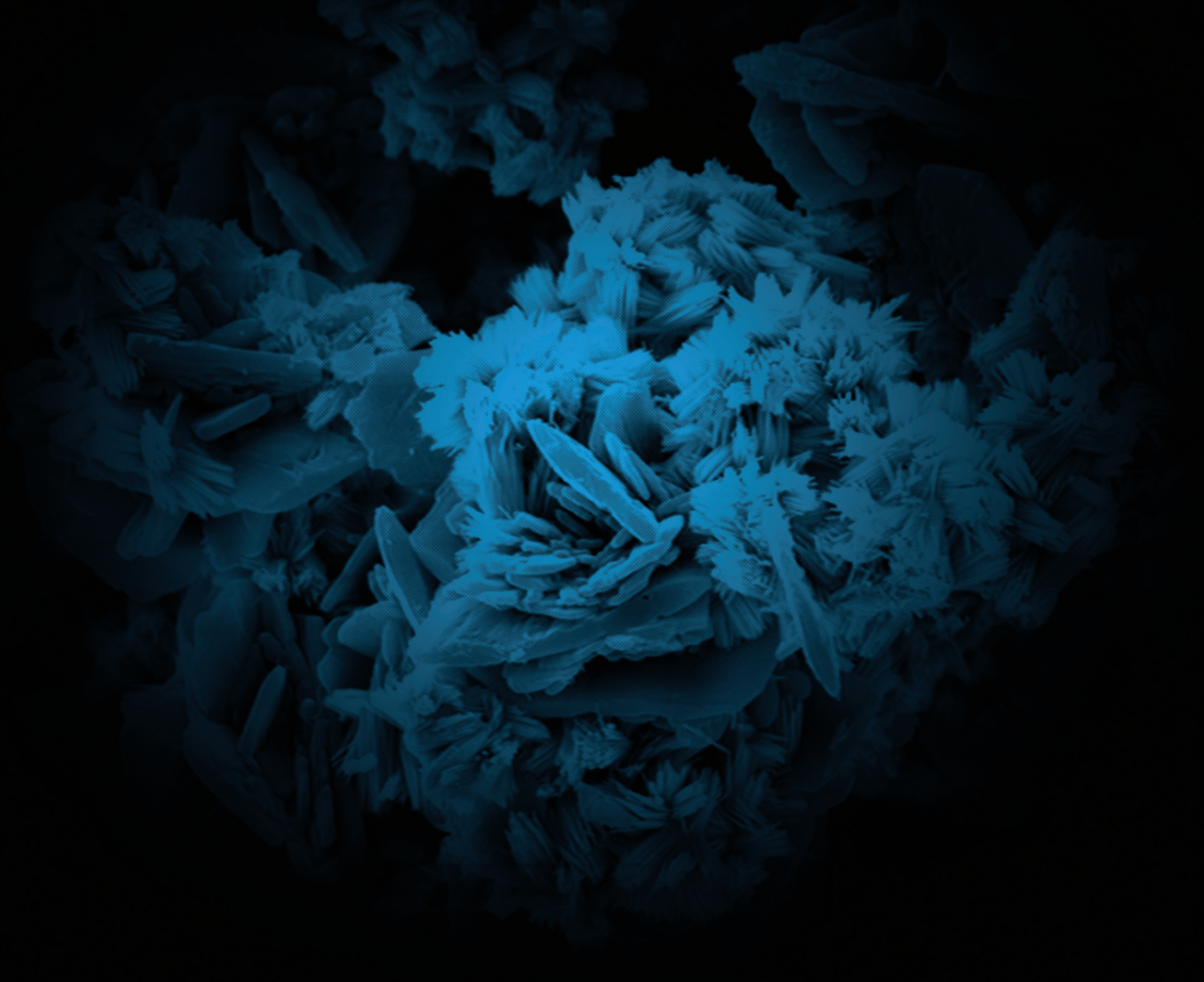




Material Science and Metallurgy

Parashivamurthy K. I.

MATERIAL SCIENCE AND METALLURGY

K. I. Parashivamurthy

Professor and Head
Department of Mechanical Engineering
Government Engineering College
Chamarajanagara
Karnataka

PEARSON

Chennai • Delhi • Chandigarh

Copyright © 2012 Dorling Kindersley (India) Pvt. Ltd

Licensees of Pearson Education in South Asia

No part of this eBook may be used or reproduced in any manner whatsoever without the publisher's prior written consent.

This eBook may or may not include all assets that were part of the print version. The publisher reserves the right to remove any material present in this eBook at any time.

ISBN 9788131761625

eISBN 9789332509634

Head Office: A-8(A), Sector 62, Knowledge Boulevard, 7th Floor, NOIDA 201 309, India
Registered Office: 11 Local Shopping Centre, Panchsheel Park, New Delhi 110 017, India

Dedicated to my mother, Smt. Rudramma,
and my father, Sri. lyannappa

This page is intentionally left blank.

Brief Contents

Preface	xvii
Acknowledgements	xvii
About the Author	xix
1. Atomic Structure	1
2. Crystal Structure	13
3. Crystal Imperfections	39
4. Atomic Diffusion	50
5. Mechanical Behaviour of Metals	63
6. Fracture	86
7. Creep	94
8. Fatigue	104
9. Solidification of Metals and Alloys	113
10. Solid Solutions	122
11. Phase Diagrams	127
12. Iron Carbon Equilibrium Diagram	147
13. Isothermal and Continuous Cooling Transformation Diagrams	158
14. Heat Treatment	167
15. Composite Materials	188
16. Properties of Ferrous and Non-ferrous Materials	213
17. Powder Metallurgy	227
18. Ceramic Materials	236
19. Corrosion of Metals and Alloys	245
Index	259

This page is intentionally left blank.

Contents

Preface	xvii
Acknowledgements	xvii
About the Author	xix
1. Atomic Structure	1
1.1 Present Theory of Atom	1
1.2 Quantum States	3
1.2.1 Quantum Numbers	4
1.3 Electronic Configuration	5
1.3.1 Principle of Minimum Energy	5
1.3.2 Pauli's Exclusion Principle	6
1.4 Forces of Attraction	6
1.4.1 Primary Forces of Attraction (Chemical Bond)	7
1.5 Secondary Bonds (van der Waals Forces)	9
<i>Exercises</i>	10
<i>Objective-type Questions</i>	10
2. Crystal Structure	13
2.1 Crystal (Space) Lattice and Unit Cell	14
2.2 Crystal Systems	15
2.3 Structures of Common Metallic Materials	17
2.3.1 Body-centred Cubic (BCC) Structure	18
2.3.2 Face-centred Cubic (FCC) Structure	20
2.3.3 Hexagonal Closed-packed (HCP) Structure	22
2.4 Crystallographic Planes and Directions	25
2.4.1 Miller Indices for Planes	25
2.4.2 Miller Indices of Direction	27
2.5 Miller Bravais Indices	28
2.6 X-ray Diffractions	30
2.6.1 Bragg's Law	30
2.7 Methods to Determine Crystal Structure	32
2.7.1 Laue Back Reflection Method	32
2.7.2 Rotating Crystal Method	33
2.7.3 Debye-Scherrer or Powder Method	33
<i>Exercises</i>	35
<i>Objective-type Questions</i>	36

3. Crystal Imperfections	39
3.1 Classification of Imperfections (Based on Geometry)	39
3.1.1 Point Imperfections	40
3.1.2 Line Imperfections	43
3.1.3 Surface Imperfections	45
3.2 Volume Imperfections (Stacking Fault)	47
Exercises	47
Objective-type Questions	47
4. Atomic Diffusion	50
4.1 Diffusion Mechanisms	51
4.2 Types of Diffusion	52
4.3 Fick's Laws of Diffusion	53
4.3.1 Fick's First Law of Diffusion—Steady-state Diffusion	53
4.3.2 Fick's Second Law—Unsteady-state Diffusion	54
4.4 Activation Energy for Diffusion (Arrhenius Equation)	56
4.5 Factors Affecting Diffusion	59
4.5.1 Temperature	59
4.5.2 Crystal Structure	59
4.5.3 Concentration Gradient	59
4.5.4 Crystal Imperfection	59
4.5.5 Grain Size	59
4.6 Applications of Diffusion	59
Exercises	60
Objective-type Questions	60
5. Mechanical Behaviour of Metals	63
5.1 Stress and Strain	63
5.1.1 Stress	63
5.1.2 Strain	63
5.2 True Stress–Strain Curves	64
5.2.1 True Stress	64
5.2.2 True Strain	64
5.3 Deformation of Metals	65
5.3.1 Types of Metal Deformation	65
Exercises	82
Objective-type Questions	84
6. Fracture	86
6.1 Ductile Fracture	86
6.2 Brittle Fracture (Cleavage Fracture)	88
6.3 Theoretical Cohesive Strength of Materials	89

6.4 Griffith's Theory of Brittle Fracture 90

Exercises 92

Objective-type Questions 92

7. Creep

94

7.1 Creep Curve 94

7.1.1 Primary Creep 95

7.1.2 Secondary or Steady-state Creep 95

7.1.3 Tertiary or Viscous Creep 95

7.2 Effect of Temperature on Creep Deformation (Low Temperature and High Temperature Creep) 95

7.3 Transient Creep 96

7.4 Viscous Creep 96

7.5 Mechanism of Creep 97

7.5.1 Dislocation Climb 97

7.5.2 Sliding of Grain Boundary 97

7.5.3 Diffusion of Vacancy 98

7.6 Creep Properties 98

7.7 Creep Fracture 98

7.8 Elastic After-effect (an Elastic Behaviour or Delayed Elastic) 99

7.8.1 Stress Relaxation 99

7.9 Creep Testing 100

7.10 Factors Affecting Creep 101

Exercises 101

Objective-type Questions 102

8. Fatigue

104

8.1 Types of Fatigue Loading 105

8.1.1 Completely Reversed Loading 105

8.1.2 Repeated Loading 105

8.1.3 Irregular Loading 106

8.2 Mechanism of Fatigue Failure 106

8.2.1 Orowan's Theory 107

8.2.2 Wood's Theory 107

8.2.3 Cottrell and Hull Theory 107

8.3 Fatigue Properties 108

8.4 S-N Diagram 108

8.5 Factors Affecting Fatigue 108

8.6 Fatigue Test 109

8.7 Fatigue Fracture 110

Exercises 110

Objective-type Questions 111

9. Solidification of Metals and Alloys 113

- 9.1 Mechanism of Solidification of Metals 113
- 9.2 Nucleation 114
 - 9.2.1 Homogenous or Self-nucleation 114
 - 9.2.2 Heterogeneous Nucleation 116
- 9.3 Crystal Growth 117
- 9.4 Dendrite Growth 117
 - 9.4.1 Volume Shrinkage 118
- 9.5 Effect of Super-cooling or Under-cooling on Critical Radius of a Nucleus 118
- 9.6 Casting Metal Structure 119
- Exercises 119*
- Objective-type Questions 119*

10. Solid Solutions 122

- 10.1 Solid Solutions 122
- 10.2 Substitutional Solid Solution 123
 - 10.2.1 Disordered Substitutional Solid Solution 123
 - 10.2.2 Ordered Substitutional Solid Solution 123
 - 10.2.3 Hume Rothery's Rule 124
- 10.3 Interstitial Solid Solution 124
 - 10.3.1 Metallic Compounds (Intermediate Phases) 125
- Exercises 125*
- Objective-type Questions 125*

11. Phase Diagrams 127

- 11.1 Cooling Curves 127
 - 11.1.1 Cooling Curve for Pure Metals or Solidification of Pure Metals 128
 - 11.1.2 Cooling Curve for Binary Alloy 128
- 11.2 Construction of Phase Diagram 129
- 11.3 Interpretation of Phase Diagram 130
 - 11.3.1 Prediction of Phase 130
 - 11.3.2 Prediction of Chemical Composition of Different Phases for a Given Temperature 131
 - 11.3.3 Prediction of Amount of Phase (Lever-arm Rule) 131
- 11.4 Gibbs Phase Rule 132
- 11.5 Classification of Phase Diagrams 134
 - 11.5.1 According to Number of Components in the System 134
 - 11.5.2 According to Solubility of Components 134
- 11.6 Liquid and Solid-state Transformation 140
 - 11.6.1 Eutectic Reaction (Transformation) 140

11.6.2	Peritectic Reaction	140
11.6.3	Eutectoid Reaction	141
11.6.4	Peritectoid Reaction	142
11.7	Complex Alloy Systems	142
11.8	Ternary Phase Diagram	143
	<i>Exercises</i>	143
	<i>Objective-type Questions</i>	145

12. Iron Carbon Equilibrium Diagram

147

12.1	Solidification of Pure Iron (Constitution of Iron or Allotropy Modification of Iron)	147
12.2	Iron Carbon Phase Diagram	148
12.3	Phases of Iron Carbide, Phase Diagram	149
12.3.1	δ -Ferrite	149
12.3.2	Austenite	150
12.3.3	Ferrite	150
12.3.4	Cementite	150
12.3.5	Pearlite	150
12.3.6	Ledeburite	150
12.3.7	Solubility of Carbon in Iron	150
12.4	Reaction of Iron Carbon System	151
12.4.1	Peritectic Reaction	151
12.4.2	Eutectoid Reaction	151
12.4.3	Eutectic Reaction	151
12.5	Steels	151
12.5.1	Solidification and Transformation of Hypoeutectoid Steel (0.4% Carbon Steel)	151
12.5.2	Solidification and Transformation of Eutectoid Steel (0.8% Carbon Steel)	152
12.5.3	Solidification and Transformation of Hypereutectoid Steel (1.5% Carbon Steel)	152
12.6	Cast Iron	153
12.6.1	Solidification and Transformation of Hypoeutectic Cast Iron (4% Carbon Cast Iron)	153
12.6.2	Solidification and Transformation of Eutectic Cast Iron (4.33% Carbon Cast Iron)	154
12.6.3	Solidification and Transformation of Hypereutectic Cast Iron (6.23% Carbon Cast Iron)	154
12.7	Critical Temperature of the Iron and Iron Carbon Diagram	154
	<i>Exercises</i>	155
	<i>Objective-type Questions</i>	156

13. Isothermal and Continuous Cooling Transformation Diagrams	158
13.1 Construction of TTT Diagram	158
13.2 Effect of Cooling Rate on TTT Diagram	161
13.2.1 Definitions	162
13.3 Continuous Cooling Transformation (CCT) Curve	162
13.4 Effect of Carbon Content and Alloying Elements	163
<i>Exercises</i>	164
<i>Objective-type Questions</i>	165
14. Heat Treatment	167
14.1 Heat Treatment Purposes	167
14.1.1 Temperature up to which the Metal or Alloy is Heated	168
14.1.2 Length of Time the Metal or Alloy is Held at this Temperature (Holding Time)	168
14.1.3 Rate of Cooling	168
14.1.4 Quenching Media	168
14.2 Heat Treatment of Steel	168
14.2.1 Treatments that Produce Equilibrium Condition	169
14.2.2 Treatments that Produce Nonequilibrium Condition	173
14.3 Martempering (Interrupted Quenching)	175
14.4 Austempering (Isothermal Transformation)	176
14.5 Hardenability	177
14.5.1 Jominy End-quench Tests	177
14.6 Surface Hardening	178
14.6.1 Method in which Whole Component is Heated	178
14.6.2 Method in which only Surface of Component is Heated	180
14.7 Heat Treatment of Nonferrous Metals	182
14.7.1 Precipitation Hardening (Age Hardening)	182
14.7.2 Annealing	184
<i>Exercises</i>	184
<i>Objective-type Questions</i>	185
15. Composite Materials	188
15.1 Particulate Reinforced Composites	189
15.2 Fibre Reinforced Composites	189
15.3 Laminated Composite Material	190
15.4 Polymer Matrix Composites	190
15.5 Metal Matrix Composite	191
15.6 Ceramic Matrix Composites	191
15.7 Agglomerated Composite Material	192

15.8	Manufacturing Methods for Composite Materials	192
15.9	Manufacturing Method for Particulate Reinforced Composites	192
15.9.1	Liquid-state Methods	192
15.9.2	Solid-state Methods	195
15.10	Manufacturing of Fibre-reinforced Polymer Matrix Composites	197
15.10.1	Open Mould Process	197
15.10.2	Closed Mould Process	200
15.11	Manufacture of Laminated Composite	201
15.11.1	Solid-state Bonding of Composite	201
15.12	Mechanical Behaviours of a Composite Material	202
15.12.1	Determination of E_1 (Longitudinal Direction or Iso-strain Condition)	203
15.12.2	Determination of Young's Modulus in the Direction of E_2 (Transverse Direction or Iso-stress Condition)	204
15.12.3	Determination of Poisson's Ratio ν_{12}	206
15.12.4	Determination of G_{12} (Shear Modulus)	206
15.13	Properties of Composite Materials	207
15.14	Advantages of Composites	207
15.15	Limitations of Composites	208
15.16	Applications	208
	<i>Exercises</i>	209
	<i>Objective-type Questions</i>	210

16. Properties of Ferrous and Non-ferrous Materials

213

16.1	Ferrous metals	213
16.1.1	Steels	213
16.1.2	Pig Iron	217
16.1.3	Wrought Iron	218
16.1.4	Cast Iron	218
16.2	Non-ferrous Metals and Alloys	220
16.2.1	Copper and Copper-based Alloys	220
16.2.2	Aluminum and Its Alloys	223
	<i>Exercises</i>	224
	<i>Objective-type Questions</i>	225

17. Powder Metallurgy

227

17.1	Method of Producing Powders	228
17.1.1	Atomization of Molten Metal	228
17.1.2	Electrodeposition	228
17.1.3	Reduction of a Compound	229
17.1.4	Crushing and Milling	229
17.2	Blending of Powder	229
17.3	Compaction (Cold and Hot)	229

17.4	Pre-sintering and Sintering	230
17.5	Finishing Operations	230
17.6	Heat Treatment	230
17.7	Characteristics of Powder and Its Parts	231
17.8	Applications of Some Powder Metallurgy Parts	231
17.9	Advantages of Powder Metallurgy Components	232
17.10	Disadvantages of Powder Metallurgy	232
	<i>Exercises</i>	233
	<i>Objective-type Questions</i>	233

18. Ceramic Materials

236

18.1	Classification of Ceramics	236
18.1.1	Based on Fusing or Melting Temperature	236
18.1.2	Based on Nature of Reaction	237
18.1.3	On the Basis of Chemical Composition of the Refractories	237
18.1.4	Based on the Nature of Materials	237
18.2	Characteristics of Refractories	239
18.3	Properties of Ceramic Materials	239
18.4	Application of Ceramics	239
18.4.1	Traditional Ceramics	239
18.4.2	Industrial Ceramics	240
18.4.3	Automotive Ceramics	240
18.4.4	Tribological Ceramics	241
18.4.5	Conductive Ceramics	241
18.4.6	Nuclear Ceramics	242
18.4.7	Optical Ceramics	242
18.4.8	Pigments	242
	<i>Exercises</i>	242
	<i>Objective-type Questions</i>	243

19. Corrosion of Metals and Alloys

245

19.1	Electrochemical Theory of Corrosion	245
19.2	Galvanic Cell	246
19.3	Electrode Potential	247
19.3.1	Primary Reference Electrode	248
19.3.2	Secondary Reference Electrode	249
19.4	Standard Electrode Potential and Electrochemical Series	250
19.5	Types of Corrosion	251
19.5.1	Uniform Corrosion	251
19.5.2	Galvanic Corrosion	251
19.5.3	Pitting Corrosion	251
19.5.4	Stress Corrosion	252

19.6	Prevention and Control of Corrosion	252
19.6.1	Proper Design and Selection of Metals	253
19.6.2	Change of Environment	253
19.6.3	Change of Metal Potential	253
19.6.4	Protective Coatings	254
19.6.5	Passivation	254
19.7	Metallic Coatings	255
19.7.1	Nickel Plating	255
19.7.2	Chromium Plating	255
19.7.3	Silver Plating	255
19.7.4	Cadmium Plating	256
19.7.5	Gold Plating	256
19.8	Organic Protective Coatings	256
19.9	Disadvantages of Corrosion	256
	<i>Exercises</i>	257
	<i>Objective-type Questions</i>	257

Index

This page is intentionally left blank.

Preface

Material Science and Metallurgy is one of the basic and core subjects for mechanical/industrial engineering and diploma courses. This book is the result of my long experience of teaching the subject, and I hope it will meet the requirements of engineering degree and diploma students. Efforts have been made to present the subject in simple language for better understanding of the students, and the problems have been solved in S.I. units. This book provides a simplified and systematic approach to difficult theoretical concepts in material science and metallurgy and helps the student to pursue an advanced level course later. Importance has been given to the requirement of students by taking all precautions and taking into consideration all the problems that a student may face while studying. It can serve as an excellent reference book for mechanical/industrial engineering and diploma students. I hope that this book will be useful for teaching faculty, students and industrial personnel.

This book contains 19 chapters. Chapters 1 to 8 deal with the fundamentals of material science, Chapters 9 to 16 deal with the basics of metallurgy including heat treatment, Chapters 17 and 18 deal with advanced materials and Chapter 19 deals with the corrosion behaviour of metals and alloys. All the important chapters are covered and hence, it is hoped that this book is very handy and useful to engineering (UG and PG) and diploma students across the country. For any suggestions and comments about this book, please feel free to contact me.

Acknowledgements

I thank Dr Sree Sree Shivakumara Swamiji, President; Sree, Sree Siddalinga Swamiji, Vice President, Siddaganga Math, Tumkur; Dr M. N. Channabasappa, Director; Dr Shivakumaraiah, Principal; Prof. Basavarajaiah, Dean Planning and all ex-colleagues of Siddaganga Institute of Technology, Tumkur; for their constant support and encouragement in writing this book. I thank my wife Smt. Usharani T. G. and my daughter Kum. Chinmayee P. for their support in preparing the draft manuscript. I also thank Dr K. G. Chandrashekara, Principal, and all my colleagues, Government Engineering College, Chamarajanagar, for their support and encouragement. I also thank the publisher, Pearson Education, Chennai, for the neat execution of the book.

K. I. Parashivamurthy

This page is intentionally left blank.

About the Author



K. I. Parashivamurthy obtained his B.E. in Mechanical Engineering during 1990, his M.Tech. in Metal Casting Science and Engineering in 1993 from Bangalore University and his Ph.D. in Ferrous Composite Materials, where he developed titanium carbide reinforced ferrous matrix composites for power plant applications at the Central Power Research Institute (CPRI), Bangalore, Bangalore University, in 2003. He joined as a lecturer in the Department of Mechanical Engineering, Siddaganga Institute of Technology, Tumkur, during 1993 and worked at various capacities like Assistant Professor, Professor and Head of the Department till November 2010. He is currently working as Professor and Head, Department of Mechanical Engineering, Government Engineering College, ChamaraJanagara, Karnataka. He has eighteen years of teaching experience and is actively involved in developing the curriculum of autonomous institutions like Siddaganga Institute of Technology, Tumkur, and M. S. Ramaiah Institute of Technology, Bangalore. He is on the Board of Examiners (BOE) for various autonomous institutions. He has presented/published about twenty research papers, both of international and national repute in journals and conferences. He has attended the *Forum for Material Testing* organized by Zwck/Roell Testing Machines, Ulam, Germany, in 2006. He has participated in the *International Conference on Materials Science & Technology 2007 Conference and Exhibition (MS&T'07)*, September 2007, Detroit, Michigan, the USA.

K. I. Parashivamurthy

This page is intentionally left blank.

Atomic Structure

INTRODUCTION

The uses of various properties of materials are mainly dependent on their structure. It is found that all structural units, large or small, are made up of molecules and atoms. To begin with, the concept of atom has gained strength to explain the properties of materials. In 1809, John Dalton predicted that the matter is composed of smallest particles in the nature called ‘atoms’. These particles in an element are hard, spherical and invisible to the naked eye. Hence, from the famous Dalton’s theory, the term ‘atom’ came into existence with the help of cathode rays. Further, in 1897, J. J. Thomson using cathode rays proved that the matter is made up of small electrons. Each atom consists of electrons which have a fixed negative charge of 1.6021×10^{-19} coulomb (C) and a mass of 9.11×10^{-28} g at rest. The electrons are represented by ‘e’. However, the atoms never have completely negative charge. Therefore, the investigations continued which led to the discovery of a positive part of atom.

Later in 1919, Lord Rutherford discovered the second subatomic particle called ‘proton’. It is represented by ‘H’ and has a mass of 1.00756 atomic mass unit (amu). Proton is heavier than electron by 1,836 times and it possesses the same amount of charge as that carried by an electron. Finally, James Chadwick in 1932 discovered the third particle called the ‘neutron’ which is represented by ‘N’. It is a fundamental particle without any charge. It possesses a mass of 1.008 amu, which is approximately equal to the mass of a proton.

1.1 PRESENT THEORY OF ATOM

Each atom is made up of fundamental or basic particles like nucleus and electrons. The nucleus consists of an equal number of protons and neutrons. It is concentrated in the centre of the atom. It is much smaller than the atom and is approximately 10^{-14} m in diameter. The atomic structure of an atom is shown in Figure 1.1.

2 Atomic Structure

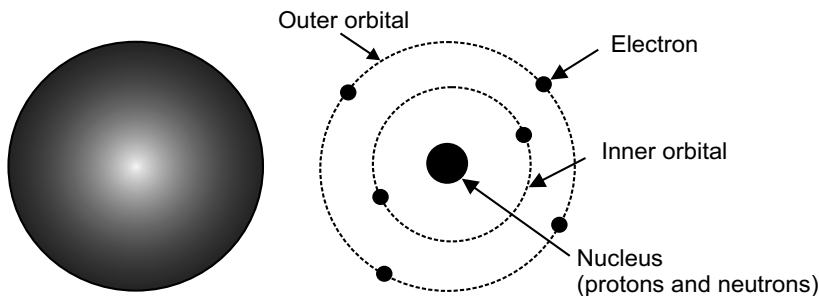


Fig. 1.1 The atomic structure of an atom

Proton has a mass of 1.672×10^{-24} g and charge of $+1.602 \times 10^{-19}$ C. In general, the number of protons in the nucleus is known as the atomic number (Z) for the element. The number of protons in the nucleus determines the charge on the nucleus and, therefore, the identity of the element.

The neutron is another particle within the nucleus. It has an uncharged mass of 1.672×10^{-24} g, slightly greater than that of the proton. The sum of protons and neutrons in the nucleus of an atom is known as the atomic weight or atomic mass number. It is generally expressed by the symbol A . The number of neutrons is equal to the difference between the mass number A and the atomic number Z . When the atoms are neutrally charged, they will have the same number of protons and electrons. The electrostatic charge on an electron is equal in magnitude to that of a proton.

The specific number of molecules in 1 g-mol of a substance, defined as the molecular weight in grams, is called Avogadro's number. This value represents the sum of protons and neutrons necessary to produce mass of 1 g and it is a universal constant having a value of 0.6023×10^{24} per mol.

1 L Hydrogen 1.00794																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 N Oxygen 15.9994	9 O Oxygen 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050											13 Al Aluminium 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfer 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

Fig. 1.2 The periodic table for various elements

An isotope can be defined as an element having atoms of different atomic weights. It is one of two or more species of atoms of a chemical element with the same atomic number and nearly identical chemical behaviour but with different atomic masses and physical properties. Every chemical element has one or more isotopes. For example, carbon has three isotopes C^{12} , C^{13} and C^{14} and all isotopes are identical in structure. Similarly, hydrogen has three isotopes and chlorine has two. The physical, nuclear and radioactive properties are different for different isotopes. Atoms of different elements having the same atomic mass called isobars, e.g. Ar^{40} , K^{40} and Ca^{40} . The chemical nature, the number of electrons and the electronics configuration in the isobars is dissimilar. The elements having equal neutrons in the nucleus are known as isotones, e.g. C^{13} , N^{14} , etc. Figure 1.2 shows the periodic table of elements and the atomic numbers that have been assigned to various elements.

The electron is the most important basic particle of an atom and it has a comparatively less mass of 9.109×10^{-28} g (1/1,836 that of the proton) and a unit charge of -1.602×10^{-19} C, which is equal in magnitude to the charge of each proton, i.e. $+1.602 \times 10^{-19}$ C. The electrons travel in circles around the nucleus in clearly measurable circular or elliptical orbits in which they can remain without any loss of energy. Only those orbits that are characterized by discrete integral quantum numbers are acceptable. The alternative explanation of the location of an electron is in terms of wave equation that specifies the possibility of the electron being at any point in a system which consists of the atom under consideration and all other atoms associated with it.

For a better understanding of an atomic structure, consider C^{12} , the most common isotope of carbon, shown in Figure 1.3. It contains six protons and six neutrons in its nucleus for an atomic mass of 12 amu. Avogadro's number of C^{12} atoms would have a mass of 12 g.

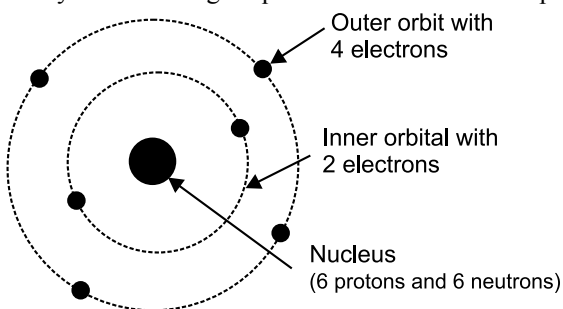


Fig. 1.3 The atomic model for the isotope of Carbon C^{12}

1.2 QUANTUM STATES

The electrons revolve around the nucleus in certain fixed orbits called stationary states or energy levels without the emission of radiant energy (Figure 1.4). These stationary orbits are called principal quantum number (n). The characteristic properties of elements are determined by the energies of the various electrons in its atom. These energies in turn are dependent on these quantum numbers. The energy will be emitted or absorbed only when an electron jumps from one orbit to another. The emission or absorption of energy is not continuous but discrete in the form of small packets of energy called quanta ($h\nu$).

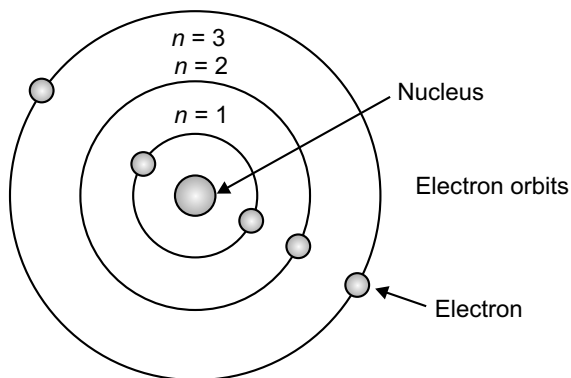


Fig. 1.4 Electron structure of an atom

4 | Atomic Structure

The frequency of the emitted radiation is given by the relationship

$$E_1 - E_2 = h\nu$$

where E_1 is the energy of the higher orbit, E_2 the energy of the lower orbit, h Plank's constant = 6.624×10^{-27} erg-s and ν the frequency of the emitted radiation. This relationship is called Bohr's frequency condition.

According to the electromagnetic theory, the accelerated electron should emit electromagnetic radiation. Therefore, an electron in an orbit will emit radiation. Bohr derived the expressions for energies of various orbits and radii of the circular orbits (quantum numbers) and the relationships are as follows:

Radius of an orbit

$$r = \frac{n^2 h^2}{4\pi^2 m Z e^2}$$

Energy of each orbit

$$E = \frac{2\pi^2 m Z e^4}{n^2 h^2}$$

where n is the correspondence number of the orbit, h Plank's constant (6.63×10^{-27} erg-s), m the mass of the electron (9.109×10^{-28} g), e the charge of the electron (4.8×10^{-10} esu) and Z the atomic number of the atom (element).

Bohr's theory provided a convincing explanation for the frequencies of the various lines obtained in the hydrogen spectrum. It provided a general explanation for the emission and absorption of atomic spectra of the elements. Its contribution is mainly in establishing the concept of quanta numbers. However, it does not explain the spectra of atoms containing more than one electron, fine structure, Zeeman effect and Stark effect.

Modern concept of atomic model, known as wave mechanics (quantum mechanics) model of an atom, explained all the defects by introducing two more quantum numbers called the magnetic quantum number (m) and the spin quantum number (s). This theory has assumed the particle nature and the wave nature of the electron and the Heisenberg's uncertainty principle.

1.2.1 Quantum Numbers

An electron orbital is called quantum state and it has the following quantum numbers. In modern atomic theory, position or state of the electron in an atom is described by four quantum numbers. The four quantum numbers and the values they take may be summarized as in the following subsections.

1.2.1.1 Principle Quantum Number 'n'

The principle quantum number represents the number of main orbits in which the electrons are accommodated.

$$n = 1, 2, 3, \dots, n$$

K, L, M, N, etc. are main shells

The number of electrons that can be accommodated in each shell is given by $2n^2$, where n is the principle quantum number.

1.2.1.2 Secondary or Azimuthal Quantum Number 'l'

$$l = 0, 1, 2, 3, \dots (n-1)$$

s, p, d, f, ... are subshells

The secondary quantum number is also called orbital angular momentum quantum number. It is related to the shape of orbit. The l defines suborbitals which give the subshells. The number of subshells in a given main shell is same as its principal quantum number n .

$n = 1$	K shell	1s
$n = 2$	L shell	2s 2p
$n = 3$	M shell	3s 3p 3d
$n = 4$	N shell	4s 4p 4d 4f and so on

The number of electrons that can be accommodated in each subshell is given by $2(2l + 1)$ where l is the secondary or azimuthal quantum number.

1.2.1.3 Magnetic Quantum Number, $M = +1...0.... -1$

The magnetic quantum number is called 'orientation quantum number' because it gives the orientation or distribution of the electron cloud in the magnetic field. Hence, $l = 0$ and $m = 0$. Therefore, for each value of l , there will be $(2l + 1)$ values of m .

$l = 0,$	$m = 0$
$l = 1,$	$m = +1, 0, -1$
$l = 2,$	$m = +2, +1, 0, -1, -2$

This means that the s-orbital is uniformly distributed around the nucleus. So, the s-orbits are circular. $l = 1, m = +1, 0, -1$. This means that the p-orbital can orient in three directions depending upon the values of m . These orientations of the p-orbital are called p_x, p_y and p_z orbitals and they are all dumbbell shaped.

1.2.1.4 Spin Quantum Number, $s = \frac{1}{2}$ and $-\frac{1}{2}$

The spin quantum number refers to the spin of an electron around the nucleus on its own axis. This quantum number has been introduced to account for the spin. Since an electron can spin in two directions, clockwise and anticlockwise (two opposite directions), there are two possible values of s that are equal and opposite. These two values are $\frac{1}{2}$ and $-\frac{1}{2}$. These spins are also designated by arrows pointing upwards and downwards as $\uparrow\downarrow$ corresponding to $s = \frac{1}{2}$ and $s = -\frac{1}{2}$ respectively.

1.3 ELECTRONIC CONFIGURATION

The filling of orbital by electrons is called electron configuration. It is required that the following rules be adopted.

1.3.1 Principle of Minimum Energy

The principle of minimum energy is explained based on the spectroscopic notation for describing the quantum state of electrons. According to the principle of minimum energy, the incoming electrons initially occupy the lowest energy level first. When this level is completely filled, the next electron goes to the next higher energy state. Hence, orbits are filled in the order of increasing energy. Figure 1.5 gives the order of filling of electrons in an atom. The total capacity of subshells is $s = 2, p = 6, d = 10, f = 14, k = 2, l = 8, m = 18$ and $n = 32$. Therefore, the increasing order is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p and so on.

6 | Atomic Structure

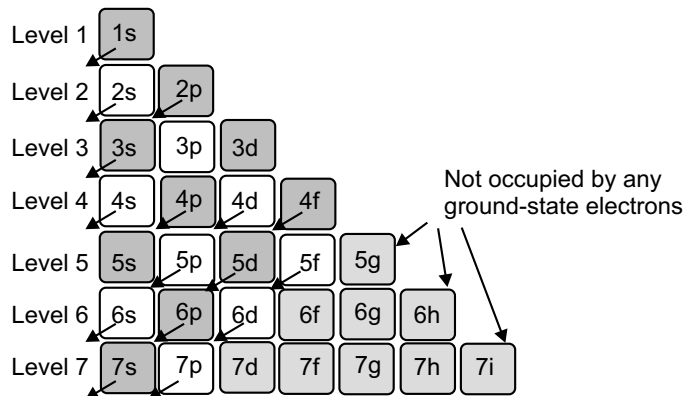


Fig. 1.5 The order of filling of electrons in an orbital

1.3.2 Pauli's Exclusion Principle

Pauli's exclusion principle states that no two electrons can have the same set of values for the four quantum numbers. It means that only one electron can occupy a given quantum state. The maximum number of electrons in any main shell is given by $2n^2$; whereas in a subshell it is given by $2(2l + 1)$.

s-orbital = 2

p-orbital = 6

d-orbital = 10

f-orbital = 14 and so on

Hence, the electron configuration can be written as follows:

	Atomic number	Configuration
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Iron	10	$1s^2 2s^2 2p^6$
Magnesium	12	$1s^2 2s^2 2p^6 2s^2 = [\text{Ne}]^{10} 3s^2$
Argon	18	$[\text{Ne}]^{10} 3s^2 3s^6$
Calcium	20	$[\text{Ar}]^{18} 4s^2$ and so on

1.4 FORCES OF ATTRACTION

The atoms in liquid and solid states are held together by the forces of attraction. Since most of the materials used in engineering are solids and liquids, it is, therefore, desirable to understand the attractions that hold the atoms together. Such interatomic forces between the atoms are referred to as bonds. Without these interatomic and intermolecular forces, all matter would be in gaseous state due to thermal vibration. When a gas condenses to form a liquid or a solid, the pull between the atoms is much stronger than the gravitational force and it is said that the atoms form bonds between one another. Bonding between atoms determines, to a large extent, the physical and electrical properties of solid

materials. Some materials possess greater mechanical strength of their atoms with a strong bonding between each other in lattice.

Various types of bonds arise due to interatomic attractions which are themselves caused by the electron distribution (or structure) of the atoms. So, these forces of attraction and, thus, the bonds formed can be divided into two: (1) primary forces of attraction and (2) secondary forces of attraction.

1.4.1 Primary Forces of Attraction (Chemical Bond)

The primary bond, also known as a chemical bond, is the strongest bond between the atoms and can be further divided into three groups:

1. Ionic or electrostatic bonds
2. Covalent bonds
3. Metallic bonds

These bonds are distinguished on the basis of the positions assumed by the bonding electrons during the formation bond.

1.4.1.1 Ionic Bond

The electrostatic attraction between the oppositely charged ions is called the ionic bond. In the ionic bond, the atoms should have low ionization energy, i.e. only a small amount of energy should be needed to pull out an electron from its outer energy level. The ionic bond is the simplest bond established between two atoms by an electron transfer. It results from the mutual attraction of positive and negative charges. It is formed when the outermost orbit electrons of one atom are transferred to another atom. The ionic bond is formed when the atoms involved lose or gain electrons to stabilize their outer electron shell configuration. The other atom should be able to accept the electron in its outer energy level readily, i.e. the atom should have high electron affinity value.

An example of simple ionic bond formation is sodium chloride:

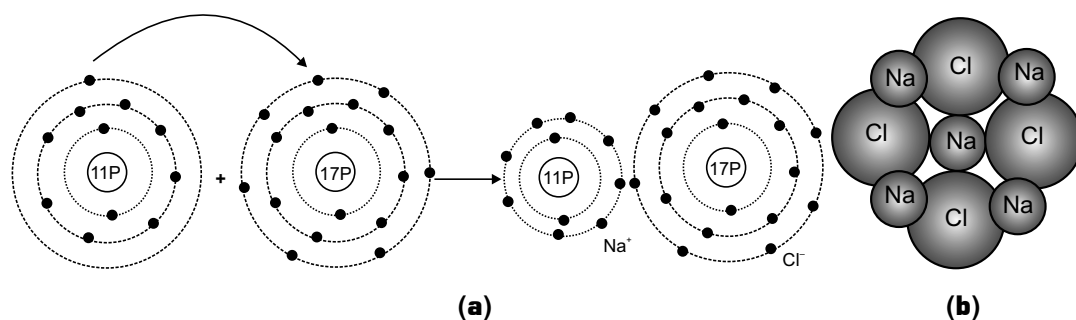
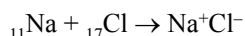


Fig. 1.6 (a) Electron transfer from sodium to chlorine and (b) three-dimensional structure of sodium chloride

Figure 1.6(a) and (b) shows the ionic bond of NaCl. The atomic number of Na is 11 and that of chlorine is 17. For stable configuration of both atoms, sodium donates an electron whereas chlorine accepts the electron. Thereby, sodium becomes sodium ion and chlorine atom becomes chlorine ion. The electrostatic attraction between sodium and chlorine ions gives rise to an ionic bond. The

8 | Atomic Structure

major condition in ionic bonded materials is that the number of positive charges equals the number of negative charges. Thus, the composition of sodium chloride is NaCl, magnesium chloride is MgCl_2 , lithium chloride is LiCl, magnesium sulphide is MgS, magnesium fluoride is MgF_2 and so on. The tendency to lose or gain electrons is one basis for classifying elements as metals or nonmetals. Metals generally lose electrons and non-metals gain them.

1.4.1.2 Covalent Bond

The covalent bond is formed when electrons of an atom of outermost orbits are shared by the electrons of outermost orbit of the other atom. An electron pair bond is formed when pairs of electrons are shared by several atoms, so that the shared electrons can contribute towards the stable electron structure for each of the sharing atoms. So, covalent bond is not electrostatic in nature. The compounds thus obtained are called covalent compounds. For example, $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$

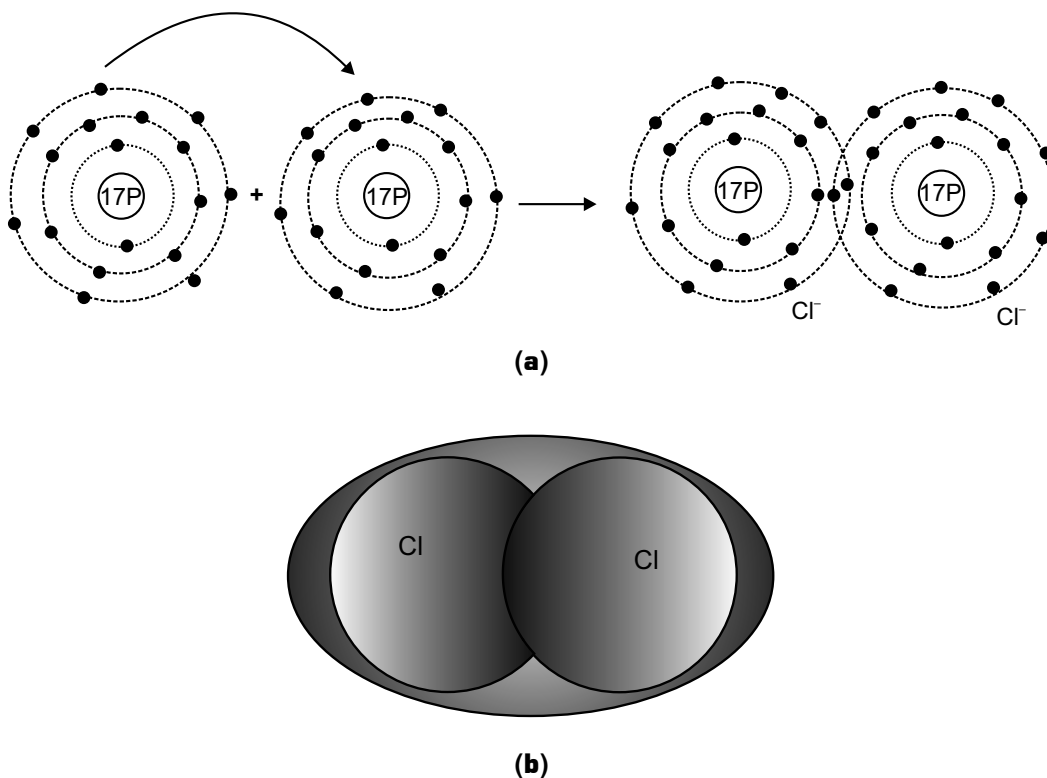


Fig. 1.7 (a) Electron sharing in chlorine and (b) three-dimensional covalent bond in chlorine

Figure 1.7(a) and (b) shows a covalent molecule of chlorine. The atomic number of chlorine is 17. It has 17 electrons in its orbits and has only 7 electrons in the outermost orbit. Therefore, it requires one electron to become stable configuration. Two chlorine atoms share one electron to produce covalent-bonded chlorine molecule. Stable covalent bonds formed in the solid state, particularly in engineering materials, include many of the organic compounds like plastics, rubber, paint, dyes, etc.

1.4.1.3 Metallic Bond

The metallic bond is formed by valency electrons to move freely from one atom to another by electron sharing in metals. It is defined as the force that binds a metal atom to a number of electrons within its sphere of influence. The metal atoms have freely held outermost energy level like a sea or a cloud of electrons in which metal ions are embedded. The metallic bond is developed due to the attraction between the positive metal ion and the electron cloud.

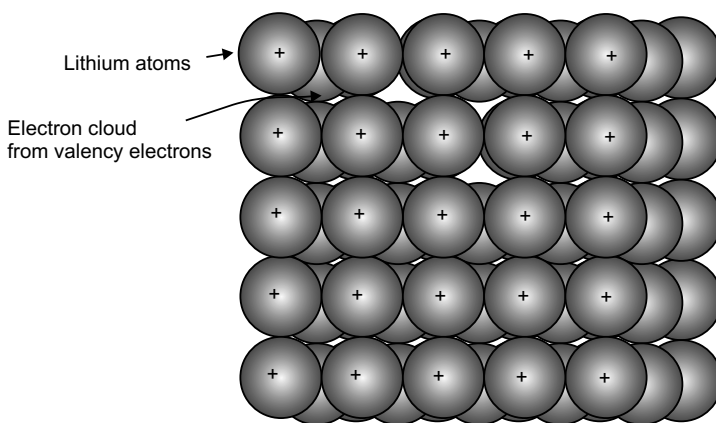


Fig. 1.8 Three-dimensional structure of lithium metal in metallic bond

Consider the case of lithium. It has only one electron in the outermost shell with its electron configuration of $1s^2 2s^1$. X-ray analysis shows that each lithium atom is surrounded by eight other lithium atoms. It is not possible for one lithium atom to get bonded to eight other atoms through covalent bonds, as it contains only one valance electron. However, it has four valance orbits ($2s$, $2p_x$, $2p_y$ and $2p_z$). Hence, the valence electrons of all the neighbouring atoms come close to one another and they all move around the centre of each lithium atom in the vacant valency orbital. In most cases, the outermost electron shell of each of the metal atoms overlaps with a large number of neighbouring atoms. As a result, the valence electrons continuously move from one atom to another and are not connected with any specific pair of atoms. These electrons are more or less free to travel through the solid and are responsible for the metallic bond.

In short, the valence electrons in metals, unlike those in covalently bonded substances, are nonlocalized, that is, they are capable of wandering relatively freely throughout the entire crystal. The atoms that the electrons leave behind become positive ions, and the interaction between such ions and the valence electrons gives rise to the binding force that holds the metallic crystal together.

The metals are ductile and malleable due to the atoms without any change in their position. This is a result of external force with respect to the surrounding cloud of electrons. Thus, the metals can behave in a definite ductile fashion under stress because a group of positive ions break their bonding at one location, slip to a new position and establish their bonds.

1.5 SECONDARY BONDS (VAN DER WAALS FORCES)

van der Waals forces is the result of mutual interaction of electrons and nuclei of molecules or atoms. Secondary bonds are weak forces of electrostatic forces of attraction between the atoms. These

10 | Atomic Structure

forces constitute forces of attraction as well as forces of repulsion when the atoms approach the particular boundary limit. These secondary bonds are also called van der Waals forces or intermolecular forces of attraction. The inert gas condenses to form solids at sufficiently low temperature although they are not expected to form any of these bonds. Similarly, in case of CH_4 (methane), CO_2 and H_2SO_4 , no spare electrons are available for forming the bonds to solidify. The type of bond exhibited by them is called secondary bond. These bonds are weak when compared to primary bonds, but are still important in determining the certain physical characteristics of materials such as plastics, graphite and paraffin.

