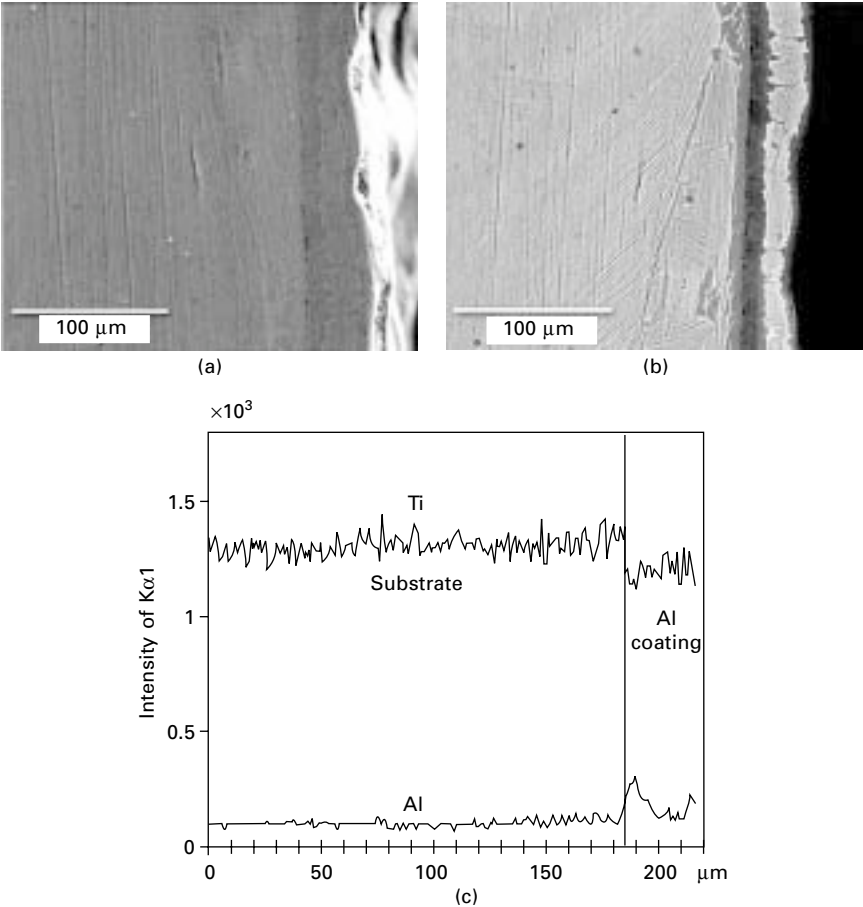
With an increase of annealing temperature, a gradual levelling of coating happens (Fig. 19.6a,b). Annealing at 1000 °C gives a homogeneous and even microstructure on the aluminium coating (Fig. 19.6b). In the high magnification micrograph of the aluminium coating, micropits are present after annealing



19.6 Surface microstructural evolution of aluminium coating during annealing treatments: (a) 800 °C; (b) 1000 °C; (c) 900 °C; (d) 1000 °C; (e) 1100 °C; (f) morphology after 1100 °C.

at 900 °C. The sizes of the micropits increase, and the coating becomes porous as the annealing temperature rises to 1000 °C (Fig. 19.6c,d). With subsequent increase of temperature up to 1100 °C, the coating structure coalesces (Fig. 19.6e), and the surface morphology becomes flat (Fig. 19.6f). Thus, the annealing treatment results in the gradual levelling of the MA-coating surface, which is very rough in the as-synthesised condition (Fig. 19.3d).

After annealing at 1100 °C, the MA-coating itself shows a structure with high apparent density (Fig. 19.7a). However, there are some pores and peeling in some areas along the coating/substrate interface (Fig. 19.7a,b). Figure 19.7b shows a different composition of aluminium coating. The jump in



19.7 Cross-section microstructure of aluminium coating after annealing at 1100 °C: (a) secondary electron image; (b) back-scattered electron image; (c) concentration profile.

aluminium concentration is at the interface (Fig. 19.7c), consistent with the clear contrast in the back-scattered electron image (Fig. 19.7b). The diffusion layer in the coating adjacent to the substrate is formed. The substrate itself has a coarse grain lamellar structure. The concentration of aluminium in the near surface region of the substrate is about 16 at.% after annealing at 1100 °C, twice the aluminium concentration in the substrate.