EXERCISES

1. Give a brief history of the development of atomic concept.
2. Describe atomic number and atomic weight.
3. State and explain proton, neutron and electron.
4. State and describe isotopes, isobars and isotones.
5. Name the three different particles of which the atoms are composed off.
6. Describe the modern concept of atom.
7. What is meant by quantum number?
8. What is electron configuration? Write electron configurations for iron, magnesium and calcium.
9. Describe the principle of minimum energy in an atom.
10. State and explain Pauli's exclusion principle.
11. Explain the electronic configurations in atoms.
12. Write a note on the significance of quantum number.
13. Explain ionic bond with an example and a neat diagram.
14. What is meant by secondary forces of attraction? Explain in detail.
15. State and explain the primary forces of attraction and describe the covalent bond.
16. Describe metallic bond with a neat diagram.

OBJECTIVE -TYPE QUESTIONS

1. The elemental proton was discovered by _____.
(a) Johan Dalton (b) Lord Rutherford
(c) J. J. Thomson (d) Bohr
2. Proton has a mass of _____.
(a) 1.786×10^{-24} (b) 1.136×10^{-24}
(c) 1.672×10^{-24} (d) 1.726×10^{-24}
3. The atomic number Z indicates _____.
(a) Number of protons in the atom (b) Number of protons and electrons
(c) Number of protons and neutrons (d) None of the above

4. The atomic mass of an atom is _____.
(a) Sum of protons, neutrons and electrons
(b) Sum of protons and electrons
(c) Sum of neutrons and electrons
(d) Sum of protons and neutrons
5. Maximum number of electrons in the n th main energy level of an atom is _____.
(a) $\sqrt{n^2}$
(b) $2n^2$
(c) $n\sqrt{2}$
(d) $2\sqrt{n}$
6. In secondary quantum number $l = n - 1$. If $n = 3$, _____.
(a) M shell and subshell 2p 3s 3d
(b) M shell and subshell 2s 3p 3d
(c) M shell and subshell is 3s 3p 3d
(d) M shell and subshell 2p 3s 3d
7. Principle of minimum energy state that _____.
(a) Incoming electrons occupy the highest energy level first
(b) Incoming electrons occupy the lowest energy level first
(c) Incoming electrons occupy the middle position of energy level first
(d) None of the above
8. The particle which is electrically neutral is _____.
(a) Neutron
(b) Proton
(c) Electron
(d) Nucleus
9. Electrons revolve around the nucleus and they will spin on their own axes in two directions. These are _____.
(a) Two electrons rotate in opposite directions
(b) Two electrons rotate in the same direction
(c) Both (a) and (b)
(d) None of the above
10. Energy will be emitted when an electron _____.
(a) Never jumps from one orbit to the other
(b) Jumps from lower orbit to higher orbit
(c) Jumps from higher orbit to lower orbit
(d) None of the above
11. Electron configuration for iron is _____.
(a) $1s^2 2s^1 2p^6$
(b) $1s^2 2s^2 sp^8$
(c) $1s^2 2s^2 2p^1$
(d) $1s^2 2s^2 2p^6$
12. The maximum number of electrons in any main shell is given by $2n^2$, whereas in a subshell it is given by $2(2l + 1)$. Therefore, the total number of electrons in d orbital is _____.
(a) 10
(b) 12
(c) 04
(d) 14
13. Electrons in an ionic bond _____.
(a) Transfer from one atom to the other
(b) Share between atoms
(c) Few electrons are shared and few are transferred
(d) None of the above

12 | Atomic Structure

14. Example for an ionic bond is _____.
(a) NaCl (b) Cl₂
(c) H₂ (d) Plastic
15. Metallic bond is produced by _____.
(a) Electron transferring in metals
(b) Movement of electron from one atom to another by electron sharing in metals
(c) Both (a) and (b)
(d) None of the above

ANSWERS

1.	b	2.	c	3.	a	4.	d	5.	b	6.	c
7.	b	8.	a	9.	a	10.	c	11.	d	12.	a
13.	b	14.	a	15.	a						

Crystal Structure

INTRODUCTION

The engineering materials are aggregate of atoms, which bind to one another in a regular pattern. Their properties mainly depend upon the nature of the atom and on the manner in which the atoms are assembled. Crystallography is the study of the arrangement and dispersion of atoms within the solid. Solids are generally classified into crystalline solids and amorphous (noncrystalline solids) solids (Figure 2.1).

In a crystalline solid, the atoms are arranged in a definite pattern constantly repeated in three dimensions. Therefore, the crystalline solids have a definite geometrical configuration, characteristic of the substance. Each atom is fixed at a definite angular orientation and is at a definite distance to all other atoms surrounding it. These arrangements are responsible for rigidity, definite volume, diffusion and melting point. Some examples of crystalline solids are aluminium, copper and iron.

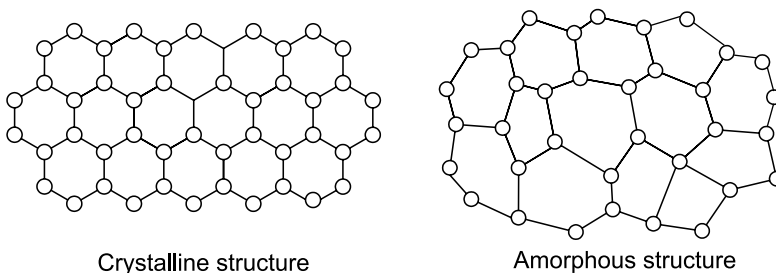


Fig. 2.1 Crystalline and amorphous structures of a solid

Amorphous solids have no definite geometrical form and no regularity in the arrangement of atoms in a solid state. The internal structure is not based on a regular repetition pattern. Although they are rigid and incompressible, they do not have sharp melting points. Examples of amorphous solids include glass, ceramic, rubber, bakelite and cellulose.

2.1 CRYSTAL (SPACE) LATTICE AND UNIT CELL

The atoms of crystals are arranged in repeating three-dimensional patterns. An array of atoms is arranged in definite angular arrangement of the space positions called space lattice or crystal lattice. The repeating patterns in crystals are due to atomic coordination within the material which contribute to the physical shape of the crystal as shown in Figure 2.2.

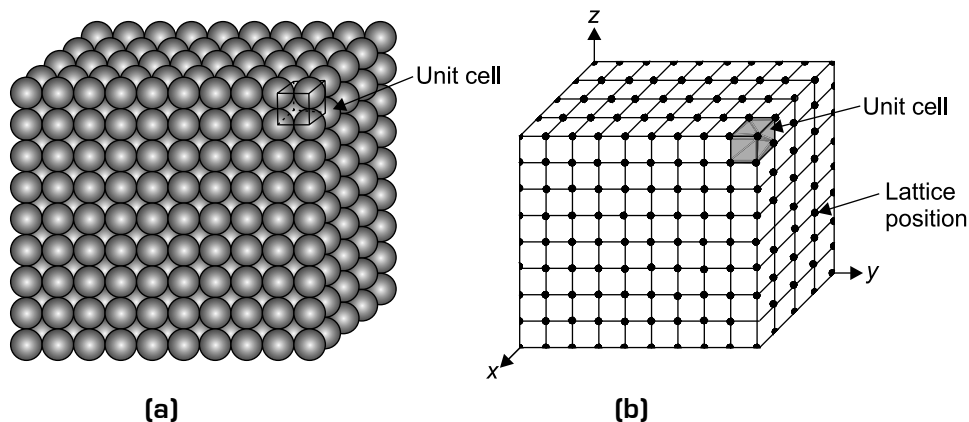


Fig. 2.2 Space lattice of a solid: (a) Three-dimensional structure and (b) skeleton structure

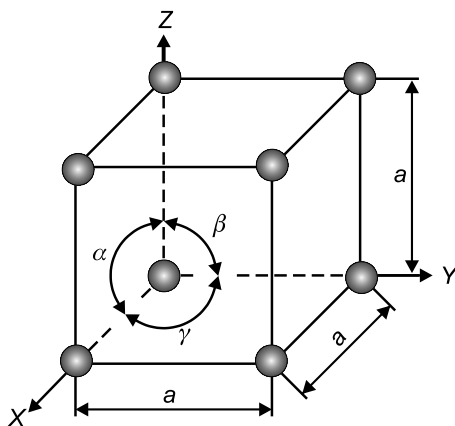


Fig. 2.3 The unit cell of a lattice

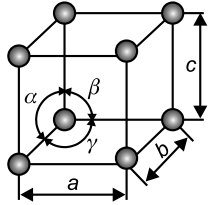
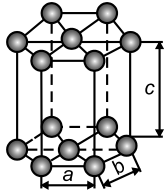
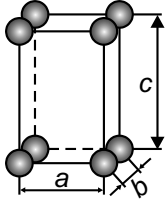
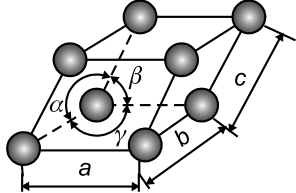
The smallest portion of a crystal lattice that can be used to describe the lattice is called the unit cell and is shown in Figure 2.3. It represents the space lattice as a whole since it is identical with every other cell in the lattice. It can be constructed by joining unit cell repeatedly in three dimensions. The lattices of various metals differ in the size and shape of their unit cells.

The size and shape of the unit cell can be described by the three vectors of the magnitude $\vec{a}$, $\vec{b}$ and $\vec{c}$ drawn from one corner of the cell called crystallographic axis. The angles between them, i.e. α , β and γ , which subtended with the axis are called 'interfacial angles'. These lengths and angles are called 'lattice parameters' or 'lattice constants' of the unit cell. The dimensions of the space lattice,

given by lattice constants in Angstroms ($1 \text{ \AA} = 10^{-10} \text{ m}$), represent the distances between the parallel planes of atoms comprising the unit cell and the angles α , β and γ is expressed in degrees or radians. The lattice parameters may or may not be equal. In fact, this gives rise to the formation of different crystal systems.

2.2 CRYSTAL SYSTEMS

The atoms coordinate with neighbours to form a solid with specific patterns. These patterns are in seven crystal systems. A. J. Bravais, a French mathematician, showed that there could be only 14 basic unit cells associated with the seven crystal systems. These 14 lattices are popularly known as Bravais lattices and are shown in Figure 2.4(a) and (b).

Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	

(Contd)

(Contd)

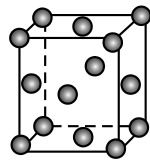
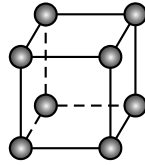
Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

(a)

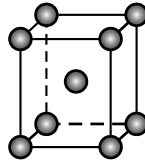
Simple monoclinic	End-centred monoclinic	Triclinic	Hexagonal
Rhombohedral	Simple orthorhombic	Body-centred orthorhombic	End-centred orthorhombic

(Contd)

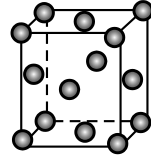
(Contd)

Face-centred
orthorhombic

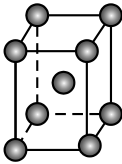
Simple cubic



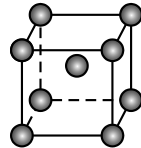
Body-centred cubic



Face-centred cubic



Simple tetragonal

Body-centred
Tetragonal

(b)

Fig. 2.4 (a) Bravais lattice of seven crystal systems and (b) Bravais 14 lattice structure

2.3 STRUCTURES OF COMMON METALLIC MATERIALS

In metals, the arrangement of the atoms is highly symmetrical with dense packing. The common types of unit cells with which the metallic elements crystallize are as follows:

1. Body-centred cubic (BCC)
2. Face-centred cubic (FCC)
3. Hexagonal close-packed (HCP)

Some concepts are useful in understanding the structure of the materials. The fundamental quantities used to describe this crystal structure are as follows:

1. **Atomic Radius:** It is defined as half the distance between the nearest atoms in a crystal.
2. **Coordination Number:** An atom in a crystalline structure is surrounded by many other atoms and the number of atoms surrounding a central atom is definite. The coordination number is the number of nearest atoms surrounding the given atom. The greater the coordination number, the more closely packed will be the structure.
3. **Density Packing Factor:** It is the ratio of volume occupied by the atoms in a unit cell to the total volume of unit cell. It is also called packing factor. $PF = v/V$, where v is the volume of atoms in the unit cell and V is the volume of the unit cell.

2.3.1 Body-centred Cubic (BCC) Structure

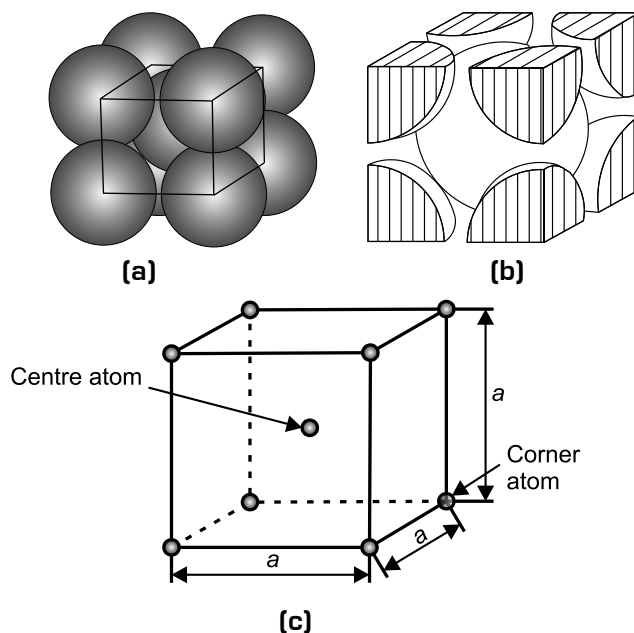


Fig. 2.5 (a) Three-dimensional BCC structure lattice, (b) cut section of a unit cell and (c) skeleton view of a BCC structure

The BCC structure is shown in Figure 2.5(a) through (c). In the BCC lattice, there are eight atoms at eight corners of the unit cell and one atom at the body centre. The central atom is surrounded by eight equidistant neighbours' atoms and each corner atom is shared by other adjoining eight cubes. This type of unit cell is found in metals like iron, magnesium, tungsten and chromium.

Coordination Number: For any corner atom of the BCC unit cell, the nearest atoms are the body-centred atoms. There are eight unit cells in neighbours with eight body-centred atoms. Hence, the coordination number for a BCC structure is 8 atoms.

Atomic Radius: In a BCC structure, the atoms touch each other along the diagonal of the cube. The diagonal in this cube is $4r$.

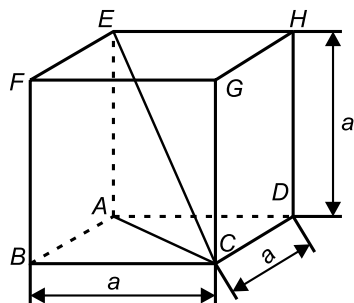


Fig. 2.6 The unit cell of a BCC

But from triangle ABC (see Figure 2.6)

$$AC^2 = BC^2 + BA^2$$

$$AC^2 = a^2 + a^2$$

$$AC^2 = 2a^2$$

From triangle AEC

$$EC^2 = AC^2 + AE^2 = 2a^2 + a^2 = 3a^2$$

$$EC^2 = 3a^2, \text{ Also } EC = 4r$$

$$\therefore (4r)^2 = 3a^2$$

$$16r^2 = 3a^2$$

$$r^2 = \frac{3a^2}{16}$$

$$r = \frac{a\sqrt{3}}{4}$$

Atoms/Unit Cell: The unit cell of a cube contains eight atoms at the corners, which are shared by the eight adjoining cubes and one atom at the centre of the cube (Figure 2.5(c)). Hence, the atoms per unit cell are as follows:

$$8 \text{ atoms at the corner} \times \frac{1}{8} = 1 \text{ atom}$$

$$1 \text{ centre atom in the unit cell} = 1 \text{ atom}$$

$$\text{Total} = 2 \text{ atoms}$$

Density Packing Factor: It can be defined as ratio of volume of atoms/unit cell to volume of unit cell.

$$\text{Atomic packing factor} = \frac{\text{Volume of atoms/unit cell}}{\text{Volume of unit cell}}$$

$$\text{Volume of atoms per unit cell} = \text{Number of atoms} \times \frac{4\pi r^3}{3}$$

The BCC structure consists of a total of 2 atoms per unit cell

$$\text{Volume of atoms per unit cell} = 2 \times \frac{4\pi r^3}{3}$$

Also,

$$r = \frac{a\sqrt{3}}{4}$$

$$= \frac{8}{3} \pi \left(\frac{a\sqrt{3}}{4} \right)^3 = \frac{\pi a^3 \sqrt{3}}{8}$$

$$\text{Volume of unit cell} = a^3$$

$$\text{Packing factor} = \frac{\frac{\pi a^3 \sqrt{3}}{8}}{a^3} = \frac{\pi \sqrt{3}}{8}$$

$$\text{PF} = 0.68$$

The packing factor of the BCC centre cell will be 68%.

Problem 2.1

Iron has a BCC crystal structure with an atomic radius of 0.124 nm. Its atomic weight is 55.85 g/mol. Calculate and compare its theoretical density with the experimental value which is 7.87 g/cm³.

Solution

$$\text{Atomic radius} = 0.124 \text{ nm or } 1.24 \text{ \AA}$$

$$\text{Atomic weight} = 55.85 \text{ g/mol}$$

$$\text{Gram/atom} = \frac{55.85}{0.602 \times 10^{24}}$$

$$\text{Density} = \frac{\text{Mass/unit cell}}{\text{Volume/unit cell}} = \frac{\frac{\text{Atoms}}{\text{unit cell}} \times \frac{\text{Gram}}{\text{atom}}}{a^3}$$

$$\text{For BCC crystal structure } r = \frac{a\sqrt{3}}{4}$$

$$a = \frac{4r}{\sqrt{3}} = \frac{4 \times 1.24}{\sqrt{3}} = 2.86 \text{ \AA}$$

In a BCC crystal structure, there are 2 atoms per unit cell.

Therefore,

$$\text{Density} = \frac{2 \times \frac{55.85}{0.602 \times 10^{24}}}{(2.86)^3 \times 10^{-24}} = 7.89 \text{ g/cm}^3$$

Theoretical density of iron is almost equal to the experimental value.

2.3.2 Face-centred Cubic (FCC) Structure

The FCC lattice has 14 atoms of which 8 are located at the corner of the cube and 6 at the centre of the side face. The packing in this lattice is more compact than in the BCC lattice as indicated in Figure 2.7 (a) through (c). This type of unit cell is found in metals like copper, silver, gold and aluminium.

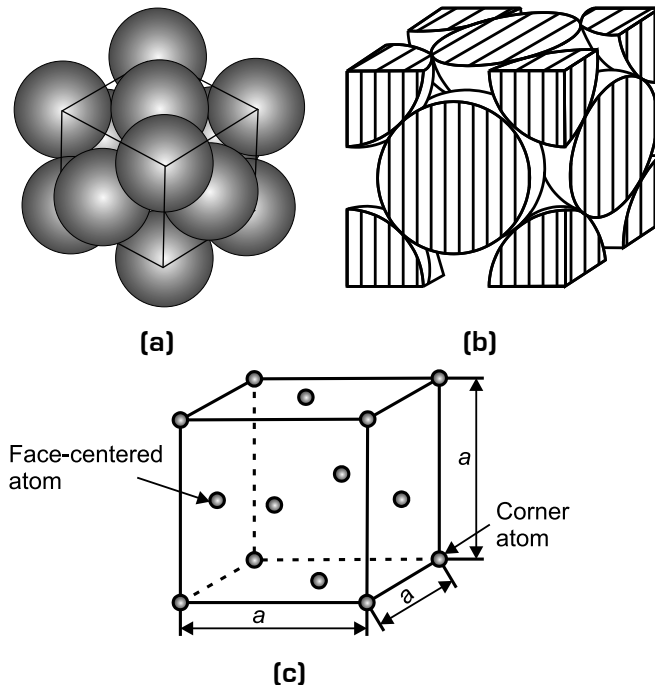


Fig. 2.7 (a) Three-dimensional FCC structure lattice, (b) cut section of a unit cell and (c) skeleton view of an FCC structure

Coordination Number: In an FCC structure, there are eight atoms, one atom each at the corner of the unit cell and one atom at the centre of each face. For any corner atom of the unit cell, the nearest atoms are face-centred atoms. Thus, the coordination number for an FCC structure = 4 centre atoms below the horizontal plane + 4 centre atoms above the horizontal plane + 4 centre atoms on the horizontal plane.

Hence, the coordination number for an FCC structure is $4 + 4 + 4 = 12$ atoms.

Atomic Radius: Figure 2.7(a) and (b) shows that the atoms touch each other along the diagonal of any face of the cube.

The length of the diagonal of the face is $4r$.

From the triangle BCD (see Figure 2.8)

$$BD^2 = BC^2 + CD^2$$

$$BD^2 = a^2 + a^2 = 2a^2$$

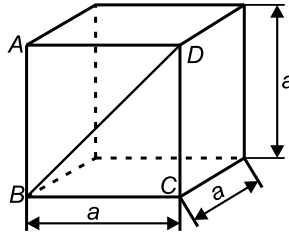


Fig. 2.8 The unit cell of an FCC

$$\begin{aligned}\text{Also, } BD &= 4r \\ (4r)^2 &= 2a^2 \\ 16r^2 &= 2a^2 \\ r^2 &= \frac{2a^2}{16} \\ r &= \frac{a\sqrt{2}}{4}\end{aligned}$$

Atoms per Unit Cell: In the FCC crystal structure, there are eight atoms, one at the each corner of the cube and six face-centred atoms of the six planes of the cube. Corner atoms are shared by eight adjacent cubes and the face atoms by two adjacent cubes. So the total number of atoms in a FCC unit cell will be

$$\begin{aligned}8 \text{ atoms at the corner} \times \frac{1}{8} &= 1 \text{ atom} \\ 6 \text{ face-centred atom in the unit cell} \times \frac{1}{6} &= 3 \text{ atoms} \\ \text{Total} &= 4 \text{ atoms}\end{aligned}$$

Density packing factor

$$\text{Density of packing:} = \frac{\text{Volume of atoms/unit cell}}{\text{Volume of unit cell}}$$

$$\text{Volume of atoms per unit cell} = \text{Number of atoms} \times \frac{4\pi r^3}{3}$$

The FCC structure consists of a total of 4 atoms per unit cell.

$$\text{Volume of atoms per unit cell} = 4 \times \frac{4\pi r^3}{3}$$

$$4 \times \frac{4}{3} \pi \left(\frac{a\sqrt{2}}{4} \right)^3 = \frac{16}{3} \times \pi \left(\frac{a^3 \times 2 \times \sqrt{2}}{64} \right) = \frac{\pi \sqrt{2} a^3}{6}$$

$$\text{Volume of unit cell} = a^3$$

$$\text{Packing factor} = \frac{\pi \sqrt{2} a^3 / 6}{a^3} = \frac{\pi \sqrt{2}}{6} = 0.74$$

The atomic packing factor of an FCC structure is 74%.

Problem 2.2

If the atomic radius of aluminium is 0.143 nm, calculate the volume of its unit cell in cubic metres.

Solution

Radius $r = 0.143 \text{ nm}$ or $1.43 \times 10^{-10} \text{ m}$.

Aluminium consists of an FCC crystal structure and an atomic radius $r = \frac{a\sqrt{2}}{4}$

or

$$a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.43 \times 10^{-10}}{\sqrt{2}} = 4.04465 \times 10^{-10} \text{ m}.$$

$$\text{Volume of the unit cell} = a^3 = 6.6167 \times 10^{-29} \text{ m}^3.$$

Problem 2.3

Iridium has an FCC crystal structure with density of 22.4 g/cm³ and an atomic weight of 192.2 g/mol. Calculate the radius of an iridium atom.

Solution

$$\text{Density} = \frac{\text{Mass/unit cell}}{\text{Volume/unit cell}} = \frac{\frac{\text{Atoms}}{\text{unit cell}} \times \frac{\text{Gram}}{\text{atom}}}{a^3} = \frac{4 \times \frac{192.2}{0.602 \times 10^{24}}}{\left(\frac{4r}{\sqrt{2}}\right)^3 \times 10^{-24}}$$

$$22.4 = \frac{1.277 \times 10^{-21}}{2.2627 \times 10^{-23} r^3}$$

$$r^3 = 2.5196$$

$$r = 1.36 \text{ \AA} \text{ or } 0.136 \text{ nm.}$$

2.3.3 Hexagonal Closed-Packed (HCP) Structure

The hexagonal close-packed structure consists of one atom each at the all corners of the hexagonal unit cell, one atom each at the centre of the two hexagonal planes and three atoms in the centre of the unit cell in a triangular fashion such that one atom lies in alternate triangular prisms as shown in Figure 2.9(a) through (d).

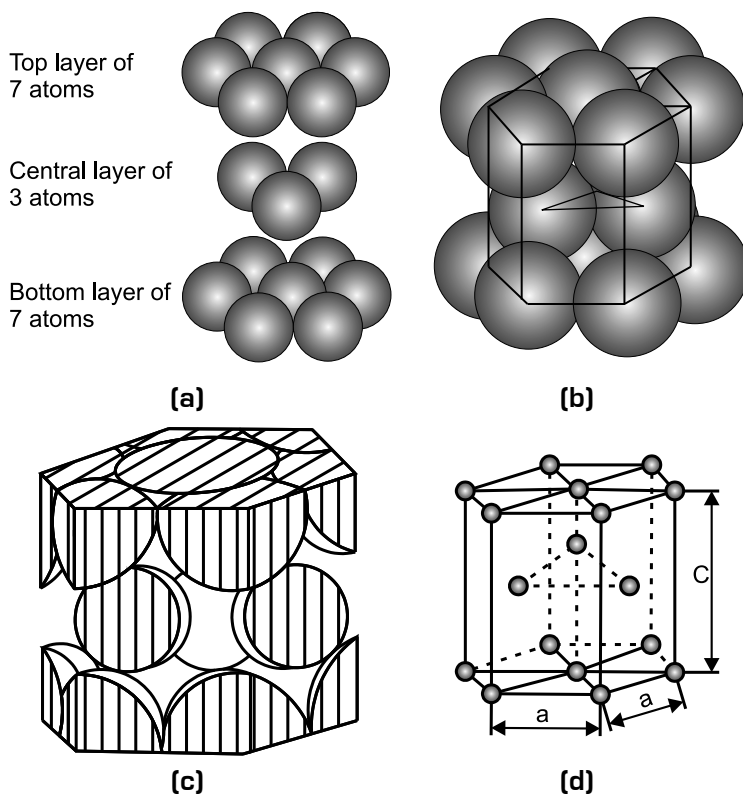


Fig. 2.9 (a) and (b) Three-dimensional hexagonal structure lattice (c) Cut section of a unit cell and (d) Skeleton view of face hexagonal structure

Coordination Number: Consider the bottom layer. The central atom has 6 nearest atoms in the same plane. Further, at a distance of $c/2$, there are top and bottom layers each having 3 atoms touching

the central atom. Therefore, in total, there are 6 atoms on the horizontal plane, 3 atoms above the plane and 3 atoms below the plane. Hence, the coordination number for the HCC structure is 12 atoms.

Atomic Radius: In the HCP structure, corner atoms touch each other.

Atomic radius for HCP = $a/2$ of sphere.

Atoms per Unit Cell: Each corner atom is shared by the six adjacent unit cells and the hexagonal face centred atoms are shared by the two adjacent unit cells. The atoms at the centre of the unit cell are not shared by any unit cells.

Consider the top layer, which has totally 7 atoms. Each corner atom contributes $\frac{1}{6}$ atoms to the unit cell and the centre atom contributes $\frac{1}{2}$ the atom to the unit cell.

Total contribution of the top layer = $6 \times \frac{1}{6} \times \frac{1}{2} = \frac{3}{2}$.

Similarly, the bottom layer also contributes $3/2$ atoms.

The central layer contributes 3 atoms, because all the central layer atoms are well inside the unit cell.

Total number of atoms in the unit cell = $\frac{3}{2} + \frac{3}{2} + 3 = 6$ atoms.

Atomic Distance or c/a in Hexagonal Packed Structure

Let c be the height of the unit cell and a the distance between two neighbouring atoms. The base of the regular HCP structure is made up of 6 equilateral triangles, and consider $\triangle ABO$ in the bottom layer of the HCP structure.

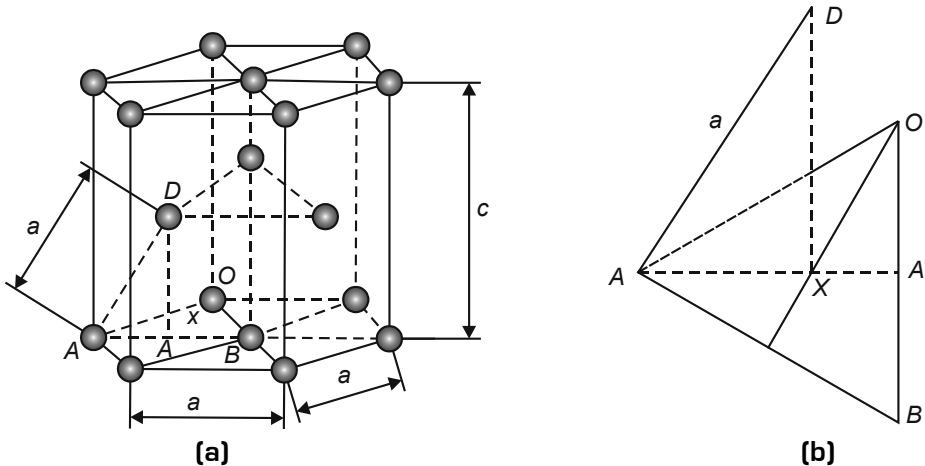


Fig. 2.10 Miller indices on the plane $ABCD$ of the cube: (a) hexagonal lattice with base six equilateral triangles and (b) vertical height between centers of triangle to one of the atom at the center layer

From Figure 2.10,

$$\cos 30 = \frac{AA'}{AB}, AA' = AB \cos 30 = a \times \frac{\sqrt{3}}{2} = \frac{a\sqrt{3}}{2}$$

$$\text{But, } Ax = \frac{2}{3} AA' = \frac{2}{3} \times \frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$

In $\triangle AxO$

$$AD^2 = Ax^2 + Dx^2$$

$$Dx^2 = AD^2 - Ax^2 = a^2 - \left(\frac{a}{\sqrt{3}}\right)^2 = a^2 - \frac{a^2}{3} = \frac{3a^2 - a^2}{3} = \frac{2a^2}{3}$$

$$\text{But, } Dx = \frac{c}{2}$$

24 | Crystal Structure

$$\left(\frac{c}{a}\right)^2 = \frac{2a^2}{3}$$

$$\left(\frac{c}{a}\right)^2 = \frac{4 \times 2}{3}$$

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

Density of Packing:

$$\text{Density of packing} = \frac{\text{Volume of atoms/unit cell}}{\text{Volume of unit cell}}$$

$$\text{Volume of atoms per unit cell} = \text{No. of atoms} \times \frac{4\pi r^3}{3}$$

The HCP structure consists of a total of 6 atoms per unit cell

$$\text{Volume of atoms per unit cell} = 6 \times \frac{4\pi r^3}{3} = 8\pi r^3$$

$$\text{Volume of unit cell} = \text{Area of the hexagon} \times C$$

$$= 6 \times \text{area of } \triangle ABO \times C$$

$$= 6 \times \frac{1}{2} OO' \times OB \times c$$

$$= 6 \times \frac{1}{2} \times a \times \frac{\sqrt{3}}{2} \times OB \times c$$

$$= 6 \times \frac{1}{2} \times a \times \frac{\sqrt{3}}{2} \times a \times c \quad \because BO = a$$

$$= 3 \times \frac{\sqrt{3}}{2} \times a^2 \times c$$

$$\text{Packing factor} = \frac{8\pi r^3}{\frac{3\sqrt{3}a^2}{2} \times C}$$

$$\text{But, } 2r = a \text{ and } \frac{c}{a} = 1.633$$

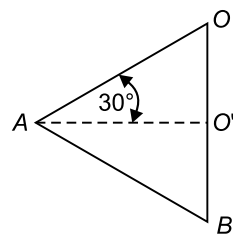
$$\text{Packing factor} = \frac{8\pi r^3}{\frac{3\sqrt{3}}{2} \times (2r^2) \times \frac{c}{a} \times a}$$

$$\text{Packing factor} = \frac{8\pi r^3}{\frac{3\sqrt{3}}{2} \times (2r^2) \times 1.633 \times (2r)}$$

$$\text{Packing factor} = \frac{8\pi r^3}{3 \times \sqrt{3} \times 1.633 \times 4 \times r^3}$$

$$\text{Packing factor} = 0.74$$

The atomic packing factor of HCP structure is 74%.



$$\cos 30 = \frac{OO'}{AB}$$

$$OO' = AB \cos 30$$

$$OO' = a \times \frac{\sqrt{3}}{2}$$

Problem 2.4

Titanium has an HCP crystal structure and a density of 4.51 g/cm³.

1. What is the volume of its unit cell in cubic metres?
2. If the c/a ratio is 1.58, compute the values of c and a .

Solution

$$\text{Density} = \frac{\text{Mass/unit cell}}{\text{Volume/unit cell}} = \frac{\frac{\text{Atoms}}{\text{unit cell}} \times \frac{\text{Gram}}{\text{atom}}}{a^3}$$

$$4.51 = \frac{6 \times \frac{46.67}{0.602 \times 10^{24}}}{a^3 \times 10^{-24}}$$

$$a^3 = 1.06 \times 10^{-28} \text{ m}^3$$

Volume of the unit cell is $= 1.06 \times 10^{-28} \text{ m}^3$

Also, $a = 4.6896 \times 10^{-10} \text{ m}$

$A = 4.6896 \text{ \AA}$

If $\frac{c}{a} = 1.58$

$c = 1.58 \times a$

$c = 1.58 \times 4.6896$

$= 7.409 \text{ \AA}$

Problem 2.5

Copper has an FCC structure and an atom radius of $1.278 \text{ \AA}$. Calculate its density. The atomic weight of copper is 63.54 and the Avogadro number is 0.602×10^{24} .

Solution

$R = 0.128 \text{ nm}$ ($1.28 \text{ \AA}$)

Atomic weight = 63.5 g/mol

Number of atoms per unit FCC unit cell is 4

Volume of unit cell $= a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = \left(\frac{4 \times 1.278}{\sqrt{2}}\right)^3 = 3.614 \text{ \AA}$

$$\text{Density} = \frac{\frac{4 \times 63.5}{0.602 \times 10^{24}}}{(3.614)^3 \times 10^{-24}} = 8.938 \text{ g/cm}^3$$

The density of copper is 8.94 g/cm^3 .

2.4 CRYSTALLOGRAPHIC PLANES AND DIRECTIONS**2.4.1 Miller Indices for Planes**

In 1839, W.H. Miller, an English crystallographer, put forward a method to identify the planes in a lattice. Some symbols can be used to describe the orientation of atoms in the crystal lattice. The orientation in space of any particular plane with respect to the axis can be specified and can be symbolically represented. This method is popularly known as Miller indices.

Miller indices are the system of notations, which denote the orientation of the crystallographic planes of atoms in a crystal, represented by a set of three numbers. Miller indices are defined as the reciprocal of the rational fractional intercepts which the plane makes with the crystallographic axes and are represented in terms of h , k and l values corresponding to $\vec{a}$, $\vec{b}$ and $\vec{c}$ vectors along x , y and z axes. Both the fractions and infinity are eliminated.

The intercepts m , n and p of any significant plane within a crystal may be represented as reciprocal intercepts in the form of $1/m$, $1/n$ and $1/p$. These fractions have a common denominator q , which is a small integer, and they can be reduced to the value of h/q , k/q and l/q , where $h = q/m$, $k = q/n$ and $l = q/p$. The numerical values of (h, k, l) so derived are always either whole numbers or zero. By omitting the common denominator q , h, k, l may be stated as (hkl) , the miller indices of the plane.

In a cube, the axes are the three coordinates x, y and z that can be fixed originating from the origin. Then the Miller indices of any plane are obtained by noting the intercept of that plane about the x, y and z axes respectively in terms of unit length.

A specific plane cannot be identified by its Miller indices. It should be done by a linear measurement in a specified direction from some fixed point as reference.

2.4.1.1 Procedure for Finding Miller Indices

The procedure for finding Miller indices is as follows:

- 1. Select the origin of reference as some point, which is outside the plane of rest so that intercept zero is avoided.
- 2. Determine the intercepts of the plane on the reference axis in terms of fractions and multiples of unit distances a, b and c along the axis.
- 3. Table the reciprocals of these numbers.
- 4. Reduce the resulting reciprocal to the smallest possible rational fraction, which has a common denominator.
- 5. Omit the common denominator and enclose the numbers of those fractions in brackets to identify them as Miller indices.

Any plane which intercepts an axis on the negative side of the origin has a negative value to that particular intercept and this appears finally as negative Miller indices.

Consider a cubic structure and mark one corner as origin 'O'. Designate the crystal axes as x, y and z originating from the origin. For example, consider Figure 2.10.

The Miller indices for the plane $ABCD$ have to be found. This plane $ABCD$ intercepts only the x -axis at one unit and does not intercept the y and z axes. This plane is parallel to y and z axes. Hence, to find the Miller indices, it is considered that the y and z axes are at infinity. Find the intercept of the plane with respect to x, y and z .

Axis	x	y	z
Intercept	1	∞	∞
Reciprocal	$1/1$	$1/\infty$	$1/\infty$
Miller indices	1	0	0

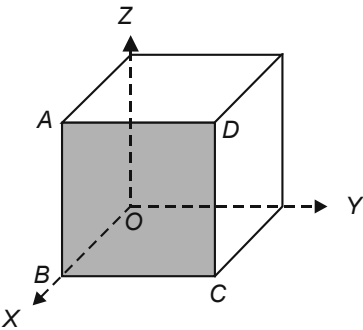


Fig. 2.10 Miller indices on the plane $ABCD$ of the cube

Miller indices of the plane $ABCD$ is (100) .

The Miller indices of any plane are represented by a set of numbers within the ordinary bracket. If the set of numbers is enclosed in a flower bracket like $\{100\}$, it refers to all sets of planes originating from numbers such as $(100) (010) (001)$.

If a plane cuts any axis on the negative side of the origin, the index will be negative. Then it is indicated by writing the negative sign just above the number. For example, consider the plane $PQRS$ shown in Figure 2.11. Since this plane intercepts with the origin, to find out the intercepts of this plane, different axes shift the origin itself as shown in the figure. Then the Miller indices of this plane is as follows:

Axis	x	y	z
Intercept	∞	-1	∞
Reciprocal	$1/\infty$	$-1/1$	$1/\infty$
Miller indices	0	-1	0

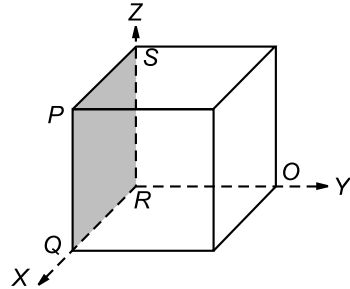


Fig. 2.11 Miller indices on the plane $PQRS$ of the cube

Miller indices of the plane $PQRS$ is $(0\bar{1}0)$

If the Miller indices of a particular plane are in fractions, then the fractions should be cleared as the Miller indices are always represented by a whole number. For example, consider the crystallographic plane PQR as shown in Figure 2.12. The intercepts are 6, 3 and 2 on x , y and z axes respectively. Then the Miller indices are as follows (Figure 2.12):

Axis	x	y	z
Intercept	6	3	2
Reciprocal	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$

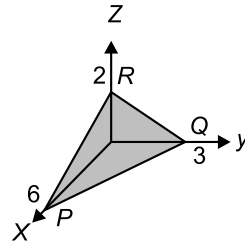


Fig. 2.12 Miller indices on the plane PQR

Take LCM and multiply by 6 throughout

Miller indices	$\frac{1}{6} \times 6$	$\frac{1}{3} \times 6$	$\frac{1}{2} \times 6$
	1	2	3

Miller indices for the plane PQR is (123) .

Common Miller indices are observed when the planes are parallel to each other and are placed on one side of the origin. For example, $(1, 2, 6)$ and $(2, 3, 12)$ are parallel to plane $(6, 3, 1)$.

In a cube crystal, some lattice face like (001) can be considered to be either (100) or (010) by rotating the cube or by rotating the reference axes through a right angle.

2.4.2 Miller Indices of Direction

The indices of direction can be defined as a significant direction of a plane within the space lattice or crystal structure. The crystallographic direction is the line joining of any two lattice points. The Miller

indices and directions are always represented by a set of numbers in a square bracket. The Miller directions can be found by noting the coordinates of the end point with reference to x , y and z axes.

Consider Figure 2.13. The Miller indices for directions are shown as follows:

Consider the crystallographic directions OA , OB and OC as shown in the figure.

Then the Miller indices for the direction are

Line	x	y	z	Miller direction
OA	1	0	1	$[101]$
OB	1	0	0	$[100]$
OC	1	1	1	$[111]$

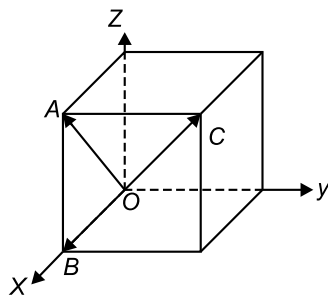


Fig. 2.13 The Miller indices for direction

2.5 MILLER BRAVAIS INDICES

Miller Bravais indices are the notations used to represent the crystallographic planes and directions in the hexagonal lattice. In this system, four axes are considered as the reference axes, i.e. three coplanar axes, a_1 , a_2 and a_3 , and a perpendicular axis passing through the centre as shown in Figure 2.14.

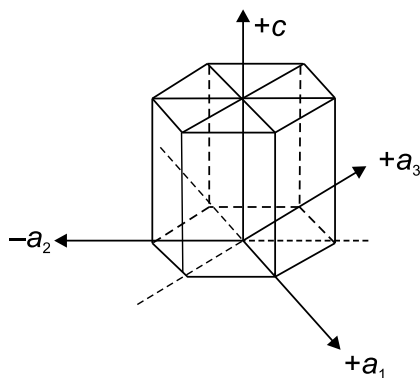


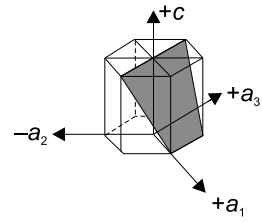
Fig. 2.14 Miller Bravais indices

The Miller Bravais indices for the planes are as follows.

	a_1	a_2	a_3	c
Intercepts	1	1	∞	1
Reciprocals	1/2	1/1	1/ ∞	1/1
	1	1	0	1

Miller Bravais indices

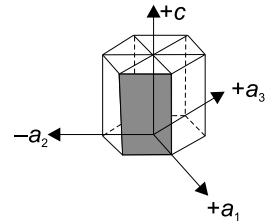
1101



	a_1	a_2	a_3	c
Intercepts	1	∞	-1	∞
Reciprocals	1/1	1/ ∞	-1/1	1/ ∞
	1	0	-1	0

Miller Bravais indices

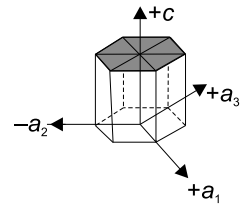
$10\bar{1}0$



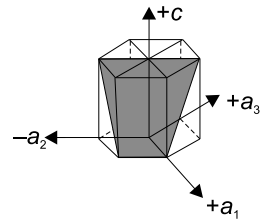
	a_1	a_2	a_3	c
Intercepts	∞	∞	∞	1
Reciprocals	1/ ∞	1/ ∞	-1/ ∞	1
	0	0	0	1

Miller Bravais indices

0001



Axis	a_1	a_2	a_3	c
Intercept	1	∞	-1	1
Reciprocal	1/1	1/ ∞	-1/1	1/1
MBI	1	0	-1	1



Miller Bravais indices is $(10\bar{1}1)$.

2.6 X-RAY DIFFRACTIONS

The crystals can have infinite numbers of atoms arranged in a three-dimensional pattern repeatedly and produce rows of planes of high atomic density. These high-density atoms act as dimensional diffraction grating for x-rays. Any crystal will have an interatomic spacing of the order of 1 or 2 Å. The x-rays used in x-ray diffraction usually have the wavelengths of the order of 1–3 Å. The wavelengths of x-rays almost equal the interatomic spacing of metals and hence the x-rays are diffracted by crystals.

When the x-rays fall on the crystal structure with a known frequency, the atoms interacting with the electrons start vibrating with the frequency of x-rays and redirect the x-rays with no change in frequency. On the basis of Bragg's law, when a parallel beam of x-rays strike the single atomic plane, it is reflected by the atoms and the angle of incidence is equal to the angle of reflection. This angle is called the Bragg's angle. The Bragg's law is based on the assumption of planes that the atoms reflect the x-rays by striking on the crystals.

2.6.1 Bragg's Law

When the x-rays are directed on a crystallographic material, they are deflected by the planes of atoms in the crystals or by the crystallographic planes.

Consider the parallel planes of atoms as shown in Figure 2.15. When x-rays are made to fall on these planes, these are deflected and diffracted back from these planes. The rays may be reflected from the atom at the surface plane or from the sub-surface planes. It means that the x-rays are reflected not only from the surface planes but also from the sub-surface planes as shown in Figure 2.15.

Let a monochromatic beam of x-ray of wavelength λ be incident on the plane at an incident angle θ . Beam of x-rays is reflected at successive layers. Ray number 1 is reflected from atom A in plane 1, whereas ray number 2 is reflected from atom B lying in plane 2. These two reflected rays will be in phase or out of phase with each other depending on their path differences. These path differences can be found by drawing perpendiculars AM and BN on ray number 2.

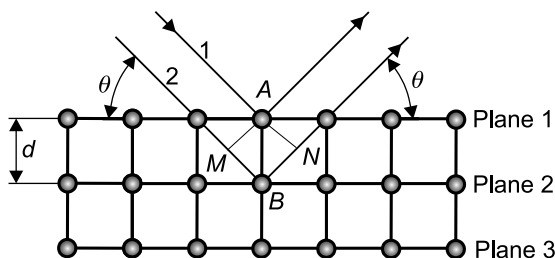


Fig. 2.15 Bragg's law

The ray number 2 travels extra distance $= MB + BN$
 $= d \sin \theta + d \sin \theta = 2d \sin \theta$

The path difference between two successive rays must be equal to an integral number of wavelengths, i.e. $n\lambda = 2d \sin \theta$, where n is an integer, λ the wavelength and d is the interplanar distance.

It is the relation between the wavelength of x-rays and the distance between the crystallographic planes and the angle of incidence. This is known as Bragg's law and it relates the wavelength with that

of the spacing between the crystallographic planes. Each θ in the above equation is associated with a specific set of lattice planes (h, k, l). Thus,

$$n\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}}$$

where $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ and a is the lattice constant.

Problem 2.6

X-rays of a known wavelength are reflected by a total angle of 44.3° in Cu specimen whose lattice constant is $3.615 \text{ \AA}$. Separate determination indicates that this diffraction for copper is of the first order line of d_{111} . Find the wavelength.

Solution

Given that $2\theta = 43.4$, $\theta = 21.7$

$$a = 3.615 \text{ \AA}$$

$$d_{111}, n = 1, \lambda = ?$$

From Bragg's law, $n\lambda = 2d \sin \theta$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{3.615}{\sqrt{1^2 + 1^2 + 1^2}} = 2.087 \text{ \AA}$$

$$1\lambda = 2 \times 2.087 \times \sin 21.7 = 1.541 \text{ \AA}$$

$$\lambda = 1.541 \text{ \AA}$$

Problem 2.7

X-rays with a wavelength of $1.54 \text{ \AA}$ are used to calculate a spacing of (200) plane in aluminium. The Bragg's angle θ is 22.4 . Find the size of the unit cell.

Solution

$$\theta = 22.4, a = ?.$$

Assume that $n = 1$ and $\lambda = 1.54 \text{ \AA}$.

From Bragg's law, $n\lambda = 2d \sin \theta$

$$= 1 \times 1.54 = 2 \times d \times \sin 22.4$$

$$d = 2.02 \text{ \AA}$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$2.02 = \frac{a}{\sqrt{2^2 + 0^2 + 0^2}} = 4.04 \text{ \AA}$$

$$a = 4.04 \text{ \AA}$$

Problem 2.8

An x-ray diffraction analysis of a crystal is made by rays of wavelength $0.58 \text{ \AA}$. Reflections are made and are observed at angles of (1) 6.45 , (2) 9.15 and (3) 13 . What interplanar spaces are present in the crystal?

Solution

$$\lambda = 0.58$$

$$1. \theta = 6.45$$

From Bragg's law, $n\lambda = 2d \sin \theta$

$$d = \frac{\lambda}{2 \sin \theta} = \frac{0.58}{2 \sin 6.45} = 2.58 \text{ \AA}$$

$$2. \theta = 9.15$$

$$d = \frac{\lambda}{2n \sin \theta} = \frac{0.58}{2 \sin 9.15} = 1.82 \text{ \AA}$$

$$3. \theta = 13$$

$$d = \frac{\lambda}{2n \sin \theta} = \frac{0.58}{2 \sin 13} = 1.28 \text{ \AA}$$

2.7 METHODS TO DETERMINE CRYSTAL STRUCTURE

The x-ray diffraction method gives details about the crystal size, orientation of the atoms in the crystal and determines whether the crystals distorted or cold worked. The following are the three important methods of determining the crystal structure:

1. Laue back reflection method
2. Rotating crystal method
3. Debye–Scherrer or the powder method

2.7.1 Laue Back Reflection Method

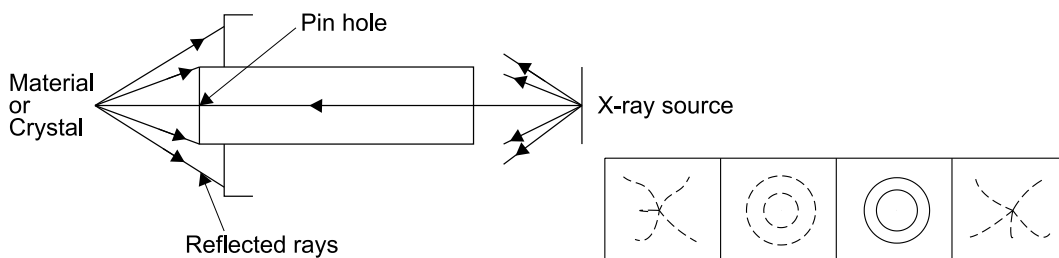


Fig. 2.16 Laue back reflection method

Figure 2.16 shows the Laue back reflection method for determining the crystal structure. When a beam of x-rays is directed on a specimen of metal, at a certain position on the crystallographic planes, the diffraction is towards the back. The image is recorded on the photographic film provided in the apparatus as a series of spots. The interception of the pattern of image obtained on the film gives the crystal structure and other details of the material. Some of the patterns, which are obtained with the corresponding details, are also shown in Figure 2.16.

The Laue back reflection method is used to for single crystal structure as well as for polycrystalline structure.

2.7.2 Rotating Crystal Method

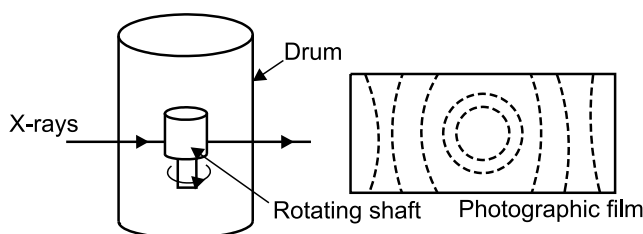


Fig. 2.17 The rotating crystal method

In the rotating crystal method, single crystal is rotated about a fixed axis. When a monochromatic radiation passes through this specimen, the resulting reflections are recorded on a photographic film when monochromatic x-rays fall on the crystal as shown in Figure 2.17. Once the crystal orientation is known, the angles and interplanar distances can be calculated.

This method can be used only for single crystal structure and cannot be used for polycrystalline structure.

2.7.3 Debye–Scherrer or Powder Method

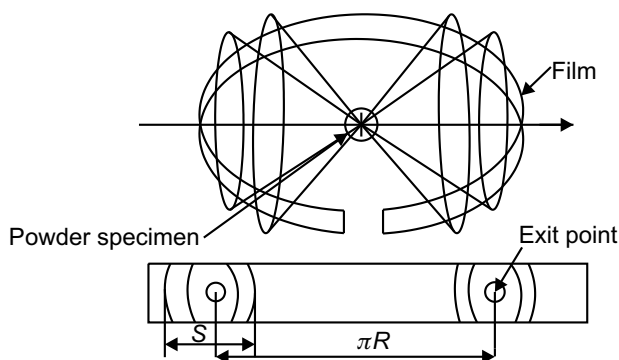


Fig. 2.18 Debye–Scherrer method

In Debye–Scherrer method, a sample of the crystal is crushed into powder and placed in a thin-walled glass tube. A narrow monochromatic x-ray beam is made to impinge the specimen, randomly oriented crystals, in the powder form. The powder specimen is placed at the centre in the capillary tube or pasted on a thin wire. The cameras known as Debye–Scherrer, positioned around the specimen, consist of a cylindrical film castle. The x-ray beam enters through a small aperture in the camera and impinging on the powder specimen gets deflected and reflected from different crystallographic planes and is recorded by the photographic film as a series of lines of varying curvature as shown in Figure 2.18. From the spacing of the lines on the photographic films and the known dimensions of the camera, the angles of the radiation are calculated.

34 | Crystal Structure

$\theta = \frac{n \cdot 90S}{2\pi R}$, where R is the radius of curvature and S is the distance in the film.

θ is related to the spacing of the atomic planes d and the wavelength of x-rays. Then, using the Bragg's law, the size, interplanar spacing, crystal structure, etc. of the crystal can be calculated.

From Bragg's law, $n\lambda = 2d \sin \theta$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$n\lambda = 2 \frac{a}{\sqrt{h^2 + k^2 + l^2}} \sin \theta$$

Let $\sqrt{h^2 + k^2 + l^2} = \sqrt{Q^2}$, then

$$n\lambda = 2 \frac{a}{\sqrt{Q^2}} \sin \theta$$

Consider first-order rays $n = 1$

$$\sin \theta = \frac{\lambda}{2a} \sqrt{Q^2}$$

Let $\left(\frac{\lambda}{2a}\right)^2 = c$, then

$$\sin^2 \theta = Q^2 c$$

The Q^2 values are different for different crystal lattices and are mainly dependent on Q . By finding the ratio of Q^2 values, the crystal lattice structure can be established. It is a widely used experimental technique to determine the crystal structure.

1:2:3:4:5:6:8—Simple cubic structure

1:2:3:4:5:6:7—Body-centre cubic structure

3:4:8:11:12:16—Face-centre cubic structure.

Problem 2.9

From a powder camera of diameter 114.6 mm and using x-rays of wavelength 1.54 Å, the following S values in millimetres are obtained for a material: 86, 100, 148, 180, 188, 232 and 272. Determine the structure and lattice parameters of the metal.

Solution

$$\lambda = 1.54 \text{ Å}, R = d/2 = 114.6/2 = 57.3 \text{ mm}$$

S value	θ	$\sin^2 \theta$	$Q^2 \times c$
86	21.5	0.1346	3×0.0448
100	25	0.1788	4×0.0447
148	37	0.3620	8×0.0452
180	45	0.5003	11×0.0454
188	47	0.5352	12×0.0446
232	58	0.7195	16×0.0449
272	68	0.8596	19×0.0452

The ratio is 3:4:8:11:12:16:19 and hence, the structure is face-centre cubic.

Also, $c = \left(\frac{\lambda}{2a}\right)^2$ For highest angle $\theta = 68$ the corresponding $c = 0.452$.

Therefore, $0.452 = \left(\frac{1.54}{2a}\right)^2$

$$a = 3.62 \text{ \AA}$$

It means that the squares of the sin of the angle at which the reflections occur are in whole numbers. The Q^2 are values are different for different cubic lattice. Each reflecting planar has a corresponding value of Q . By determining the ratios of these Q^2 values, the type of lattice can be found out very easily.

1:2:3:4:5:6:8—Simple cubic structure

1:2:3:4:5:6:7—Body-centre cubic structure

3:4:8:11:12:16—Face-centre cubic structure

Problem 2.10

X-rays of wavelength $1.54 \text{ \AA}$ is used to calculate the spacing of (200) planes in aluminium. The Bragg's angle for this reflection is 22.4 . Find the size of the unit cell of the aluminium crystal?

Solution

$$\lambda = 1.54 \text{ \AA}$$

$$\text{Plane } (h, k, l) = (2, 0, 0)$$

$$\theta = 22.4$$

From Bragg's law, $n\lambda = 2d \sin \theta$. Assume that $n = 1$.

$$\lambda = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin \theta = \frac{2a}{\sqrt{2^2 + 0^2 + 0^2}} \sin 22.4$$

$$1.54 = a \sin 22.4$$

$$a = \frac{1.54}{\sin 22.4} = 4.041 \text{ \AA}$$

EXERCISES

1. Define atomic packing factor. Explain how the packing factor of FCC is greater than that of BCC.
2. Explain the following crystal structures with a neat sketch: (a) body-centred cubic and (b) face-centred cubic.
3. Define atomic packing factor and coordination number and prove from the fundamentals that the atomic packing factor of FCC is greater than that of BCC.
4. For the BCC structure, show that the unit cell edge length a and the atomic radius R are related through $a = \frac{4r}{\sqrt{3}}$.
5. Draw neat sketches of BCC and FCC unit cells and from the fundamentals calculate their atomic packing factors.

36 | Crystal Structure

6. Prove that the atomic packing factor of BCC crystal is greater than that of the simple cubic crystal.
7. Determine the following for FCC and HCP space lattices: basic atoms, coordination number, lattice constant and atomic packing factor.
8. Differentiate between BCC and FCC crystal structures, considering the number of atoms per unit cell, the coordination number and the atomic packing factor.
9. Silver is an FCC and its atomic radius is $1.444 \text{ \AA}$. How large is its unit cell?
10. Nickel has an FCC crystal structure with a lattice parameter of 0.352 nm . What is the value of its atomic radius in nanometres?
11. Explain clearly how the properties of diamond are different from those of graphite though they are basically of the same element.
12. The distance between (111) plane in a BCC structure is $2.03 \text{ \AA}$. What is the size of the unit cell and radius of the atom?
13. What are Miller and Miller Bravais indices? How are Miller indices arrived at for planes and directions?
14. Explain clearly how the Miller indices are designated to the crystallographic planes.
15. Explain clearly the crystallographic planes and directions.
16. Sketch neatly the following planes and directions in the cubic lattice:
(110), (111), (101), (100), (124), (111), and (012), $(\bar{1}\bar{1}\bar{1})$, [112], [110].
17. Write the procedure to arrive at Miller indices of a crystal plane which intercepts at 2, 2 and 3 units on x , y and z axes respectively from the intersection of these axes.
18. Illustrate the three steps used in determining the Miller indices of a given plane.
Sketch the following: Planes (110), (111), (326); and directions [100], [110], [111].
19. Using a suitable example, show the method of obtaining Miller indices for crystallographic planes and directions for cubic crystals.
20. What is diffraction? Derive the Bragg's equation in x-ray crystallography.
21. The (111) plane of a cubic crystal is inclined at 26° to an x-ray beam. If the interplanar distance is $1.506 \text{ \AA}$, compute the x-ray wavelength that gives first-order reflection. What is the lattice constant of the crystal?
22. A diffraction pattern of a cubic crystal of lattice parameter $3.16 \text{ \AA}$ is obtained with monochromatic x-rays of wavelength $1.54 \text{ \AA}$. The first four lines on this pattern have the Bragg's parameters $\theta = 20.3, 29.2, 36.7$ and 43.6 respectively. Identify the crystal structure.

OBJECTIVE -TYPE QUESTIONS

1. In an amorphous material, _____.
 - (a) Atoms are arranged in a definite geometrical form
 - (b) Atoms are arranged in a non-geometrical form

- (c) Atoms are arranged in a systematic order
(d) Atoms are arranged in a 3D fashion
2. The copper shows _____.
(a) Crystalline structure (b) Noncrystalline structure
(c) Amorphous structure (d) Both crystalline and noncrystalline structures
3. _____ is a BCC structure.
(a) Gold (b) Copper
(c) Aluminium (d) Iron
4. Bravais lattice consists of _____.
(a) 16 basic unit cells in 36 system of crystals
(b) 7 basic unit cells in 14 system of crystals
(c) 14 basic unit cells in 7 system of crystals
(d) 12 basic unit cell in 7 system of crystals
5. Coordination number is _____.
(a) The number of atoms below the horizontal plane
(b) The number of atoms above the horizontal plane
(c) The number of nearest atoms which are surrounding the given atom
(d) None of the above
6. In a BCC structure, total number of atoms per unit cell are _____.
(a) 4 (b) 2 (c) 6 (d) 5
7. Coordination number for an FCC structure is _____.
(a) 12 (b) 8 (c) 10 (d) 11
8. Coordination number for an HCP structure is same as that of _____.
(a) BCC (b) FCC (c) SC (d) None of the above
9. Titanium is an example for _____.
(a) HCP (b) BCC (c) FCC (d) None of the above
10. Millar indices represent _____.
(a) Orientation of the crystallographic planes
(b) Direction of the crystallographic plane
(c) Both (a) and (b)
(d) None of the above
11. The atomic packing factor of aluminium is _____.
(a) 34% (b) 74% (c) 68% (d) 52%
12. Miller Bravais indices are used for representing _____.
(a) Crystallographic planes and directions in the BCC lattice
(b) Crystallographic planes and directions in the FCC lattice
(c) Crystallographic planes and directions in the hexagonal lattice
(d) Both (a) and (b)

38 | Crystal Structure

13. Rotating crystal method is used only for _____.
 (a) Polycrystalline materials (b) Single crystal materials
 (c) both (a) and (b) (d) Noncrystalline materials
14. In Debye–Scherrer method, θ will be _____.
 (a) $n \frac{10 S}{2\pi R}$ (b) $n \frac{90 S}{2\pi R}$ (c) $n \frac{35 S}{2\pi R}$ (d) $n \frac{45 S}{2\pi R}$
15. The Q^2 value for a BCC structure is _____.
 (a) 1:2:3:4:5:6:7... (b) 1:2:3:4:5:6:8...
 (c) 3:4:8:11:12:16... (d) 3:6:10:14:16...

ANSWERS

1.	b	2.	a	3.	d	4.	c	5.	c	6.	b
7.	a	8.	b	9.	a	10.	a	11.	b	12.	c
13.	b	14.	b	15.	a						

3

chapter

Crystal Imperfections

The metals are made up of infinite number of atoms in space whose arrangement conforms to a particular symmetry. Crystal imperfections refer to some irregularities in crystal structures in one or more atomic distances. Such defects have an effect on the properties of materials like strength, cold formability, diffusion rate and melting temperature of the solid. Sometimes, crystal defects are introduced intentionally into the lattices in a controlled manner to achieve the required properties.

The solid materials are crystalline in structure. The crystals are divided into two groups, real crystals and ideal crystals. If the arrangement of atoms in a crystal is perfect, regular and continuous throughout the crystal, it is known as an 'ideal crystal'. In practice, the ideal crystals rarely exist. The crystals in any material have many defects, which may be due to various reasons. There will be irregularity or defects in the arrangement of atoms within the crystal. These types of crystals are known as 'real crystals'. The real crystals will have many imperfections which alter the mechanical, electrical and magnetic properties in the crystalline solids.

3.1 CLASSIFICATION OF IMPERFECTIONS (BASED ON GEOMETRY)

The imperfections classified on the basis of their geometry are as follows:

1. Point imperfections
 - (a) Vacancy defect
 - (b) Impurity defect
 - (c) Interstitial defect
 - (d) Electronic defect
2. Line imperfections
 - (a) Edge defect
 - (b) Screw defect
3. Surface imperfections
 - (a) Tilt defect
 - (b) Twin boundary
 - (c) Grain boundary

3.1.1 Point Imperfections

The point imperfections are zero-dimensional imperfections and these are restricted to one or two atomic diameters in the crystal lattice. This defect is completely localized at one point. The missing atoms, displaced atoms and extra atoms are involved at the lattice site. The point imperfections are of four types which are discussed in the following subsections.

3.1.1.1 Vacancy Defect

The most important of point defect is the vacancy or absence of an atom at a lattice site within the metal. It is the unoccupied atom position within a crystal as indicated in Figure 3.1 (a) and (b). The atoms can frequently change their positions leaving empty lattice site called vacancies. There may be single, two or more atoms vacant in the crystal lattice. Vacancy may arise due to imperfect packing during solidification or from the thermal vibrations of the atom at elevated temperature. Increased thermal energy may make an individual atom jump out of its positions of lowest energy and sufficient vacancies are generated in the crystal structure.

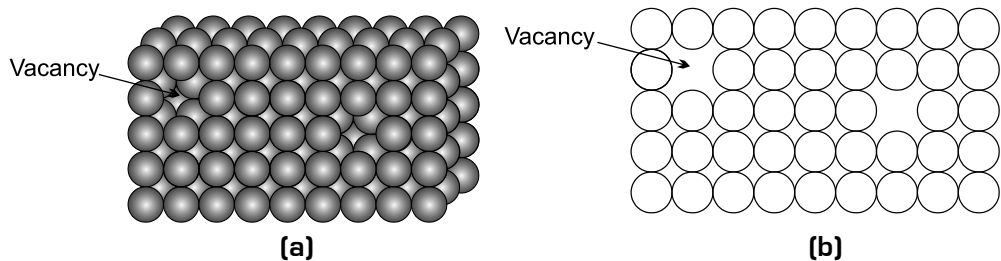
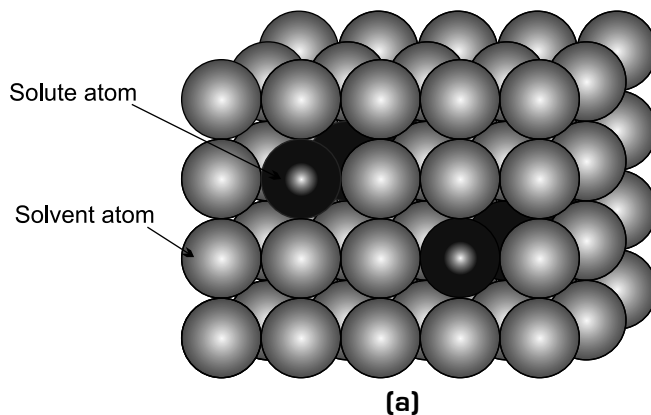


Fig. 3.1 The vacancy defect: (a) Three-dimensional view and (b) two-dimensional view

3.1.1.2 Impurity Defect

The impurities may be foreign atoms or any foreign particles included in the crystal structure. There are two types of impurities depending upon the cause for the defect. When the impurities are in the form of foreign atoms occupied in the lattice sites and the atomic diameter is more or less same as the parent atom diameter, it is known as substitutional impurities which are shown in the Figure 3.2 (a) and (b).



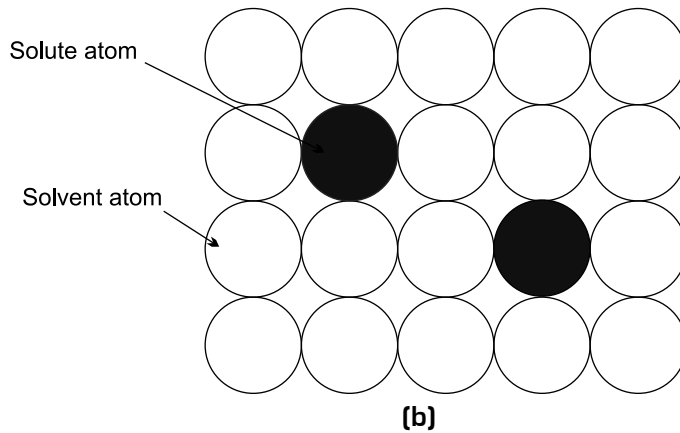


Fig. 3.2 Substitutional impurity: (a) Three-dimensional view and (b) two-dimensional view

3.1.1.3 Interstitial Defect

If a foreign atom occupies the position between the atoms of the original lattice, it is known as interstitial defect as shown in Figure 3.3 (a) and (b). This defect arrives when an atom or a slag occupies in void position in the lattice. The interstitial atom tends to push the surrounding atom further apart, unless the interstitial atom is smaller than the rest of the atoms in the crystal.

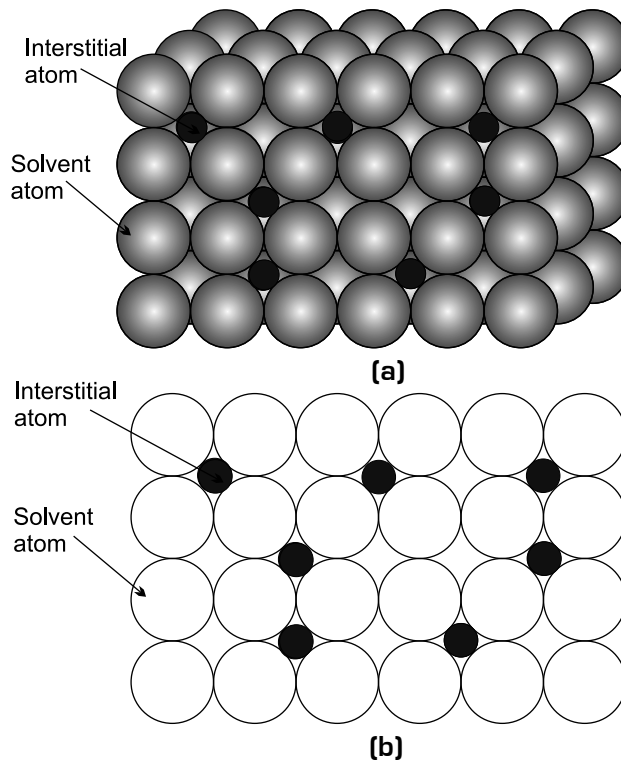


Fig. 3.3 Interstitial defects: (a) Three-dimensional view and (b) two-dimensional view

3.1.1.4 Electronic Defects

The ionic crystal structure has an error in the charge distribution between the atoms known as electronic defects. Consider zinc oxide. The zinc ions can occupy as the interstitial charge and this leads to a large number of positive charges at that place. In other places, if the zinc ions are missing, there is a gain of negative charge due to loss of positive charges. Thus, a vacancy or an interstitial impurity may produce an excess or a deficiency of positive or negative charges. There are two types of electronic defects, Frenkel defect and Schottky defect.

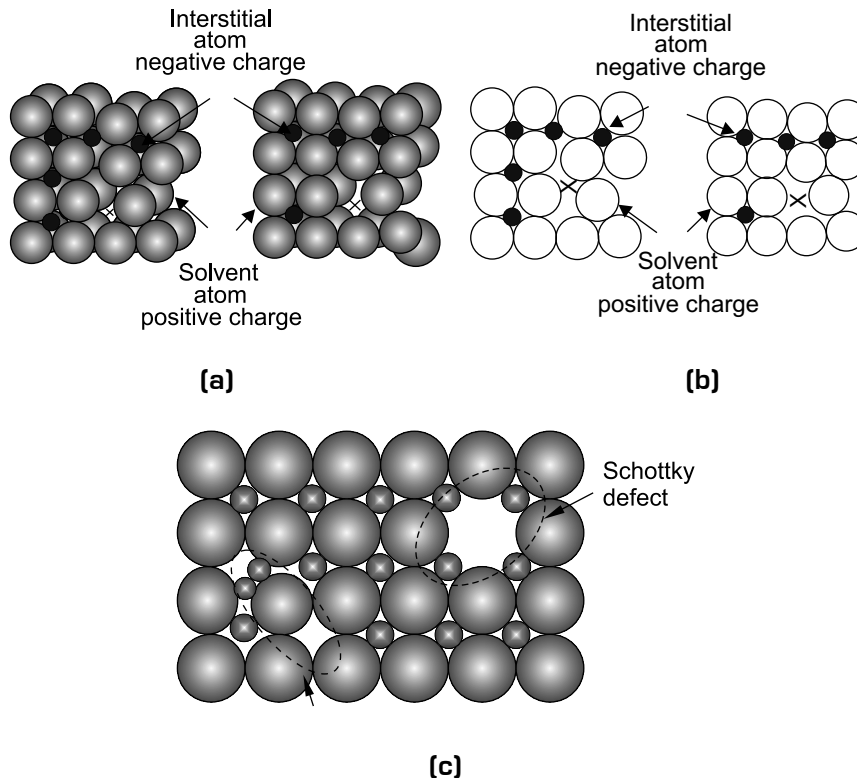


Fig. 3.4 The electronic defects: (a) Three-dimensional view of Frenkel defects; (b) two-dimensional view of Frenkel defects and (c) three-dimensional view of Frenkel and Schottky defects

Frenkel Defects: In any ionic crystal, cations being smaller in size can occupy an interstitial close to its original site thus causing an error in the charge distribution and no net change in the electrical charge. The defect of vacancy and interstitial in ionic crystals is called Frenkel defect which is shown in Figure 3.4. The closed crystal structure exhibits negligible Frenkel defect because an additional energy is required to force the ion to a new position. This defect is, however, increased by the unbalance of electric charge created locally by their formation.

Schottky Imperfections: A pair of positive and negative ions missing from the interior place of the crystal structure is called Schottky defect. These defects involve vacancies of pairs of ions of opposite charge in an ionic or ceramic crystal. Schottky imperfection is also called ion vacancy.

3.1.2 Line Imperfections

A dislocation can be defined as a disturbed region between two substantially perfect parts of a crystal. These are a linear disturbance of atomic arrangements on the slip plane through the crystal. These are also called line defects. There are one-dimensional imperfections that appear along the surface and also in the crystal. These are also called dislocations. The dislocation defect is caused when a plane of atoms is displaced from its original line of array. The dislocation may give rise to internal space and is responsible for the phenomenon of slip by which most of the materials deform plastically. The dislocations in a crystal are a result of growth accidents, thermal stress and external stress. The two types of dislocations are edge dislocation and screw dislocation.

3.1.2.1 Edge Dislocation

Edge dislocation is a one-dimensional defect. In this defect, the disturbed region is centred on the edge of the plane. Hence, it is known as edge dislocation. It is produced when misalignment of some atoms produce lattice distortion. A row of atoms is absent or is displaced by a unit distance within a crystal structure. In a perfect crystal, the dislocation appears in the form of a missing row of atoms from the top to the bottom of the crystal but ends midway within a crystal as shown in Figure 3.5(a). This dislocation is formed during the solidification of metals and alloys and plastic deformation. It is symbolically represented by ' $\perp$ ' for incomplete planes.

The magnitude and direction of dislocation measured by a vector is called Burgers vector. For finding dislocation, draw a path in the clockwise direction in the disturbed region as shown in Figure 3.5(b). From the figure, the magnitude of the vector P gives the Burgers vector. This is perpendicular to the edge dislocation. The direction of Burgers vectors depends on the direction of the path considered and it may be clockwise or anticlockwise.

Figure 3.5(b) shows the mechanism of edge dislocation. In Figure 3.5(a), the crystal is shown in its original form. A dislocation is indicated where in a few atoms are squeezed out of plane by pressure of an extra row of atoms in the upper half of the crystal. The application of shear stress (τ) causes a general distortion of the crystal so that the atom B moves closer to A where atom D moves further away. Therefore, the bond between B and C is broken and a new bond is formed between A and B . Thus, the dislocation is shifted through perpendicular atomic distance to the right.

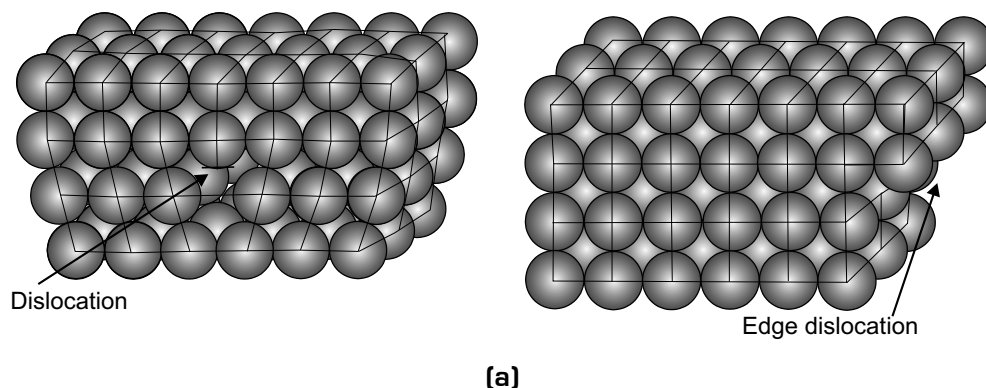


Fig. 3.5 Edge dislocation of a lattice: (a) Three-dimensional view, (b) two-dimensional view and (c) skeleton view

Continued

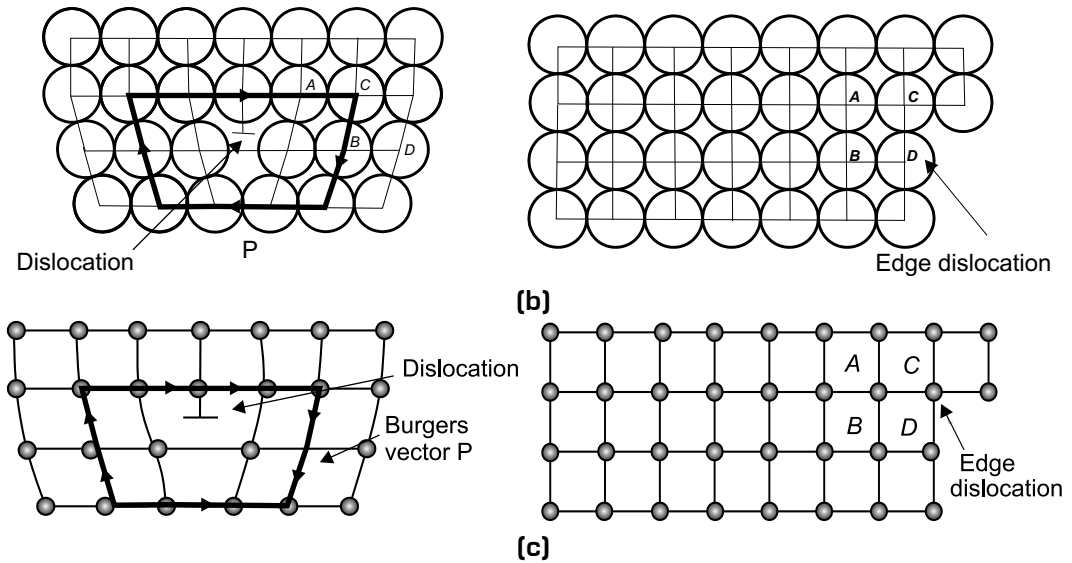


Fig. 3.5 Continued

3.1.2.2 Screw Dislocation

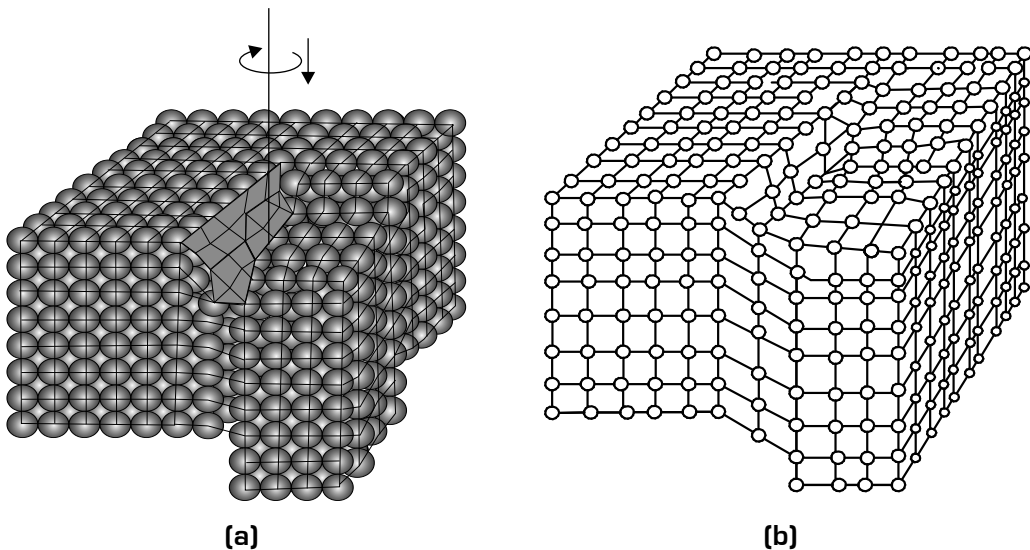


Fig. 3.6 The screw dislocation of a lattice: (a) and (b) Three-dimensional view and (c) Burgers vector of screw dislocation

Screw dislocation is a linear defect where the atoms are displaced along the line of dislocation. Shear stress distorts the crystal structure as shown in Figure 3.6 (a) and (b). The stress displaces the crystal and causes dislocation. The line moves in the direction indicated as shown in Figure 3.6(b). The dislocation displacement follows the helical path, known as screw dislocation. These dislocations are

easily created in the metal during crystal growth along the edge dislocation and also originate from partial slipping of a crystal plane.

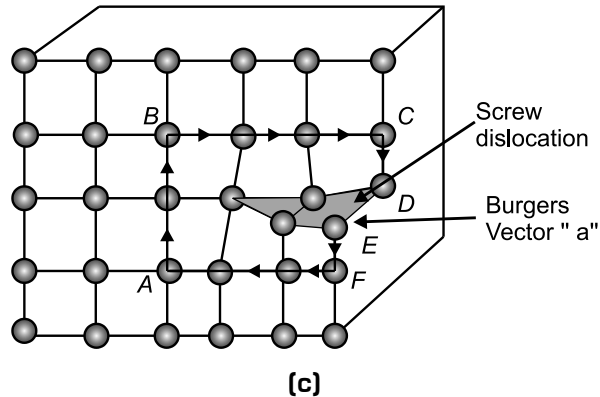


Fig. 3.6 Continued

Burgers vector in the case of screw dislocation is parallel to the line of dislocation. Consider a crystal as shown in Figure 3.6(c). In a crystal plane, path $ABCDEF$ shows the screw dislocation. The magnitude of vector "a" will displace the atom by one interatomic distance towards the forward producing screw dislocation with respect to the bottom part of the crystal structure. The magnitude and direction of the vector 'a' give rise to Burgers vector, and it is parallel to the line of dislocation.

Consider path $ABCDEF$, shown in Figure 3.6(c). In this path, the magnitude of vector 'a' will be displaced. Over the plane along the line DE to one interatomic distance to the front with respect to the rest of the crystal structure.

3.1.3 Surface Imperfections

Surface distortion is a two-dimensional imperfection that lies in the metal with polycrystalline structures. These defects also appear above the surface having a thickness of few atomic diameters. Some of the surface imperfections are grain boundary, twin boundaries and tilt boundaries.

3.1.3.1 Grain Boundary Imperfection

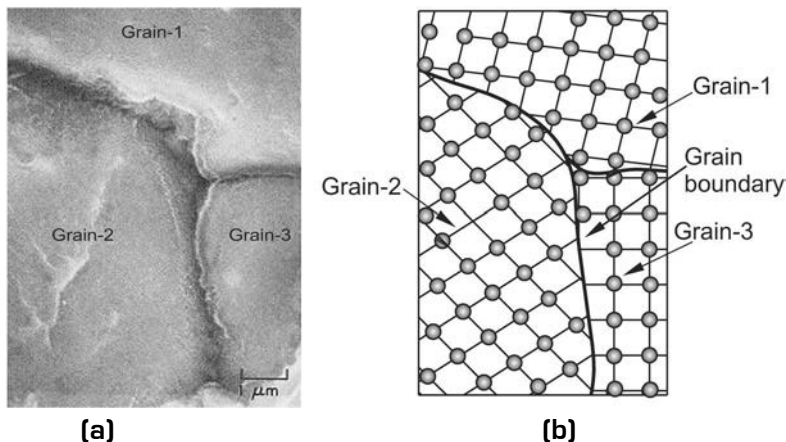


Fig. 3.7 The grain boundary defects: (a) Pictorial view and (b) skeleton view

46 | Crystal Imperfections

In polycrystalline metals, different crystals are oriented in different directions. Every crystal has a fixed orientation with respect to the atomic pattern, which will not match with that of the adjacent crystal. The grain boundary distortion obtained at the junction of two different orientations of the polycrystalline crystals due to the mismatch in the orientation of adjacent grains at the boundaries is shown in Figure 3.7. Inside the crystal, the atoms are arranged perfectly; at the boundaries, the atoms are not arranged perfectly and thereby a disturbed region is formed. The mismatch and orientation with the adjacent grain produce a less efficient packing of atoms along the boundary and slides even under a small load.

3.1.3.2 Tilt Boundary Imperfection

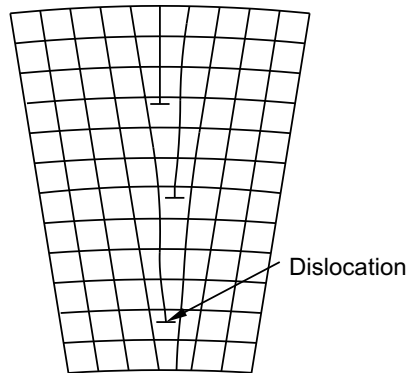


Fig. 3.8 The tilt boundary defect

Tilt boundary defects are created when neighbouring crystallographic planes are tilted towards each other by a small angle as shown in Figure 3.8. It is formed when an array of edge dislocation pile up one above the other and the two nearest crystals have an aligned dislocation. This type of boundary is associated with relatively little energy and is composed of edge dislocation lying one above the other in the boundary.

3.1.3.3 Twin Boundary Imperfection

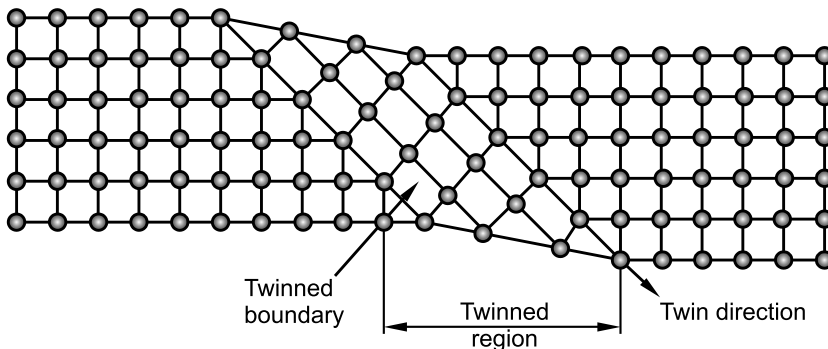


Fig. 3.9 Schematic diagram showing twin boundary

Twin boundary distortion is a dislocation or sliding of few atoms in plane and it is separated into two parts which look like a mirror image of each other. This is called twin boundaries and is shown in Figure 3.9. This twin portion of the plane can be observed when a material is subjected to some form of shear stress. When stress is applied on the plane of the crystal, a few number of atoms in certain regions move by a definite distance proportional to the distance of the twinning plane. The twin boundaries form either during annealing heat treatment process (called annealing twins) or during the plastic deformation (called mechanical twins). It is also a two-dimensional distraction and may result in the crystal growth or deformation of metals.

3.2 VOLUME IMPERFECTIONS (STACKING FAULT)

The volume imperfections such as crack or stacking fault will be formed when there is dissimilarity in the stacking sequence of atomic crystal structure. A stacking fault is an infrequency in the packing sequence of the layer of atoms, e.g. the atoms arranged in a sequence other than the normal sequence.

EXERCISES

1. Define ideal and real crystals.
2. Classify and explain the crystal imperfections in order of their geometry.
3. Explain point defects with a neat sketch.
4. Discuss Frenkel and Schottky defects.
5. Discuss the different types of line defects.
6. Explain line dislocation with a neat sketch.
7. What is Burgers vector? Draw vectors for line and screw dislocations.
8. Differentiate between the line and screw dislocations.
9. Using neat sketches explain the following imperfections:
 - (a) Dislocations,
 - (b) Grain boundary and
 - (c) Point defects.
10. Explain in detail the surface defects.
11. Differentiate between the edge and screw dislocations with neat sketches.
12. Draw the sketch and explain grain boundary and tilt boundary defects.
13. Write a note on twin boundary imperfection.
14. What are the effects of line defects, point defects and surfaces defects in crystals?

OBJECTIVE -TYPE QUESTIONS

1. Physical and mechanical properties of a metal are affected by _____.
 - (a) Physical shape
 - (b) Colour
 - (c) Imperfection
 - (d) Both (a) and (b)

48 | Crystal Imperfections

2. Real crystals are _____.
(a) Always perfect (b) Never perfect
(c) Both (a) and (b) (d) None of the above
3. Because of imperfections in a crystal lattice, _____.
(a) Theoretical stress is lower than the actual stress
(b) Theoretical stress is higher than the actual stress
(c) Theoretical stress is equal to the actual stress
(d) Theoretical and actual results cannot be compared
4. Point defect is an example for _____.
(a) One-dimensional defect
(b) Two-dimensional defect
(c) Three-dimensional defect
(d) Both one- and two-dimensional defects
5. Carbon in an iron crystal structure is an example for _____ defect.
(a) Vacancy (b) Interstitial
(c) Surface (d) Substitutional
6. Substitutional impurity implies _____.
(a) Solute atom replaces the solvent atom
(b) Solute atom occupies the void space in the crystal
(c) Atomic diameter of the solute is too small than that of the solvent
(d) None of the above
7. In a crystal, electronic defect is also known as _____.
(a) Error in charge distribution
(b) Error in atom distribution
(c) Error in crystal arrangement
(d) Error in vacancy of an atom
8. Ideal crystals have _____.
(a) Line defects (b) Only point defects
(c) Electronic defects (d) No defects
9. Frenkel defect is nothing but _____.
(a) Cations being smaller in size occupy an interstitial in void space
(b) Anions being smaller in size occupy an interstitial in void space
(c) Both cations and anions being smaller in size occupy an interstitial in void space
(d) Anion being larger in size occupy an interstitial in void space
10. In some ionic crystal structures, a pair of ions missing is called _____.
(a) Frenkel defect (b) Schottky defect
(c) Line defects (d) Surface defects
11. A row of atoms being absent or displaced by a unit distance within a crystal structure is known as _____.
(a) Line defects (b) Point defects
(c) Surface defects (d) None of the above
12. Dislocations are mainly responsible for increase in _____.
(a) Fracture (b) Wear resistance
(c) Strength (d) None of the above

13. Burgers vector is a vector used for measuring the magnitude of _____.
 (a) Surface defects (b) Dislocations
 (c) Point defects (d) None of the above
14. Example for surface defects is _____.
 (a) Line defects (b) Impurities
 (c) Grain boundary defects (d) Point defects
15. Volume defects can be _____.
 (a) Schottky defect (b) Twin defects
 (c) Stacking fault (d) None of the above

ANSWERS

1.	c	2.	b	3.	b	4.	d	5.	b	6.	a
7.	a	8.	d	9.	a	10.	b	11.	a	12.	c
13.	b	14	c	15.	c						

Atomic Diffusion

INTRODUCTION

Diffusion can be defined as the movement of atoms or molecules between different regions in a solid lattice structure. In any metal, as the temperature is raised, more and more atoms vibrate energetically and a group of atoms relocate themselves in the lattice. The atoms in a solid are continuously jumping from one position in the structure to a neighbouring position. The diffusion of atoms or molecules brings several changes in a solid solution and is very important for metallurgists. Many phase changes that occur in alloys involve a redistribution of the various kinds of atoms. The homogenization of a cast alloy is due to the diffusion of atoms from a region of high concentration to a region of low concentration. Figure 4.1 illustrates the diffusion of nickel atoms in the lattice of copper metal.

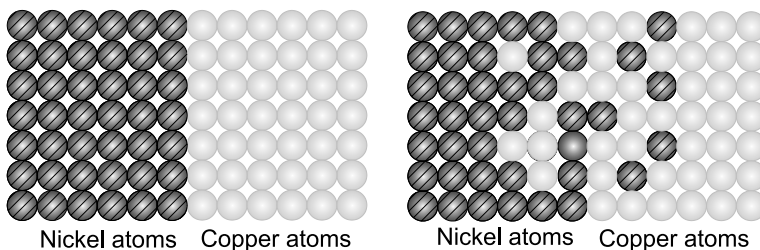


Fig. 4.1 The diffusion of nickel atoms in a copper lattice

Diffusion is caused by the random movement of individual atoms and will occupy the specified positions within a material. The thermal agitation supplies the required activation energy to the atoms to jump from one atomic site to a neighbouring site. The energy variation, caused by the collisions between the atom and the neighbouring atom, can throw the atom in any direction. The path of the atom is totally unpredictable and may be random or zigzag. However, when a large number of atoms make such movements they produce a systematic flow down of the concentration gradient.

4.1 DIFFUSION MECHANISMS

In perfect crystals, the movement of atoms is difficult as there is no place for the atoms to move. However, most of the crystals consist of imperfections thereby allowing the atoms to diffuse in the material. Several atomic mechanisms have been proposed to explain the diffusion. All of these mechanisms are based on the vibration energy of the atoms in a solid.

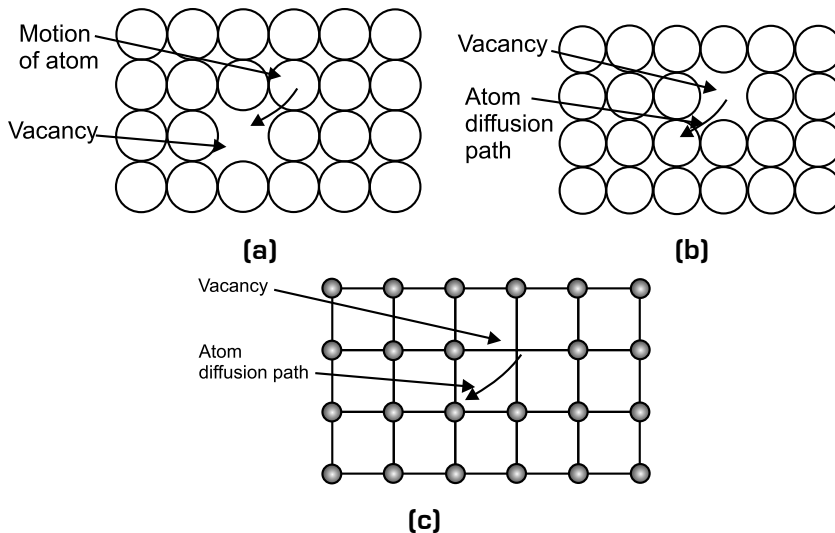


Fig. 4.2 Vacancy diffusion: (a) and (b) Path of atom flow in two dimensions and (c) flow of atom in skeleton of lattice

The vacant lattice sites are common in any crystal lattice at any temperature above absolute zero. These vacant sites greatly facilitate the jumping of adjoining atoms. The jumping of atoms to nearest vacant lattice site is illustrated in Figure 4.2. It involves the diffusion of atoms by jumping to a nearest vacant lattice site. This is a very important mechanism for the diffusion of metals. As a result of jumping of the atoms, the vacancies are moved through the lattice and the atoms shift randomly from one lattice position to another. Such diffusion, over a period of time, produces concentration changes. The vacancies are continuously being created and destroyed at the surface.

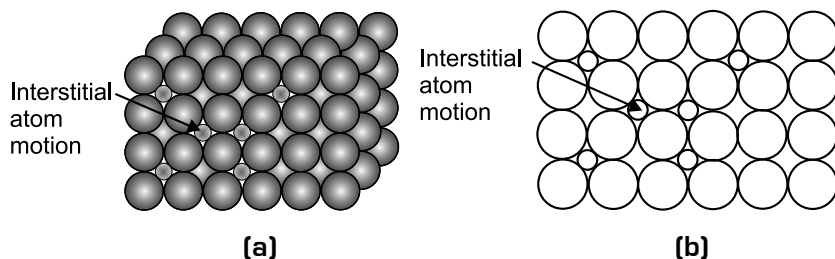


Fig. 4.3 Interstitial diffusion: (a) Interstitial diffusion in three dimensions and (b) interstitial diffusion in two dimensions

The interstitial mechanism may occur when a solid is composed of two or more elements whose atomic radii differ significantly. The large atom occupies the lattice sites while the smaller atom fit into

the void created by the large atom. Carburization of low carbon steel is the best example for interstitial diffusion mechanism. Figure 4.3 indicates that the carbon atoms fit in the lattice of iron. The atomic radius of carbon is $0.71 \text{ \AA}$ and it can fit in the void created by iron which has an atomic radius of $2.65 \text{ \AA}$. The carbon atoms are responsible for ameliorating the strength and hardness of iron.

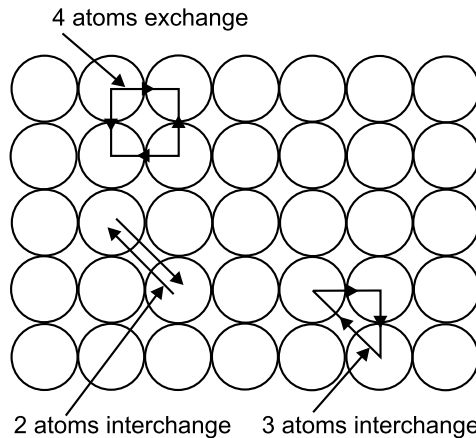


Fig. 4.4 Direct interchange diffusion in self-diffusion

In the direct interchange mechanism, two or more adjacent atoms jump past each other and exchange their own positions due to thermal agitation of atoms. The number of atom sites remains constant during diffusion (Figure 4.4). This mechanism results in the local distortion due to the displacement of atoms surrounding the jumping pairs.