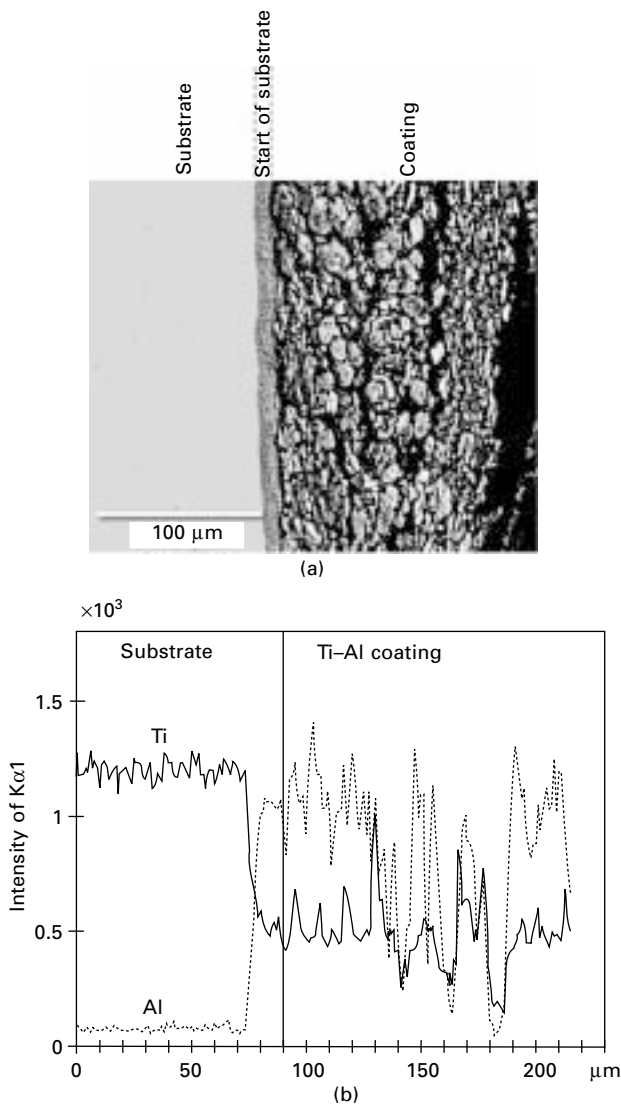
Thus, significant changes in the structure of the aluminium coating occur after annealing at temperatures above 800 °C. At about 880 °C, α -Ti (hcp) to β -Ti (bcc) transformation in the substrate should occur. The intense interdiffusion between substrate and coating leads to recrystallisation of the coating structure. Moreover, at temperatures exceeding 900 °C, the growth of β -grains in the substrate occur. The concentration of aluminium at the near-interface region increases significantly upon heating. As a result, α -Ti to β -Ti transformation in the substrate and near-surface region of the substrate does not occur simultaneously. Annealing at temperatures above 900 °C leads to recrystallisation of the near-surface region and stabilising α -Ti at the interface. Then, the lines of β -phase are not in the X-ray diffraction patterns of the aluminium coating after annealing treatment above 900 °C (Fig. 19.4a).

19.4 Annealing treatment of the titanium/aluminium coating

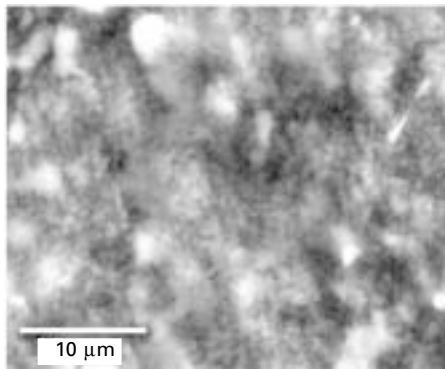
Annealing of titanium/aluminium coatings at 600 °C induces the formation of Al_3Ti (Table 19.1 and Fig. 19.4b). Aluminium completely reacts on the formation of Al_3Ti . The peaks of α -Ti are in the X-ray diffraction pattern after annealing at 600 °C (Fig. 19.4b), showing that particles of pure titanium are present in the coating. The coating is porous (Fig. 19.8a), consisting of non-uniform particles. A layer with a thickness of about 12 μm from the start of the substrate is enriched by aluminium (Fig. 19.8b). However, in comparison with the aluminium coating, the diffusion layer is substantially thinner (Fig. 19.5a,b). After annealing at 600 °C, the surface microstructure of the titanium/aluminium coating is porous and rough, along with the formation of very fine particles on the surface (Fig. 19.8c). A comparison of the two types of coatings might indicate that in the case of the aluminium coating, formation of Al_3Ti results from interdiffusion between the titanium substrate and the aluminium layer. In the case of the titanium/aluminium coating, Al_3Ti is formed mainly as a result of reaction between titanium particles and the aluminium matrix in the coating, which also leads to the porosity.