4.2 TYPES OF DIFFUSION

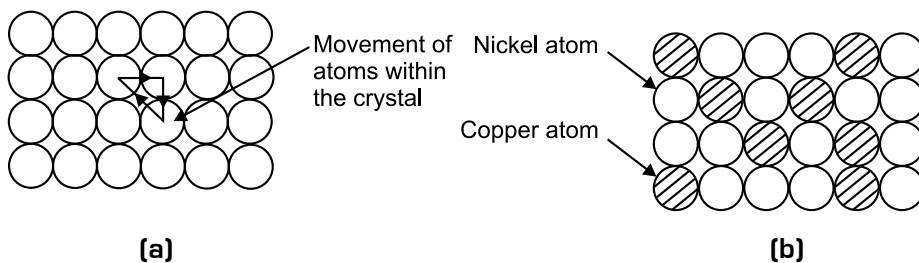


Fig. 4.5 (a) Atoms jump within their lattice and (b) inter-diffusion of a copper-nickel system

On the basis of the movement of atoms within the metal or from one metal to another, diffusion can be classified as self-diffusion, inter-diffusion, volume diffusion and grain boundary diffusion. The movement of atoms within a material or from one crystal to another crystal of the same material is called self-diffusion. As shown in Figure 4.5(a), the atoms exchange their lattice position by jumping which is due to thermal agitation. Here, the moving atoms and the solid are of the same chemical element. Inter-diffusion means the movement of atoms from the crystal lattice of one component to the crystal lattice of another component. It takes place in alloys. For example, in Cu–Ni system, inter-

diffusion implies the diffusion of Ni through the lattice structure of Cu as indicated in Figure 4.5(b). Volume diffusion indicates the migration of a group of atoms from one place to another within the material and it takes place in bulk quantity. Grain boundary diffusion is the movement of atoms from one grain to another grain at the grain boundary. When the atoms are diffused along the surface of the planes, it is called surface diffusion.

4.3 FICK'S LAWS OF DIFFUSION

Fick, a Greek scientist, expressed the diffusion of atoms or molecules in a mathematical equation called Fick's laws of diffusion. These laws are described in the following sections.

4.3.1 Fick's First Law of Diffusion—Steady-state Diffusion

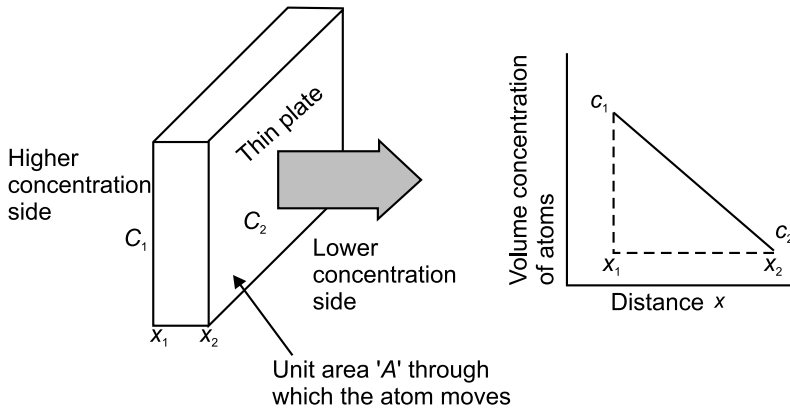


Fig. 4.6 Steady-state diffusion of atoms

The quantitative relation between the concentration gradient and the amount of atoms displaced by diffusion is given by the Fick's first law. Fick's first law states that the group of atoms (rate of diffusion J) moving across a unit surface in unit time is proportional to dc/dx (concentration gradient) under steady-state flow and it can be represented graphically as shown in Figure 4.6.

Fick considered the diffusion phenomenon similar to electrical conductivity. The rate of diffusion can be expressed by

$$J = \frac{F}{R} \quad (1)$$

where J is the rate of diffusion in atoms in m^2/s , F is the driving force and R is the resistance to movement of atoms.

The resistance (R) in diffusion is decreased by rise in temperature. In general, the resistance of the diffusion is decreased with the increase in temperature. If R is greater than F , the diffusion is not possible. If R is equal to F , the rate of diffusion is minimum. When F is greater than R , the rate of diffusion will be rapid.

Therefore,

$$R = \frac{dl}{A} \quad (2)$$

54 | Atomic Diffusion

where d is a constant, L is the distance of atomic movement and A is the area of plane of diffusion.

Substituting Equation (2) in Equation (1), we get

$$J = \frac{FA}{dL} = \left(\frac{F}{L}\right) A \frac{1}{d} = \left(\frac{F}{L}\right) AD \quad (3)$$

where $\frac{1}{d} = D$, the coefficient of diffusion.

The coefficient of diffusion can be defined as the amount of substance diffusing in unit time across a unit area through a unit concentration gradient and is generally expressed in cm^2/s .

If F is greater than R , the rate of diffusion is very rapid. Hence, Equation (3) becomes

$$\frac{dm}{dt} = -DA \frac{dc}{dx} \quad (4)$$

where J is the rate of diffusion $= \frac{dm}{dt}$, dm is total number of atoms diffused in a short time dt and $\frac{F}{L}$ is the concentration gradient that exists at the plane equal to $\left(-\frac{dc}{dx}\right)$. The negative sign indicates that diffusion takes place down the concentration gradient. Equation (4) represents the Fick's first law of diffusion and it is considered that there will not be any change in concentration gradient with time and it holds good for steady-state condition.

4.3.2 Fick's Second Law—Unsteady-state Diffusion

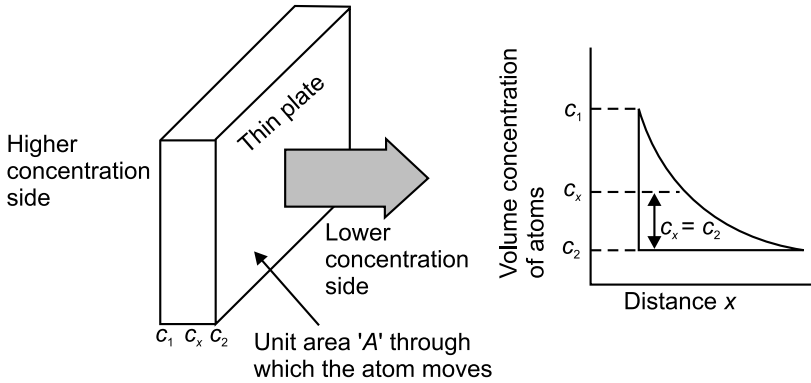


Fig. 4.7 Unsteady state of diffusion of atoms

In practice, diffusion process is an unsteady state. This is because, the concentration at a given point changes with time, and hence the diffusion flux also varies with time, i.e. $\frac{dc}{dt} \neq 0$. The Fick's second law takes this into account. According to Fick's second law, the rate of diffusion will depend upon the change in the concentration gradient with time. The corresponding concentration profile is schematically represented in Figure 4.7 and it is given by the equation

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \times \frac{dc}{dx} \right)$$

where $\frac{dc}{dt}$ is the rate of change of concentration at a given position x , D is the diffusion coefficient in m^2/s and x is the distance between atoms flow in diffusion direction in m .

In this equation, if we assume that the diffusion coefficient D is a constant (i.e. independent of concentration), then the Fick's second law can be written as

$$\frac{dc}{dt} = D \times \frac{d^2c}{dx^2} \quad (5)$$

Equation (5) is used to find the diffusion of atoms in a solid crystal structure (like in carburizing, nitriding, etc). As per this, the solution to Fick's second law is

$$\frac{(c_x - c_0)}{(c_s - c_0)} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where c_0 is the initial uniform concentration of an element in the solid, c_s is the surface concentrations of the diffusing element, c_x is the concentration of a diffusing element at a distance x from the surface, erf is the Gaussian error function, x is the depth from surface in m , D is the diffusivity of diffusing concentration in m^2/s and t is the time in s .

In this equation, the expression $\text{erf}\frac{x}{2\sqrt{Dt}}$ is the Gaussian error function. The error function values are as follows:

S. No.	z	$\text{erf}(z)$	S. No.	z	$\text{erf}(z)$
1.	0	0	19.	0.85	0.7707
2.	0.025	0.0282	20.	0.90	0.7970
3.	0.05	0.0564	21.	0.95	0.8209
4.	0.10	0.1125	22.	1.0	0.8427
5.	0.15	0.1680	23.	1.1	0.8802
6.	0.20	0.227	24.	1.2	0.9103
7.	0.25	0.2763	25.	1.3	0.9340
8.	0.30	0.3286	26.	1.4	0.9523
9.	0.35	0.3794	27.	1.5	0.9661
10.	0.40	0.4284	28.	1.6	0.9763
11.	0.45	0.4755	29.	1.7	0.9838
12.	0.50	0.505	30.	1.8	0.9891
13.	0.55	0.5633	31.	1.9	0.9928
14.	0.60	0.6039	32.	2.0	0.9953
15.	0.65	0.6420	33.	2.2	0.9981
16.	0.70	0.6778	34.	2.4	0.9993
17.	0.75	0.7112	35.	2.6	0.9998
18.	0.80	0.7421	36.	2.8	0.9999

where z is the independent variable, i.e., $z = \frac{x}{2\sqrt{D}}$, and $\text{erf}(z)$ is the dependent variable.

4.4 ACTIVATION ENERGY FOR DIFFUSION (ARRHENIUS EQUATION)

In any diffusion mechanism, the atoms will relocate themselves in the lattice. Energy transformation involves the rearrangement of atoms to a new configuration. For this transformation, the atoms must get higher energy before any process can take place. The rearrangement of the atoms not only depends on the temperature, but also on the arrangement of atoms in the lattice. The energy required by an atom to change its position is called the activation energy.

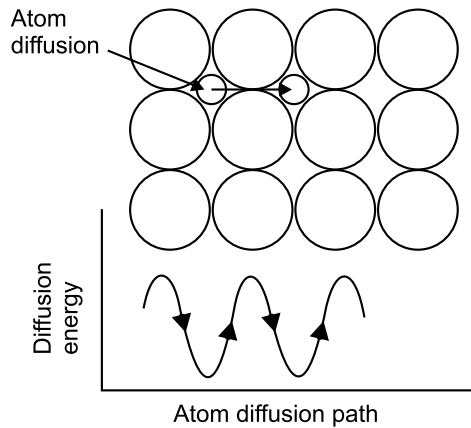


Fig. 4.8 The activation energy

The diffusion of atoms will not take place unless the atom is activated by the transition state that requires additional activation energy Q . The activation energy corresponds to the top of the energy barrier as shown in Figure 4.8. The rate of diffusion depends on the number of atoms which possess sufficient energy to reach the transition point, and the frequency or velocity with which those atoms can cross the energy barrier. The probability of an atom having sufficient energy to cross the energy barrier from one place to the other is given by Maxwell–Boltzmann distribution law. It states that ‘A fraction of atoms acquiring sufficient energy to cross the barrier is proportional to the factor exponential to the power $e^{\frac{-Q}{kT}}$, where Q is the activation energy, k the Boltzmann constant and T the absolute temperature.’

Therefore, the rate of diffusion will be equal to the concentration of the activated atoms and their frequency of crossing the energy barrier. This leads to the Arrhenius equation $D = D_0 e^{\frac{-Q}{RT}}$, where D_0 is a constant related to the frequency of the atoms crossing towards the barrier, Q is the activation energy, k is the rate constant, R is the gas constant and T is the absolute temperature.

Problem 4.1

A steel tank in a process industry contains nitrogen at 400 K and a constant pressure of 15 atm. Vacuum exists outside the tank. Nitrogen concentration at the inner surface of the tank is equal to 12 kg/m³. The constant D_0 and the activation energy for diffusion process between nitrogen and steel

are $5 \times 10^{-7} \text{ m}^2/\text{s}$ and 75 kJ/mol respectively. Calculate the rate at which the nitrogen escapes through the tank wall. The thickness of the tank is 6 mm .

Solution

$$Q = 75 \text{ kJ/mol} = 75 \times 10^3 \text{ J/mol}$$

$$D_0 = 5 \times 10^{-7} \text{ m}^2/\text{s}$$

$$T = 400 \text{ K}$$

$$R = 8.314 \text{ J/mol K}$$

Nitrogen concentration $c_1 = 12 \text{ kg/m}^3$ (inner wall)

Nitrogen concentration $c_2 =$ (outside vacuum)

Tank thickness $= 6 \times 10^{-3} \text{ m}$

$$J = ?$$

$$J = -D \frac{dc}{dx}$$

$$J = -D \left(\frac{c_1 - c_2}{dx} \right)$$

$$c_1 - c_2 = 12 - 0 = 12 \text{ kg/m}^3$$

$$dx = 6 \times 10^{-3}$$

$$D = D_0 e^{\frac{-Q}{RT}}$$

$$D = 5 \times 10^{-7} e^{\frac{-75 \times 10^3}{8.314 \times 400}}$$

$$D = 8.028 \times 10^{-17} \text{ m}^2/\text{s}$$

$$J = \frac{-8.02 \times 10^{-17} \times 12}{6 \times 10^{-3}}$$

$$J = 16.05 \times 10^{-14} \text{ kg/m}^2$$

Problem 4.2

Calculate the diffusion rate of carbon at 700°C assuming that the constants $D_0 = 4.9 \times 10^{-5} \text{ m}^2/\text{s}$ and $Q = 153.2 \text{ kJ/mol}$.

Solution

$$Q = 153.2 \text{ kJ/mol} = 153.2 \times 10^3 \text{ J/mol}$$

$$D_0 = 4.9 \times 10^{-5} \text{ m}^2/\text{s}$$

$$T = 700 + 273 = 973 \text{ K}$$

$$D = ?$$

$$D = D_0 e^{\frac{-Q}{RT}}$$

$$D = 4.9 \times 10^{-5} e^{\frac{-153 \times 10^3}{8.314 \times 973}}$$

$$D = 2.92 \times 10^{-13} \text{ m}^2/\text{s}$$

58 | Atomic Diffusion

Problem 4.3

Calculate the value of diffusivity D in m^2/s for the diffusion of copper in austenite (FCC) at 972°C . Use the following values:

$$D_0 = 2.0 \times 10^{-5} \text{ m}^2/\text{s}$$

$$Q = 142 \text{ kJ/mol}$$

$$R = 8.321 \text{ J/mol K}$$

Solution

$$Q = 142 \text{ kJ/mol} = 142 \times 10^3 \text{ J/mol}$$

$$R = 8.314 \text{ J/mol K}$$

$$D_0 = 2.0 \times 10^{-5} \text{ m}^2/\text{s}$$

$$T = 927 + 273 = 1200 \text{ K}$$

$$D = ?$$

$$D = D_0 e^{\frac{-Q}{RT}}$$

$$D = 2.0 \times 10^{-5} e^{\frac{-142 \times 10^3}{8.314 \times 1200}}$$

$$D = 1.32 \times 10^{-11} \text{ m}^2/\text{s}$$

Problem 4.4

The diffusivity of copper atoms in FCC copper lattice is $8.0 \times 10^{-21} \text{ m}^2/\text{s}$ at 400°C and $6.0 \times 10^{-5} \text{ m}^2/\text{s}$ at 800°C . Calculate the activation energy in J/mol for diffusion of copper atoms in FCC copper lattice in this temperature range.

Solution

$$\text{Temperature} = 400^\circ\text{C} = 673 \text{ K}$$

$$\text{Temperature} = 800^\circ\text{C} = 1073 \text{ K}$$

$$\text{Diffusivity of copper at } 673 \text{ K} = D_{673} = 8.0 \times 10^{-21} \text{ m}^2/\text{s}$$

$$\text{Diffusivity of copper at } 1073 \text{ K} = D_{1073} = 6.0 \times 10^{-5} \text{ m}^2/\text{s}$$

$$R = 8.314 \text{ J/mol}$$

$$Q = ?$$

$$D = D_0 e^{\frac{-Q}{RT}}$$

$$D_{673} = D_0 e^{\frac{-Q}{8.314 \times 673}} \quad (1)$$

$$D_{1073} = D_0 e^{\frac{-Q}{8.314 \times 1073}} \quad (2)$$

Dividing Equation (1) by Equation (2)

$$\frac{8.0 \times 10^{-21}}{6.0 \times 10^{-5}} = \frac{D_0 e^{\frac{-Q}{8.314 \times 673}}}{D_0 e^{\frac{-Q}{8.314 \times 1073}}}$$

$$1.33 \times 10^{-6} = e^{\frac{-Q}{5595-32}} - \frac{-Q}{8920-92}$$

$$1.33 \times 10^{-6} = e^{Q\left(\frac{-1}{5595-32} + \frac{Q}{8920-92}\right)}$$

$$1.33 \times 10^{-6} = e^{-6.66 \times 10^{-5}Q}$$

$$\ln(1.33 \times 10^{-6}) = -6.66 \times 10^{-5}Q$$

$$Q = 203158 \text{ J/m}$$

4.5 FACTORS AFFECTING DIFFUSION

The various factors which affect diffusion are discussed in the following sections.

4.5.1 Temperature

The diffusion takes place by the thermal agitation of atoms in a metal. The influence of temperature on the diffusion is calculated by using the relation $D = D_0 e^{\frac{-Q}{RT}}$, where D , D_0 and R are independent of temperature. Rise in temperature increases the rate of diffusion. The diffusion coefficient will change according to the Arrhenius equation.

4.5.2 Crystal Structure

The diffusion is a structurally sensitive property. If the atoms are more densely packed, the diffusion rate decreases. The FCC structure has slower rate of diffusion than the BCC structure. More open is the structure, greater is the diffusion because the activation energy required is less.

4.5.3 Concentration Gradient

The diffusion coefficient is independent of concentration. Higher is the concentration gradient, higher will be the diffusion; and lower the concentration gradient, lower the diffusion.

4.5.4 Crystal Imperfection

The crystal imperfection, such as vacancy distribution, in a crystal will increase the rate of diffusion. For the activation energy, the diffusion of impurities of interstitial type is faster than the diffusion of substitution type.

4.5.5 Grain Size

The grain boundary diffusion is faster than the diffusion within the grain. It is to be expected that the overall diffusion rate could be higher in a fine-grained structure.

4.6 APPLICATIONS OF DIFFUSION

Many components like gear, camshafts, piston pins, etc. require a very hard wearing surface to withstand the constant wear in service conditions and at the same time, a strong core which will

60 | Atomic Diffusion

withstand the shock loads. The treatments given to steels to achieve this are called surface heat treatments. This combination of widely differing properties can be combined in a single piece of steel by surface hardening. In this method, the hardness of the surface is improved by diffusing interstitial elements like carbon, nitrogen or both into the surface of steel. Here, carbon or nitrogen diffuses into the steel surface under concentration gradient.

Some alloy cast ingots are inhomogeneous due to the cooling rate, alloy concentration and the type of casting technique. A chemically inhomogeneous solid solution tends to become homogeneous through diffusion. Homogenization of any alloys can be achieved by heating at a relatively low temperature and cooling slowly to diffuse the solute atoms uniformly throughout the casting. Some of the examples are cast aluminium–copper and magnesium–aluminium alloys.

EXERCISES

1. What is diffusion? Explain the different factors which affect the diffusion.
2. What are the mechanisms and what are the factors affecting this phenomenon?
3. Differentiate between the interstitial and vacancy diffusion.
4. Discuss inter-diffusion process.
5. State and explain Fick's laws of diffusion.
6. Classify the diffusion process.
7. Explain briefly any two factors affecting the diffusion.
8. State the two laws of diffusion and give their mathematical expressions.
9. Derive the equation for steady-state diffusion.
10. What is meant by diffusion coefficient? Derive its units in MKS system.
11. High activation energy is needed in case of movement of atoms without imperfections. Substantiate the above statement with an example.
12. What is Arrhenius equation? Explain with illustration.
13. The following data have been obtained for diffusion of a particular case:

Temperature, K	Diffusion coefficient, D
700	1.9×10^{-10}
800	5.0×10^{-10}
900	6.58×10^{-9}
1000	5.00×10^{-8}
1100	2.68×10^{-7}

From an Arrhenius plot, calculate the activation energy for diffusion.

OBJECTIVE -TYPE QUESTIONS

1. Diffusion that takes place in a crystal is due to _____.
 - (a) Thermal agitation
 - (b) Cold working
 - (c) Both (a) and (b)
 - (d) None of the above

2. In decarburizing process, the atoms are diffused _____.
(a) Out of crystal (b) Into the crystal
(c) Within the crystal (d) All of the above
3. The homogenization of a cast alloy is the result of diffusion atoms from _____.
(a) Diffusion of atoms from a region of high concentration to a region of low concentration
(b) Diffusion of atoms from a region of low concentration to a region of high concentration
(c) Both (a) and (b) (d) None of the above
4. Diffusion that takes place within the single crystal structure is known as _____.
(a) Self-diffusion (b) Inter-diffusion
(c) Volume diffusion (d) Both (a) and (b)
5. Carburization of a low carbon steel is the best example for _____.
(a) Substitutional diffusion (b) Interstitial diffusion
(c) Both (a) and (b) (d) None of the above
6. Group of atoms moving across a unit surface in unit time is proportional to dc/dx under the steady-state flow is known as _____.
(a) Fick's second law of diffusion (b) Boltzmann diffusion
(c) Fick's first law of diffusion (d) None of the above
7. Diffusivity increases with _____.
(a) Increase in temperature (b) Metal having high melting temperature
(c) Metal having high latent heat of diffusion
(d) All of the above
8. Fick's second law can be written as _____.
(a) $\frac{dc}{dt} = D_x \frac{d^2c}{dx^2}$ (b) $\frac{dc}{dt} = D_x \frac{dc}{dx^2}$
(c) $\frac{dc}{dt} = D_x \frac{dM}{dx^2}$ (d) $\frac{dc}{dt} = x \frac{d^2c}{dx^2}$
9. The energy required by an atom to change its position by diffusion in the crystal is called _____.
(a) Mechanical energy (b) Thermal energy
(c) Activation energy (d) Vibration energy
10. When temperature decreases, _____.
(a) The rate of diffusion decreases
(b) The rate of diffusion increases
(c) The rate of diffusion remains unchanged
(d) None of the above
11. Rate of diffusion is higher for a crystal having _____.
(a) Fine grain (b) Coarse grain
(c) Higher packing factor (d) None of the above
12. Diffusion is more sensitive to _____.
(a) Type of alloy (b) Size of the metal
(c) Time (d) Temperature

62 | Atomic Diffusion

13. In diffusion, _____.
(a) Diffusion coefficient is independent of concentration
(b) Diffusion coefficient is dependent on concentration
(c) Both (a) and (b) (d) None of the above
14. Natural diffusion that takes place in a metal is _____.
(a) Surrounding temperature (b) Metal vibration
(c) Metal cold working (d) None of the above
15. Grain boundary movement of atoms implies _____.
(a) Movement of atoms from one grain to another grain at the grain boundary
(b) Movement of atoms within the grain
(c) Movement of atoms from one grain surface to the inner part
(d) All of the above

ANSWERS

1.	a	2.	b	3.	a	4.	a	5.	b	6.	c
7.	a	8.	a	9.	c	10.	a	11.	a	12.	d
13.	a	14.	a	15.	a						

Mechanical Behaviour of Metals

INTRODUCTION

When a metal is subjected to force it deforms and the deformation is either permanent or temporary and is produced under various physiological processes called mechanical behaviour of metals. This behaviour includes elastic action, plastic deformation and fracture.

For the designing and manufacturing of any solid material, the engineers must be aware of certain properties of metals. Among all the types of properties, the mechanical properties are the most important. Fracture is the end result of the plastic deformation. It takes place by the separation of a body under stress into two or more parts due to excess deformation. The fracture may be brittle, ductile, fatigue or creep.

5.1 STRESS AND STRAIN

The Hook English scientist published a research paper in 1678, that for many materials, the displacement under a load was proportional to force and establishing the notion of displacement with force. In 1705, Jacob Bernoulli described, in his research paper, that the deformation was to give force per unit area, or stress, as a function of the elongation per unit length, or strain, of a metal under tension.

5.1.1 Stress

Stress can be defined as the resistance developed in a material by the action of external force. When a material is loaded, its atoms get ready to withstand the load. The total of all the interatomic forces will balance the external load. The stress is also referred as the engineering or conventional stress and it is expressed as the load acting on a unit cross-sectional area.

$$\text{Stress } (\sigma) = \frac{\text{Load}}{\text{Original cross-sectional area}} = \frac{P}{A_0}$$

5.1.2 Strain

When a material is subjected to a load, it deforms and results in an increase or decrease in its dimensions. The amount of deformation in the direction of load is called strain. It is also referred to

64 | Mechanical Behaviour of Metals

as the engineering or conventional strain. In tensile deformation, elongation per unit length is called longitudinal strain. The ratio between the unit lateral contraction or lateral strain and the longitudinal strain is called 'Poisson's ratio'.

$$\text{Strain } (\varepsilon) = \frac{\text{Change in length}}{\text{Original length}} = \frac{\delta l}{A_o}$$

5.2 TRUE STRESS–STRAIN CURVES

5.2.1 True Stress

In the plastic range, both the reduction in area and strain can be very large and these dimensions change with loadings. True stress can be defined as loading by instantaneous area, i.e.,

$$\sigma_{\text{true}} = \frac{\text{Load}}{\text{Instantaneous cross-sectional area}}$$

True stress is also expressed in terms of normal strain.

$$\sigma_T = \frac{P}{A_i} = \frac{P}{A_i} \times \frac{A_o}{A_o} = \frac{P}{A_o} \times \frac{A_o}{A_i}$$

where P is the load in N , A_o is the original c/s area in mm^2 , A_i is the instantaneous c/s area in mm^2 , σ_T is the true stress.

Volume of original specimen = Volume of deformed specimen

$$\therefore A_o L_o = L_i A_i \quad \therefore \frac{A_o}{A_i} = \frac{L_i}{L_o}$$

Also

$$\varepsilon = \frac{L_i - L_o}{L_o} = \frac{L_i}{L_o} - 1$$

and

$$\begin{aligned} \varepsilon + 1 &= \frac{L_i}{L_o} = \frac{A_o}{A_i} \\ &= \frac{P}{A_o} (\varepsilon + 1) = \sigma (\varepsilon + 1) \end{aligned}$$

5.2.2 True Strain

True strain is nothing but strain that is based on the actual length at that time of increment instead of on the original length. True strain is defined such that the increment, caused by an increase in length δl , is based on the instantaneous length.

$$\varepsilon_T = \frac{\text{Increase in length } \delta l}{\text{Instantaneous length}}$$

True strain is also expressed in terms of normal strain.

$$\begin{aligned} \varepsilon_T &= \sum \left(\frac{L_1 - L_o}{L_o} \right) + \left(\frac{L_2 - L_1}{L_1} \right) + \left(\frac{L_3 - L_2}{L_2} \right) + \dots \\ \therefore \varepsilon &= \frac{L - L_o}{L_o} = \frac{L}{L_o} - 1 \end{aligned}$$

$$\varepsilon_T = \int_{L_0}^L \frac{\delta l}{L} = \text{Log}_e \frac{L}{L_0} \quad \because \frac{L}{L_0} = \varepsilon + 1$$

$$\varepsilon_T = \text{Log}_e (1 + \varepsilon)$$

where L_0 is the original length in mm, L_1 is the first increment in mm, L_2 is the second in increment in mm, etc. and ε_T is the true strain.

5.3 DEFORMATION OF METALS

In the mechanical working on metals, numerous metallic shapes are formed by different processes to form proper shapes and dimensions. The different processes used are rolling (for rails, beams, plates, etc.), forging (for crankshafts, axles), spinning or drawing (for tanks, tubes and other light shapes), extrusion (for rods, tubes, etc.), machining, etc. The basic reasons for the use of metallic substances as materials of construction are due to the property of plastic flow or the ability of the solid material to be permanently deformed without rupture. The deformation of metals is necessary to form various metallic shapes without rupture.

5.3.1 Types of Metal Deformation

Deformation is of two types—elastic deformation and plastic deformation. This classification of deformation is based on the type of strain produced or the basic mechanism of the deformation due to loading in the metal.

5.3.1.1 Elastic Deformation

When the solid is loaded, it is deformed; but it returns to its original position when unloaded. Under these conditions, a linear relationship exists between elastic stress and strain, expressed by Hook's law. Hook's law states that the stress is directly proportional to the strain within the elastic limit. According to Hook's law,

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\varepsilon}$$

The ratio between the stress and strain under elastic deformation is known as modulus of elasticity or Young's modulus. It is a characteristic of the type of the metal and its magnitude depends upon the force of attraction between the atoms of a metal.

Mechanisms of Elastic Action

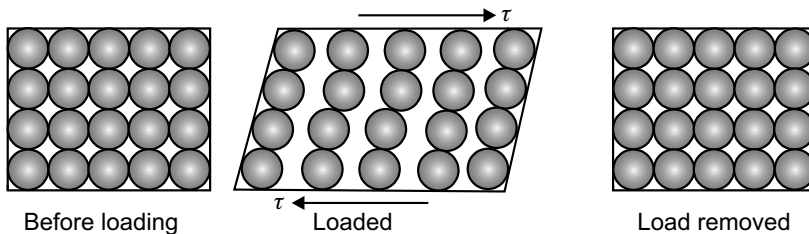


Fig. 5.1 Elastic deformation of a metal

Consider a metal loaded by tensile force. The metal elongates elastically by simple separation of its atoms in the direction of loading. The atoms are displaced from their normal equilibrium position just enough to develop attractive forces between them which will balance the applied load. Release of the applied force allows the atoms to return to their normal equilibrium positions as shown in Figure 5.1. The strain produced in elastic deformation may be linear, shear or lateral strain depending upon the type of loading.

5.3.1.2 Stress–strain Diagram for Ductile Metal

The study of stress–strain curves for different materials gives information on their basic mechanical behaviour. A stress–strain curve provides information on the elastic limit, yield strength, ultimate tensile strength, toughness and stiffness for a given material.

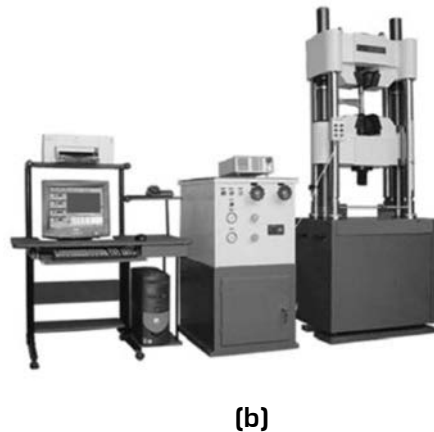
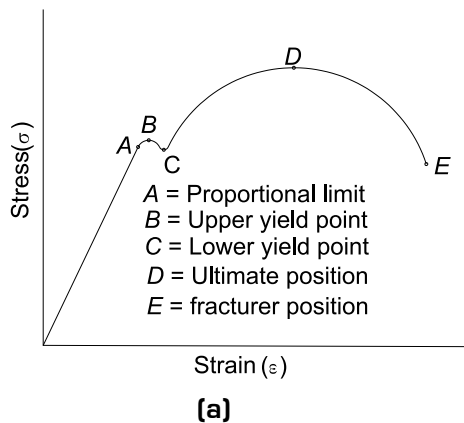


Fig. 5.2 (a) Stress–strain diagram for medium ductile metal and (b) testing machine

It is plotted using stress on the x-axis and strain on the y-axis. A typical stress–strain curve for a ductile material (mild steel) is shown in Figure 5.2. It can be seen that the curve is a straight line up to a certain value of the load, thereafter it deviates from the linearity and again rises in a somewhat parabolic shape until the breakage occurs.

In a ductile material, at the beginning of the test, the materials deform elastically. The strain, both longitudinal and lateral, at first increases proportionally to the stress and the specimen returns to its original length on removal of the stress. Beyond the elastic limit, the applied stress produces plastic deformation so that a permanent deformation remains even after the removal of the applied load. In this stage, the resultant strain begins to increase more quickly than the corresponding stress and continues to increase till the yield point is reached. At the yield point, the material suddenly stretches and the stress continuously decreases with elongation. In the beginning of the plastic deformation, the atoms start to move from one position to another due to the stress. Because of dislocations, each crystal starts losing its rigidity and the stress slightly decreases at a point called upper yield point. Line dislocations move from one position of crystal to the grain surface by dislocation pile up and it becomes perfect and each grain starts to resist the applied load during yielding. The point from where the curve starts to rise is indicating the lower yield point. Further, as the stress values on the specimen increase, the area of cross section starts decreasing. Finally, the deformation gets localized at a place, and what is commonly known as the ‘necking’ occurs and the specimen breaks. After the necking has begun, the normal stress decreases until the material fractures at the point of minimum cross-section area within the neck.

5.3.1.3 Comparison of True Stress and True Strain

The engineering stress is calculated based on the original area of cross section, without considering the reduction in area that take place with deformation. Such a stress–strain diagram that is based on the original area of cross section of a specimen is termed engineering or conventional stress–strain diagram. In the stress–strain diagram shown in Figure 5.3, the load is divided by the original area of cross section of the specimen. At every point of testing, the original cross-sectional area is only taken for computing the stress. But in practice, the cross-sectional area keeps reducing with deformation, and hence the stress value keeps rising. This is because, the material becomes stronger due to work hardening. Also, with each increment of plastic elongation, the gauge length keeps increasing. By using the instantaneous values of dimensions, we will be able plot a true stress and true strain diagram and the curve appears as shown in Figure 5.3. The yield point and proportionality limit are practically the same.

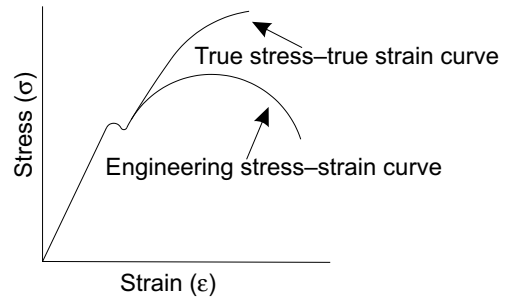


Fig. 5.3 Comparison of engineering stress–strain curve with true stress–true strain curve for ductile metal

5.3.1.4 Stress–strain Diagram for Different Metals

The deformation in a metal can be either ductile or brittle depending upon the type of material. Highly brittle materials, like cast iron, do not undergo any plastic deformation and they fail immediately after the elastic limit (Figure 5.4(a)). Medium ductile materials, like mild steel, show well-defined

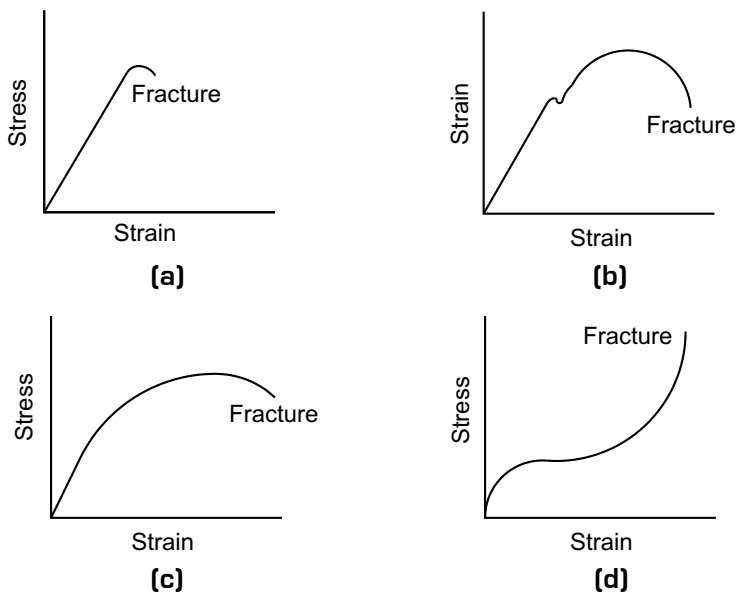


Fig. 5.4 Stress–strain diagram for different metals: (a) Brittle metal, (b) medium ductile metal, (c) high ductile metal and (d) nonlinear elastic metal

yield point, elongation beyond the elastic limit and ultimate tensile strength (Figure 5.4(b)). On the other hand, high ductile materials, like pure aluminium, pure copper, etc., do not show any specific yield point but easily deform after exceeding the elastic limit (Figure 5.4(c)). The nonlinear elastic materials, like rubber, will not show any linearity in the elastic deformation and it is difficult to find the yield point, ultimate strength, etc. (Figure 5.4(d)).

5.3.1.5 Linear Elastic Properties

The elastic properties in linear range are those which represent the ability to resist load, deformation and capacity to absorb energy in the elastic range.

1. **Elastic strength:** A material has a high elastic strength if it resists the load without yielding and without being permanently deformed. It is measured by stress which represents the transmission from the elastic range to the plastic range. Once the elastic strength limit is exceeded, the plastic deformation starts.
2. **Proportionality limit:** The stress which a material can withstand without being permanently strained is called 'elastic or proportionality limit'. In most of the materials, the proportionality between the stress and strain leads throughout, almost, the entire range of elastic action. Elastic strength is, therefore, measured as the stress making the end of this proportionality. This can be found by a stress-strain diagram.
3. **Resilience:** It is the capacity of a material to absorb energy when loaded within its elastic limit and release energy when unloading.

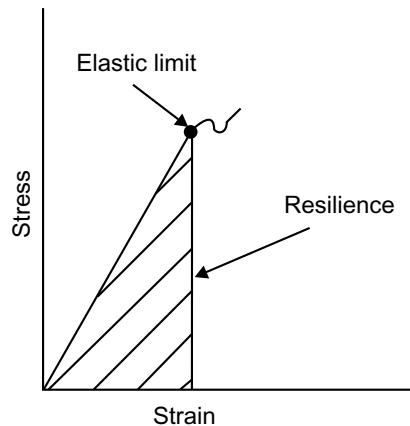


Fig. 5.5 The resilience of tensile specimen

Area below the curve shows resilience of the metal as shown in Figure 5.5. When a bar is elongated by a tensile force, the energy it absorbs comes directly from the work done by the applied forces so long as the deformation is both elastic and linear. This energy is stored in the material in a recoverable form as strain energy. The resilience is given by the area under the linear region of the stress-strain curve for a material.

The strain energy stored per unit volume in material up to the end of proportionality is called modulus of resilience. In some materials the resilience energy is higher. Such materials, commonly called the resilient materials, have the capacity to store higher strain energies, hence can absorb shocks and vibrations. Such materials are used as spring materials.

4. **Stiffness:** It refers to the property of a material due to which it resists the elastic deformation.

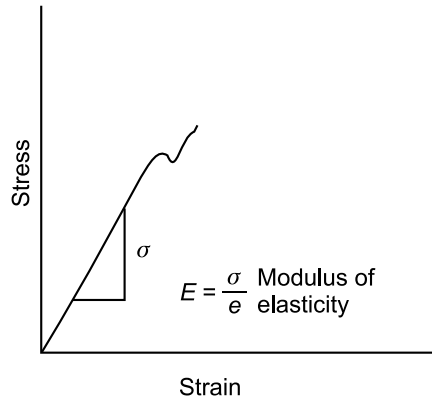


Fig. 5.6 Stiffness

The material has a higher stiffness value when its deformation in the elastic range is relatively small. For a given material, the modulus of elasticity is the measure of the stiffness. Lower the elastic deformation (lower the strain), higher is the modulus and hence higher is the stiffness. Obviously, a stiffer material will have a larger slope if the material follows the Hook's law. Its stiffness is measured by E and it can be found graphically by the slope of the straight line (see Figure 5.6).

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\epsilon}$$

5.3.1.6 Nonlinear Elastic Properties

There are certain materials like rubber, polymers, etc. that show a nonlinear behaviour. Thus, their elastic region is nonlinear (not a straight line, but a curve) as shown in Figure 5.7.

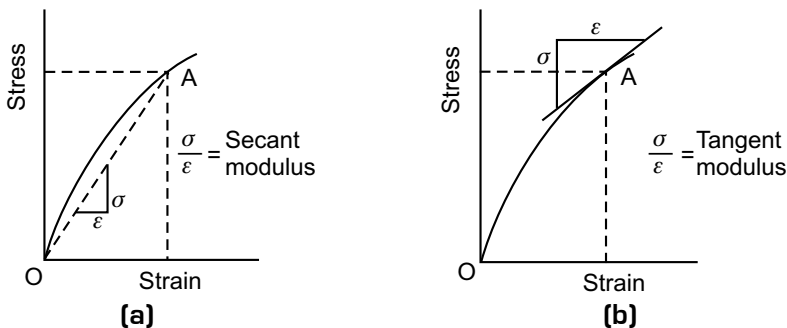


Fig. 5.7 Nonlinear elastic properties: (a) Secant modulus and (b) tangent modulus

1. **Stiffness:** Stiffness of a material does not follow Hook's law, and the stress–strain relation is not a constant. In such a case, the average stiffness is best measured at a given stress and it is also known as the secant modulus as shown in Figure 5.7(a). The line OA represents the slope of the secant and the value obtained for the secant modulus depends on the location 'A' which is usually specified in terms of stress at A . Similarly, the tangent modulus is measured as the slope of the

stress–strain curve at a given stress value [Figure 5.7(b)], whereas the secant modulus is given by the slope of a secant drawn between the origin and a given stress value.

2. **Resilience:** The resilience strain energy is stored is equal to the area under stress–strain diagram and the proportional limit does not exist in nonlinear case. Even the material is elastic; the strain energy stored is always not fully recoverable.

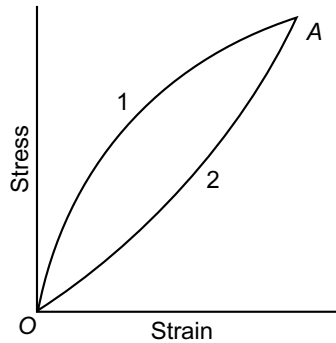


Fig. 5.8 Resilience for nonlinear elastic materials

Figure 5.8 shows a typical stress–strain diagram of rubber, a nonlinear elastic material. Curve (1) represents loading from O to A the area below this curve gives the strain energy stored per unit volume when rubber is elongated. When the rubber is unloaded, the resultant curve is (2) and is lower than the lower curve and the area under this curve is smaller than the curve (1). Some energy has been lost in the form of internal friction in the rubber and is represented by the area between two curves. Hence, total strain energy stored is not completely recoverable.

5.3.1.7 Plastic Deformation of Metals

In plastic deformation, stress exceeds the elastic range and the atoms or molecules in a metal permit permanent elongation. During the testing of metals, when stress exceeds the elastic limit, plastic deformation is observed. Stress beyond the elastic limit, a permanent and non-recoverable deformation takes place. Plastic deformation refers to the breaking of bonds from the original neighbouring atoms and then re-bonding with new neighbouring atoms. As compared to tension or compression, most of the metals are significantly weaker in shear. The plastic deformation observed in the processes like rolling, drawing, pressing, etc. are used to manufacture the metal articles.

5.3.1.8 Plastic Deformation by Single Crystal

Plastic deformation in a single crystal is associated with sliding, dislocation or twinning of the atoms within grains. Three modes of plastic deformation have been observed, namely, deformation by slip, deformation by dislocation and deformation by twinning.

Slip: The most common mechanism of plastic deformation in crystalline materials is slip and this can be defined as the mechanism by which there is a large displacement of one part of the crystal relative to another along a particular crystallographic plane and in a certain crystallographic direction.

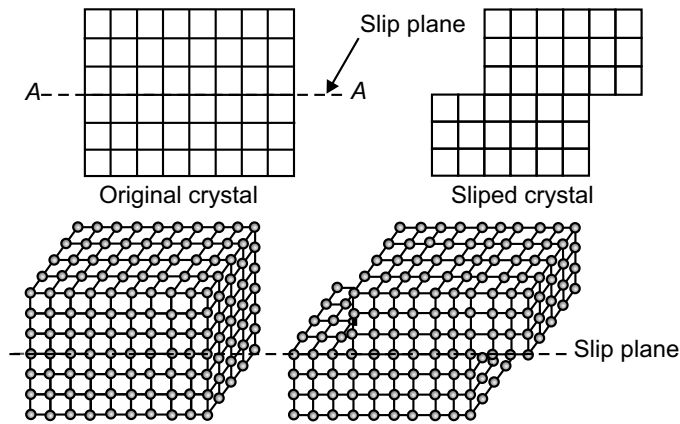


Fig. 5.9 Deformation by slip

Figure 5.9 shows the slip process in a single crystal under shear load. As a result of plastic deformation, the crystal is divided into a number of layers or slip blocks, in reference to each other, which are separated by a thin layer. As a result of the deformation, the thin layers of the crystal are displaced in such a manner that the whole process does not return and the slipped layer is not returned to the original shape of the atomic block after the withdrawal of the external force. The slip occurs along certain direction under planes as show in Figure 5.9. The shear stress which produces slip on a crystal plane is called critical shear stress.

Critical resolved shear stress: The slip in a single crystal depends upon the magnitude of the shear stress produced by the external load. Slip begins when the stress on the slip plane in the direction reaches a value called the critical resolved shear stress.

To calculate the resolved shear stress from a single crystal, it is necessary to know the orientation with respect to the tensile axis of the plane on which the slip appears.

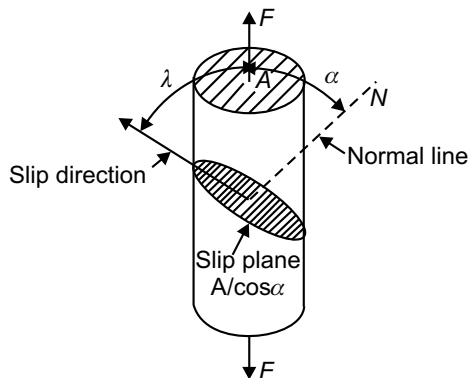


Fig. 5.10 Critical resolved stress

Consider a cylindrical crystal with cross-sectional area A . The angle between the normal to the slip plane and the tensile axis is α and that the slip direction makes with the tensile axis is λ . The area of the slip plane inclined at an angle α will be $(A/\cos \alpha)$ and the component of the axial load in the slip plane in the slip direction is $F \cos \lambda$. Hence, the critical resolved shear stress is given by (see Figure 5.10)

$$\frac{F \cos \lambda}{A / \cos \alpha} = \frac{F \cos \lambda \times \cos \alpha}{A}$$

This equation gives the shear stress on the slip direction. When the shear stress is maximum, $\alpha = \lambda = 45^\circ$ and the equation becomes equal to $F/2A$. If the tension axis is normal to the slip plane, i.e. $\lambda = 90^\circ$, or if it is parallel to the slip plane, i.e. $\alpha = 90^\circ$, the resolved shear stress is zero and this means that the slip will not occur.

Deformation by Dislocation: A dislocation is a disturbed region between the two perfect parts of the crystal. The movement of the dislocation produces a step and slip band. The motion of the dislocation through a crystal lattice requires a stress for smaller than the theoretical shear stress. In a deformation, an edge dislocation moves when a shear stress is applied perpendicular to the slip line and screw dislocation moves when a shear stress is applied parallel to the slip plane.

Consider a crystal with atomic planes, 1, 2, 3, 4, 5 having edge dislocation as shown in the Figure 5.11(a). From the figure, the extra plane of the atom to the edge dislocation is at 4. The plane 4 is only a half plane due to the presence of an edge dislocation. Due to the action of shear stress, the atoms start moving from right to left by pushing the atoms of planes 5 and 6 by breaking the bond between the atoms at below the slip plane and reform the bond in the next position. By this process, the edge dislocation line has moved from its initial position between the planes 3 and 5 to a new position between the planes 4 and 6. This process continues under the stress as shown in Figure 5.11(b) and (c) and the dislocation moves to right and appears in the form of the steps in the crystal structures. This extra half-plane forms an edge at the right end, which is one atomic distance wide.