Annealing the titanium/aluminium coating at 700 °C reduces the intensity of the Al_3Ti and α -Ti diffraction peaks in the X-ray pattern (Fig. 19.4b). Ti_3Al lines along with the wide asymmetric peaks of the Al_2Ti phase are present. The Al_2Ti and TiAl compounds have close lattice plane spacing.

The wide asymmetric peaks of Al_2Ti in the X-ray pattern are overlapping diffraction lines from Al_2Ti and TiAl . Al_2Ti , TiAl and Ti_3Al are formed as a result of the reaction between Al_3Ti and Ti particles on heating up to 700°C . After subsequent increase of annealing temperature from 700 to 900°C , the volume fraction of Al_3Ti gradually decreases while the volume fraction of Ti_3Al , Al_2Ti and TiAl increases. Titanium in the titanium/aluminium coating



19.8 Titanium and aluminium coating after annealing at 600°C : (a) back-scattered electron image showing cross-section microstructure; (b) concentration profile; (c) surface microstructure.



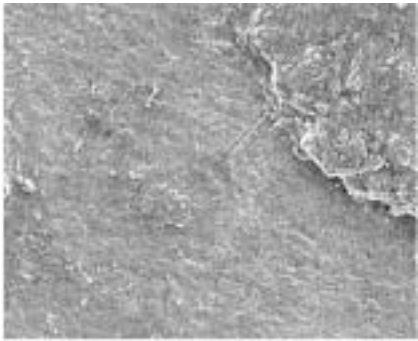
(c)

19.8 Continued

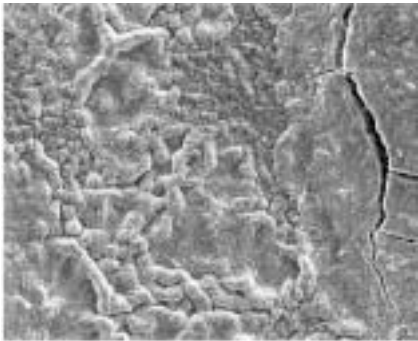
completely reacts on the formation of these compounds after treatment at 800 °C (Fig. 19.4b). Al_3Ti decomposes only on heating up to 1000 °C. Annealing at 1000 °C gives Al_2Ti , TiAl and Ti_3Al on the titanium/aluminium coating (Table 19.1 and Fig. 19.4b). In addition, the peaks of the X-phase are in the X-ray diffraction pattern after treatment at 1000 °C. What is important is that the diffraction peaks of $\alpha\text{-Ti}$ are again present after annealing at 1000 °C (Fig. 19.4b). Then, with an increase of annealing temperature to 1100 °C, the intensity of $\alpha\text{-Ti}$ peaks increases dramatically, while the intensity of the Ti_3Al lines decreases. This can be related to the rapid release of aluminium into the substrate when the mobility of the atoms increases. The TiAl compound on the titanium/aluminium coating does not decompose completely after annealing at 1100 °C (Table 19.1 and Fig. 19.4b).

With an increase of temperature from 800 to 1000 °C, the microstructure of the coating becomes very inhomogeneous, with a very rough and irregular hillock-like structure (Fig. 19.9a,b). Large microcracks appear on the smooth areas (Fig. 19.9b). With subsequent increase of annealing temperature from 1000 to 1100 °C, the microstructure of the titanium/aluminium coating starts levelling (Fig. 19.9c). The surface is porous (Fig. 19.9d). The coating structure coalesces as the annealing temperature rises from 1000 to 1100 °C. The microcracks start healing (Fig. 19.9e). During the annealing treatment, the surface morphology of the titanium/aluminium coating becomes less rough compared to the as-synthesised MA-coating (Figs. 19.2d and 19.9f).