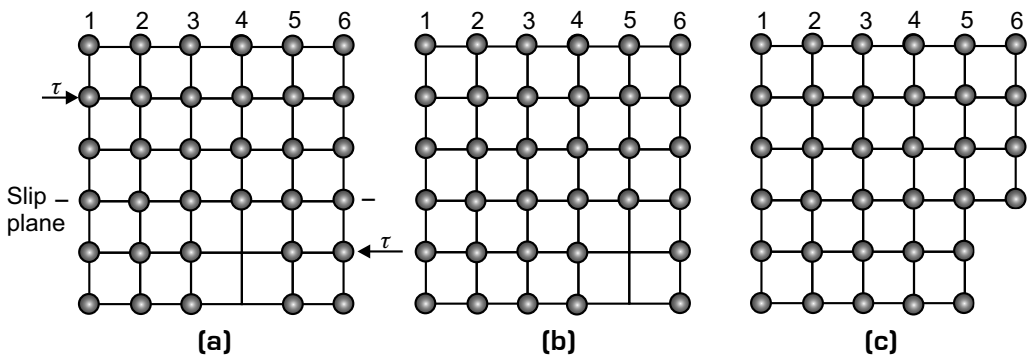


Fig. 5.11 Deformation by dislocation: (a) Dislocation line between the planes 3 and 5, (b) between 4 and 6 and (c) dislocation at the surface in the form of edge

Twins and Twinning: Twinning refers to the plastic deformation of metals by sliding of atoms in few atomic thicknesses. It is a common deformation in certain metallic materials like tin, iron and zinc. Figure 5.12 shows the geometry of the twinning when a plane is subjected to stress. One twinning plane will move parallel to the other under the influence of the stress along the slipping plane. In twinning, instead of whole blocks of atoms moving different distances along the slipping planes, each plane of atoms moves a definite distance and the total movement of atoms in the twinning plans

is proportional to the distance from the reference plane. The twinning deformation takes place when the applied shear stress produces atomic displacement in such a way that the lattice makes a mirror image across the twinning plane. In a twinning deformation, the plane along which the twinning takes place is called the twinning plane, and the direction in which the twin moves is called the twinning direction. The distance between the two twinned planes is called the twin region.

The twins are of two types—The twin which may be produced by the mechanical deformation is called mechanical twin and the twin produced as a result of the thermal stress called the annealing twin. The mechanical twins are produced due to an immediate result of applied stress in the usual manner. The annealing twins appear only in the annealed metals. Annealing twins occur during annealing process after plastic deformation to reduce the internal stress.

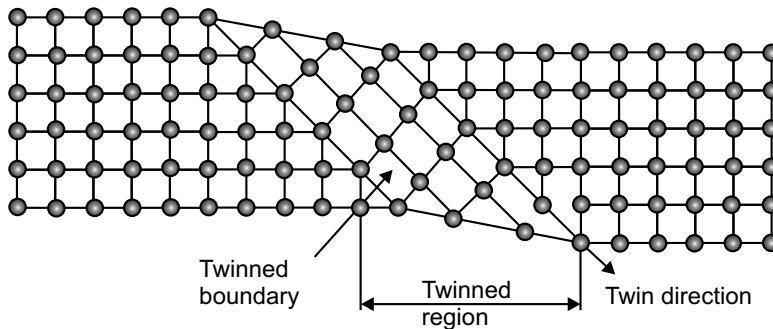


Fig. 5.12 Twinning of a plane

The main differences between the slip and mechanical twinning are as follows:

Slip Deformation	Twin Deformation
Steps appear on the deformed surface.	Well-defined region on the deformed surface.
Volume of metal deformation is more.	Volume of deformation is less.
Crystallographic direction does not change after slip deformation.	Crystallographic orientation changes after twin deformation.
Slip appears in a number of atomic spacing	Twin displacement takes place in less than one interatomic distance.
Slips require low shear stress to cause deformation.	Twinning requires higher shear stress to cause deformation.
Slip is common in FCC crystal structure.	Twinning is common in BCC crystal structure.

5.3.1.9 Deformation in a Polycrystalline Crystal

The commercial metals are polycrystalline aggregates. They are made up of a large number of crystals or grains and this polycrystalline material will not deform like a single crystal because each crystal or

grain is not free to deform as it is surrounded by a number of crystals. There is an added influence of grain boundary and each crystal has different orientation. Every grain boundary in a polycrystalline is surrounded by other grains. Therefore, a large stress is required for deformation. Each grain restricts deformation of the other grain because of the orientation difference between the grains.

The yield strength of polycrystalline metals is very complex. There are four factors which show that a polycrystalline material does not have a unique elastic limit. Therefore, when the metal is loaded, various grains do not have the same elastic stresses. The resolved shear stresses vary with the grain orientation and the critical shear stress is required for slip formation. These factors indicate that the polycrystalline metal does not have a unique elastic limit. Hence, in the polycrystalline material, a gradual initiation of plastic deformation will take place.

Plastic deformation in the polycrystalline material will never be uniform due to the random orientation of the grain. When the grains are smaller, there are more number of grain boundaries through which the dislocation has to pass. Hence, it requires higher stress to deform. The yield stress is more dependent on the grain size.

5.3.1.10 Yield Point Phenomenon

In certain materials, the yield does not begin gradually but comes suddenly and results in large plastic deformation at a more or less constant stress without any strain hardening. The stress–strain diagram for this type of behaviour is a discontinuous curve as shown in Figure 5.13.

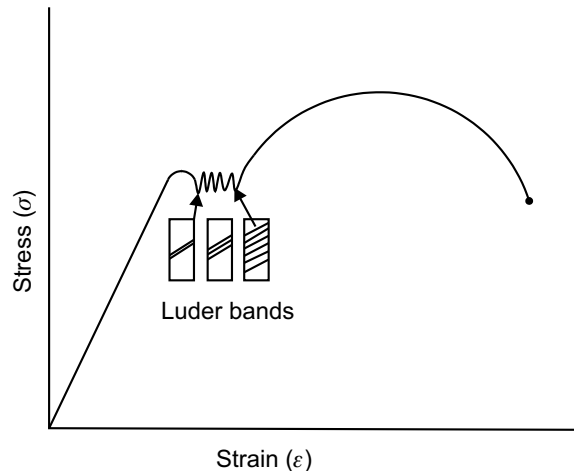


Fig. 5.13 Yield point phenomena

Sometimes yielding disturbs and even follows a sharp drop at a particular stress. The peak stress is called upper yield point and the lower stress is called lower yield point. Yielding is due to the dislocation rearrangement in the sample which causes the stress–strain curve to drop sharply and rise gradually. This is called yield point phenomenon. Elongation occurs at decrease or constant stress during the yield deformation and a certain type of band appears on the surface of the metal which is visible. With the continued strain, the band spreads along the length of the specimen. These bands which are generally inclined at 45° to tensile axis are called Luder bands.

5.3.1.11 Mechanical Properties—Plastic Region

Yield Strength: The start of plastic deformation is also called yielding, and the stress required to cause yielding is known as yield strength. It is given by the relation,

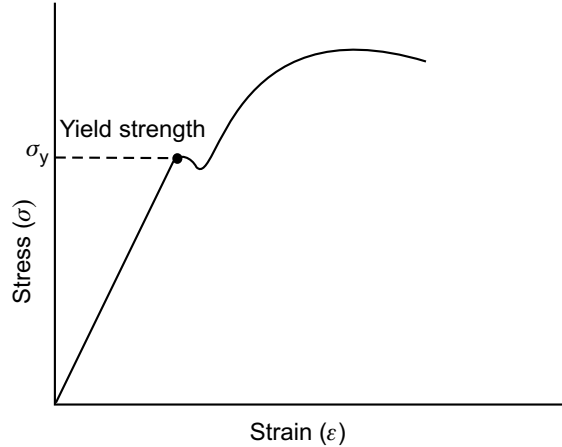


Fig. 5.14 Yield strength

$$\sigma_y = \frac{P_y}{A_0} \text{ MPa (MN/m}^2\text{)}$$

where P_y is the load at which the yield begins and A_0 is the original area of cross-section in mm^2 (see Figure 5.14).

Offset Yield Strength: Certain brittle materials like cast iron do not exhibit a definite yield point. They simply show a gradual change in curvature, indicating the transition from the elastic to the plastic region. Hence, the yield strength cannot be obtained. In such cases, the yield strength is determined by offset method.

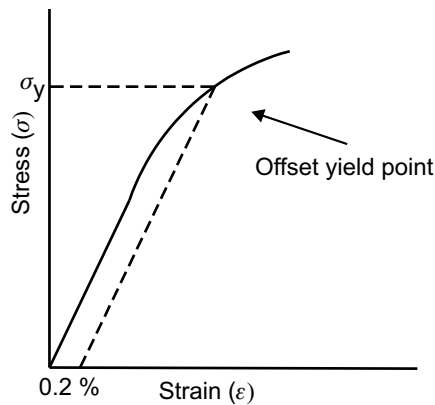


Fig. 5.15 Offset yield strength

76 | Mechanical Behaviour of Metals

In this method, a straight line is drawn parallel to the linear region of the stress–strain curve at some specified strain offset, which is usually 0.2% of the failure strain (i.e., 0.002 strains). The corresponding stress at which this offset line meets the stress–strain curve is taken as the yield strength of the material (see Figure 5.15). This strength is termed offset yield strength or the proof stress.

Ultimate Tensile Strength—UTS (σ_u): The ultimate tensile strength can be defined as the maximum stress that can be sustained by a material in tension.

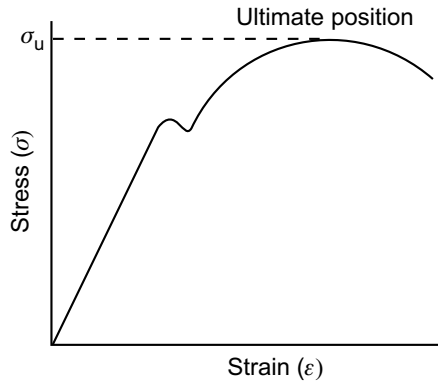


Fig. 5.16 Ultimate tensile strength

$$\sigma_u = \frac{P_u}{A_0} \text{ MPa (MN/m}^2\text{)}$$

where P_u is the ultimate load in N and A_0 is the original area of cross section in mm^2 (see Figure 5.16).

Fracture Strength: When the load crosses the ultimate value, the curve drops gradually and at this point, the specimen fractures. The stress at which the fracture of the specimen takes place is called the fracture strength. It is given by,

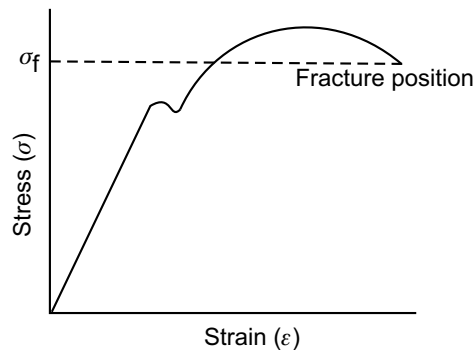


Fig. 5.17 Fracture strength

$$\sigma_f = \frac{P_f}{A_o} \text{ MPa (MN/m}^2\text{)}$$

where P_f is the fracture load in N and A_o is the original area of cross section in mm^2 (see Figure 5.17).

Ductility: Ductility is an important mechanical property in the plastic range of a material. It is a measure of the degree of plastic deformation taking place till the material fails in tension. A general definition of ductility is the ability of a material to be drawn into wires. A material that does not undergo considerable plastic deformation is termed brittle. Ductility is generally expressed as percent elongation or percent reduction in area:

$$\text{Percent elongation} = \frac{L_f - L_o}{L_o} \times 100$$

where L_f is the fracture length in mm and L_o is the original gauge length in mm

$$\text{Percent reduction in area} = \frac{A_o - A_f}{A_o} \times 100$$

where A_o is the original area of cross section in mm^2 and A_f is the area of cross section at the point of fracture in mm^2 .

Generally, non-ferrous metals (like aluminium, copper, etc.) are more ductile than ferrous metals. In fact, copper is so ductile that its area of cross section reduces almost to a point at fracture.

Malleability: Malleability is another measure of the degree of plastic deformation of a material under compression. The general definition of malleability is the ability of a material to be rolled into thin sheets. Aluminium, copper and gold are examples of highly malleable materials.

Toughness:

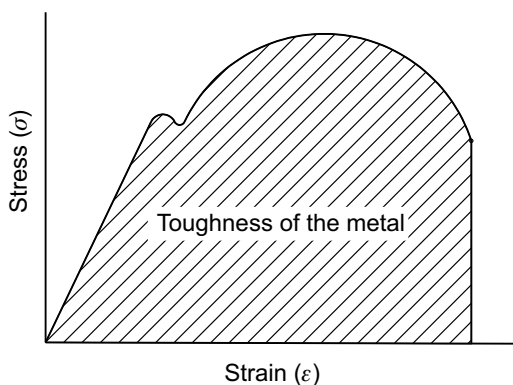


Fig. 5.18 Toughness of the metal

Toughness is the ability of a material to absorb energy both in the elastic and plastic ranges. Thus, the total area under the stress–strain curve represents the toughness of a material (see Figure 5.18). That means, higher the plastic deformation, higher is the toughness of a material. Brittle materials do not undergo considerable deformation, hence their toughness is minimum.

5.3.1.12 Work Hardening (Strain Hardening)

The increase in the hardness and strength of a metal produced by the previous cold working of a metal is called work hardening. Most of the metals, such as iron, copper, aluminium, nickel, etc., are not appreciably hardened by cold working because they can recrystallize at room temperature.

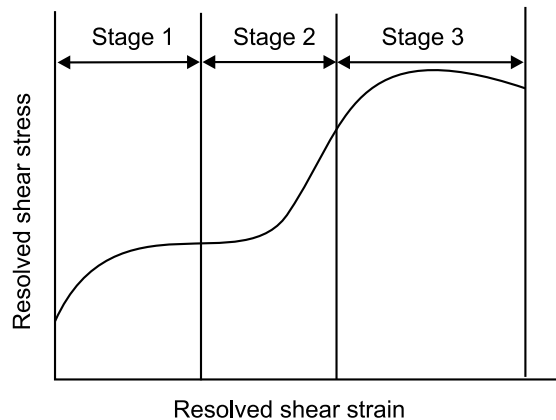


Fig. 5.19 Work hardening

Ductile materials show increase in the strength and hardness when plastically deformed at a temperature lower than the crystallization temperature. This is called ‘work hardening’. The work hardening of a metal is due to the movement of dislocations. During the deformation, dislocations pile up at the boundary in the crystals causing density dislocations. The applied stress on the slip plane is opposed by the newly developed back stress produced by dislocation pile ups. The higher the amount of the dislocation density, more the effect of the work hardening, i.e. the resistance of the metal to deform is increased in strength as well as hardness. This increased hardness accompanying plastic deformation results in the increase of the tensile strength and the yield strength of the solids as well as decrease in ductility.

There are three stages for hardening of a work hardenable metal as shown in Figure 5.19. Corresponding to the stage one, work hardening rate is practically low. Here, dislocations lie easily under the applied stress. In stage two, the work hardening rate is higher than that of the stage one due to the action the dislocation. Here, the dislocations are moved on interacting slip plane. In the third stage, work hardening decreases due to the lower dislocations.

The work hardening process is used in many manufacturing processes in industries. The cold rolling of low carbon stainless steels increases the tensile strengths and the yield point to more than double the original values.

5.3.1.13 Strain Ageing

The yield strength of the material is increased and the ductility is decreased due to the natural ageing or heating at a relatively low temperature after cold working called strain ageing. In most ductile materials, it is observed that the metal receives greater stress to produce further deformation after yielding due to work hardening. Strain hardening in crystalline material is largely accounted by dislocations.

Figure 5.20 shows the effect of strain on stress-strain curve for low carbon steel. The curve *OAB* shows the stress-strain curve of low carbon steel strained through the yield point elongation to a strain corresponding to point B. The specimen is then unloaded and retested without great delay or any heat treatment. It is noted that while reloading, the yield point does not occur.

Consider the specimen to be strained up to *C* and unloaded. After ageing for several days at room temperature or several hours at an ageing temperature, if this specimen is reloaded, the yield point reappears. Also, the yield point will be increased by ageing treatment. The appearance of the yield point is due to the diffusion of carbon and nitrogen atoms to dislocation during the ageing period from atmosphere. It is a phenomenon in which the mechanical properties of the ductile material change when they are strained beyond the elastic range and are aged. In the polycrystalline materials, dislocations find additional obstacles in the form of crystal boundaries and inclusion of foreign matter. Thus, the polycrystalline materials have high rates of strain hardening than a single crystal.

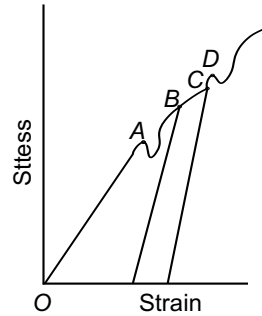


Fig. 5.20 Stress-strain diagram indicating strain hardening

5.3.1.14 Bauschinger Effects

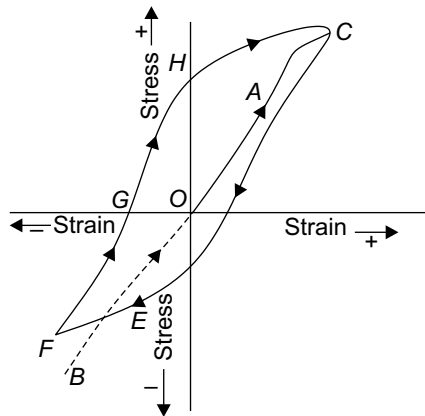


Fig. 5.21 The Bauschinger effect

The Bauschinger effect is a general phenomenon observed in polycrystalline metals on reversal of the loads. The initial yield stress of material in tension is A . If some material were to be tested in compression, the yield strength will be at point B . Now consider a new specimen which is loaded in tension, along OAC . If the specimen is unloaded and then loaded in compression, the specimen starts to yield at point E which is lower than its original compression yield strength. On further testing in tension, the yield stress has increased from point A to C . This phenomenon is called Bauschinger effect (see Figure 5.21). The increase in yield strength during tensile loading can be explained by strain hardening effect. During plastic deformation, the dislocations pile up at grain boundaries resulting in creation of back stress which oppose the applied stress. In compression load, the dislocation starts to move in the opposite direction which they come from at lower stress produced during tensile loading. This results in reduced compression yield strength.

5.3.1.15 Elastic After-effect

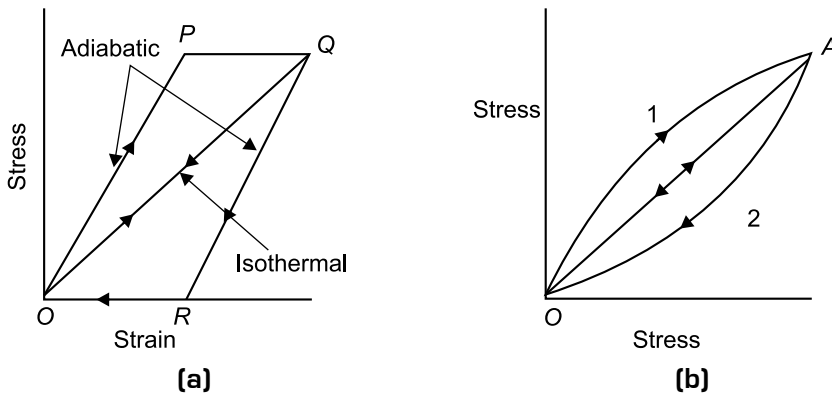


Fig. 5.22 Stress-strain diagram: (a) Quick loading and unloading condition and (b) slow or smooth loading and unloading condition

Elastic after-effect is one of the important phenomena of tensile deformation and it appears due to thermoelastic action. When a member is elongated, its volume increases and at the same time the temperature in the metal drops. If the elongation takes place slowly enough so that the thermal equilibrium is maintained, the process is said to be isothermal. On the other hand, if the elongation is rapid and there is insufficient time for heat transfer, the process is adiabatic and the temperature of the member is reduced.

If a member is loaded adiabatically to a certain stress and if the stress is held constant so as to allow the member absorb heat, further expansion will take place until the result is the same as that of the isothermal process. This behaviour of a member is denoted as shown in Figure 5.22(a). The same process can be observed during unloading from point Q . Isothermal unloading follows the line QO and adiabatic unloading follows the line QR parallel to OP and after the same time it returns to the origin.

If a smooth cycle of loading and unloading is carried out, the curve obtained is as shown in Figure 5.22(b). Here, the energy dissipated is equal to the area inside the loop called the elastic hysteresis loop. The size and shape of the hysteresis loop varies with the frequency of the cyclic loading. Lower the frequency, smaller is the loop and vice versa.

The elastic after-effect is caused partly due to the slow evolution of heat by the stress and the effect of this heat on thermal expansion. This effect is also partly due to the diffusion of impurities in pure materials and partly due to the mechanical hysteresis resulted by the grains.

5.3.1.16 Ductile–Brittle Transition

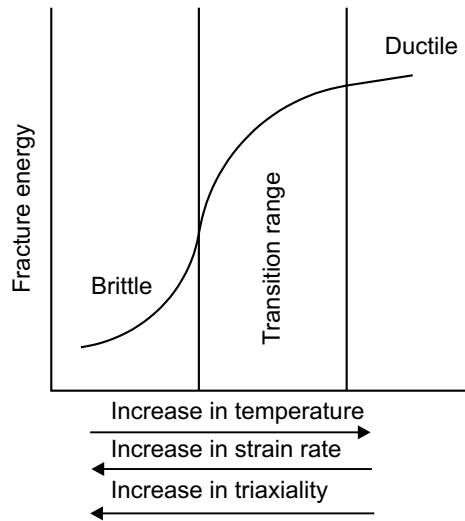


Fig. 5.23 Ductile to brittle transition

If any member is loaded, three main factors influence yielding and fracture. The three factors are (i) triaxiality, (ii) rate of loading and (iii) temperature. The yield stress increases with increase in triaxiality. Then the fracture stress is relatively unaffected. The yield stress decreases with increase in temperature. The fracture stress also decreases but only by a small amount. For example, in low carbon steel, yield stress increases sharply with increase in strain rate or decrease in temperature. Ductile metals tend to become brittle as triaxiality increases. Impact loading of member provides evidence of transition strain rate above which the ductile materials become brittle. The transition phenomenon can be shown by the curve in Figure 5.23. It is a well-known fact that brittle materials require less energy for fracture than ductile materials of approximately same strength as indicated in Figure 5.23. Transition from ductility to brittle behaviour is, therefore, accompanied by drop in the fracture energy. The phenomena of ductile transition can be represented graphically as shown in the figure.

5.3.1.17 Notch Effect

The tendency of normally ductile material is to behave in a brittle manner in the presence of notches. This is called notch sensitivity. This property depends on the response of the material to changes in the strain rate triaxiality and temperature. Materials like carbon steels and plastics are highly notch sensitive. The FCC metals are not generally notch sensitive. The materials that are originally brittle are not considered notch sensitive. Notch sensitivity is measured by the sharpness of the transition in the fracture.

EXERCISES

1. List and define the important properties determined in a tensile test.
2. Draw the conventional stress–strain diagrams for ductile and brittle materials under tensile load and explain the different properties of the materials.
3. Draw a schematic stress–strain–curve for mild steel and explain the determination of various mechanical properties from the curve.
4. With the help of a neat schematic conventional Stress–strain diagram for mild steel under tension, explain clearly the behaviour of the material till fracture.
5. Draw a stress–strain diagram for a low carbon steel specimen and explain the significance of important parameters like elastic limit, yield point and ultimate stress.
6. A tensile test was conducted on a 2 m length steel wire of 0.6 mm diameter. Determine the Young’s modulus of the material by plotting a stress versus strain graph using the following data.

Load	0	5	10	15	20	25	30
Extension (mm)	0	0.173	0.346	0.519	0.692	0.866	1.089
7. Explain the nonlinear elastic properties of materials subjected to static tension.
8. Define true stress and true strain and obtain the expressions for these in terms of engineering stress and strain.
9. Explain with a neat sketch the mechanism of plastic deformation by slip.
10. Explain with a sketch the mechanism of plastic deformation by twinning.
11. With neat sketches explain the differences between slip and twin.
12. Differentiate between slip and twinning deformations using neat sketches.
13. With neat figures explain how slip takes place when edge dislocations are present in a slip plane.
14. What is meant by critical resolved shear stress? What is the maximum value of CRSS and what is the condition under which it is obtained?
15. Derive an expression for the critical resolved shear stress for slip in a single crystal.
16. Explain clearly the twinning mechanism using a neat sketch.
17. Brittle materials are better in compression compared to tension. Explain why?
18. Using neat sketches explain the behaviour of rubber subjected to tensile test.
19. Explain discontinuous yielding and mention the effect of the same on the surface quality of rolled products.
20. Define the following:

(i) Elastic strength	(ii) Stiffness
(iii) Resilience	(iv) Toughness
(v) Ductility	
21. With a stress–strain curve explain the Bauschinger effect and the reasons for the same.

22. What is Bauschinger effect? Explain briefly its effect in the deformation of metals.
23. Explain the meaning of resilience, stiffness and toughness.
24. What is discontinuous yielding and why does it occur?
25. Explain the mechanism of elastic action when subjected to static tension.
26. What is offset yield strength and how is it found?
27. What is strain hardening? Explain the reasons for the same.
28. Explain the mechanism of strain hardening. When it is advantageous and when it is undesirable. How does it differ from conventional hardening methods?
29. What are the mechanisms that contribute to the strain hardening of a single crystal? Explain clearly two major mechanisms.
30. Explain the following:
 - (i) Critically resolved shear stress
 - (ii) Strain hardening
31. What is the effect of grain boundaries on the strain hardening characteristics of a polycrystalline aggregate?
32. Briefly explain the following:
 - (i) Strain ageing
 - (ii) Bauschinger effect
33. Define the following properties and state the measures used to assess the levels of these properties in a material:
 - (i) Tensile strength
 - (ii) Stiffness
 - (iii) Resilience
 - (iv) Ductility
 - (v) Toughness
34. Define the term '0.002% proof stress'.
35. Explain the method of determining the yield strength when a metal does not have a distinct yield point.
36. Briefly explain the following:
 - (i) Linear and nonlinear elastic properties
 - (ii) True stress and true strain
 - (iii) Yield point phenomenon
 - (iv) Strain hardening
37. What are the differences between strain hardening and strain ageing phenomena?
38. Explain with a neat sketch indicating 'Luder bands', the yield point phenomenon of ductile materials.
39. Presence of dislocations in metallic crystals successfully explains the discrepancy between the observed and theoretical yield strength values of metals. Discuss.
40. Explain why strain-hardening rate of a polycrystalline aggregate is much greater than that of a single crystal of the same metal.
41. Explain the following:
 - (i) True stress and true strain
 - (ii) Strain hardening and reasons
 - (iii) Recovery, recrystallization and grain growth

OBJECTIVE-TYPE QUESTIONS

1. Elastic deformation is due to _____.
 (a) Slipping of atoms (b) Dislocation of atoms
 (c) Simple separation of atoms (d) All of the above
2. True stress in nothing but _____.
 (a) Load by original area (b) Load by instantaneous area
 (c) Yield load by original area (d) None of the above
3. During tensile testing, discontinuous curve at yielding point is _____.
 (a) Due to strain hardening
 (b) Due to work hardening
 (c) Due to dislocation rearrangement
 (d) Due to ageing
4. Linear elastic properties can be observed in _____.
 (a) Mild steel (b) Rubber
 (c) Both (a) and (b) (d) None of the above
5. Energy stored during elastic deformation is known as _____.
 (a) Stiffness (b) Toughness
 (c) Resilience (d) Ductility
6. Higher the stiffness of metal, _____.
 (a) Higher the elastic deformation
 (b) Restricts the elastic deformation
 (c) Higher the plastic deformation
 (d) Fracture at low stress
7. Nonlinear elastic materials _____.
 (a) Stress proportional to the strain
 (b) Follow Hook's law
 (c) Follow proportional limit
 (d) Doesn't follow the Hook's law
8. Secant modulus is determined for _____.
 (a) Steel (b) Copper
 (c) Rubber (d) Ceramics
9. Critical resolved shear stress is _____.
 (a) The shear stress which produces slip on a crystal plane
 (b) The compressive stress which produces slip on a crystal plane
 (c) The shear stress which produces dislocation on a crystal plane
 (d) The shear stress which produces twinning on a crystal plane
10. Which of the statements is false in relation to twinning?
 (a) Crystallographic orientation changes after twin deformation.
 (b) Twin displacement takes less than one interatomic distances.
 (c) Twinning requires higher shear stress to cause deformation.
 (d) Twinning does not require stress to cause deformation.

11. The _____ deformation takes place when applied shear stress produces atomic displacement in such a way that the lattice makes a mirror image across the twinning plane.
 - (a) Slip
 - (b) Dislocation
 - (c) Twin
 - (d) All of the above
12. Yield strength of a metal mainly depends on _____.
 - (a) Grain size
 - (b) Dislocation
 - (c) Both (a) and (b)
 - (d) Single crystal
13. The Luder bands generally appear in _____.
 - (a) 12° to tensile axis
 - (b) 65° to tensile axis
 - (c) 75° to tensile axis
 - (d) 45° to tensile axis
14. Offset yield strength is measured in _____.
 - (a) Mild steel
 - (b) Pure copper
 - (c) Rubber
 - (d) Cast iron
15. The Bauschinger effect is related to _____.
 - (a) Both tensile and compressive loading
 - (b) Both compressive and shear loading
 - (c) Both tensile and shear loading
 - (d) Tensile, compressive and shear loading

ANSWERS

1.	c	2.	b	3.	c	4.	a	5.	c	6.	b
7.	d	8.	c	9.	a	10.	d	11.	c	12.	c
13.	d	14	b	15.	a						

Fracture

INTRODUCTION

Fracture is the separation or fragmentation of a solid body under stress into two or more parts. It is the end result of a plastic deformation process. Material fails in service if it deforms excessively. Failure may occur under different types of loads like tensile, compressive, shear, torsional or a combination of these. Theoretically, a pure metal can elongate almost 100% by reduction in cross section. Most of the metals contain many impurities and the cohesion between different grains and atoms will be loose in the deformation process. Voids and dislocations grow under stress. The voids join together and form a continuous fracture surface followed by the failure of the remaining portion of the metal.

Depending upon the energy absorption or the shape change due to a fracture, there are two types of fractures—ductile fracture and brittle fracture. The type of fracture depends on the following factors:

1. Nature of the material (ductile or brittle)
2. Temperature (at high temperature ductile fracture results)
3. Type and rate of loading

6.1 DUCTILE FRACTURE

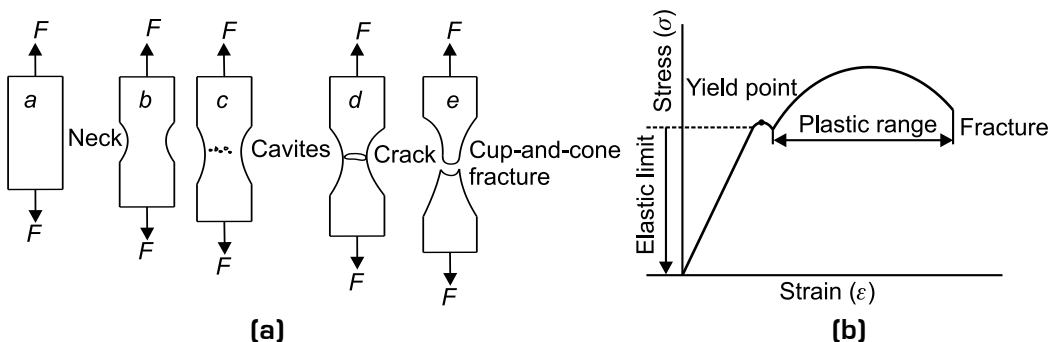
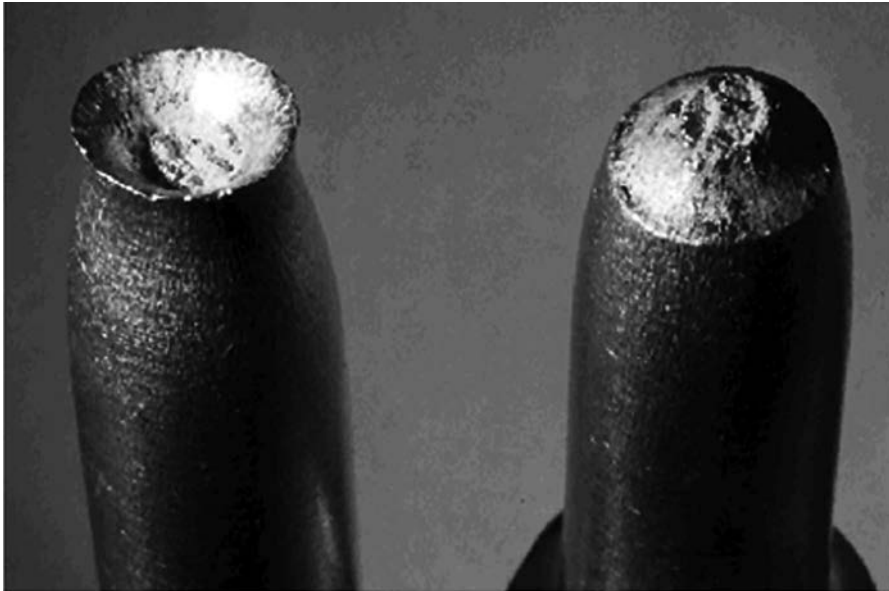


Fig. 6.1 The ductile fracture: (a) Stages of ductile fracture, (b) stress-strain diagram for ductile metal and (c) surface of fractures



(c)

Fig. 6.1 Continued

The ductile fracture occurs after an appreciable amount of plastic deformation prior to or during the propagation of a crack. It is clearly indicated by a large plastic deformation of the material. It is occurred by a slow tearing of the metal with the expenditure of the energy. The ductile fracture in a moderately ductile material under tensile stress is shown in Figure 6.1. There are three stages under which the ductile fracture of engineering materials in tension occurs. (1) In the initial stage (Figure 6.1(a) and (b)), after the elastic range of the specimen under the tensile load, the necking of the sample begins. A tri-axial state of the stress is introduced in the region as a result of neck formation. Many cavities formed in the region under the continued straining is called crack. This crack grows in the direction perpendicular to the specimen axis, until it approaches the specimen surface area. (2) In the centre of the sample, the cavities begin to coalesce into a crack in the centre of the specimen (Figure 6.1(c)). (3) With further increase in load, the crack further spreads the surface in the direction of 45° to the tensile axis and finally fracture occurs in the form of cup and cones. Development of cup-and-cone fracture in the neck begins at the point of plastic instability where the increase in the strength due to the strain hardening and decrease in cross-sectional area takes place at the maximum load.

The single crystals and the polycrystals of ductile metals show necking when they are highly pure. Most of the metals contain impurities and alloying constituents as second phases. During the ductile fracture, cohesion between different grains and atoms will be loose. Voids and dislocations grow under stress. The voids join together and form a continuous fracture surface followed by the fracture of the remaining annulus (central portion). In alloys, the central fracture surface shows numerous cup-like depressions. Their shape is influenced by the type of the stress. They will be circular in the case of tensile stress and parabolic in the case of shear stress.

6.2 BRITTLE FRACTURE (CLEAVAGE FRACTURE)

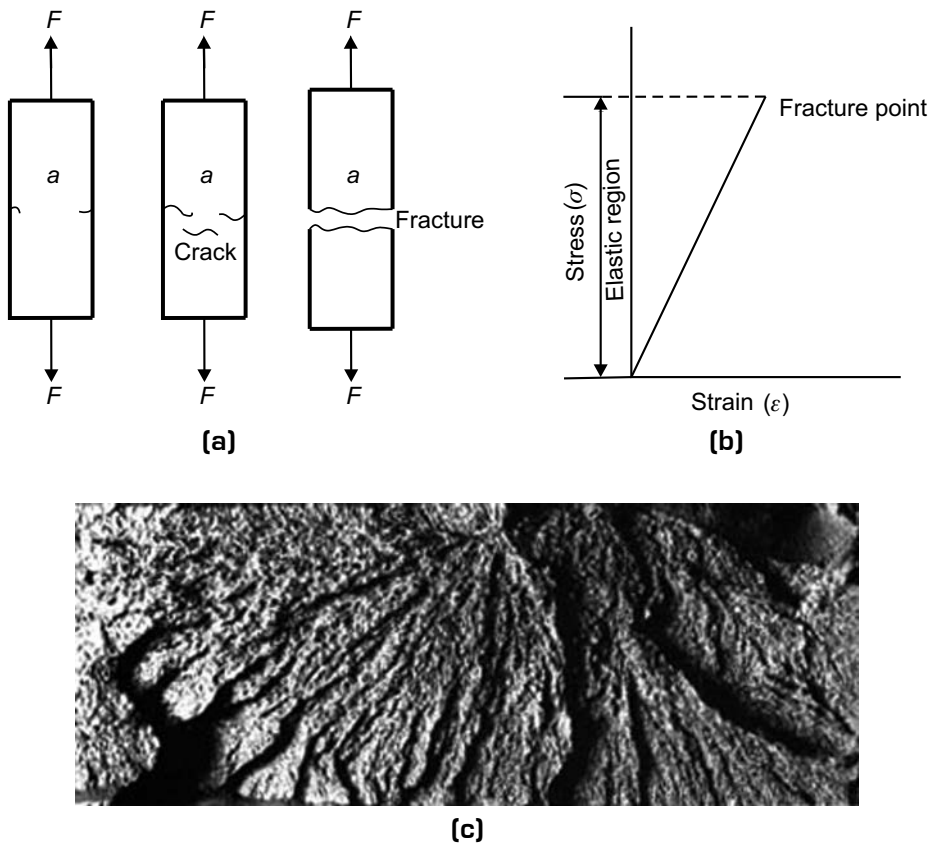


Fig. 6.2 (a) Stages of brittle fracture, (b) stress-strain diagram for brittle metal and (c) surface of fractures

The brittle fracture in metals is characterized by the rapid rate of crack propagation with minimum energy absorption and negligible deformation. The fracture proceeds along crystallographic planes or cleavage planes. It is identified by the presence of large smooth areas separated by steps or feathers or river markings or cleavage tongues as they are called. Fracture occurs by a very rapid rate of propagation of a crack after little or no plastic deformation. There will not be any elongation in the brittle fracture; and if there is any, it will be less than 1%. The stress and strain curve for a brittle fracture is as shown in Figure 6.2. The brittle fracture occurs in two stages—crack nucleation and crack propagation. In crack nucleation, the crack passes along the grain boundaries. In some cases, brittle fracture can be caused by grain boundary films. In crack propagation, the crack is not close to the crystal boundaries. It occurs within the elastic limit and suddenly. Usually, in brittle fracture, the materials will fracture into a number of pieces. The broken pieces of brittle fracture can be fitted together and, thus, the original shape and the dimensions of the specimen restored.

6.3 THEORETICAL COHESIVE STRENGTH OF MATERIALS

The strength in a material is due to the cohesive forces between the atoms of the material. Higher and stronger the magnitude of cohesive forces, higher the elastic constant, strength and the melting point of the materials.

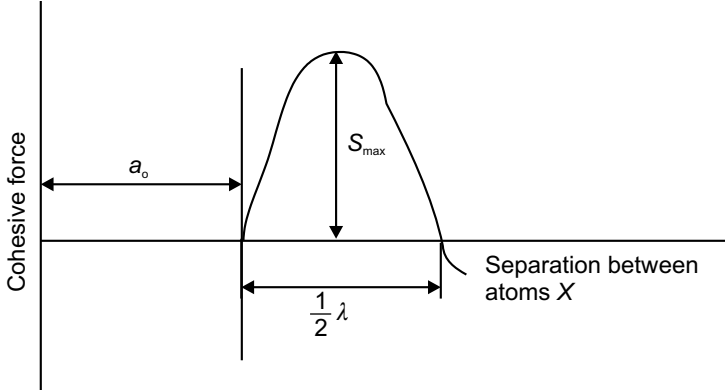


Fig. 6.3 Cohesive forces between two atoms

Figure 6.3 shows the variation of cohesive forces between two atoms as function of separation distance between the atoms. The curve represents the resultant of the attractive and repulsive forces between the atoms. The interatomic distance in unstrained condition is indicated by a_0 . If a crystal is subjected to a tensile load, the separation between the atoms will be increased with the increase in distance between the two atoms. The repulsive force first decreases rapidly than the attractive force. As the load is further increased, the repulsive force goes on decreasing and a point is reached where the repulsive force will be negligible and the attractive force reaches maximum. From this point onwards, with the increase in load, the attractive force goes on decreasing due to the increase in the separation distance of atoms. The cohesive force at this point is equal to the cohesive strength of the material. The material has to be plastically deformed by the applied stress and should be sufficient enough to overcome the cohesive strength of the material. Assume that the cohesive force curve represents a sine curve, then

$$\sigma = \sigma_{\max} \sin \frac{2\pi x}{\lambda} \quad (1)$$

where σ is the cohesive force, $\sigma_{\max}$ is the maximum theoretical cohesive strength, x is the displacement of atoms given by $x = a - a_0$, λ is the wave length and a_0 is interatomic space.

For small values of x , $\sin x = x$

Therefore,

$$\sigma = \sigma_{\max} \frac{2\pi x}{\lambda}$$

or

$$\sigma_{\max} = \frac{\sigma \lambda}{2\pi x} \quad (2)$$

$$E = \frac{\sigma}{e} \text{ or } \sigma = Ee$$

Also,

$$e = \frac{a - a_0}{a_0} = \frac{x}{a_0}$$

$$\sigma = E \times \frac{x}{a_o}$$

$$\sigma_{\max} = E \frac{x}{a_o} \frac{\lambda}{2\pi x} = \frac{E\lambda}{2\pi a_o} \quad (3)$$

When fracture occurs in a brittle material, all work preceding the fracture goes into the creation of two new surfaces. Each of these surfaces has a surface energy of γ_s erg/cm². The work done per unit area of surface in creating the fracture is the area under stress displacement curve which is given by U_o .

$$U_o = \int_0^{2/\lambda} \sigma_{\max} \sin \frac{2\pi x}{\lambda} = \frac{\lambda \sigma_{\max}}{\pi} \quad (4)$$

But this energy is equal to the energy required to create the two new fracture surfaces.

$$\frac{\lambda \sigma_{\max}}{\pi} = 2\gamma_s$$

$$\lambda = \frac{2\pi\gamma_s}{\sigma_{\max}} \quad (5)$$

Substituting the value of λ in Equation (3) and simplifying, we get

$$\sigma_{\max} = \frac{\lambda E}{2\pi a_o} = \frac{2\pi\gamma_s E}{\sigma_{\max} 2\pi a_o}$$

$$\sigma_{\max}^2 = \frac{\gamma_s E}{a_o}$$

$$\sigma_{\max} = \sqrt{\frac{\gamma_s E}{a_o}}$$

6.4 GRIFFITH'S THEORY OF BRITTLE FRACTURE

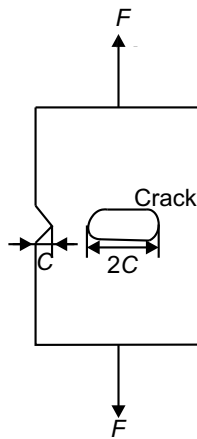


Fig. 6.4 Griffith's model for brittle fracture

The brittle fracture occurs with little or no plastic deformation. Crack appears suddenly and the metal gets fractured at unpredictable stress level. Griffith proposed a model, as shown in Figure 6.4, for

understanding the discrepancy between the theoretical strength and the actual fracture strength of the brittle material. He assumed that the brittle materials will contain a number of fine cracks which act as a notch to raise the stress due to the stress concentration. When a metal is stressed under tensile stress, then theoretical cohesive strength can be attained at this localized area with this stress concentration. The theoretical cohesive strength is reached at these regions even at a nominal stress which is well below the theoretical value of the cohesive strength.

Griffith established the following criteria for the propagation of crack, 'A crack will propagate when the increase in elastic strain energy is at least equal to the energy required to create a new crack surface.' In this theory, the energy method is employed to estimate the stress necessary to cause the crack propagation.

The elastic strain energy per unit volume is given by

$$U_e = -\frac{\sigma^2}{E} \times \text{Width} \times \text{Area} = -\frac{\sigma^2}{E} \times 2C \times \pi C = -\frac{2\pi C^2 \sigma^2}{E}, \text{ where } \sigma \text{ is the tensile stress acting normal to}$$

crack and E is the Young's modulus. Here, negative sign indicates decrease in the elastic strain energy.

The surface energy of the flat crack of length $2C$ and that of unit width is

$$U_s = (2\gamma C)2 = 4\gamma C$$

where γ is surface energy per unit area of crack surface. This equation is multiplied by 2 because there are two new crack surfaces.

Applying Griffith's criteria, if the crack is to propagate in length, it does not change the net energy of the system. In addition to this, it will propagate and produce brittle fracture. The total energy change during the process is

$$\begin{aligned} U &= U_e + U_s \\ &= -\frac{2\pi\sigma^2 C^2}{E} + 4\gamma C \end{aligned}$$

To know the maximum stress at which the crack begins, differentiate the above equation and equate it to zero.

$$\begin{aligned} -\frac{d\left(\frac{2\pi\sigma^2 C^2}{E}\right)}{dC} + \frac{d(4\gamma C)}{dC} &= 0 \\ \frac{2\pi\sigma^2 C}{E} &= 4\gamma \end{aligned}$$

or

$$\sigma^2 = \frac{2\gamma CE}{\pi C^2}$$

$$\sigma_{\text{crit}} = \sqrt{\frac{2\gamma E}{\pi C}}$$

The above equation shows that the stress necessary to cause brittle fracture and limitation of Griffith's theory is applicable only for brittle fracture. It can be seen from this equation that the stress required to fracture a metal is lower if the existing crack is longer and the energy consumed in plastic deformation is smaller. It is believed that in some cases, micro-cracks exist in the metal due to solidification or hot working. Such cracks will accumulate as barriers to dislocation movement. They, in turn, propagate and contribute brittle failure. The increase in the work temperature promotes plastic deformation making the metal ductile.

EXERCISES

1. Explain the various types of fractures observed in metals.
2. What are the two major types of fractures of metals? Differentiate between them.
3. Explain the Griffith's theory of brittle fracture and also derive an expression for the fracture stress which is just required to propagate a crack.
4. State and explain the Griffith's theory of brittle fracture. Is this theory applicable to ductile materials? Explain.
5. Explain the theoretical cohesive strength of materials and derive an expression for the same.
6. Using Griffith's criterion, derive an expression for the fracture stress that would just propagate a crack of certain length into a brittle fracture.
7. Differentiate between ductile and brittle fractures.

OBJECTIVE -TYPE QUESTIONS

1. Ductile fracture shows _____.
 (a) Regular surface (b) Narrow surface
 (c) Cup-and-cone shape (d) All of the above
2. Ductile fracture appears _____.
 (a) After large deformation (b) With minimum deformation
 (c) Without deformation (d) All of the above
3. Fracture _____.
 (a) Is a end result of deformation (b) Appears during deformation
 (c) Both (a) and (b) (d) None of the above
4. Before ductile fracture _____.
 (a) Yielding of metals takes place (b) Tri-axial stress develop in a point
 (c) Crack nucleates and enlarges (d) Cross section increases
5. Brittle fracture takes place _____.
 (a) By large deformation (b) By tearing of metal
 (c) By cleavage fracture (d) By stress concentration
6. Brittle fracture _____.
 (a) Occurs after large deformation (b) Occurs suddenly
 (c) Broken pieces cannot be fitted together (d) None of the above
7. High cohesive strength of metal should have _____.
 (a) Lower melting point (b) Low yield strength
 (c) Fracture within elastic limit (d) Higher elastic constant
8. Brittle fracture occurs when _____.
 (a) No plastic deformation (b) Cracks appear slowly
 (c) Stress level is predictable (d) All of the above

9. Cohesive force between the two atoms _____.
 (a) Repulsive force will be negligible and the attractive force is maximum.
 (b) Repulsive force will be maximum and the attractive force is negligible
 (c) Both (a) and (b) (d) None of the above
10. As per the Griffith equation, _____.
 (a) Energy is required for deformation
 (b) Simple separation of atoms is required
 (c) Energy is absorbed in plastic deformation
 (d) Energy is required to create a new crack surface

ANSWERS

1.	c	2.	a	3.	c	4.	b	5.	c	6.	b
7.	d	8.	a	9.	a	10.	d				

7

chapter

Creep

INTRODUCTION

The materials have to sustain steady or constant loads for long periods of time in many of their applications. It may be under different temperature conditions. Under these conditions, the materials may undergo plastic deformation with time without any increase in the load which results in fracture. Thus, the time-dependent deformation or strain occurring under a constant stress is known as creep. Some examples of creep are blades of turbine rotor, steel cables and concrete.

7.1 CREEP CURVE

A creep curve is a plot of the creep strain versus the time taken to fracture the specimen. The plot is obtained by conducting creep test. During the test, the creep strain at various time intervals is measured and plotted as a function of elapsed time. The curve drawn between the total creep deformation and the time duration is shown in Figure 7.1. The creep curve shows the three stages of the creep—primary, secondary and tertiary. These stages are identified based on the deformation behaviour of the metal with time.

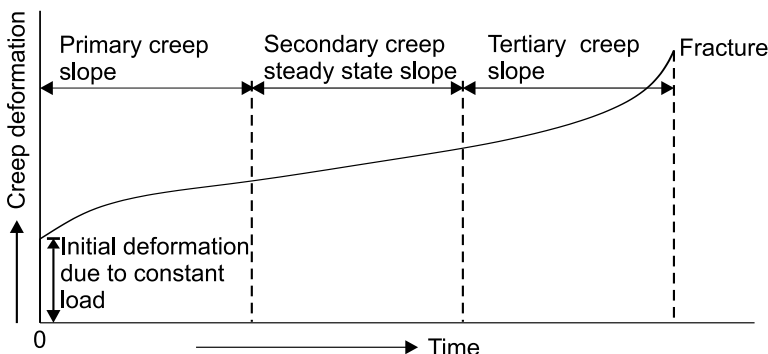


Fig. 7.1 Creep curve

7.1.1 Primary Creep

The stage of the creep during which the creep rate decreases with time due to the work hardening (strain hardening) because of the plastic deformation is called primary creep. It usually occurs in the elastic region of the material. This creep is also called transient creep or cold creep. The material can revert to its original dimensions if it is unloaded in this stage.

7.1.2 Secondary or Steady-state Creep

The stage of the creep in which the creep rate is minimum is called secondary or steady-state creep. As the rate of creep decreases to an essentially constant value, the metal enters the second stage of creep and this stage is of longest duration in the creep curve. The metal constantly deforms because the rate of re-softening balances the rate of strain hardening. In this stage, a balance exists between the rate of strain hardening and rate of softening due to recrystallization. In this stage, the creep rate is constant and hence, the curve is linear. The second stage of creep is also known as hard creep. The creep deformation at this stage is shown by a steady-state or a constant slope in the curve.

7.1.3 Tertiary or Viscous Creep

The tertiary creep is marked by a rapid increase in the creep rate and failure of the specimen for a short duration of time. If the magnitude of constant load and the temperature are sufficiently high, this creep results. In this stage, the creep deformation accelerates as viscous flow until the material is fractured. Failure by creep is usually referred by the term rupture or creep rupture. This is shown by the increasing the slope up to the fracture in the curve.

7.2 EFFECT OF TEMPERATURE ON CREEP DEFORMATION (LOW TEMPERATURE AND HIGH TEMPERATURE CREEP)

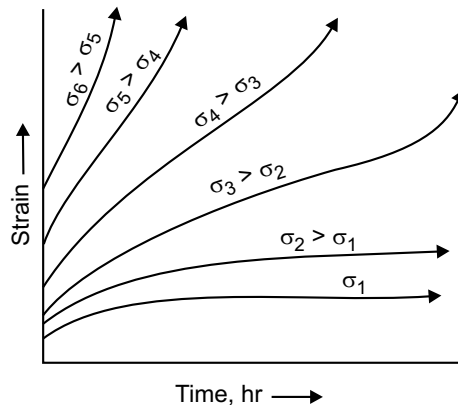


Fig. 7.2 Effect of temperature on the creep (low and high temperature creep)

At a low temperature, where recovery is not possible, the transient creep results. At low temperatures, the creep deformation obeys the mechanical equation of state, i.e. the rate of strain at a given time depends only on the present stress and strain values but not on the previous strain history. Under low temperature, because of the strain hardening of the material, the creep deformation can take place only up to an extent, which restricts further deformation (see Figure 7.2).

At a high temperature, the progress of the creep very much depends on the prior strain and thermal hysteresis of the material. It does not obey the mechanical equation at a high temperature. This results in a steady state wherein the material deforms continuously, even under a small static load, until the material is fractured.

A high temperature creep can be observed only at higher temperatures, when the recrystallization of the material can take place, whereas the transient creep can be observed even at absolute zero temperature. Therefore, the transient creep is usually referred as cold creep and the viscous creep as hot creep.

7.3 TRANSIENT CREEP

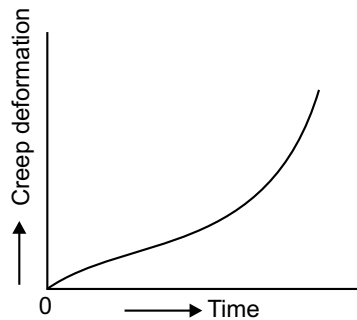


Fig. 7.3 Transient creep behaviour

Transient creep, shown in Figure 7.3 by a small increase in slope of the curve, is also known as primary creep. This occurs in the material in its elastic range and the material can obtain its original dimensions when the load is removed. Deformation takes place slowly.

In this creep, owing to the constant load applied on the material, the material deforms with a loss of time and the deformation ceases after a certain time when the stress applied is balanced by strain hardening. This is the cold creep which takes place at low temperatures, even at absolute zero temperature. The transient creep obeys the mechanical equation of state.

7.4 VISCOUS CREEP

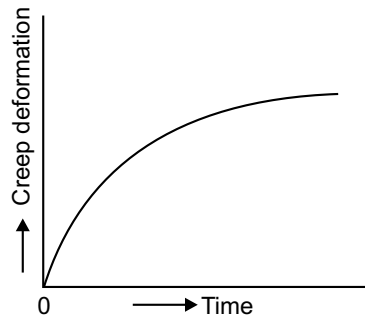


Fig. 7.4 Viscous creep behaviour

The viscous creep cannot be seen at small stress and at low temperatures. This takes place in the materials only at a high temperature where the recrystallization of material can take place. In the materials that strain harden due to deformation, the viscous creep occurs when the strain hardening effect is just balanced by the softening effect due to high temperature. At a high temperature, the viscous creep occurs even at stress below the yield stress of the materials (see Figure 7.4). This is also considered as high temperature or hot creep.

7.5 MECHANISM OF CREEP

The following are the mechanisms that will take place during the process of creep:

1. Climb of dislocation
2. Sliding of grain boundary
3. Diffusion of vacancy

7.5.1 Dislocation Climb

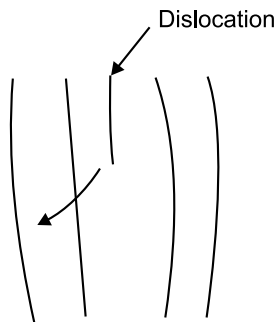


Fig. 7.5 Dislocation climb in creep behaviour of metals

At a high temperature, a considerable atomic movement causes the dislocation to climb up or down. In a climb of edge dislocation, there may be diffusion of atoms due to the applied stress. Thus, the edge dislocation is moved from one end to the other and the rate of creep is governed by the rate of escape (movement of) of dislocation beyond the obstacles (see Figure 7.5).

7.5.2 Sliding of Grain Boundary

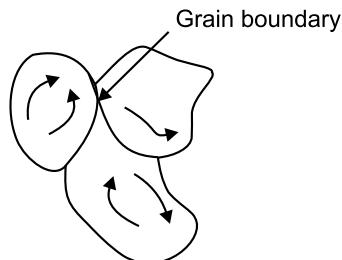


Fig. 7.6 Grain sliding in creep behaviour of metals

The grain boundaries become soft at low temperatures and at high strength. The grain boundary plays a major role in the creep of polycrystals at high temperature as they slide through each other. At a high temperature, the ductile metals begin to lose their ability to strain harden and become viscous because of sliding of grain boundary (see Figure 7.6).

7.5.3 Diffusion of Vacancy

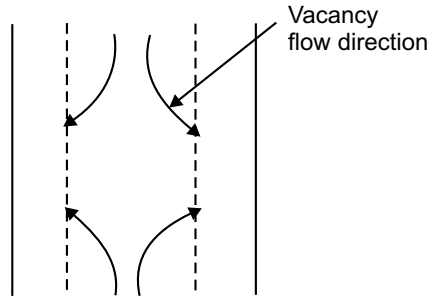


Fig. 7.7 Diffusion of atoms in a vacancy mechanism in creep behaviour

In the diffusion of vacancy mechanism, atom vacancies control the creep rate. It depends on the migration of vacancies from one side of the grain to another. Vacancies move in response to the applied stress in the direction as shown in Figure 7.7.

7.6 CREEP PROPERTIES

The most important creep properties are creep strength and creep rupture strength. The creep strength of a metal can be defined as the highest stress that a material can withstand for a specified length of time without excessive deformation. Creep strength is also called as the creep limit. However, these properties vary with the temperature. The creep fracture strength is the stress at which the material gets fractured. When the plastic deformation is accompanied with a reduction in the cross section of the material, the creep usually ends with fracture if it is allowed to continue for a long time.

7.7 CREEP FRACTURE

The creep fracture occurs in many ways. In the case of ductile materials, the creep fracture may take place at a higher temperature and under longer stress. The metals start to lose their ability to strain harden due to temperature. Therefore, the fracture may take place at a nearly uniform elongation without the formation of a neck. The metals get fractured with very large plastic deformation. The grain boundary shearing is the main cause for the deformation and fracture. In metals, the movement of all grains towards each other causes the cracks and one crack large enough to open spreads across the member until fracture. At high stress, moderate temperature and at short time, the fracture is usually the same as in a simple tension. A ductile material may form a neck before fracture. At stress acting for long times, the deformation is sometimes almost negligible and the fracture tends to be a brittle fracture.

7.8 ELASTIC AFTER-EFFECT (AN ELASTIC BEHAVIOUR OR DELAYED ELASTIC)

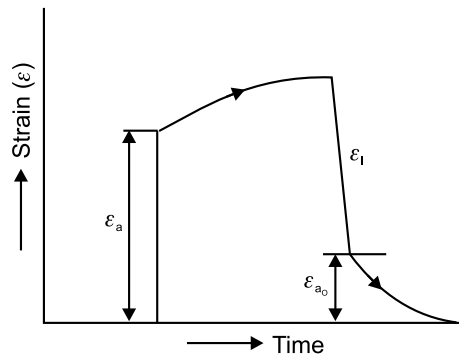


Fig. 7.8 Elastic after-effect during tensile creep

The time-dependent change of strain on loading and unloading is known as elastic after-effect. Consider a material subjected to a certain constant stress below the elastic limit. Due to this sudden stress, the material will strain instantaneously up to a level, and if the load is not removed, the material will gradually deform due to the creep until the strain reaches an essentially constant value as shown in Figure 7.8. If the load is removed suddenly at this stage, the strain develops instantaneously up to a certain level. A certain amount of strain still remains in the material, which decreases slowly with time.

7.8.1 Stress Relaxation

The stress relaxation is a phenomenon observed in some materials, which have been subjected to stress under constant load. It is the process in which there is a reduction in stress in a material over a period of time under an applied constant stress at a constant temperature and there will be no change in the dimensions of the component. This process is just the reverse of creep process. In this process, the material loses its stress with time whereas in the creep process, the material deforms with time, both under constant load. A few examples of components undergoing stress relaxations are nut and bolt, rivets, electrical wire and guy, and other parts that may be under tension, compression or bending loads.

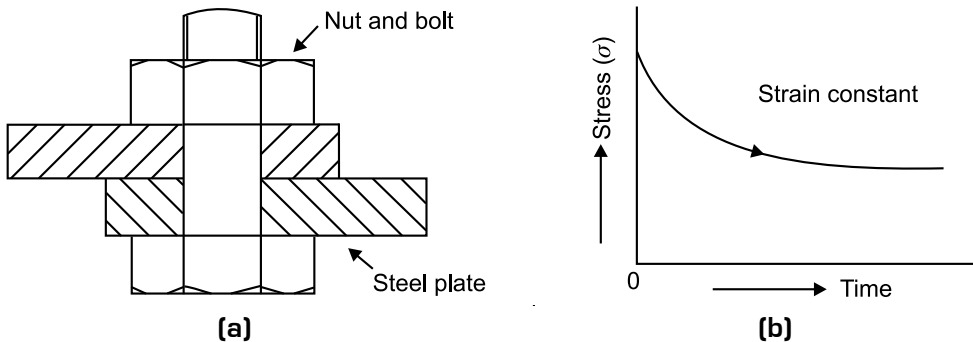
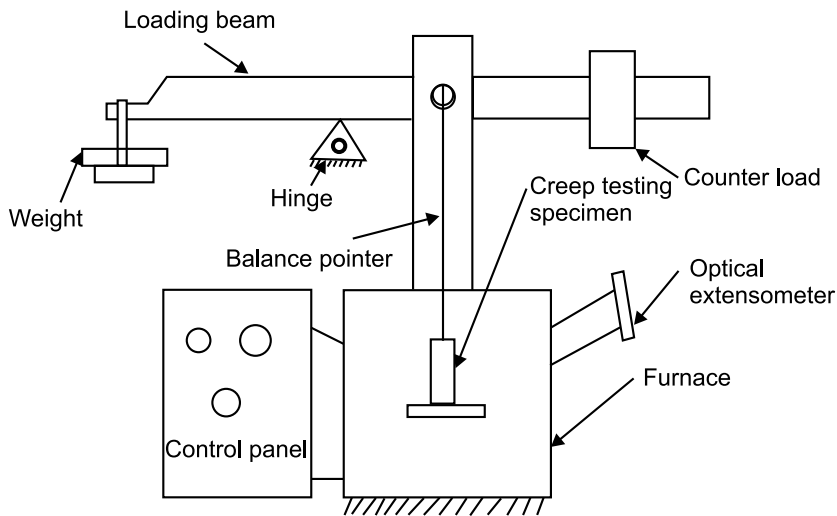


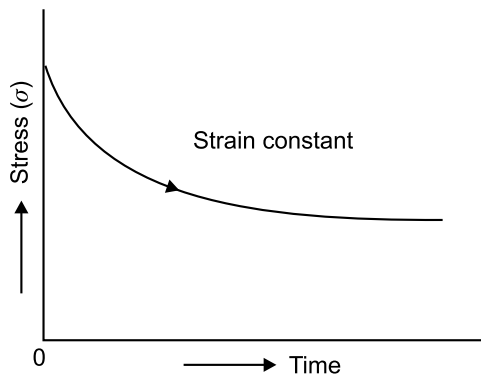
Fig. 7.9 (a) Stress relaxation in a nut-and-bolt experiment and (b) stress relaxation curve

A stress relaxation test is a creep test performed under unsteady stress. When two plates hold in tight contact are frequently found to have relaxed considerably after long period of time as a result of creep as shown in the Figure 7.9. During the testing of the specimen, deformation is observed as a function of time. Because of creep the metal is plastically deformed by dislocation and strain rate increases with time.

7.9 CREEP TESTING



(a)



(b)

Fig. 7.10 (a) Creep testing set-up and (b) creep testing graph

The advanced technologies require materials which are loaded and heated up simultaneously and are very fast. Materials to be used in space, aerospace and thermal power plant are tested under actual or predicted service conditions. Short time high temperature tests are developed on these lines. A special test specimen is heated by furnace under high load (predetermined load). The temperature and the elongation are recorded by special instrumentation.

During the creep test, a specimen is held at a constant load and at a constant temperature. The specimen is placed inside the furnace and heated for four to five hours, so that its temperature becomes uniform throughout. It is then subjected to a constant load by a lever and dead weight system. The creep deformation starts in the specimen, which is recorded at certain interval of time. Optical extensometer records the strain in the specimen. The deformation produced is measured as a function of time. The values so obtained are plotted on a curve with stress on the y -axis and time (log scale) on the x -axis. The curve obtained appears as the curve shown in the Figure 7.10.

7.10 FACTORS AFFECTING CREEP

As discussed so far, the creep occurs due to the grain boundary softening of the metal or an alloy. Thus, we can interpret the important criteria, i.e. their effect on either grains or grain boundaries. The alloying elements, i.e., those which dissolve and strengthen in the solid solution or grains, e.g., Ni, Co and Mn, will increase the creep strength and the steel carbide forming elements like Ti, Mo, W, etc. which segregate at the grain boundaries, decrease the creep strength. Similarly, heat treatment processes like normalizing and annealing improve the creep properties of steels. The steel made by electric induction furnace is found to possess better creep properties than steels made by other methods. In electric induction melting, all the inclusions (and slag) will be removed which segregate at the grain boundaries. The coarse-grained steels are superior to the fine grained ones. The proportion of grain boundary to grain (area) is small in the case of coarse-grained steels. The atmosphere of service of the material influences the creep property of the metal. Corrosive and oxidizing atmospheres decrease the creep properties.

EXERCISES

1. What is creep in metals? Draw a typical creep curve and explain the stages of creep.
2. What is meant by creep in metals? Draw a typical three-stage creep curve of a metal? Which stage is of practical significance? Justify your answer.
3. Draw a creep curve showing the three stages of creep. Write a sentence about each stage.
4. Explain the different stages of creep.
5. With the help of a creep curve, explain the mechanism of creep.
6. Explain clearly the two major mechanisms that contribute to the creep of metals.
7. Draw S–N diagrams showing the fatigue limit and explain briefly.
8. Explain the phenomenon of viscous creep and the conditions under which it is predominant.
9. State and explain the methods to determine the creep strength of metals. Write a note on creep properties of metals.
10. Using the creep curve, explain the three stages of creep. What is the effect of temperature on these stages?

102 | Creep

11. Define creep strength and creep rupture strength. Describe any one method of determinations of these properties. Name the four important creep mechanisms.
12. Explain the following:
 - (i) Transient and viscous creeps
 - (ii) Creep properties
 - (iii) Stress relaxation

OBJECTIVE -TYPE QUESTIONS

1. Creep is a unique property which is commonly observed in _____.
 - (a) Boiler shell
 - (b) Rotating axils
 - (c) Overhead cables
 - (d) All of the above
2. The part which does not come across the creep deformation is _____.
 - (a) Turbine rotor
 - (b) Furnace parts
 - (c) Overhead beam
 - (d) Vehicle engine
3. Creep can be stated as _____.
 - (a) Time-dependent stress under constant temperature
 - (b) Time-dependent strain under constant stress
 - (c) Time-dependent strain with varying load
 - (d) Time-dependent stress with varying temperature
4. The decreasing creep rate because of working hardening process is known as _____.
 - (a) Tertiary creep
 - (b) Secondary creep
 - (c) Primary creep
 - (d) All of the above
5. $\frac{de}{dt}$ is constant at _____.
 - (a) Primary creep
 - (b) Tertiary creep
 - (c) Secondary creep
 - (d) None of the above
6. In a steady-state creep, _____.
 - (a) Rate of work hardening balances the rate of softening
 - (b) Only work hardening can be observed
 - (c) Only softening can be observed
 - (d) All of the above
7. Temperature and stress level are high in the case of _____.
 - (a) Steady-state creep
 - (b) Transient creep
 - (c) Viscous creep
 - (d) None of the above
8. High temperature creep is characterized by _____.
 - (a) Twinning of atoms
 - (b) Dislocation of atoms
 - (c) Slip of atoms
 - (d) Grain sliding
9. Viscous creep is _____.
 - (a) Nonexistent at low temperature and low stress
 - (b) Nonexistent at high temperature and high stress
 - (c) Nonexistent at medium temperature and high stress
 - (d) All of the above

10. The mechanism not related to creep is _____.
 - (a) The glide of dislocation leading to creep
 - (b) The climb of dislocation leading to creep
 - (c) The sliding of grain boundary
 - (d) Griffith theory
11. At high temperature, the atomic movement permits the dislocations to jog is known as _____.
 - (a) Dislocation glide
 - (b) Dislocation climb
 - (c) Diffusion of atoms
 - (d) Grain boundary sliding
12. Grain boundary plays a major role in the creep of _____.
 - (a) Single crystalline
 - (b) Polycrystalline
 - (c) Mixed crystalline
 - (d) All of the above
13. The stress at which the material will not excessively deform at constant load is known as _____.
 - (a) Creep strength
 - (b) Creep limit
 - (c) Creep fracture strength
 - (d) All of the above
14. The stress at which the material gets creep fractured is known as _____.
 - (a) Ultimate strength
 - (b) Fracture strength
 - (c) Yield strength
 - (d) Creep strength
15. The creep curve is a plot between _____.
 - (a) Stress and the time on log graph sheet
 - (b) Stress and the time on normal graph sheet
 - (c) Total creep and the time on log graph sheet
 - (d) Total strain and time on normal graph sheet

ANSWERS

1.	d	2.	d	3.	a	4.	b	5.	b	6.	b
7.	b	8.	b	9.	a	10.	d	11.	b	12.	b
13.	a	14	b	15.	c						

Fatigue

INTRODUCTION

The materials when subjected to fluctuating or repeated dynamic loads will fracture at a stress or load much lower than the stress required for causing a fracture under continuous application of steady loads. This phenomenon of fracture is known as fatigue and it takes place by loss of strength, loss of ductility and increased uncertainty in both strength and service life. The fatigue failure is a dynamic phenomenon and all rotating parts such as axles of motor vehicles, crankshaft, shafts of machine and the wings of aircraft are some of the examples subjected to fluctuating stress and fatigue fracture. The fatigue failure of a material depends upon a number of factors such as fatigue loading, magnitude of the load, nature of the material and temperature. The fatigue failure occurs without prior notice and it is similar to a brittle fracture as shown Figure 8.1. This can occur in all types of materials.



Fig. 8.1 Fatigue fracture of the rim of a car wheel

8.1 TYPES OF FATIGUE LOADING

There are many types fatigue loading that can cause fatigue behaviour. The applied stress may be tension/compression (axial), bending (flexural), twisting (torsional) (twisting) or a combination of any of these conditions which are reverse loading, alternative fluctuating loading, repeated loading and irregular loading.

8.1.1 Completely Reversed Loading

Figure 8.2 shows a complete reversed cycle of stress. The load is reversed in a definitive time interval and the stress magnitude is equal to the maximum stress and the average stress is zero. The stress will be varied in an interval of time with a same magnitude on both the positive and negative sides. The amplitude is symmetrical about the mean. Tensile is considered as positive and compressive stress as negative. This type of stress is developed by rotating the shaft operating at a constant speed, without overloads. It is the most useful form of fatigue loading used in practice. For example, this reversed loading can be seen when the rotating axle or shaft experiences the bending stress; and the rotating shaft on two bearings at a constant load will undergo such fatigue cycle.

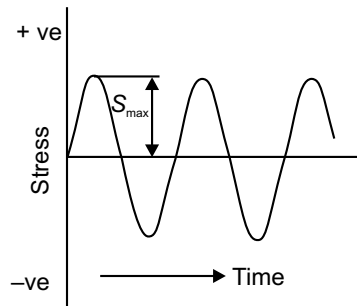


Fig. 8.2 Completely reversed cycle of stress

An alternative fluctuating stress is produced by a steady stress due to the constant load. The tensile or compression load will be applied on to the material that is already stressed to a certain extent. In this, the mean stress is equal to the steady stress and the maximum stress is equal to the sum of the mean stress and the stress amplitude as indicated in Figure 8.2. These types of load will vary on both the sides of the constant stress, whereas there is no limit for variation on the positive and negative sides. The example of this is a weight added to the beam near the end where it is connected to the crank.

8.1.2 Repeated Loading

In repeated loading, the maximum and minimum stress values are not equal and this type of loading is a push-pull type of loading where the applied stress will not vary on both the sides but varies on only one side. There is no limit for the magnitude of the applied stress variation (see Figure 8.3). For example, the leaf springs in a car undergo repeated stress cycles, as the number of passengers and the road conditions vary.

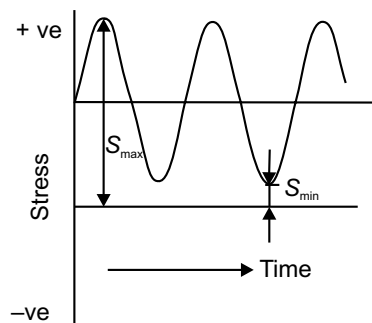


Fig. 8.3 Repeated cycle of stress

8.1.3 Irregular Loading

A type of loading in which the stress variation is highly random, as shown in Figure 8.4, is known as irregular loading. The applied stress values are not regular and vary in each cycle. Example of random loaded component is the aircraft wing, which undergoes a series of varying stress levels due to gust loads while takeoff, flying and landing.

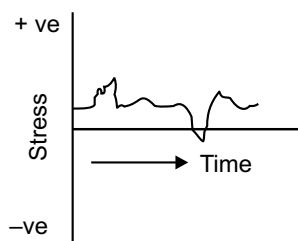


Fig. 8.4 Irregular cycle of stress

8.2 MECHANISM OF FATIGUE FAILURE

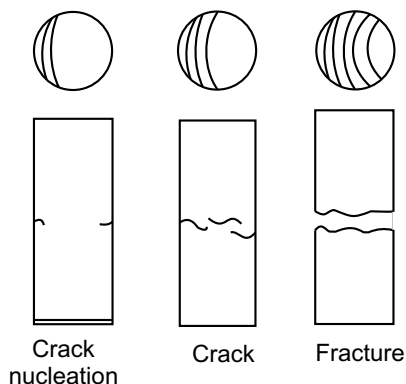


Fig. 8.5 Stages of fatigue fracture

The fatigue failure that occurs due to simple alternative tensile and compressive stress is shown in Figure 8.5. A fatigue fracture always starts as a small crack under repeated loading of the stress. As the crack expands, the load carrying the cross section of the metal component is reduced due to the increasing stress on this section. Ultimately, a point is reached where the remaining cross section is no longer strong enough to carry the load and it finally results in a fracture. A number of theories have been proposed by different research works which are discussed in the following subsections.

8.2.1 Orowan's Theory

The metals contain a small crack or weak regions in those areas of the specimen which are favourable for deformation. If the stress is such that the total plastic strain in the weak region exceeds the critical value, the crack is formed. This crack creates stress concentration due to which a new localized plastic region is formed in which the process is performed repeatedly until the crack becomes large enough and results in a fracture.

8.2.2 Wood's Theory

Wood conducted microscopic observation on the slip produced by fatigue. The slip produced by fatigue stress is a systematic buildup of fine slip movements corresponding to movements of the order of 10^{-7} cm rather than in steps of 10^{-5} to 10^{-4} cm, which are observed for static slip bands. According to Wood, the fine slip movements of fatigue could build up notches at surface, which act as stress increase, and a fatigue crack starts in this manner, which ultimately leads to fatigue fracture.

8.2.3 Cottrell and Hull Theory

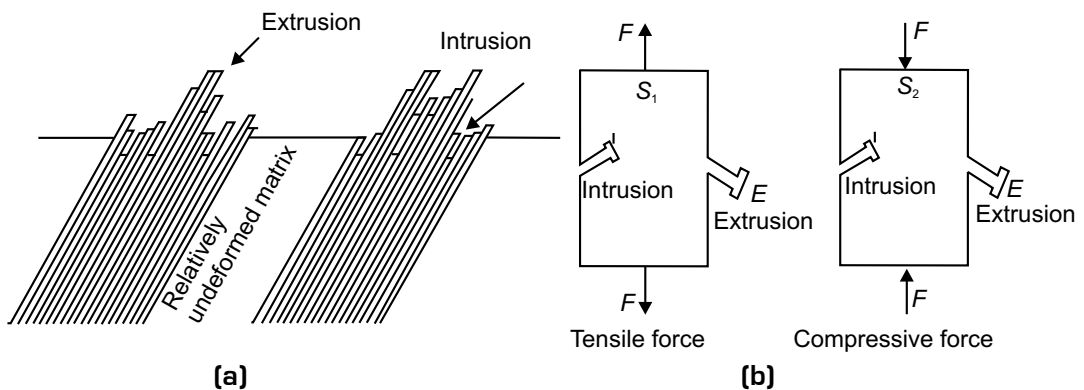


Fig. 8.6 The intrusion and extrusion of dislocation during fatigue loading: (a) Actual deformation of metal and (b) intrusion and extrusion dislocation developing based on the type of load

Cottrell and Hull suggested a model involving the interaction of edge dislocation on two slip systems. Two different slip systems with different directions and planes of slip produce slip steps at surface forming intrusions and extrusions. Also, it is believed that the fatigue crack starts instantaneously at the surface. S₁ and S₂ are the source-producing slip steps on the surface of intrusion, I, and extrusion, E (See Figure 8.6).

8.3 FATIGUE PROPERTIES

The most important fatigue properties are fatigue life, fatigue limit and fatigue strength. Fatigue life is nothing but the total number of stress cycles required to bring about the fracture under the given loading conditions. As measured experimentally, fatigue life for a given specimen under a given condition is a property of the individual specimen. Fatigue limit is the stress level below which a material can withstand an infinite number of fatigue cycles without failure.

8.4 S-N DIAGRAM

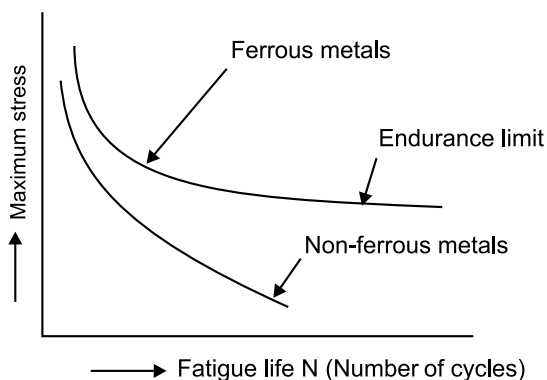


Fig. 8.7 S-N diagram

The fatigue testing samples are tested and each sample is broken at different stress. The breaking stress and the number of revolutions the specimen had undergone before the failure are recorded. The vertical axis shows the maximum stress ($\sigma_{\max}$) and horizontal axis represents the cycles to failure or fatigue life (N) in a semi-log graph sheet called S-N diagram. Figure 8.7 shows the variation of fatigue life with stress. From the S-N curves, it can be seen that at the higher stress levels, failure occurs by small number of cycles. At lower stress values, the number of cycles to failure increases. When a series of stress is plotted against the number of cycles to failure at each stress on a graph, the curve becomes perfectly horizontal at some particular stress for ferrous metals. This stress is known as the endurance limit (EL) or fatigue limit. If any ferrous metal or alloys are loaded to a stress which is below its endurance limit, failures do not occur. However, for non-ferrous metals, there is a gradual decrease in stress, which increases in N value and consequently there is no such fatigue limit for non-ferrous materials.

8.5 FACTORS AFFECTING FATIGUE

The fatigue of a metal component under fatigue loading is influenced by a number of factors such as surface condition, temperature, frequency of stress cycle and environment condition.

The fatigue strength and fatigue life are structure-sensitive properties. The fatigue strength of metals increases with the decreasing grain size. The fatigue life is affected by chemical composition, grain size and amount of cold working on the metal. The surface irregularities such as cracks or rough surface cause stress concentration and reduce the fatigue limit. The surface roughness can be

reduced by cladding or coating on the metal with low melting metals, such as zinc, and polymers like paint. The fatigue strength is highest at a low temperature and decreases gradually with increase in temperature. For better fatigue strength, the metal should be at a low temperature. For most metals, the frequency of the stress cycle has little effect on the fatigue life. At lower frequency, the metals have high fatigue life. Corrosive environment may create pits on the metal component, which then acts as notches, which increases the stress and ultimately reduces the life of the component.

Another way of improving the fatigue strength is by heat treatment. Many iron alloys can be hardened by being heated to a high temperature and then by quenching in water. This treatment when applied locally to the surface layer substantially increases their fatigue strength. Further increase in strength can be achieved by combining heat treatment with chemical action of elements like carbon and nitrogen, which diffuse into the surface layers of iron at high temperatures. Finally, effective immunity against chemical corrosion can be secured by plating the surface of metals with protective coatings.

8.6 FATIGUE TEST

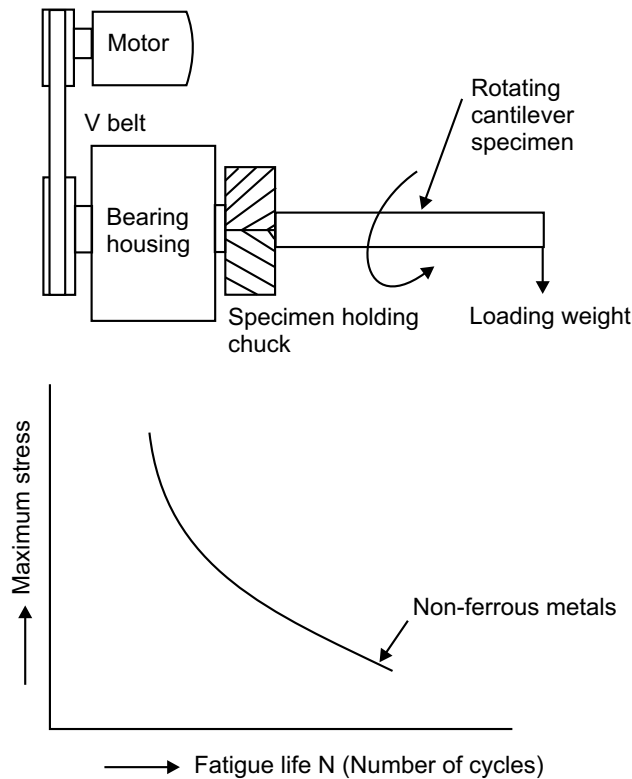


Fig. 8.8 Fatigue testing set-up

The experimental set-up consists of bearing housing coupled with a chuck to hold the specimen. One end of the specimen is fixed to the chuck and other end is loaded as shown in Figure 8.8. The

specimen rotates at constant speed and it creates load reversal in its layer of the metal. During one revolution of the specimen, the upper surface of loaded specimen is in tension and the lower surface is in compression with neutral axis at the centre. The number of rotations of the specimen is measured using tachometer.

For a given load, the number of cycles the material can service before failure (N) is noted down. Such experiments are conducted for various stress levels. Finally, plot the graph stress verses number of cycles. The typical S–N diagram is shown in Figure 8.8.

8.7 FATIGUE FRACTURE

The fatigue fracture occurs in materials which are subjected to a cyclic stress repeatedly. It occurs suddenly without prior notice and is similar to the fracture in brittle materials. This fracture appears at all temperatures. The metals deform initially due to the cyclic stress and get strain harden. The nucleation of fracture takes place as a result of localized plastic flow. On further cyclic loading, the metal becomes brittle due to work hardening and also by the decreasing ductility. The stress concentration becomes equal to the cohesive strength of the material leading to cracking. The small cracks spread in the boundary of the grains and lead to fatigue fracture.

EXERCISES

1. Define fatigue. State and explain the different types of fatigue loading.
2. Define fatigue in metals. Describe the various types of fatigue loading with examples.
3. Write a note on different types of fatigue loading.
4. Explain the mechanism of fatigue failure. What factors affect the fatigue failure?
5. Discuss various metallurgical features that affect fatigue.
6. How would you conduct a test to assess the fatigue life of a material? Explain briefly.
7. Define the properties of a material in fatigue and briefly explain an experiment used to measure any one of the property.
8. Explain the mechanism of fatigue crack growth in ductile materials.
9. Explain how the S–N diagram is obtained experimentally.
10. What is S–N diagram? How is it drawn? How is it useful to convert fatigue life to fatigue strength?
11. How does fracture occur in fatigue loading of a metallic material? Discuss the important features of a fatigue fracture.
12. What is the most likely method of failure of a shaft subjected to completely reversed loading? Draw the corresponding stress cycle diagram and explain the terms stress amplitude, mean stress and stress ratio for the above case.
13. Explain the important feature that is noted in the S–N diagram for ferrous materials.
14. Explain the different mechanisms of fatigue failure? Write a note on S–N diagram.

OBJECTIVE -TYPE QUESTIONS

1. Stress amplitude varying with time is known as _____.
 (a) Dynamic stress (b) Normal stress
 (c) Varying stress (d) Fluctuating stress
2. Fatigue occurs in a metal due to _____.
 (a) Loss of strength (b) Loss of ductility
 (c) Increased uncertainty (d) All of the above
3. Fatigue refers to _____.
 (a) Material failure under the action of constant stress
 (b) Material failure under the action of repeated stress
 (c) Material failure under the action of dynamic stress
 (d) All of the above
4. The stress amplitude is symmetrical in the case of _____.
 (a) Fluctuating loading (b) Reversed loading
 (c) Repeated loading (d) Irregular loading
5. An example of fatigue behaviour is _____.
 (a) Crank shaft (b) Electrical cable
 (c) Furnace parts (d) Building roof
6. Repeated fatigue load is characterized as _____.
 (a) Maximum and minimum stress values are equal
 (b) Maximum and minimum stress values are not equal
 (c) Stress amplitude vary with both sides
 (d) None of the above
7. Fatigue fracture starts with _____.
 (a) Small crack under repeated loading
 (b) Nucleating of crack at the centre of the metal
 (c) Tearing of metal under fluctuating stress
 (d) Slipping of metals
8. The theory which states that 'metal contain a small crack is favourable for deformation' is _____.
 (a) Wood's theory (b) Orowan's theory
 (c) Cottrell and Hull theory (d) None of the above
9. Wood's theory for fatigue is based on _____.
 (a) Both dislocation and slip deformation
 (b) Small crack is favourable for fatigue deformation
 (c) Interaction of edge dislocation
 (d) Slip produced by fatigue stress
10. Fatigue life is _____.
 (a) Total stress cycle required to bring fracture at a given load
 (b) Total time required to bring fracture at a given load
 (c) The load applied to bring fracture at a given time
 (d) All of the above

112 | Fatigue

11. The stress which a material can withstand without getting fractured is called _____.
 (a) Fatigue life (b) Fatigue strength
 (c) Fatigue limit (d) None of the above
12. Endurance limit for non-ferrous materials is _____.
 (a) Constant with number of cycles (b) Decreasing with number of cycles
 (c) Increasing with number of cycles (d) All of the above
13. S-N diagram indicates _____.
 (a) Maximum stress versus fatigue life (b) Varying stress versus fatigue life
 (c) Time versus fatigue life (d) Fatigue life versus varying stress
14. Fatigue life is a _____.
 (a) Temperature-sensitive property (b) Structure-sensitive property
 (c) Load-sensitive property (d) All of the above
15. Fatigue fracture occurs _____.
 (a) Suddenly (b) By large deformation
 (c) At a low temperature (d) None of the above

ANSWERS

1.	d	2.	d	3.	b	4.	b	5.	a	6.	b
7.	a	8.	b	9.	d	10.	a	11.	b	12.	b
13.	a	14.	b	15.	a						

Solidification of Metals and Alloys

INTRODUCTION

Solidification is the process of phase transformation of metals and alloys from the liquid to the solid state. It is the reverse of melting. During this process, the atoms arrange themselves in an orderly three-dimensional pattern. The liquid molten metal is cast to shape and the metallographic structure is produced immediately after solidification. The properties of a material depend on the internal state of that material, i.e., size, shape and orientation of grain, and distribution of the alloying element. Besides the structure, the soundness of casting also depends upon the solidification mechanism. The understanding of the solidification of metals and alloys is most important as it is essential to produce defect-free castings. Therefore, the solidification process can control the properties of metals and alloys. The mechanism of solidification of metals and alloys is a good guide to produce a good or a sound casting.

9.1 MECHANISM OF SOLIDIFICATION OF METALS

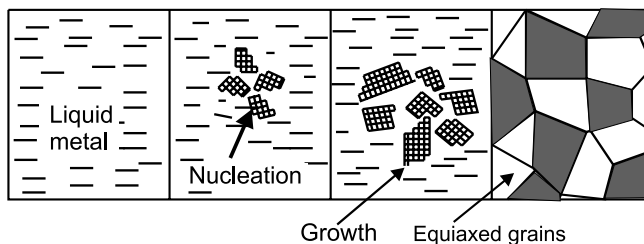


Fig. 9.1 Mechanism of solidification

When a solid metal is heated, its atoms vibrate about a fixed point called lattice point. As the temperature of the metal increases, the energy of each atom increases. At a certain temperature (depending upon the metal), the atoms become so agitated that they can escape from their fixed positions. Thus, the structure begins to lose rigidity, i.e., it begins to melt. The amount of heat required to melt the metal is known as latent heat of fusion.

The mechanism of solidification proceeds by the formation of stable nuclei in the liquid metal followed by the growth of nuclei into the crystals with the formation of grain structure (see Figure 9.1). When a molten metal is poured into a mould cavity, since the heat loss is more rapid near the mould walls, the first submicroscopic metal called nuclei crystallizes on mould surface. In pure metals (aluminium, copper, etc.), the melt is difficult to crystallize if no nuclei in the form of impurities are present to start solidification. In such a case, the melt under-cools or super-cools to form seed crystals and the solidification continues at a constant temperature. In an alloy system, the solidification takes place over a temperature range and nucleation appears in the form of very small crystals on the substrate or impurities. The nuclei are formed as the crystal growth proceeds with the release of energy at the crystal melt interface. As the crystal grows, they tend to develop spike-like structure and change into equiaxed grain or develop a tree-like structure called dendrite structure (dendron meaning tree in Greek). The crystal growth takes place until the spaces between the boundaries fill up.

9.2 NUCLEATION

The nucleation is the beginning of phase transformation and is indicated by the appearance of a small cluster of atoms or molecules to form the basic crystal structure or small solids called 'nuclei'. The nucleation may involve assembling of proper kinds of atoms by diffusion. The structure of the crystal may change into one or more unstable intermediate crystals and form critical nuclei of a new solid phase. The formation of small crystals in molten metal takes place in two mechanisms—homogeneous and heterogeneous nucleation.

9.2.1 Homogenous or Self-nucleation

The formation of nuclei within its own melt without the aid of impurity or foreign particles is called homogeneous or self-nucleation. This nucleation occurs in perfectly homogeneous materials such as pure (aluminium, copper, etc.) molten metals. This is a simplest type of nucleation in which the liquid metal provides atoms to the nucleate. During the nucleation, the molten metal must be cooled below its freezing temperature. Nucleation occurring at any part of liquid or molten metal is identical, and groups of atoms form small zones.

The atoms in a molten liquid bond together to form a small crystal called 'embryo'. This embryo grows into a nucleus with the addition of atoms. In pure metals, this takes place by super-cooling and the nucleation of super-cooled grain is governed by the following two factors:

1. The free energy available from the solidification process, which depends on the volume of the particle formed
2. The energy required forming a solid–liquid interface, which is dependent on the surface area of the particle

If the size of the nucleus is less than the critical size, it may be re-dissolving in molten metal due to the agitation of atoms. This depends upon free energy (F_v) which is decreasing in the molten metal below the melting temperature and this contributes to the stability of solid metal. For developing of critical nucleus in molten metal, consider the energy changes in the nucleation process.

Assume a spherical particle generated during nucleation by the super-cooling or under-cooling of molten metal below the freezing temperature.

Free energy changes per unit volume of metal is as follows

$$f_u = -\frac{4}{3} \pi r^3 \Delta F_u \quad \dots(1)$$

where the negative sign indicates a decrease in free energy, r is the radius of particle and ΔF_u is the change in free energy/unit volume.

During solidification, the nucleated solid phase possesses a surface in between the liquid and the solid. Such a surface has a positive free energy/unit area. Free energy increases are proportional to the surface area of the particle, and free energy increase is given by

$$f_s = 4\pi r^2 \gamma \quad \dots(2)$$

The total free energy associated in the process of nucleation is the sum of volume free energy and surface free energy change. Total free energy change for a particle of radius r is

$$\begin{aligned} \Delta F &= f_u + f_s \\ \Delta F &= -\frac{4}{3} \pi r^3 \Delta F_u + 4\pi r^2 \gamma \quad \dots(3) \end{aligned}$$

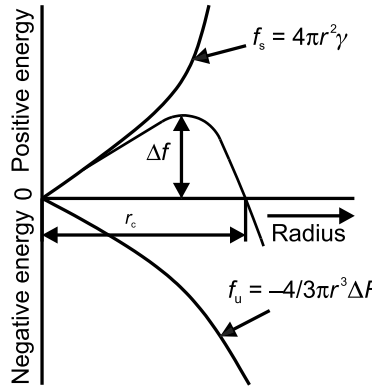


Fig. 9.2 Free energy change versus radius of particles

Figure 9.2 shows that if the particle radius increases, free energy ΔF also increases till the particle grows to a critical radius r_c . With further increase in particle radius, free energy decreases and also becomes negative.

Critical radius can be calculating by differentiating Equation (3) with respect to particle radius r and equating it to zero.

Thus, the equation becomes

$$\frac{d}{dr} \Delta F = \frac{d}{dr} \left[-\frac{4}{3} \pi r^3 \Delta F_u + 4\pi r^2 \gamma \right] = 0 \quad \dots(4)$$

$$4\pi r^2 \Delta F_u = 8\pi r \gamma \text{ since } r = r_c$$

$$r_c = \frac{2\gamma}{\Delta F_u} \quad \dots(5)$$

This is the critical particle size, which must be created before the nucleus is stable. Critical nucleus developing in the molten metal with the net effect of two factors is the total energy of the particle which reaches a maximum value at a given particle size for a given super-cooling temperature. Critical energy can be calculated by substituting r_c in Equation (3).

$$\begin{aligned}
 \Delta F &= -\frac{4}{3}\pi\left(\frac{2\gamma}{\Delta F_u}\right)^3\Delta F_u + 4\pi\left(\frac{2\gamma}{\Delta F_u}\right)^2\gamma \\
 \Delta F_u &= -\frac{4}{3}\pi\frac{8r^3}{(\Delta F_u)^2} + 4\pi\frac{4\gamma^2}{(\Delta F_u)^2}\times\gamma \\
 &= -\frac{32\pi r^3}{3(\Delta F_u)^2} + \frac{16\pi r^3}{(\Delta F_u)^2} \\
 &= 16\pi r^3\left(\frac{-2}{3} + 1\right) \\
 \Delta F &= \frac{16\pi\gamma^3}{3(\Delta F_u)^2} \quad \dots(6)
 \end{aligned}$$

The particle having a radius more than the critical radius tends to grow and also lower the free energy. Equation (6) gives the total free energy reduced to create stable nucleation.

9.2.2 Heterogeneous Nucleation

The formation of nuclei within its own melt with the help of foreign substances or substrates is known as heterogeneous nucleation. The phase transformation takes place with the help of impurities, which lower the free energy. Since large amount of under-cooling does not take place in industrial casting process, nucleation should be heterogeneous and not homogeneous. In molten metal, usually impure particles will reduce the liquid–solid interface energy and helps in nucleation and thereby reduce the amount of super-cooling.

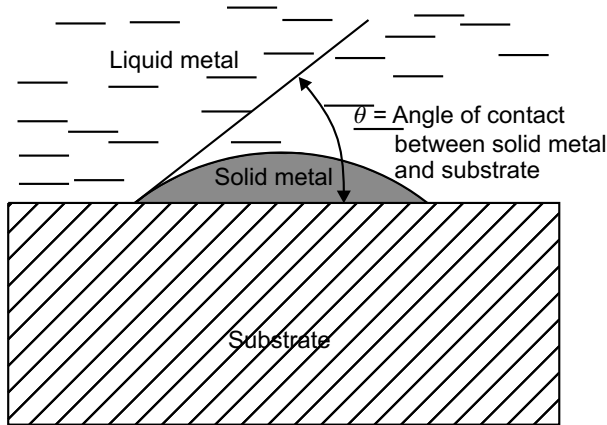


Fig. 9.3 Heterogeneous nucleation developing on the substrate

Figure 9.3 shows heterogeneous nucleation on nucleating agent. During heterogeneous nucleation, the surface energy to form a stable nucleus is reduced. If a metal is to solidify on a foreign substrate, it is essential that the surface of the substrate should be wet by a liquid metal. Once this condition is satisfied, next the liquids solidify easily on the substrate. It is because of this reason that the angle of contact between the substrate and the solid metal being deposited is an important theoretical concept in nucleation. When angle of contact θ is small, interface between solid and substrate has a low surface energy. Hence, the total free energy for formation of stable nucleus is also decreased and critical radius of the nucleus will be smaller as per the given equation $r_c = -2r\sin\theta/\Delta F_u$. When the contact angle is small, nucleation will occur at a small amount of under-cooling. If the contact angle is large, a

greater amount of under-cooling is necessary. If $\theta = 180^\circ$, the liquid metal does not easily solidify on the substrate, since solid metal and substrate interface energy is high. Sometimes, nucleating agent is added to molten metal to act as a catalyst. This substrate may be a compound, i.e., insoluble in metal, which will produce a small contact angle. Some substances in fine sizes are added in small quantities to the molten metal in order to promote heterogeneous nucleation and growth of crystals. These are called inoculants.