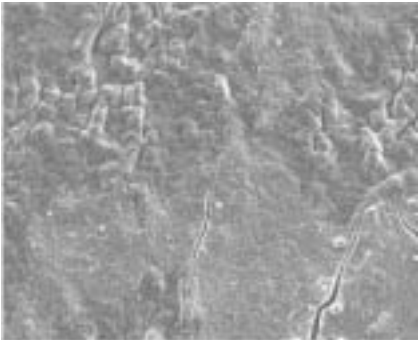
There are no peelings, microcracks or pores (Fig. 19.10a). The coating is very dense, and has a good apparent adherence to the substrate after treatment at 1100 °C. Back-scattered electron imaging shows a multilayered structure of coating, with different thicknesses (Fig. 19.10b). Instead of a smooth change in concentration from $\alpha\text{-Ti}$ to TiAl , there are the jumps in the concentration (Fig. 19.10c). The discontinuity is consistent with the clear



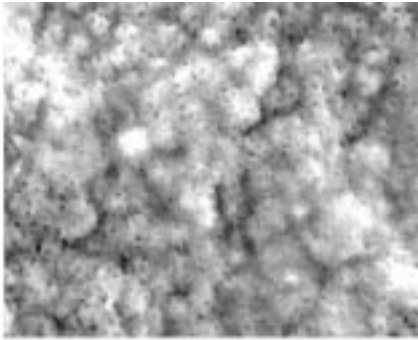
(a)



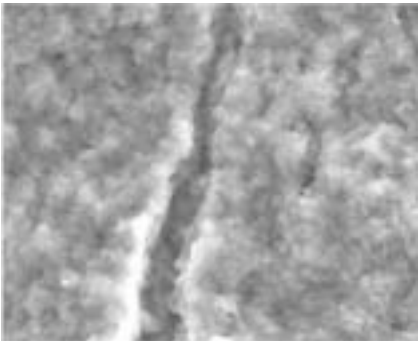
(b)



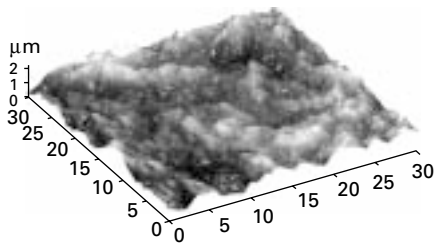
(c)



(d)

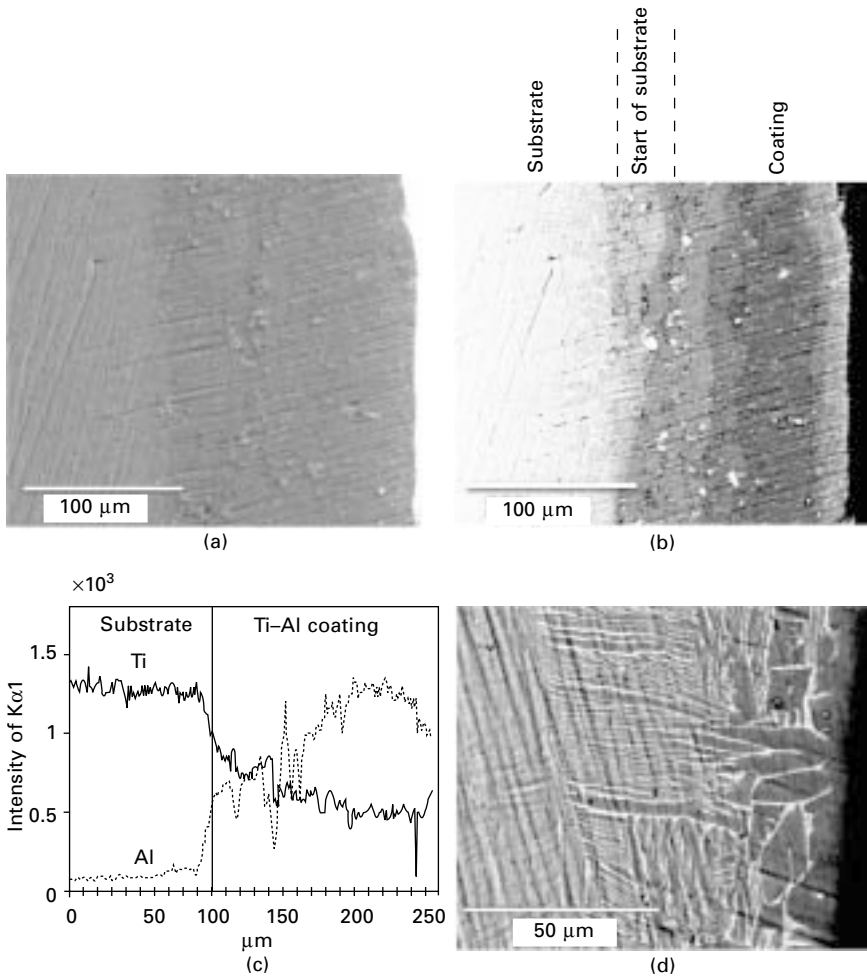


(e)



(f)

19.9 Surface microstructural evolution of titanium/aluminium coating during annealing treatments: (a) 800 °C; (b) 1000 °C; (c) 1100 °C; (d) 900 °C; (e) 1100 °C; (f) morphology after 1100 °C.