9.3 CRYSTAL GROWTH

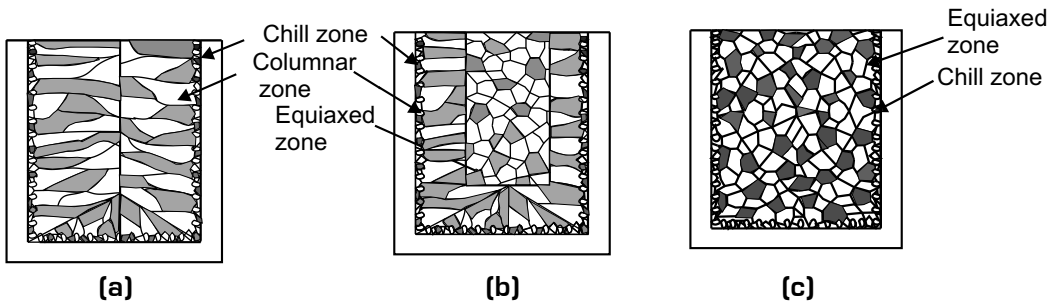


Fig. 9.4 (a) Columnar grains, (b) columnar and equiaxed grain and (c) only equiaxed grain

Once a stable nucleus is formed, it grows by acquiring atoms from the liquid. From the existing nuclei, the growth continues. The grain growth takes place gradually by the addition of atoms in certain crystallographic directions and planes in the second stage of solidification. The rate of growth depends on the atoms of under-cooling below the melting point of that metal. During solidification, latent heat of fusion is being released. This growth is controlled by the rate of heat transferred from the casting and mould. The growth occurs in a direction opposite to the heat flow. In addition, growth also depends on the crystallographic directions. In pure metals, columnar grains extend to the centre of casting but in alloys, the columnar grain growth is interrupted by equiaxed grain growth as shown in Figure 9.4. Grain growth ends when all the molten metal solidifies.

9.4 DENDRITE GROWTH

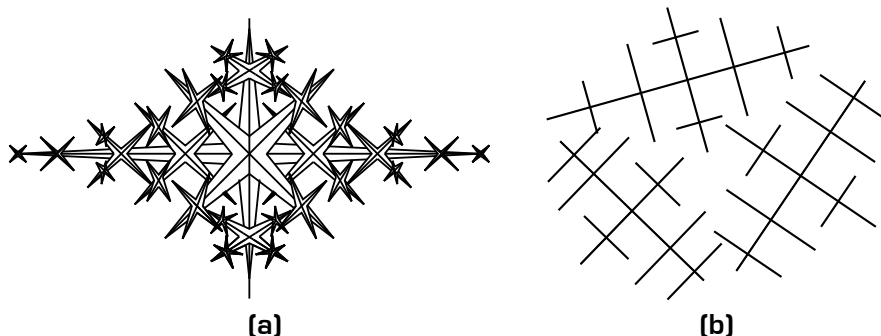


Fig. 9.5 (a) Three-dimensional dendrite growth and (b) two-dimensional dendrite growth

In an alloy, solidification occurs over a range of temperature. If the temperature gradient is in some intermediate position, then there will be some certain amount of super-cooling. Super-cooling promotes the growth of spikes, which extend into the liquid in a direction opposite to the heat flow in the form of tree-like structure called dendrite structure as shown in Figure 9.5. Dendrite growth appears because the metal-liquid interface is warmed up by the release of latent heat. This stops or reduces the growth in a particular direction and the growth starts in other directions where the temperature is low. Spikes-like solid metal appear because of this behaviour in the solidification. As new spikes warm up, the forwarded growth again stops and secondary and tertiary growth of spikes occurs to form the typical dendrite. The dendrite growth in metals can be observed by interrupting, freezing and pouring out the remaining liquid from the mould. The dendrite growth represents only about 10% of the total freezing process of pure metals, whereas it is very common in the freezing of alloys.

9.4.1 Volume Shrinkage

When molten metal is allowed to solidify, volume contraction can be observed and it can be compensated by extra molten metal made available with the help of riser. Any metal is contracted by liquid-to-liquid, liquid-to-solid or solid-to-solid transformation. The liquid contraction occurs in a liquid state. When molten metal is poured into a mould, the cavity temperature drops suddenly and liquid-to-liquid shrinkage occurs. Once the solidification starts, liquid-to-solid shrinkage in the metal starts and it needs extra liquid metal to compensate. Solidification contraction occurs during the change from liquid to solid. Finally, the size of the metal gets reduced when the temperature decreases to room temperature. Solid contraction occurs in solid state after solidification.

9.5 EFFECT OF SUPER-COOLING OR UNDER-COOLING ON CRITICAL RADIUS OF A NUCLEUS

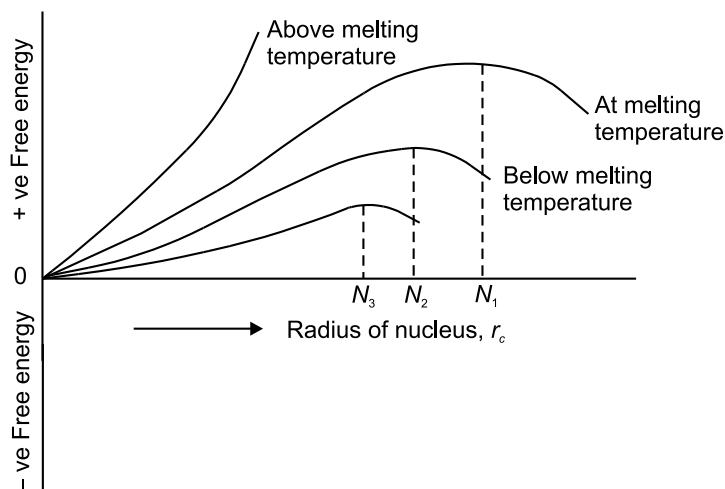


Fig. 9.6 Effect of cooling rate on nucleation

The cooling rate of the molten metal affects the size of the grain during solidification. Figure 9.6 shows the critical radius of nucleus created with a change of free energy of the system (under-cooling). If the temperature is above the melting temperature of that metal, there would be no nucleation without under-cooling of the molten metal. A few number of nucleation are promoted with a slow rate of cooling or a small degree of under-cooling and crystal size will be large (radius = N_1) as indicated in

Figure 9.6. If the molten metal cools rapidly, it leads to very high under-cooling resulting in the formation of a large number of small-sized nucleation and a large number of small grains ($\text{Radius} = N_2$). If the temperature is well below the melting point, the size of the nucleus can be very small. For many purposes, particularly for strength, small grain size is desired and this means a large number of nuclei must be made available and the cooling rate must be controlled to allow the nuclei to act. Controlled cooling and addition of nucleating agents are the standard methods for producing correct grain size in a casting.

9.6 CASTING METAL STRUCTURE

When a pure molten metal is poured into a metal mould, equiaxed grains appear immediately due to the chilling action from the mould surface and hence the metal leads to large under-cooling. The liquid metal next to the mould will start solidifying and grows towards the centre of casting by rejecting the heat in the direction opposite to the heat flow. The columnar crystal will be growing under these conditions till it reaches the centre of the casting. A columnar crystal structure is shown in Figure 9.4(a).

In the case of pure metals, when the molten metal leads to large amount of super-cooling, equiaxed grains appear. Release of heat from the molten metal is uniform in all directions of the casting. In the case of alloys, heterogeneous nucleation takes place, hence the equiaxed grains are formed under controlled solidification conditions. The commercial alloys have both equiaxed and columnar grains and they always show fine equiaxed grain at the outer skins and columnar grain at the centre (Figure 9.4(b)). In some metals, equiaxed grains can be observed both in outer and inner metal (Figure 9.4 (c)). The centre of the crystal will always be bigger in size due to the slow rate of cooling as compared to outer surface of the casting.

EXERCISES

1. Explain with neat sketches the different stages of mechanisms of solidification.
2. Explain clearly nucleation and grain growth.
3. What is meant by nucleation under-cooling and solidification under-cooling? Explain briefly
4. Explain homogeneous and heterogeneous nucleation. Under what conditions these types of nucleation take place.
5. Derive critical radius of homogeneous nucleation.
6. Explain the concept of critical radius for nucleation during solidification.
7. Differentiate between homogeneous and heterogeneous nucleation.
8. Explain with neat sketches nucleation and growth of dendrites.
9. Explain with figure the grain structure of cast metals.
10. With neat sketches, show the different types of metallic structure that can be obtained.

OBJECTIVE -TYPE QUESTIONS

1. Solidification process can control _____.

(a) The properties of metals	(b) Surface finish of the metal
(c) Colour of the metal	(d) All of the above

120 | Solidification of Metals and Alloys

2. Nucleation refers _____.
 - (a) Phase transformation is in intermediate position
 - (b) End of phase transformation
 - (c) Beginning of phase transformation
 - (d) All of the above
3. Self-nucleation appears _____.
 - (a) In alloys
 - (b) In pure metals
 - (c) With aid of impurities
 - (d) With aid of inoculants
4. Critical energy can be calculated by using the equation _____.
 - (a) $\Delta F = \frac{16\pi\gamma^3}{3(\Delta F_u)^2}$
 - (b) $\Delta F = \frac{16\pi\gamma^3}{2(\Delta F_u)^2}$
 - (c) $\Delta F = \frac{4\pi\gamma^3}{3(\Delta F_u)^2}$
 - (d) $\Delta F = \frac{16\pi\gamma^2}{3(\Delta F_u)^2}$
5. In heterogeneous nucleation, if contact angle is small, _____.
 - (a) Nucleation occurs at a small amount of under-cooling
 - (b) Nucleation occurs at a large amount of under-cooling
 - (c) Nucleation occurs without under-cooling
 - (d) Nucleation occurs at constant cooling
6. Contact angle in heterogeneous should be _____.
 - (a) Large
 - (b) Small
 - (c) 180°
 - (d) 150°
7. Crystal growth occurs _____.
 - (a) By addition of columnar grains in a certain direction
 - (b) By addition of grains in a certain orientation
 - (c) By addition of grains in a certain direction
 - (d) By addition of atoms in a certain crystallographic direction
8. Tree-like structure is called _____.
 - (a) Equiaxed
 - (b) Columnar
 - (c) Dendrite
 - (d) All of the above
9. Crystal growth can be controlled by _____.
 - (a) Controlling heat flow
 - (b) Adding alloying elements
 - (c) Adding heat to the molten metal
 - (d) None of the above
10. In alloys, _____ structure can be observed.
 - (a) Only columnar
 - (b) Only equiaxed
 - (c) Both columnar and equiaxed
 - (d) All of the above
11. In pure metal, _____ dendrite structure can be observed.
 - (a) About 10%
 - (b) About 70%
 - (c) About 90%
 - (d) 100 %
12. Solidification contraction takes place during
 - (a) Liquid to liquid cooling
 - (b) Liquid to solid cooling
 - (c) Solid to solid cooling
 - (d) All of the above

13. When molten cools very slowly, _____.
 (a) Radius of nucleation will be large
 (b) Radius of nucleation will be small
 (c) Radius of nucleation will be dependent on cooling rate
 (d) All of the above
14. Inoculants means _____.
 (a) Some substances of fine size are added in small quantities to the molten metal
 (b) Some substances of large size are added in large quantities to the molten metal
 (c) Some substances are added to the molten metal for removing gas
 (d) All of the above
15. The energy required to form a solid–liquid interface is dependent on the _____.
 (a) Volume of the particle
 (b) Number of atoms in a solid
 (c) Surface of the particle
 (d) None of the above

ANSWERS

1.	a	2.	c	3.	b	4.	a	5.	b	6.	b
7.	d	8.	c	9.	a	10.	d	11.	a	12.	b
13.	a	14.	a	15.	c						

chapter 10

Solid Solutions

INTRODUCTION

Pure metals always have low strength and high ductility and it is practically impossible to use them in industrial applications. Industrial metallic substances are composed of two or more elements in an atomic level as either a compound or a solution for improving the mechanical properties. The value of solid solution was discovered during the ancient times and is commonly known as alloys. Most important industrial solid solutions include alloy steels containing chromium, nickel, manganese, silicon along with carbon. Alloy steels have a wide range of special properties, such as hardness, toughness, corrosion resistance and ductility. Nonferrous alloys, mainly copper–nickel, bronze and aluminum alloys, are used to a great extent in industries.

10.1 SOLID SOLUTIONS

A solid solution is a homogeneous mixture of two or more kinds of atoms in a solid state or more than two types of atoms combined in a single-space lattice. If two or more than two types of metals are mixed in their liquid state, they form a liquid solution. When this mixture is solidified, the solid may retain the homogeneity that was present in the liquid state. In this, the components of different types of atoms form a common crystal lattice. The component whose lattice is retained is called the solvent and the solute atom may occupy a vacant lattice site in the parent metal. It may also exist in between the atoms in the parent lattice as indicated in Figure 10.1.

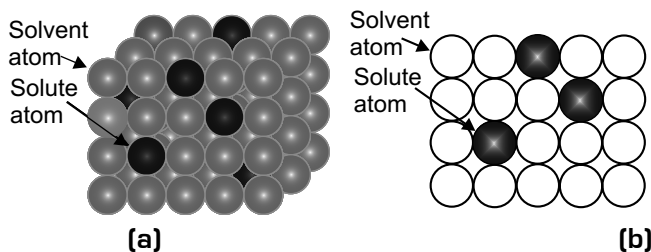


Fig. 10.1 (a) Three-dimensional substitutional solid solution and (b) two-dimensional substitutional solid solution

Brass is a solid solution of copper and zinc. A typical composition of the brass contains 64% copper and 36% zinc. The copper atoms are solvent atoms and the zinc atoms are solute atoms. The combination of these metals in a lattice structure provides strength, toughness, wear resistance and other desired properties. The solid solutions are of two types—substitutional solid solution and interstitial solid solution. Some other examples of solid solution are Ni–Cu, Au–Ag, Ag–Cu and Fe–C.

10.2 SUBSTITUTIONAL SOLID SOLUTION

In a substitutional solid solution, the solute atom substitutes the atoms of solvent in the crystal structure. The crystal structure of the parent element is unchanged, but the lattice may be distorted by the presence of the solute atoms. In a substitutional solid solution, the two atoms (solvent and solute) are equal or approximately equal in diameter and the crystal structure of the two elements must be the same. Brass is alloy of copper and zinc. The atomic diameter of copper is 1.278 Å and that of zinc is 1.332 Å and the two metals form substitutional solid solution. Figure 10.1 shows that the zinc atoms replace some copper atoms in the lattice structure of copper. Substitutional solid solutions are further classified into disordered substitutional solid solution and ordered substitutional solid solution.

10.2.1 Disordered Substitutional Solid Solution

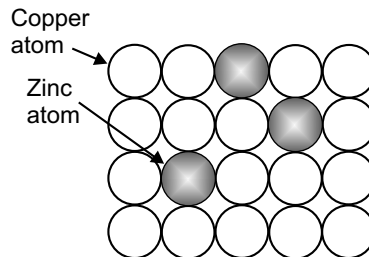


Fig. 10.2 Disordered substitutional solid solution

In a substitutional solid solution, the solute atoms do not follow any specific order, but the atoms are distributed randomly in the lattice structure of the solvent. The concentration of solute atoms can vary throughout the lattice structure. This alloy is said to be in a disordered condition. The disordered substitutional solid solutions crystallize from the molten metal (see Figure 10.2).

10.2.2 Ordered Substitutional Solid Solution

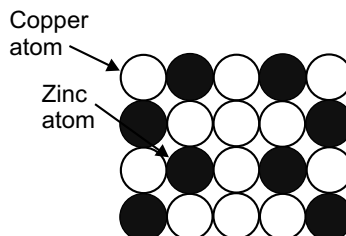


Fig. 10.3 Ordered substitutional solid solution

If the disordered substitutional solid solution is heated to its recrystallization temperature and then cooled very slowly, the atoms are rearranged due to the diffusion that takes place during cooling. This results in uniformity and definite ordering of the atoms in the lattice structure. This structure is said to be ordered substitutional solid solution (see Figure 10.3).

10.2.3 Hume Rothery's Rule

To obtain a metal with desired properties, alloying is essential in metallurgy. However, not all metals can be added to obtain substitutional solid solution. Hume Rothery, a well-known scientist, identified some factors that give complete substitutional solid solution in varying alloying elements. For obtaining a substitutional solid solution, the choice of alloying elements must be based on the following factors.

1. **Relative size factor:** If two metal atoms differ in their sizes by more than 15%, the formation of a solid solution between them will be restricted. To show the solid solubility in each other, it is essential that their atomic diameter shall be similar or the two different atoms differ in their sizes by less than 13% and this is the most important factor to obtain a solid solution.
2. **Chemical affinity factor:** If two metals possess a greater chemical affinity, they prefer to form a chemical compound rather than a solid solution, and lesser are the chances of forming a solid solution and dissolving each other. The two metal atoms should have very less chemical affinity between them to show solid solubility.
3. **Relative valence factor:** In alloying metals, the solute and solvent atoms are different in valence electrons. Hence, a metal of high valence can dissolve only a small amount of lower valence metal but the lower valence metal may have a good solubility than higher valence metal.
4. **Crystal structure factor:** It is found that metals having the same type of crystal lattice form a complete series of solid solution, i.e., the crystal lattice of solvent and solute should be same, otherwise, the solute and the solvent will not merge with each other.

10.3 INTERSTITIAL SOLID SOLUTION

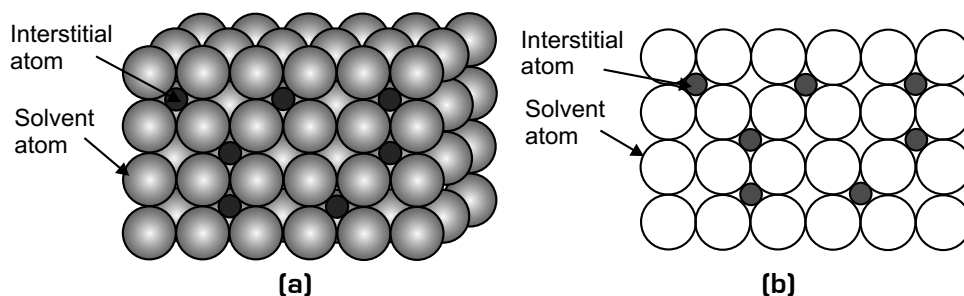


Fig. 10.4 (a) Three-dimensional interstitial solid solution and (b) two-dimensional interstitial solid solution

In an interstitial solid solution, the diameter of the solute atom is very small when compared to the solvent atoms (see Figure 10.4). These are formed when atoms of small atomic radii fit into the void

spaces of the larger solvent atoms. The diameters of carbon, boron and nitrogen atoms are less than 1 Å and can fit in the crystal structure of iron, nickel and manganese as interstitial solid solution. For example, the atomic diameter of iron is 1.24 Å and that of carbon is 0.77 Å. Because of large difference in the diameters of iron and carbon atoms, the carbon atom is unable to substitute to solvent atom and it can fit in the form of interstitial in austenite.

10.3.1 Metallic Compounds (Intermediate Phases)

In the metallurgy process, the alloying elements are added to achieve the desired properties in metals. The intermediate phases are formed in a two-component system when their mutual solid solubility is limited and the chemical affinity is high. When alloying elements are added in excess to solid solubility, a second phase called intermediate phases appears. The intermediate phases are of different types: their metallic compounds, electron compounds and Laves phases. These compounds possess either ionic or covalent bond. These compounds have non-metallic properties and poor ductility, poor electrical conductivity of and higher melting point with complex crystal structure. The metallic compounds are two types—interstitial compounds (WC , Fe_3C) and valance compounds (Mg_2Si , MgPb).

EXERCISES

1. Define solid solution, phase and component. Explain clearly the various types of solid solutions.
2. Explain the factors governing the formation of substitutional solid solutions.
3. Differentiate between the two types of solid solutions. Explain the factors that contribute it.
4. List and explain the different types of substitutional solid solutions.
5. Differentiate between interstitial solid solution and substitutional solid solution.
6. Explain in detail Hume Rothery's rule for substitutional solid solution.
7. What is meant by metallic compounds? Explain in detail with examples.

OBJECTIVE-TYPE QUESTIONS

1. Brass is an example for _____.
 (a) Interstitial solid solution
 (b) Substitutional solid solution
 (c) Metallic compound
 (d) Non-metallic compound
2. The component which retains its crystal structure is known as _____.
 (a) Solvent
 (b) Solute
 (c) Alloy
 (d) None of the above
3. Solid solution is the result of _____.
 (a) Pure metal solidifies in two types of space lattice
 (b) More than two kinds of atoms combined in two types of space lattice
 (c) More than two kinds of atoms combined in one type of space lattice
 (d) All of the above

126 | Solid Solutions

4. Substitutional solid solution forms when _____.
 - (a) The atomic diameter difference is less than 7.5%
 - (b) The atomic diameter difference is less than 15%
 - (c) The atomic diameter difference is greater than 10%
 - (d) The atomic diameter difference should be less than 4%
5. Disordered substitutional solid solution appears during _____.
 - (a) Cold working
 - (b) Forming
 - (c) Solidifying
 - (d) Heating
6. Majority of the solid solutions are _____.
 - (a) Metallic compound type
 - (b) Interstitial type
 - (c) Substitutional type
 - (d) Inter-metallic type
7. Disordered substitutional solid solutions become ordered _____.
 - (a) When a metal is heated and cooled slowly
 - (b) When a metal is deformed slowly
 - (c) When a metal is heated and quenched in water
 - (d) All of the above
8. Hume Rothery's rule is for _____.
 - (a) Interstitial solid solution
 - (b) Substitutional solid solution
 - (c) Metallic compounds
 - (d) Non-metallic compounds
9. Relative valence factor states that _____.
 - (a) Low valence metal can dissolve only a small amount of higher valence metal
 - (b) Higher valence metal can dissolve only a small amount of lower valence metal
 - (c) Low valence metal can dissolve only a small amount of low valence metal
 - (d) Higher valence metal can dissolve only a small amount of higher valence metal
10. Example for interstitial phase is _____.
 - (a) Copper in nickel
 - (b) Silver in copper
 - (c) Nickel in silver
 - (d) Carbon in iron structure

ANSWERS

1.	b	2.	a	3.	c	4.	b	5.	c	6.	c
7.	a	8.	b	9.	a	10.	d				

Phase Diagrams

INTRODUCTION

The solidification of a metal or an alloy is clearly understood by means of a phase diagram. A plot with the temperature on the vertical scale and the percentage of composition by weight on the horizontal scale is termed a phase diagram. A diagram plotted for an alloy system in this fashion is called an equilibrium or a phase diagram. The phase diagram is also known as constitutional diagram.

The applications of alloys are wide and ever-increasing in the industry when compared to pure metals. The alloys not only increase the strength of the metals, but many combinations of properties can be obtained by alloying the metals with each other in various proportions. The alloy diagrams are useful in the study of the characteristics of any series of alloys; and it is possible to predict the structure and the physical and chemical properties of any given alloy from these diagrams.

In a phase diagram, to specify completely the state of a system in equilibrium, it is necessary to specify the three independent variables—temperature, pressure and composition—which are externally controllable. If there is no variation in pressure, then the metal equilibrium can be expressed in terms of two independent variables, viz., temperature and composition.

11.1 COOLING CURVES

The phase diagrams are usually constructed from the data of cooling curve obtained by plotting falling temperature versus time for small selected alloys, which are allowed to cool under equilibrium condition. When a metal or alloy solidifies from a state of fusion, it is noticed that at the time of solidification, considerable amount of heat is given out due to changes taking place in the structure of the metal or alloy. The simplest type of curve is obtained by taking the temperature readings at fixed intervals of time with the aid of a pyrometer. This curve is used for studying the changes that occur during the solidification of alloys. If a plot is drawn between temperature and time at a constant composition, the resulting cooling curve shows a change of slope when a phase change occurs.

11.1.1 Cooling Curve for Pure Metals or Solidification of Pure Metals

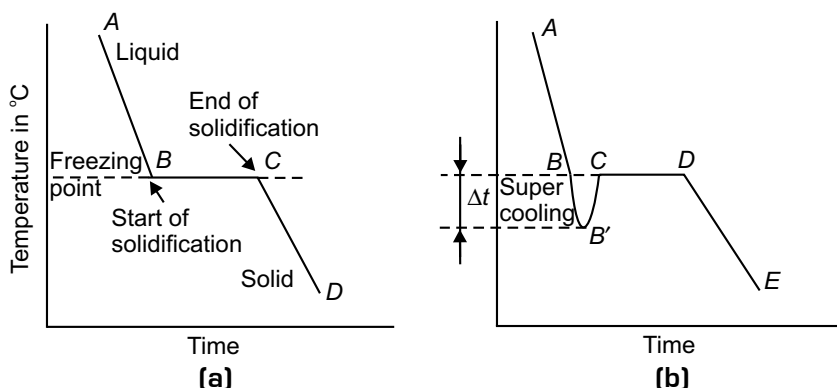


Fig. 11.1 (a) Hypothetical cooling curve and (b) actual cooling curve for pure metals

The pure metals melt and solidify at the same temperature which may be termed as melting point or freezing point. These metals are cooled under equilibrium conditions from the molten state till they solidify.

A time–temperature diagram is shown in Figure 11.1(a). Liquid metal cools from A to B. The crystal begins to form at B. From B to C molten metal liberates latent heat of fusion and the temperature remains constant until the entire liquid metal is solidified. Between B and C, the metal is partially solid and partially liquid. On further cooling, i.e., from C to D, solid metal tends to reach the room temperature. In Figure 11.1(a), the horizontal line corresponds to the solidifying or melting temperature of a single-component system at a constant pressure.

In real systems, a certain amount of under-cooling occurs before the solidification starts. That is, the melt is maintained in a metastable state at a temperature below the freezing point and most of the cooling curves are as shown in Figure 11.1(b). Nucleation of solid does not start at point B, but it starts at point B', i.e., liquid metal has super-cooled by an amount Δt . This is known as super-cooling or under-cooling. The extent of under-cooling in terms of temperature and time depends upon several factors.

11.1.2 Cooling Curve for Binary Alloy

11.1.2.1 Solidification of Alloy—Type 1

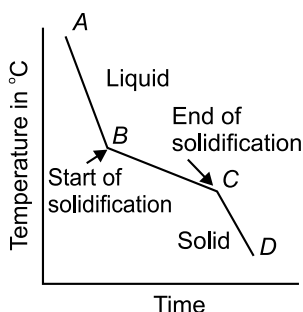


Fig. 11.2 Cooling curve for binary alloy

Consider the solidification of an alloy containing 50% X and 50% Y metals (see Figure 11.2). The alloy which has started cooling is at a temperature A and the metals X and Y are completely soluble in each other. The crystals begin to form at B . In a binary system, during the freezing period, temperature does not remain constant, rather it drops along line BC till the whole mass is solid and cool to room temperature along CD . At the room temperature, the alloy is homogeneous in the solid state similar to in the liquid state. The Cu–Ni system is an example of two metals which form a solid solution.

11.1.2.2 Solidification of Alloy—Type 2 (Eutectic Solidification)

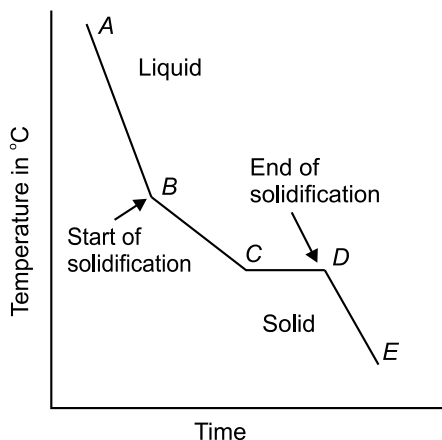


Fig. 11.3 Cooling curve for binary eutectic

In some binary alloy systems, the liquid metal cools along the curve AB until the temperature reaches point B . At point B , one component in excess will crystallize and the temperature will drop along BC as indicated in Figure 11.3. At point C , the residue liquid reaches eutectic (Greek word meaning ease melt) composition and the two components crystallize simultaneously from the eutectic mixture. The temperature remains constant until the whole mass is solid between points C and D . From D to E , the metal cools to room temperature. The Cd–Bi system is an example of two metals completely soluble in liquid state but partially soluble in solid state.

11.2 CONSTRUCTION OF PHASE DIAGRAM

The alloy diagram is constructed from a number of cooling curves of a series of alloys of the metals used in the investigation. Thus, while constructing the alloy diagram of the nickel–copper alloys, approximately, the following steps have to be followed:

1. Construct the cooling curve of pure metal A
2. Construct the cooling curve of pure metal B
3. Construct the cooling curves of about 10 different alloys of A and B , for example, an alloy of 90% A with 10% B ; an alloy of 80% A and 20% B ; and so on.

A and B are mixed in proper proportion and heated above the melting temperature of that alloy. Molten alloys are allowed to cool in equilibrium condition and the temperature at which metal starts to melt ($M, M_1, M_2, \dots$) and the temperature at which metal start to freeze ($F, F_1, F_2, \dots$) are recorded. The cooling curves thus obtained are combined to construct the phase diagram of the metals A and B .

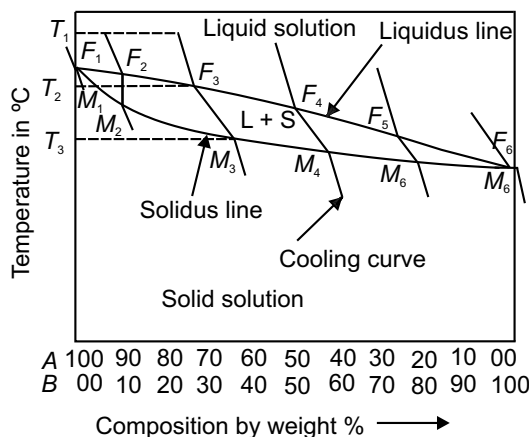


Fig. 11.4 Construction of phase diagram for two metals completely soluble both in liquid and solid phases

The resulting phase diagram as in Figure 11.4 is obtained by joining the points $F_1, F_2, \dots$ and the points $M_1, M_2, \dots$. The upper line obtained by joining the points showing the beginning of solidification is called the liquidus line. The liquidus line indicates the lowest temperature at which a given alloy of the series in the liquid starts to freeze. The lower line of the diagram is known as the solidus. The area above the liquidus line is a single-phase region. Any alloy in that region consists of a homogeneous liquid solution. At any point in the solidification range, the alloy is partly solid and partly liquid. Similarly, the area below the solidus line is a single-phase region and any alloy in this region consists of a homogeneous solid solution.

11.3 INTERPRETATION OF PHASE DIAGRAM

The following three steps are necessary for the interpretation of phase diagram.

11.3.1 Prediction of Phase

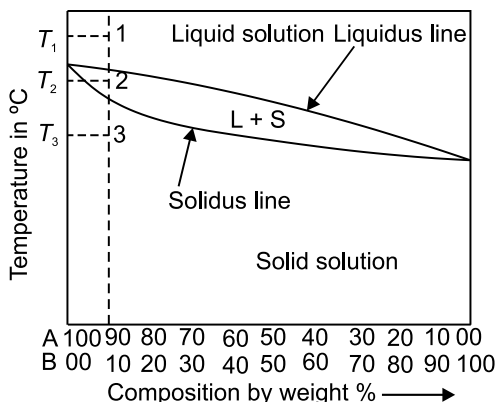


Fig. 11.5 Prediction of phase

Figure 11.5 illustrates the phases that will be present for a given alloy of composition of 90% *A* and 10% *B*. In the phase diagram given in Figure 11.5, the physical states of the alloy at points 1, 2, 3 are as follows. At point 1, since it is above the liquidus line, it consists of only the liquid solution of composition 90% of *A* and 10% of *B* at $T_1^\circ\text{C}$. At point 2, it is between the solidus and liquidus lines. It consists of liquid solid interphase with 90% of *A* and 10% of *B* at $T_2^\circ\text{C}$. At point 3, it is below the solidus line, so it consists only solid solution of 90% of *A* and 10% of *B* at $T_3^\circ\text{C}$.

11.3.2 Prediction of Chemical Composition of Different Phases for a Given Temperature

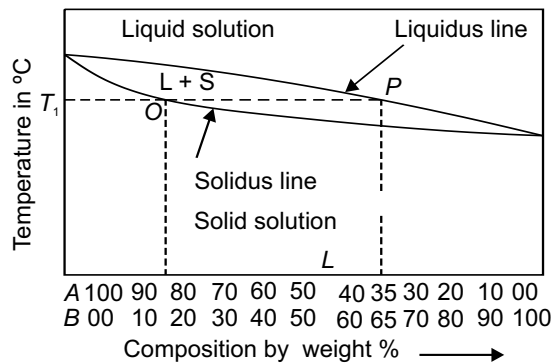


Fig. 11.6 Prediction of chemical composition

Consider the composition at a given temperature, say at $T_1^\circ\text{C}$. Draw a horizontal line. This line intercepts at *O* and *P* on solidus and liquidus line. From the points *O* and *P*, project vertical lines to confirm the composition. In Figure 11.6, at point *P*, the composition 35% of *A* and 65% of *B* starts freezing. The composition 80% of *A* and 20% of *B* starts melting.

11.3.3 Prediction of Amount of Phase (Lever-arm Rule)

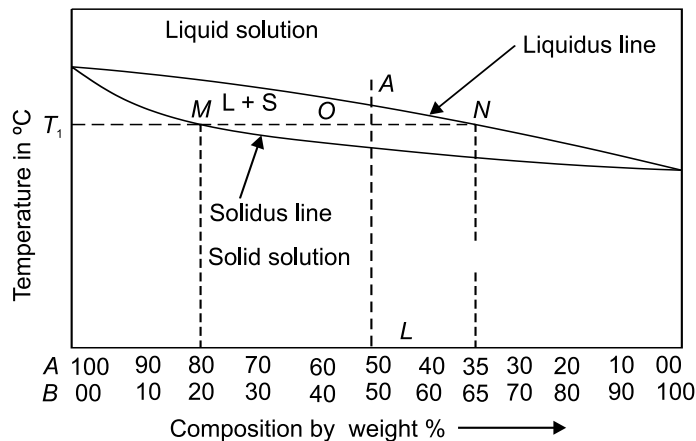


Fig. 11.7 Prediction of amount of phase

132 | Phase Diagrams

The relative amounts of the co-existing phases and their compositions during the process of solidification can be calculated at any temperature by the lever rule. A tie line (isothermal) is drawn intersecting both the solidus and the liquidus lines and the intercepts made by the liquidus and solidus curves with respect to the alloy composition. To determine the relative amount of two phases, consider two lines AL and MN , vertical and horizontal lines in phase diagram, as shown in Figure 11.7. The intersection of these two lines is treated as the fulcrum of a simple lever system. In this, the relative length of lever arms multiplied by amount of phase present must be balanced. This is known as lever rule.

Mathematically, the lever rule can be expressed as

$$\text{Total amount of solid phase} = \frac{ON}{MN} \times 100$$

$$\text{Total amount of liquid phase} = \frac{OM}{MN} \times 100$$

11.4 GIBBS PHASE RULE

The number of variable factors which define the state of a system is called the degree of freedom. Number of degrees of freedom is the quantity of independent external or internal variables like temperature, pressure and concentration which may change the formation of new phase in the system. Gibbs proved that 'number of degrees of freedom of a system in equilibrium condition is related to the number of components and the number of phases'. Mathematically, it can be expressed as

$$P + F = C + N$$

where P is the number of phases in the system, F is the number of degrees of freedom or number of physical variables, which cause phase change of metal or alloy system, C is the number of components in the system and N is the number of external factors such as temperature and pressure.

Usually in metallurgical process, the pressure will not be considered a variable as it is fixed at 1 atmospheric pressure. Thus, the above equation becomes

$$P + F = C + 1$$

or

$$F = C + 1 - P$$

The number of degrees of freedom cannot be less than 0. So,

$$C + 1 - P \geq 0$$

or

$$P \leq C + 1$$

The application of phase rule to systems of pure metal is illustrated in Figure 11.8(a).

A pure metal at above melting temperature [at point 1 in Figure 11.8(a)] has single liquid phase.

The degrees of freedom at Point 1 becomes

$$F_1 = C + 1 - P$$

$$F_1 = 1 + 1 - 1$$

$$F_1 = 1$$

This system is said to be monovariant, i.e., only the temperature can be changed to alter the phase. During cooling, liquid metal becomes solid by defusing out the latent heat.

Pure metal during solidification [at point 2 in Figure 11.8(a)] has two (liquid and solid) phases.

The degrees of freedom at Point 2 becomes

$$F_2 = C + 1 - P$$

$$F_2 = 1 + 1 - 2$$

$$F_2 = 0$$

This system is said to be nonvariant, i.e., we should not vary to change phase of the system. The temperature remains constant during solidification.

Similarly, at Point 3

$$F_3 = C + 1 - P$$

$$F_3 = 1 + 1 - 1$$

$$F_3 = 1$$

The degrees of freedom $F = 1$ indicate that the pure solid metal becomes liquid only by heating from room temperature to liquid state. During heating, solid metal absorbs latent heat and gets converted into liquid at melting temperature.

The application of phase rule to the system of binary solid solution is illustrated in Figure 11.8 (b)). As shown in the figure two metals are completely soluble in the liquid and solid state.

Binary solid solution at the above melting temperature at Point 1 in Figure 11.8(b) has a single liquid phase.

The degrees of freedom at Point 1 becomes

$$F_1 = C + 1 - P$$

$$F_1 = 2 + 1 - 1$$

$$F_1 = 2$$

This system is said to be divariant, i.e. the phase of a system can be changed by varying the composition and temperature. The figure indicates that by varying the composition the state of the system changes.

In a binary solid system, two phase and two component system (at Point 2) the degrees of freedom will be

$$F_2 = C + 1 - P$$

$$F_2 = 2 + 1 - 2$$

$$F_2 = 1$$

This system is said to be monovariant. This indicates that in a binary solid, during solidification, the temperature drops in opposition to being constant in the case of pure metal as indicated in the above example.

Similarly, at Point 3

$$F_3 = C + 1 - P$$

$$F_3 = 2 + 1 - 1$$

$$F_3 = 2$$

Degrees of freedom 2 indicate that the system is divariant and the binary solid solution becomes liquid by heating and also by varying composition at a certain temperature.

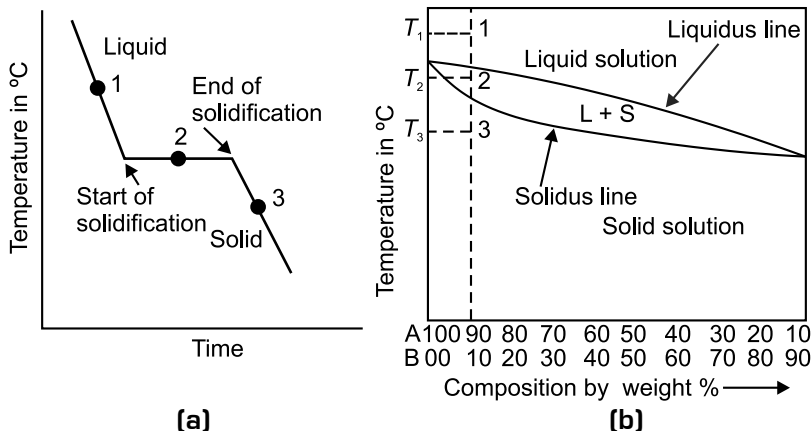


Fig. 11.8 Verification of Gibbs phase rule: (a) Cooling curve for pure metal and (b) phase diagram of two metals completely soluble both in liquid and solid states

11.5 CLASSIFICATION OF PHASE DIAGRAMS

The phase diagrams are classified into two ways:

11.5.1 According to Number of Components in the System

On the basis of number of components in the system, the phase diagrams can be classified as follows :

1. Single-component system has unary diagram
2. Two-component system has binary diagram
3. Three-component system gives rise to ternary diagram and so on

11.5.2 According to Solubility of Components

On the basis of solubility of components, the phase diagrams can be classified as follows:

1. Two metals completely soluble in liquid and solid states
2. Two metals completely soluble in liquid state but partially soluble in solid state
3. Two metals completely soluble in liquid state and insoluble in solid state
4. Two metals incompletely soluble in liquid and solid states

11.5.2.1 Two Metals Completely Soluble in Liquid and Solid States

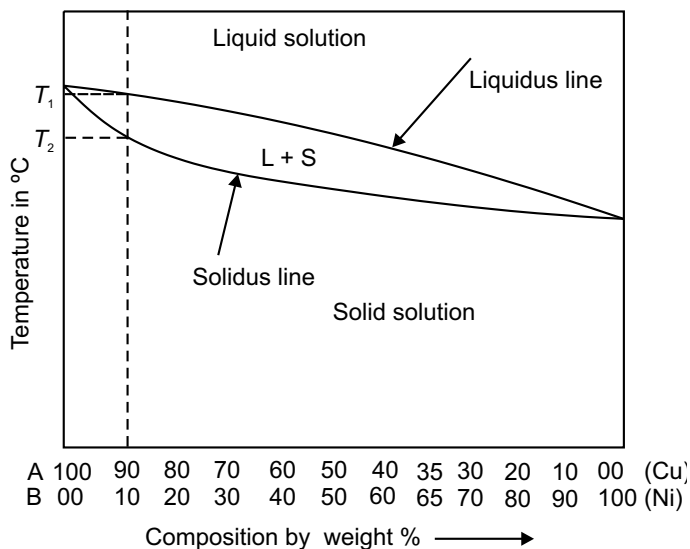


Fig. 11.9 Two metals completely soluble in liquid and solid states

Figure 11.9 shows two metals, Cu and Ni, completely soluble in liquid and solid states. Examples of other systems are antimony–bismuth. The Cu–Ni phase diagram consists of two lines, i.e., liquidus and solidus. Above the liquidus line, there is a uniform liquid solution for any alloy series. Below the solidus line there is a single-solid solution for any alloy. The two metals are completely soluble in the solid state. Hence, substitutional solid solution will be formed.

Consider solidification of alloy containing composition of 90% of copper and 10% of nickel. Solidification now can be started at temperature T_1 and as it reaches the liquidus line, it turns into solid at T_2 . In between temperatures T_1 and T_2 , the metal is partially solid and partially liquid. From T_2 temperature, the metal cools to room temperature.

Problem 11.1

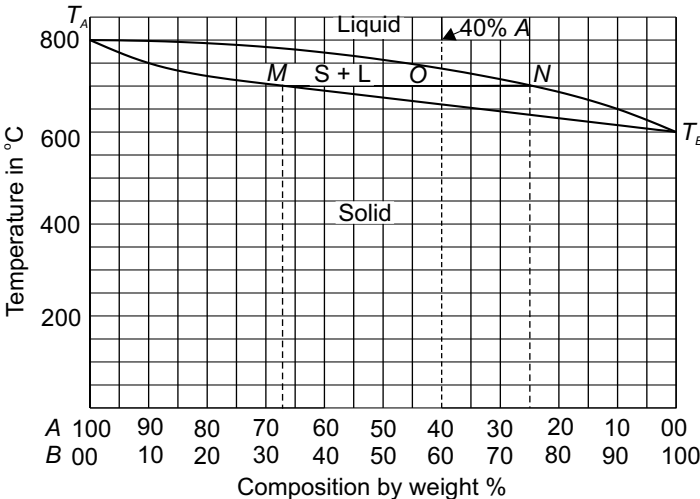
Two metals A and B have 100% mutual solubility in the liquid and solid states. The melting points of pure metals A and B are 800°C and 600°C respectively. Details of the start and end of solidification of various alloys in the series are as follows:

Alloy of Composition	Temperature at Start of Solidification ($^\circ\text{C}$)	Temperature at End of Solidification ($^\circ\text{C}$)
90% A + 10% B	798	750
70% A + 30% B	785	705
50% A + 50% B	757	675
30% A + 70% B	715	645
10% A + 90% B	650	615

1. Draw the phase diagram of the series if there are no solid-state reactions and label all regions.
2. Predict the number, type, relative amounts and concentration of phases present in an alloy of 40% A and 60% B at 700°C .

Solution

1. The following is the phase diagram.



2.

Alloy	Number Phase	Type	Relative Amounts
40% A and 60% B	02	Solid and liquid	Solid = 70.05% Liquid = 29.95%

136 | Phase Diagrams

For relative amounts, consider the lever-arm rule

$$\% \text{ Solid} = \frac{MO}{MN} \times 100 = \frac{67.5 - 40}{65 - 26} \times 100 = \frac{27.5}{39} \times 100 = 70.05\%$$

$$\% \text{ Liquid} = 100 - 70.05 = 29.95 \%$$

11.5.2.2 Two Metals Completely Soluble in Liquid State but Partially Soluble in Solid State

Many of the industrial binary alloys form two varieties of crystals when the freezing starts. These crystals carry a certain percentage of the alternate metal as a solid solution. Figure 11.9 shows equilibrium diagram of a system of components that has complete mutual solubility in liquid state and limited solubility in solid state.

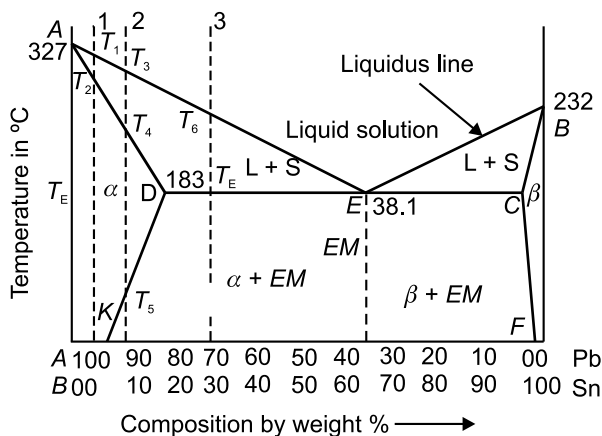


Fig. 11.10 Two metals completely soluble in liquid state and partially soluble in solid state

Consider the solidification characteristics of alloys of lead–tin (Pb–Sn) system. Lead melts at 327°C and tin melts at 232°C as shown in Figure 11.10. If a small amount of tin is added to molten metal lead, freezing point of the resulting alloy decreases as indicated by the line AE on phase diagram. On the other hand, if the small amount of lead is added to tin, the freezing point of the resulting alloy decreases. From this, each metal decreases the freezing point of the other. The line connecting these freezing points must intersect at some point called E . This point is the eutectic point in the diagram and represents 38.1% of lead and 61.9% of tin which melts/freezes at eutectic temperature 183°C (T_E). The alloy whose composition is represented by eutectic is called as eutectic composition.

Lines AE and EB are liquidus lines and lines AD , DEC and CB are solidus lines. Point D shows maximum solubility of metal tin in lead and point C shows maximum solubility of metal lead in tin at eutectic temperature. Points K and F indicate the solubility of metals tin in lead and lead in tin respectively at 0°C temperature. At point E , solid solution lead and tin simultaneously separate from the liquid phase to form eutectic mixture.

From the figure, the metal lead dissolves in tin up to 19.5% and tin in lead 2.6% at eutectic temperature. Similarly, the metal lead in tin dissolves 5% and tin in lead dissolves 6% at 0°C. But these limits of solid solubility apply only up to the eutectic temperature of T_E °C. As indicated in the diagram, these solid solutions are alpha (α) and beta (β) solid solution.

Solidification of Alloys: In alloy 1 containing 95% lead and 5% tin, solidification begins at temperature T_1 and completes at temperature T_2 . Solid solution ' α ' continuously crystallizes from molten liquid and is cooled to room temperature. Throughout the process, alloy will be ' α ' solid solution.

In alloy 2 containing 8% lead and 92% tin, solidification begins at T_3 and completes at T_4 . Alloy 2 consists of only α solid solution till it reaches temperature T_5 . On further cooling from T_5 , the solid solution will become supersaturated and solid solution decomposes and is separated at temperature below T_5 . At the room temperature, the metal consists of solid solution and eutectic mixture.

In alloy 3 containing 30% lead and 70% tin, solidification begins at T_6 and completes at T_E . Initially, α solid solution crystallizes along the solidus line moving towards maximum solubility of lead in it. At temperature T_E (eutectic temperature), the residue liquid phase reaches to eutectic composition and then metal completely solidifies in the form of eutectic mixture. The eutectic mixture contains only grains of metal lead and tin after solidifying.

Problem 11.2

Construct a phase diagram using the following data and label all the fields.