19.10 Cross-section microstructure of titanium/aluminium coating after annealing at 1100 °C: (a) secondary electron image; (b) back-scattered electron image; (c) concentration profile; (d) back-scattered electron image of the substrate at interface.

contrast difference seen in the back-scattered electron image (Fig. 19.10b,c). Figure 19.10d shows a diffusion layer from the start of the substrate. The substrate itself has a coarse grain lamellar structure, which may be formed from the coarse grains of β -Ti upon cooling. The columnar structure is formed at the near interface region, with a concentration of aluminium about 50 at.% after annealing at 1100 °C. There is a layer with fine lamellar structure between the columnar and coarse lamellar grains.

Thus, recrystallisation of the titanium/aluminium coating also starts at temperatures above 880 °C, as α -Ti to β -Ti transformation in the substrate

happens (Fig. 19.9). Formation of microcracks on heating up to 1000 °C can be a result of a strong stress being developed because of crystallographic differences between the multilayered coating and the substrate. Recrystallisation of the near surface region of the substrate, caused by the change in aluminium concentration, can lead to partial stress relaxation. Increase of atom mobility with an increase of annealing temperature results in healing microcracks.

The distinction between the aluminium and the titanium/aluminium coatings produced by MA is that the aluminide phases in the titanium/aluminium coating are formed successively during the annealing treatment (Table 19.1), similar to the titanium samples coated by the aluminium film (Romankov *et al.*, 2006, 2007). However, in the case of Romankov *et al.* (2006, 2007), Ti₃Al starts decomposing only after the decomposition of TiAl. In the case of the titanium/aluminium coating here, the volume fraction of Ti₃Al decreases dramatically, while TiAl does not decompose completely (Fig. 19.4b). The differences in structural formation and its transformation between aluminium and titanium/aluminium coatings during annealing treatments may be related to the thickness of the coatings. On the other hand, the presence of titanium particles in the as-synthesised titanium/aluminium coating may have some effect on the thermodynamics of the reactions. The powders of pure titanium and aluminium are mixed in the proportion for TiAl compound. Upon heating, aluminium mainly reacted with titanium in the titanium/aluminium coating forming aluminide phases. As a result, release of aluminium and its diffusion into the substrate may be restrained. TiAl compound is stabilised up to 1100 °C. Interdiffusion growth of aluminide phases can dominate at the substrate/coating interface. Interdiffusion gives a good apparent adherence to the substrate on heating up to 1100 °C (Fig. 19.10). However, the dynamics of interdiffusion growth may slow down in the direction of the coating surface. Also, after treatment at 1100 °C, adherence to the substrate is better for the titanium/aluminium coating than for the aluminium one (Figs. 19.5 and 19.10), which can be related with the thickness and structures of the coatings.

19.5 Summary

By means of the mechanical alloying method, aluminium and titanium/aluminium coatings can be deposited on titanium alloys. During MA processing, aluminium is better deposited on the surface in the presence of titanium particles. The MA technique produces titanium/aluminium coatings with a thickness of 200 µm and aluminium ones with a thickness of 50 µm after two-hours milling at room temperature. The titanium and aluminium coating consists of titanium particles in the aluminium matrix. As-synthesised coatings show structures with high apparent density and free of porosity. However, the surface morphology of the MA-coatings is very rough. Annealing treatment leads to levelling of the surface microstructure. Recrystallisation of the coatings

starts at temperatures above 880 °C, as α -Ti to β -Ti transformation in the substrate happens. Annealing at temperatures ranging between 600 and 1100 °C gives different aluminide phases on the surface. In the case of the aluminium coating, Al_3Ti and Ti_3Al are formed upon heating up to 1100 °C. In the case of the titanium/aluminium coating, Al_3Ti , Al_2Ti , TiAl and Ti_3Al are formed on the surface. After heating at 1100 °C, the titanium and aluminium coating shows a multilayered structure with high apparent density, free of porosity, and a good adherence to the substrate.

Thus, the MA method allows the production of very thick Ti–Al coatings after a relatively short time at room temperature. No special milling atmosphere is required. Ti–Al intermetallic coatings can be produced by subsequent annealing treatment. The MA method is likely to be useful for the fabrication of other diffusion coatings as well.

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