Melting point of Ag = 961°C

Melting point of Cu = 1083°C

Eutectic temperature = 780°C

Eutectic composition = 28% Cu

Maximum solubility of Cu in Ag = 9% at 780°C

Maximum solubility of Ag in Cu = 8% at 780°C

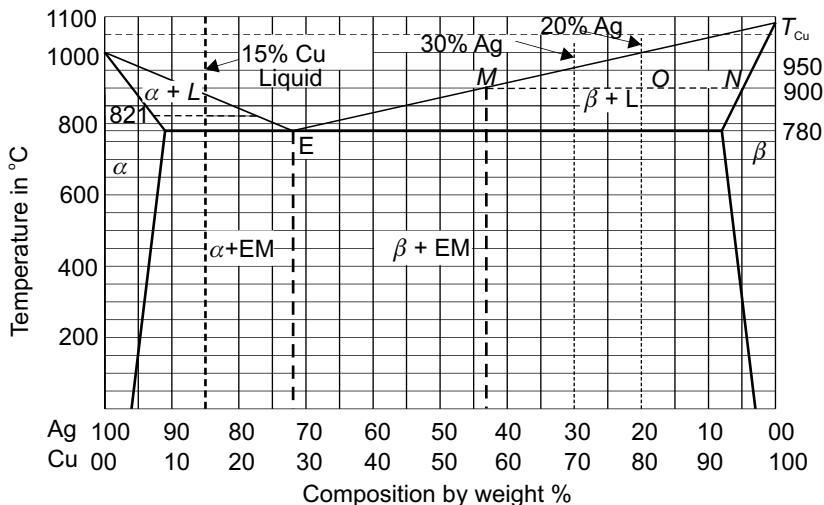
Maximum solubility of Cu in Ag = 2% at 400°C

Maximum solubility of Ag in Cu = 0% at 400°C

Determine the following:

1. Temperatures at which solidification starts and ends for 30% Ag alloy
2. Temperature at which a 15% Cu alloy has 50% liquid phase and 50% solid phase
3. Percentage composition of liquid and solid phases in a 20% Ag alloy at 900°C

Solution



138 | Phase Diagrams

1. For an alloy of 30% silver, solidification starts from 950°C and ends at 780°C.
2. Temperature at which 15% copper is 50% liquid and solid is 821°C.
3. Consider lever-arm rule for an alloy of 20% silver at 900°C

$$\% \text{ Solid} = \frac{MO}{MN} \times 100 = \frac{43.5 - 20}{43.5 - 5} \times 100 = \frac{23.5}{38.5} \times 100 = 61.03\%$$

$$\% \text{ Liquid} = 100 - 61.03 = 38.97\%$$

11.5.2.3 Two Metals Completely Soluble in Liquid State and Insoluble in Solid State

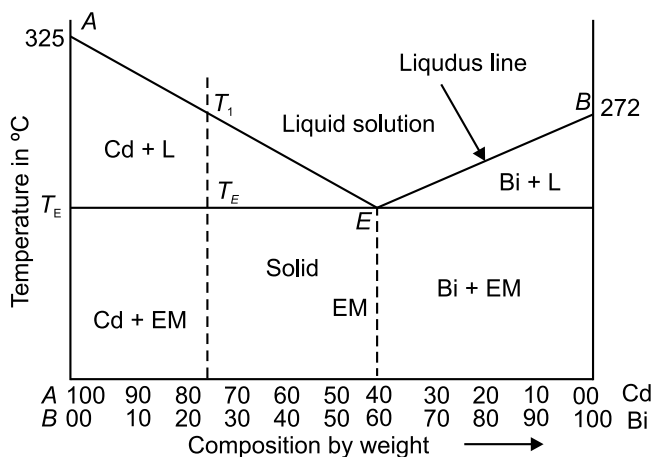


Fig. 11.11 Two metals completely soluble in liquid state and insoluble in solid state

Figure 11.11 shows a phase diagram of *A* and *B* (Bi–Cd system). From the alloy diagram, it can be noted that the melting point of cadmium is 325°C and that of bismuth is 272°C. If a small amount of cadmium is added to molten bismuth, freezing point of the resulting alloy decreases and is indicated by the line *AE* on phase diagram. On the other hand, if a small amount of bismuth is added to cadmium, the freezing point of the resulting alloy decreases. The addition of each metal to another decreases the freezing point of the other. The line connecting these freezing points must intersect at some point called *E*. This point is the eutectic point in the diagram and represents 40% cadmium and 60% bismuth which melts at eutectic temperature T_E . The alloy whose composition is represented by eutectic is called as eutectic composition. The alloy of eutectic composition melts and freezes at a specific and constant temperature and in this respect behaves as a pure metal.

Consider cooling of an alloy of 80% cadmium and 20% bismuth. At T_1 temperature, pure metal cadmium starts separating and the molten liquid metal gets poorer in cadmium and richer in bismuth. As the temperature further falls, more and more crystals of metal cadmium separate. This process continues until the composition of residue liquid attains eutectic composition (i.e., 60% cadmium and 40% bismuth). At this stage, the eutectic composition will solidify at temperature T_E °C and the alloy will solidifies like pure metals. Eutectic consists of alternate layers of metal cadmium and bismuth, which form at eutectic temperature. The eutectic alloys are entirely soluble in each other in the liquid state, but are insoluble in each other in the solid state.

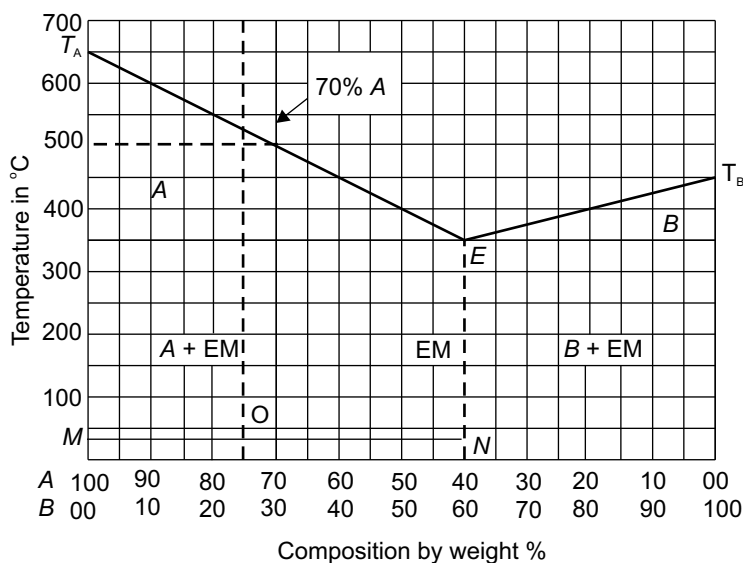
Problem 11.3

Two metals *A* and *B* are used to form an alloy containing 70% *A* and 30% *B*. Metal *A* melts at 650°C and *B* at 450°C when alloyed together. *A* and *B* do not form any compound or intermediate phase. The solid solubility of either metal is negligible. The metal pair forms a eutectic of 40% *A* and 60% *B*, which solidifies at 350°C. Assume the liquidus and solidus lines to be straight.

1. Draw the phase diagram.
2. Find the temperature at which the alloy starts and completes solidification.
3. Find the percentage of eutectic in the alloy at room temperature.

Solution

1. The following is the phase diagram.



2. The alloy of 70% *A* and 30% *B* starts solidification at 500°C and ends at 350°C.
3. Percentage of eutectic = $\frac{MO}{MN} \times 100 = \frac{100 - 70}{100 - 40} \times 100 = \frac{30}{60} \times 100 = 50\%$

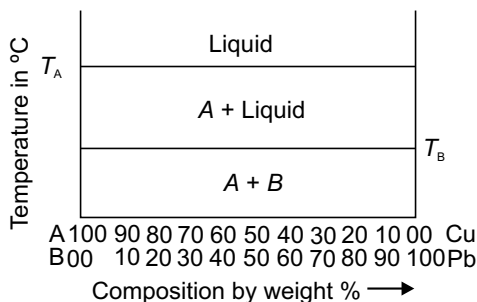
11.5.2.4 Two Metals Incompletely Soluble in Liquid and Solid States

Fig. 11.12 Two metals incompletely soluble in liquid and solid states

140 | Phase Diagrams

All metals are not soluble in each other in the liquid state, e.g., lead and zinc, or lead and copper do not mix with each other when melted (see Figure 11.12). Lead which is heavier settles down at the bottom and the lighter metal zinc or copper, as the case may be, forms a distinct and separable top layer. This property is important commercially while making certain types of bearing alloys. The specific case is that of putting droplets of lead through molten copper and making an emulsion similar to that of oil in water. This emulsion is allowed to solidify and the soft lead globules in suspension in copper form an ideal anti-friction alloy.

Practically, however, the two metals are rarely completely insoluble. When the temperature of the mixture is raised beyond a certain limit, these become soluble in each other and on cooling, these separate from each other. This liquid solubility at a high temperature is not of much practical importance.

11.6 LIQUID AND SOLID-STATE TRANSFORMATION

11.6.1 Eutectic Reaction (Transformation)

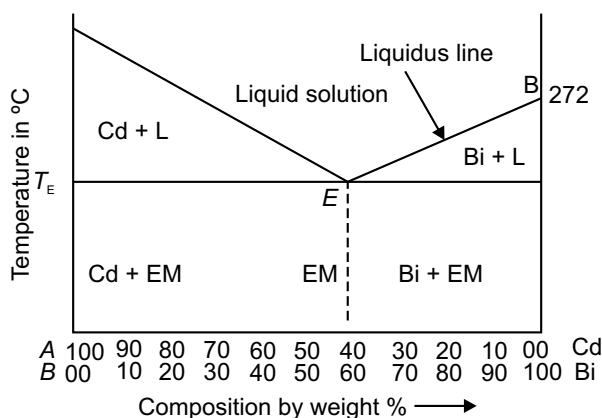
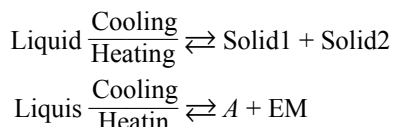


Fig. 11.13 Eutectic reaction in cadmium and bismuth system

In a eutectic reaction, the liquid solution of a fixed composition solidifies at a lower temperature than all other compositions and forms a mixture of two solid phases. This process reverses on heating. An example of metals showing eutectic reaction is bismuth and cadmium at 60% bismuth and 40% cadmium (see Figure 11.13).



11.6.2 Peritectic Reaction

Peritectic reaction is the reaction that occurs during the solidification of some alloys. In this reaction, the liquid phase reacts with the solid phase to give a solid phase of different structure, and the reaction occurs at a constant temperature.

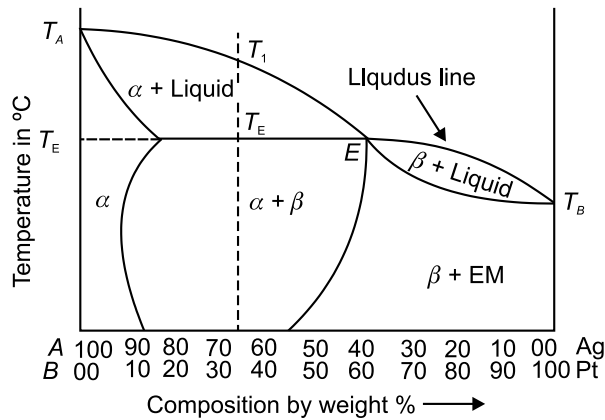
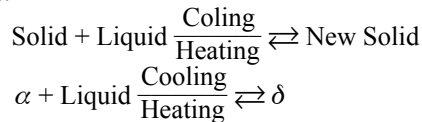


Fig. 11.14 Peritectic reaction in silver and platinum system

Assuming a very slow rate of cooling, the peritectic reaction will occur only in silver and platinum alloys that contain 12–45% Ag (see Figure 11.14). Consider a liquid of composition of 25% silver and 75% platinum. The solidification starts at T_1 °C and ' α ' begins to form till peritectic temperature (T_E). At this temperature, the ' α ' crystals begin to react with remaining liquid and form δ solid solution.

In the peritectic reaction, a liquid and a solid react isothermally to form a new solid. This reaction can generally be expressed as follows:



The new solid formed is generally an intermediate phase.

11.6.3 Eutectoid Reaction

Allotropy (pure metals) and order–disorder transformation (in alloys) are the phase changes occurring in the solid state. The most important of the solid-state transformations is the eutectoid reaction in which one solid phase decomposes isothermally into a mixture of two solid phases.

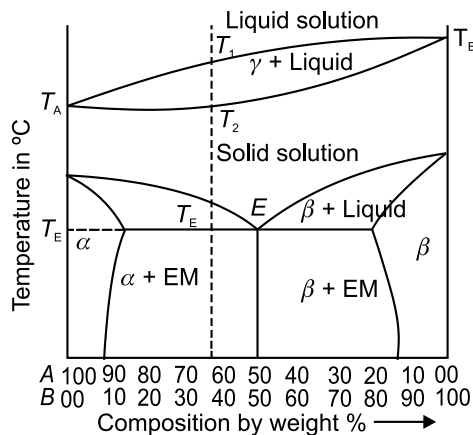
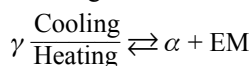
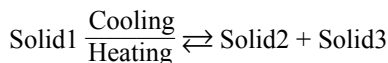


Fig. 11.15 Eutectoid reaction in silver and platinum system

142 | Phase Diagrams

Consider an alloy of 60% A and 40% B . As it is cooled slowly, γ solid solution appears. More and more of γ solid solution appears until it reaches $T_2^\circ\text{C}$. When the alloy reaches eutectoid temp T_E , the γ solid solution now starts changing to ' α ' solid solution. At the eutectoid temperature, residue γ solid solution is changed into eutectoid mixture. Microstructure at the room temperature consists of primary ' α ' which was formed between T_3 and T_4 surrounded by a eutectoid mixture of A and B (see Figure 11.15).



Another example of eutectoid reaction, which is very common, is austenite decomposing into pearlite (ferrite + cementite).

11.6.4 Peritectoid Reaction

The peritectoid reaction is a very rare reaction. In this reaction, the two solid phases, a pure metal and the other solid solution, react at peritectoid temperature to form a new solid phase.

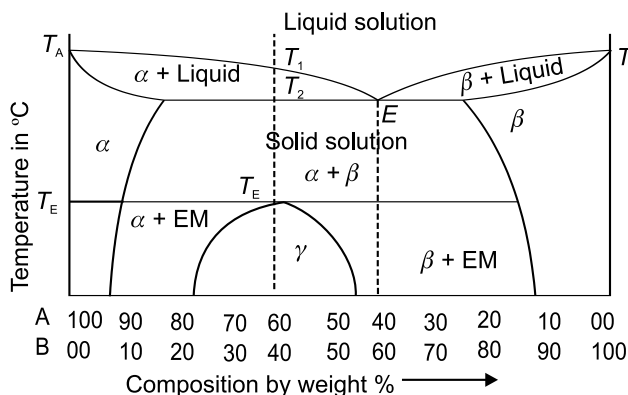
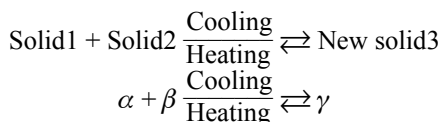


Fig. 11.16 Pertectoid reaction

In Figure 11.16, the solid phases α and β react at peritectoid temperature to form a new phase γ . Peritectoid reaction is the transformation of two solids into a third new solid.



11.7 COMPLEX ALLOY SYSTEMS

Many of the important alloys in the industry contain three or more metals in significant proportions. We now here consider the effect of the third element or metal on the binary alloy.

These effects are specified briefly as follows:

1. The three elements may form a ternary eutectic with lower melting point than the binary eutectic. Thus, the addition of bismuth to the lead–tin eutectic produces an alloy which melts in boiling water.

2. There is the possibility that all the three metals may go into solid solution; in this case the third element has not got much effect on the binary alloy.
3. The third element may combine with one of the elements of the alloy or with the impurities in the alloy to produce a profound effect. Thus, e.g., when manganese is added to steel containing sulphur, the manganese confers better forging properties to steel by combining with sulphur to form manganese sulphide (MnS), which gets ejected from the steel. Such additions of manganese to steel are very difficult to illustrate by the alloy diagram method. However, if only three components are present, an alloy diagram may be plotted by means of triangular coordinates as shown in Figure 11.17.

11.8 TERNARY PHASE DIAGRAM

The properties of a pure metal may be improved by the addition of one or more alloying elements. Most commercial alloys are complex due to more number of alloying elements. At present, no single method is available for representing the phase relationship in a multi-component system. Three-component systems are the most complex systems to represent phases with respect to three components like copper–aluminum–zinc.

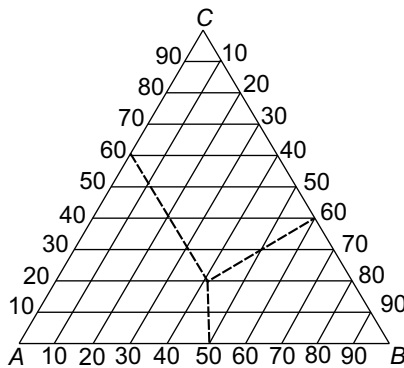


Fig. 11.17 Equilibrium diagram of a ternary alloy

Figure 11.17 shows the triangular method for plotting the three component variations in a tertiary system when the pressure and temperature are fixed. Each of the components of a ternary alloy is represented by each of the corners of an equilateral triangle. The sides of the triangle represent an alloy system of three binary alloy diagrams AB , AC and BC . The individual metals in the alloy are A , B and C . All the possible combinations of the three components are then formed from the lengths of the perpendicular from any given point Z . From the diagram it can be seen that Z represents 60% of A , 60% of B and 50% of C . To construct a diagram with the triangle as the base, the temperatures are plotted at right angles to the plane of the triangle. The development of the diagram ultimately results in a solid model, each side of the model representing one of the three binary systems.

EXERCISES

1. What is a phase diagram? How are they classified?
2. Explain the phase rule. Discuss it with examples.
3. List the usefulness of equilibrium phase diagrams.

- Draw the phase diagram for the series and label all the lines and regions assuming the liquidus, solidus and solvus curves to be straight. Predict the number, type, extent and composition of the phases present in an alloy containing 70% *A* and 30% *B* at 25°C.

22. Two metals *A* and *B* are used to form an alloy containing 70% *A* and 30% *B*. Metal *A* melts at 650°C and *B* at 450°C when alloyed together. *A* and *B* do not form any compound or intermediate phase. The solid solubility of either metal is negligible. The metal pair forms eutectic of 40% *A* and 60% *B*, which solidifies at 350°C. Assume the liquidus and solidus lines to be straight.
- Draw the phase diagram.
 - Find the temperature at which the alloy starts and completes solidification.
 - Find the percentage of eutectic in the alloy at room temperature.
23. Construct an equilibrium diagram for the following data. Indicate all necessary details.
- Two metals *A* and *B* with melting points 600°C and 900°C respectively are alloyed together. The maximum solubility of *B* in *A* is 10% and *A* in *B* is 15% at 300°C. The maximum solubility of *B* is 5% and *A* is 5% at 0°C. The alloy forms a eutectic at 40% *B* and 60% *A* at 300°C. No intermediate compounds are formed. Calculate the fraction eutectic formed just below the eutectic temperature at 60% *B*.
24. Two metals *A* and *B* of melting points 1,000°C and 800°C respectively have unlimited mutual liquid solubility. The solid solubility of *B* in *A* is a maximum of 20% at the eutectic temperature of 500°C which reduces to 10% at 0°C. The solid solubility of *A* in *B* is a maximum of 10% at the eutectic temperature which reduces to 5% at 0°C. No solid-state reactions other than those due to solubility changes occur in the series. The eutectic composition is 70% *B*. Assume solidus, liquidus and solvus lines to be straight.
- Draw the phase diagram of the series.
 - Describe the mode of solidification, solid-state reactions and room temperature microstructure of an alloy containing 40% *B*.
25. A binary alloy of *M* and *N* contains 56% solid phase and 44% of liquid phase. The composition of solid phase and liquid phase are 28% *N* and 70% *N* respectively. What is the overall composition of the alloy?
26. Two metals *A* and *B* are used to form an alloy containing 75% *A* and 25% *B*. *A* melts at 650°C and *B* at 450°C. When alloyed together, *A* and *B* do not form any compound or intermediate phase. The solid solubility of metal *A* in *B* and of *B* in *A* are negligible. The metal pair forms a eutectic at 40% *A* and 60% *B* which solidifies at 300°C. Assume the liquidus and solidus lines to be straight. Draw the phase diagram for the alloy series and find
- The temperatures at which the alloy starts and completes solidification
 - The percentage of eutectic in the alloy at room temperature

OBJECTIVE -TYPE QUESTIONS

- Cooling curve is obtained by plotting _____.
 - Time versus temperature
 - Temperature versus time
 - Time versus composition
 - Composition versus time
- During alloy solidification, the temperature is _____.
 - Constant
 - Increases
 - Decreases
 - All of the above
- Before solidification, some amount of under-cooling occurs _____.
 - In an alloy
 - In pure metal
 - In tertiary alloy
 - None of the above
- Eutectic solid solidifies at _____.
 - Varying temperature
 - Constant temperature
 - Both constant and varying temperature
 - None of the above

146 | Phase Diagrams

5. Lever-arm rule is used for identifying _____.
 (a) Amount of phase (b) Amount of temperature
 (c) Amount of heat (d) Solidifying temperature
6. Number of degrees of freedom of a system in equilibrium condition is related to _____.
 (a) Temperature and pressure (b) Only pressure
 (c) Number of components and phases present
 (d) Only temperature
7. In a monovariant system, the degrees of freedom is _____.
 (a) One (b) Zero (c) Two (d) Four
8. An example for two metals completely soluble in liquid state and partially soluble in solid state is _____.
 (a) Copper–silver (b) Copper–zinc
 (c) Lead–tin (d) Gold–copper
9. An example for two metals completely soluble in liquid and solid is _____.
 (a) Copper–nickel (b) Lead–bismuth
 (c) Lead–tin (d) All of the above
10. Bismuth and cadmium phase diagram is an example for _____.
 (a) Two metals completely soluble in liquid and solid states
 (b) Two metals completely soluble in liquid state and partially soluble in solid state
 (c) Two metals completely soluble in liquid state and insoluble in solid state
 (d) All of the above
11. In a eutectic reaction, _____.
 (a) Liquid transfers into two solids (b) Liquid transfers into one solid
 (c) Liquid transfers into three solids (d) None of the above
12. Liquid phase reacts with a solid phase to give a different solid phase called _____.
 (a) Eutectic reaction (b) Eutectoid reaction
 (c) Peritectic reaction (d) Peritectoid reaction
13. Eutectic composition refers to _____.
 (a) Two metals completely soluble in solid state
 (b) Two metals partially soluble in solid state
 (c) Two metals completely insoluble in solid state
 (d) All of the above
14. Eutectoid transformation is a _____.
 (a) Liquid to liquid transformation (b) Solid to solid transformation
 (c) Liquid to solid transformation (d) None of the above
15. Temperature at which eutectic composition solidifies is known as _____.
 (a) Solidification temperature (b) Peritectoid temperature
 (c) Eutectic temperature (d) Melting temperature

ANSWERS

1.	a	2.	a	3.	b	4.	b	5.	a	6.	c
7.	a	8.	c	9.	a	10.	c	11.	a	12.	c
13.	c	14.	b	15.	c						

chapter 12

Iron Carbon Equilibrium Diagram

INTRODUCTION

The alloys of iron are very important engineering materials which find extensive application in almost all areas. Alloys with carbon content up to 2% are known as steel where as those having carbon above 2% and up to 6.67% are termed as cast iron. Steels and cast irons with varying percentage of carbon and other alloying elements are very popular engineering materials. These alloys possess a wide range of properties, which make them very attractive and find extensive usage in all fields of engineering. For example, steel is used in all engineering applications like civil structures, automobile bodies and machine components. Similarly, cast irons are used as lathe bed, machine vise, crankshaft, etc.

12.1 SOLIDIFICATION OF PURE IRON (CONSTITUTION OF IRON OR ALLOTROPY MODIFICATION OF IRON)

Iron is an allotropic metal which shows more than one type of crystal structure during heating from room temperature to molten state or during cooling from molten state to solid state. To study the allotropic modification, molten iron is allowed to cool slowly and the cooling curve for pure iron is as shown in Figure 12.1. At temperatures above 1,539°C, iron is in a liquid state. When molten iron solidifies from liquid state at 1,539°C, it crystallizes into delta iron (δ -iron), which is BCC in crystal structure. During solidification, the temperature remains constant. On further cooling to a temperature of 1,395°C, the atoms are rearranged and the allotropic modification of iron takes place from delta iron to gamma iron. At this temperature, gamma iron is in FCC crystalline structure, which is nonmagnetic. With further drop in a temperature to 910°C, gamma iron is once again modified to BCC crystal and it is known as alpha iron (α -iron). Alpha iron at 910°C is nonmagnetic and remains nonmagnetic until the temperature of 768°C. When the metal is further cooled below the temperature of 768°C, the metal changes from nonmagnetic to magnetic iron without a change in lattice structure.

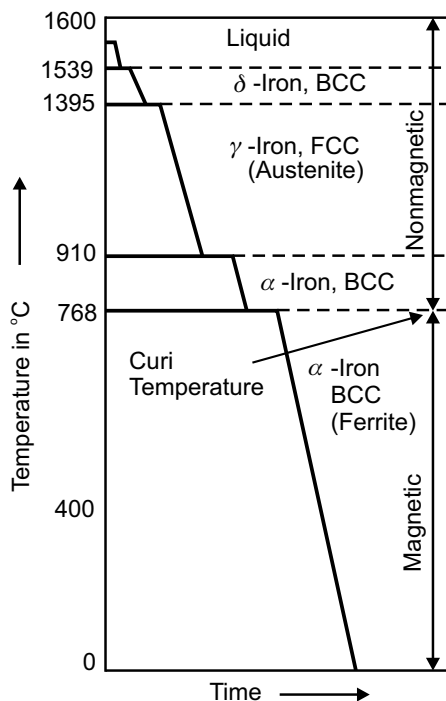


Fig. 12.1 Cooling curve for pure iron

This critical temperature is known as ‘Curie temperature’. With a further drop in temperature, no further changes take place, as indicated in the diagram. ‘alpha-Iron’ is highly magnetic and exists up to room temperature. These changes are reversible on heating from room temperature to melting point. Under normal rate of cooling, actual transformation takes place at temperature, which is lower than the temperature indicated above. Similarly, on heating, transformation occurs at temperature higher than temperature indicated above. This phenomenon is known as thermal hysteresis of pure iron.

12.2 IRON CARBON PHASE DIAGRAM

The iron carbon equilibrium diagram graphically represents the changes that take place when two variables, such as temperature and overall composition, are varied. It shows the phase present in an alloy for system of different temperatures and for different compositions. This equilibrium diagram has temperature on vertical scale and percentage of composition by weight as horizontal scale. The composition on horizontal scale represents only 6.67% by weight. This is because, a maximum of 6.67% carbon can only be added to molten iron at which it becomes saturated. Any further addition of carbon will not make it dissolve in iron; but it rather floats on the surface due to low density. This phase diagram is also known as iron and iron carbide phase diagram.

The iron carbon phase diagram is constructed by using a number of cooling curves with carbon varying from 0 to 6.67% similar to nonferrous diagrams. The effects of carbon addition to iron are shown in Figure 12.2. When carbon dissolves in molten iron, the solidification temperature of the resulting iron carbon alloy decreases. Iron carbon alloys which contain up to 2% carbon are known as steel. Iron carbon alloys holding more than 2% carbon are called cast irons. Up to 0.8% carbon steels are called as hypoeutectoid steels. The carbon content from 0.8% to 2% is called hypereutectoid steel. Similarly, from 2% to 4.43% carbon is called hypoeutectic cast iron and 4.43% to 6.67% cast iron is called hypereutectic cast iron.

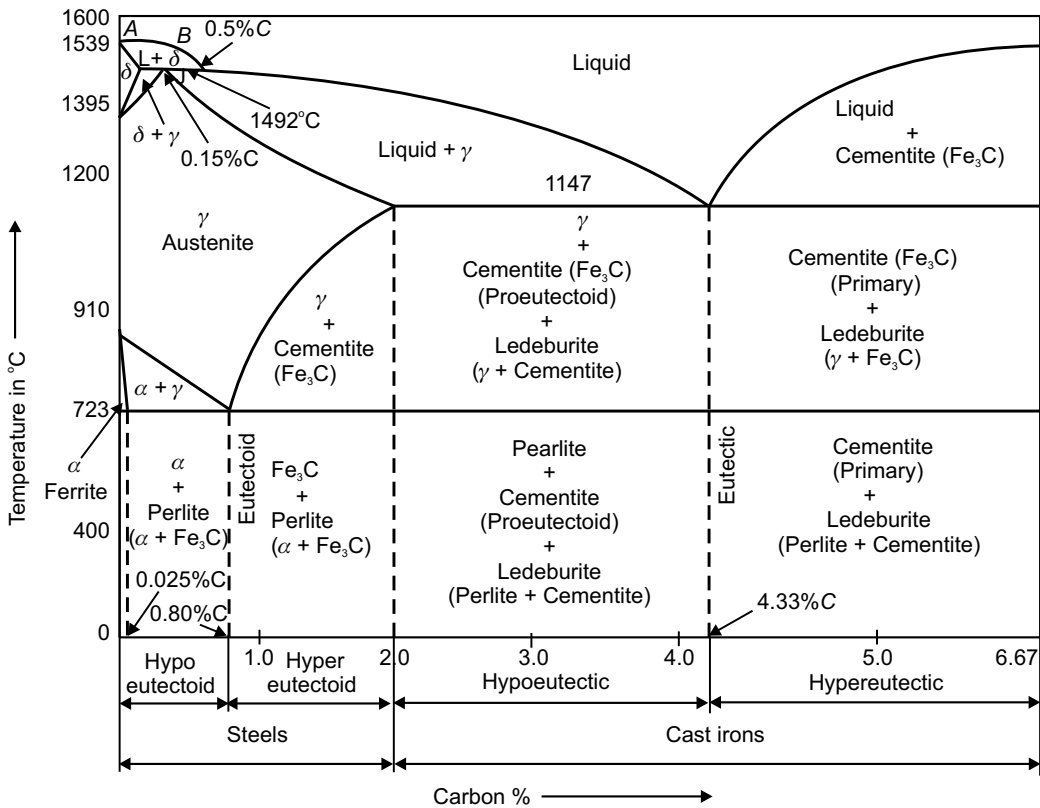


Fig. 12.2 Iron carbon phase diagram

Pure iron melts or solidifies at 1,539°C. Further, when up to 4.3% carbon is added to molten iron, the solidification temperature decreases to 1,130°C. This is indicated by a line *ABC* on the diagram. Beyond 4.3% carbon, the temperature increases as shown in the figure. This is represented by a line *CD* on the diagram. From the figure, the line *ABCD* represents liquidus line. The melting point of pure iron is marked as point *A*. Similarly, point *D* is the melting point of iron carbide. As the temperature of the liquid falls along the line *ABCD*, crystals of austenite separate from the liquid. In the same way, the crystals of iron carbide separate from liquid along line *CD*. The complete solidification of iron carbon alloys produce along the line *HJECF* called the solidus.

12.3 PHASES OF IRON CARBIDE, PHASE DIAGRAM

The phases that occur in iron carbon alloys are molten alloys, austenite, ferrite, cementite, ledeburite and pearlite.

12.3.1 δ -Ferrite

When a low carbon steel crystallizes at 1,539°C, the solid that appears is in BCC crystal structure called δ -ferrite. At 1,492°C, because of higher temperature the solubility of carbon in δ -ferrite is very

150 | Iron Carbon Equilibrium Diagram

small, between 0.1% and 0.15%, . It is soft, ductile and converted into γ solid solution by reacting with residue liquid of iron at 1,395°C.

12.3.2 Austenite

Austenite is an interstitial solid solution of carbon up to 2% at 1,147°C and it is FCC in crystal structure. It is normally unstable at room temperature and is nonmagnetic. On cooling below 723°C, it starts transferring into ferrite and pearlite.

12.3.3 Ferrite

The structural modification of pure iron at room temperature is known as ferrite. It is an interstitial solid solution of small amounts of carbon dissolved in BCC crystal structure. The maximum solubility of carbon is 0.025% at 723°C and 0.008% at room temperature. Ferrite is soft, ductile and is of low strength among all phases of iron carbon alloys.

12.3.4 Cementite

When carbon in iron exceeds the solubility limit, it forms a second phase which is commonly known as cementite. This is also called iron carbide (Fe_3C) and it contains up to 6.67% carbon by weight and has orthorhombic crystal structure. It is a typical compound of low tensile strength but high compressive strength and ferromagnetic. It is hardest structure in iron carbide system.

12.3.5 Pearlite

The mechanical mixture of ferrite and cementite formed at 727°C on very slow cooling is known as pearlite. It consists of alternate layers of ferrite and cementite. It is a product of eutectoid transformation. Pearlite is fairly soft and its hardness lies between that of ferrite and cementite. It appears like a fingerprint in structure.

12.3.6 Ledeburite

Ledeburite is eutectic lamellar mixture of austenite and cementite. It contains 6.67% carbon and is formed at 1,147°C by eutectic reaction. Further, ledeburite is unstable and transfers into ferrite and cementite at 726°C. Cementite is hard but brittle and pearlite is also fairly hard. Therefore, the transformed ledeburite is also hard and brittle.

12.3.7 Solubility of Carbon in Iron

The solubility limit for carbon in ferrite iron is shown by line GPR. This area of diagram is labeled as ' α ' (Ferrite). The maximum solubility of carbon in ferrite is 0.025% at 723°C and minimum solubility is 0.008% at room temperature.

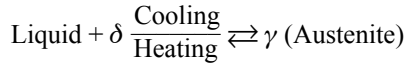
Austenite is FCC structure iron and is capable of containing up to 2% dissolved carbon. It has definite solubility for carbon, which depends upon the temperature. It is indicated in the area GSEJM in the diagram.

12.4 REACTION OF IRON CARBON SYSTEM

There are three invariant reactions that occur in iron carbon phase diagram leading to various phase transformations and structures. These reactions are peritectic reaction, eutectic reaction and eutectoid reaction.

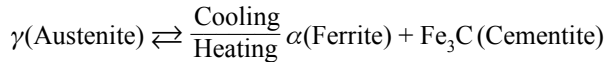
12.4.1 Peritectic Reaction

The peritectic reaction involves the isothermal transformation of liquid and solid to another solid phase at a constant temperature. In this reaction, the δ -iron reacts with residue liquid and is completely transferred to austenite on cooling at 1,492°C. The reaction can be written as



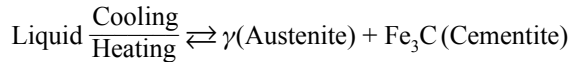
12.4.2 Eutectoid Reaction

The eutectoid reaction is solid to solid transformation at constant temperature. A solid decomposes into two solid phases. In this reaction, the austenite transfers into ferrite and cementite by eutectoid reaction on cooling at 723°C. The reaction can be written as



12.4.3 Eutectic Reaction

The eutectic reaction is liquid to solid transformation at constant temperature. A liquid is converted into two solids. In this reaction, the liquid solution is transferred into austenite and cementite on cooling at 1,147°C. The reaction can be written as



12.5 STEELS

Steels contain iron and carbon with the carbon content varying from 0.008% to 2%. In this, carbon is combined with iron in solid solution and no free carbons are present. However, in practice, the carbon range does not exceed 1.7%. Steels can be classified into three types: low carbon steels—0.2%–0.3% carbon, medium carbon steels—0.3%–0.6% carbon and high carbon steels—0.6%–1.7% carbon. Steels with carbon content from 0.025% to 0.8% are called hypoeutectoid steel. Steels with 0.8% carbon are known as eutectoid steels and steels with carbon content from 0.8% to 2% are called hypereutectoid steel.

12.5.1 Solidification and Transformation of Hypoeutectoid Steel (0.4% Carbon Steel)

The alloy is liquid above the liquids line. As the temperature decreases from the liquid line (T_1 °C), δ -delta iron starts to precipitate from the liquid phase. The δ -iron contains a maximum of 0.1% carbon. At temperature 1,427°C or T_2 °C, δ -solid solution and molten iron react to get converted into austenite. The austenite region is shown in Figure 12.3. The line GSA in the figure shows that the temperature

152 | Iron Carbon Equilibrium Diagram

transformation of austenite to ferrite starts at S , $T_3^\circ\text{C}$. Below this line, ferrite separates out from the austenite. Under very slow cooling conditions, the entire free ferrite separates from austenite when temperature reaches 723°C . At temperature 273°C , the carbon content of the austenite is 0.8% . Slightly below this temperature the austenite of the eutectoid composition decomposes with simultaneous precipitation of ferrite and cementite thus forming pearlite. Upon further cooling at room temperature, microstructure contains a mixture of free ferrite and pearlite.

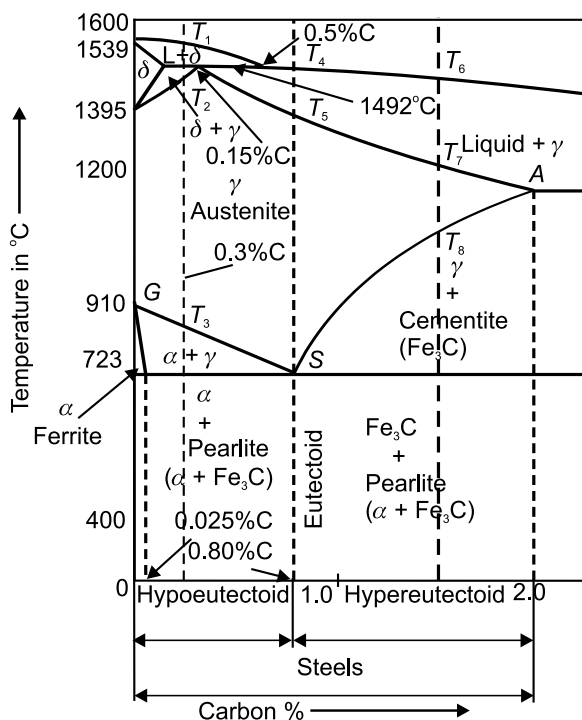


Fig. 12.3 Steel portion of iron carbon phase diagram

12.5.2 Solidification and Transformation of Eutectoid Steel (0.8% Carbon Steel)

The steel containing 0.8% carbon is called eutectoid steel. The alloy is liquid above $T_4^\circ\text{C}$ and solidification starts when temperature decreases austenitic range. This process is continuous until temperature reach $T_5^\circ\text{C}$. By the time the temperature reaches T_5 , the whole liquid solidifies as austenite. 0.8% carbon steel becomes solid solution in the form of austenite between the temperature range of T_5 and 273°C . When temperature 273°C is reached, the carbon content of the austenite is 0.8% and steel undergoes the eutectoid reaction into two new solid phases (ferrite and cementite) called pearlite. On further cooling to room temperature, the microstructure will be pearlite.

12.5.3 Solidification and Transformation of Hypereutectoid Steel (1.5% Carbon Steel)

Hypereutectoid steel contains carbon content from 0.8% to 2% . Any alloy from hypereutectoid steel is liquid above $T_6^\circ\text{C}$. Slightly below this temperature, solidification starts with the separation of austenite crystals. This process is continuous till it reaches a temperature of $T_7^\circ\text{C}$. By time the temperature

reaches $T_7^\circ\text{C}$, the whole liquid solidifies as austenite. Hypereutectoid carbon steel becomes solid solution in the form of austenite in the temperature range of T_7 and $T_8^\circ\text{C}$. On further decreasing the temperature, the solubility of the carbon content decreases along the line SA and the excess carbon precipitates as pro-eutectoid cementite upto temperature 273°C . At 273°C , the carbon content of the residue austenite is 0.8% and undergoes the eutectoid reaction and forms two new solid phases (ferrite and cementite) called pearlite. Upon further cooling to room temperature, the microstructure will be proeutectoid, cementite and pearlite.

12.6 CAST IRON

Cast iron is the name given to those alloys of iron carbon which contain more than 2% of carbon. Carbon from 2% to 4.33% is called hypoeutectic, 4.33% cast iron is eutectic and 4.33% to 6.67% cast iron is called hypereutectic cast iron. On the basis of nature of carbon present in cast iron, it may be divided into white cast iron and gray cast iron. In the gray cast iron, carbon is present in free form as graphite. Under very slow rate of cooling during solidification, carbon atoms get sufficient time to separate out in pure form as graphite. In addition, certain elements promote decomposition of cementite. Silicon and nickel are two commonly used graphitizing elements. In white cast iron, carbon is present in the form of combined form as cementite. In normal conditions, carbon has a tendency to combine with iron to form cementite.

12.6.1 Solidification and Transformation of Hypoeutectic Cast Iron (4% Carbon Cast Iron)

Hypoeutectic cast iron has carbon content between 2% and 4.33% (see Figure 12.4). Hypoeutectic cast iron of any composition solidifies at $T_1^\circ\text{C}$ on the liquids line with separation of austenite. Below

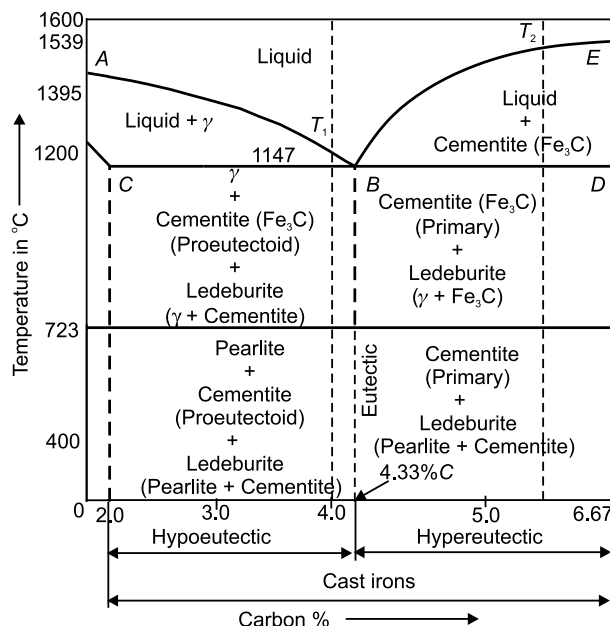


Fig. 12.4 Cast iron portion of iron carbon phase diagram

154 | Iron Carbon Equilibrium Diagram

this line, the alloy is in a two-phase state consisting of liquid and austenite crystals. As solidification progresses, the composition of residue liquid varies along the solids CB and liquids AB respectively. The austenite precipitated between $T_1^\circ\text{C}$ and $1,147^\circ\text{C}$ has 0.8% carbon. At $1,147^\circ\text{C}$, the residue liquid reduces to eutectic composition (4.33% carbon) and gets converted into eutectic mixture called austenite and cementite. The mixture of austenite and cementite is known as ledeburite. Just below $1,147^\circ\text{C}$, the cast iron consists of austenite crystals and ledeburite. Further cooling involves the separation of cementite from the austenite. The composition of austenite varies along AB. At 727°C , the austenite gets enriched with 0.8% carbon and decomposes into ferrite and cementite. The mixture of ferrite and cementite is called pearlite. The final structure at room temperature consists of ledeburite, cementite and pearlite. These transformations occur when the hypoeutectic cast iron is cooled at a normal rate.

12.6.2 Solidification and Transformation of Eutectic Cast Iron (4.33% Carbon Cast Iron)

Eutectic cast iron contains 4.33% carbon and it solidifies at a constant temperature of $1,147^\circ\text{C}$. Below $1,147^\circ\text{C}$, the microstructure consists of austenite and cementite. The mixture of austenite and cementite is also known as ledeburite. As the temperature decreases, the solubility of carbon decreases in austenite as indicated in line AB. On further cooling in temperature range $1,147^\circ\text{C}$ to 723°C , excess carbon comes out and gets modified into cementite along with iron. At 723°C , austenite contains 0.8% carbon and transforms into pearlite (ferrite and cementite). The final structure at room temperature consists of ledeburite, cementite and pearlite.

12.6.3 Solidification and Transformation of Hypereutectic Cast Iron (6.23% Carbon Cast Iron)

Hypereutectic cast iron has carbon content between 4.33% and 6.67%. Hypereutectic cast iron of any composition solidifies at $T_2^\circ\text{C}$ on the liquids line with the separation of cementite (primary). Below this line, the alloy is in a two-phase state consisting of liquid and cementite crystals. As solidification progresses, the composition of residue liquid varies along the solidus line BE. The cementite precipitates between $T_2^\circ\text{C}$ and $1,147^\circ\text{C}$. At $1,147^\circ\text{C}$, the residue liquid reduces to eutectic composition (4.33% carbon) and gets converted into eutectic mixture called ledeburite (austenite and cementite). Just below $1,147^\circ\text{C}$, the cast iron consists of cementite (primary) crystals and ledeburite. Further cooling involves the separation of cementite from the austenite. At 727°C , the austenite gets enriched with 0.8% carbon and decomposes into ferrite and cementite. The final structure at room temperature consists of cementite, ledeburite and pearlite. These transformations occur when the hypoeutectic cast iron is cooled at a normal rate.

12.7 CRITICAL TEMPERATURE OF THE IRON AND IRON CARBON DIAGRAM

Critical temperature is the temperature at which changes in composition and structure occur during heating or cooling. The critical temperature is also known as arrest point. These points or temperatures are usually represented by the following symbols:

- A_0 Temperature at which the cementite changes from ferromagnetic to magnetic during heating. It occurs at 210°C .

- A_1 Temperature at which the pearlite transforms into austenite at constant temperature. This temperature is referred as lower critical temperature. It occurs at 727°C .
- A_2 Temperature at which ferromagnetic ferrite become paramagnetic.
- A_3 Temperature at which the hypoeutectic steel is completely transformed to austenite.
- A_{cm} Temperature at which the hypereutectoid steel is completely transformed to austenite.

These critical temperatures do not occur at exactly the same temperature. Rapid heating rises these points whereas on rapid cooling, they are reduced due to thermal hysteresis. The designation for critical temperatures during heating are A_{c1} , A_{c3} and A_{cm} and during cooling they are represented as A_{r1} , A_{r2} and $A_{r_{\text{cm}}}$.

EXERCISES

1. Name three allotropic forms of iron and indicate their lattice structure.
2. Draw 'iron carbon equilibrium' diagram and demarcate the region where the following reactions take place: (i) Eutectic, (ii) Peritectic and (iii) Eutectoid. Explain the structural changes taking place at 4.3% carbon.
3. Draw a neat figure of iron–iron carbide diagram and label for transformation of austenite upon continuous cooling.
4. Draw iron–iron carbide equilibrium diagram and indicate the different phases on it. Name the composition and temperatures at which invariant reactions take place in iron–carbon system.
5. Draw a neat iron–iron carbide phase diagram and identify all phases present at different temperatures and carbon percentages.
6. Draw iron–iron carbide diagram for steel and explain the solidification of hypoeutectoid and eutectoid steel.
7. Name the phase reactions occurring in iron–iron carbide diagram. What are the temperatures and compositions at which they occur?
8. Draw the microstructures and mention the differences between a hypereutectoid steel and a hypoeutectoid steel.
9. List and explain the important properties of microconstituents found in Fe–C equilibrium phase diagram.
10. With the help of iron–iron carbide diagram, describe peritectic, eutectic and eutectoid invariant reactions with respective phases, temperatures and carbon content.
11. Describe, using suitable microstructures, the solidification of a 0.6% C steel when cooled slowly from $1,600^\circ\text{C}$ to room temperature.
12. Explain the cooling of Fe and 3% C alloy iron from its liquid state.
13. Draw iron–iron carbide phase diagram and identify the phase fields. Calculate the amount of proeutectoid ferrite, eutectoid ferrite and cementite in 0.4% carbon steel at room temperature.

OBJECTIVE-TYPE QUESTIONS

1. Pure iron solidifies approximately at _____.
 (a) 1,600°C (b) 1,400°C
 (c) 1,349°C (d) 1,539°C
2. Pure iron is nonmagnetic above _____.
 (a) 900°C (b) 1,000°C
 (c) 768°C (d) 723°C
3. Delta iron is in _____.
 (a) FCC crystal (b) HCP crystal
 (c) BCC crystal (d) None of the above
4. Maximum percentage of carbon soluble at 1,492°C in delta iron is _____.
 (a) 0.2% (b) 0.6%
 (c) 0.8% (d) 0.5%
5. Pure iron appears at room temperature in the form of _____.
 (a) Austenite (b) Pearlite
 (c) Ferrite (d) Cementite
6. 0.8% steel is also called as _____.
 (a) Eutectic steel (b) Eutectoid steel
 (c) Hypereutectoid steel (d) None of the above
7. In iron carbon phase diagram, peritectic reaction occurs approximately at _____.
 (a) 1,567°C (b) 1,559°C
 (c) 1,420°C (d) 1,492°C
8. Eutectoid reaction takes place at _____.
 (a) Below 723°C (b) Above 723°C
 (c) At 723°C (d) At 1,147°C
9. Pearlite is mechanical mixture of _____.
 (a) Gamma iron and cementite (b) Gamma iron and austenite
 (c) Austenite and cementite (d) None of the above
10. 4.33% cast iron is also known as _____.
 (a) Eutectic cast iron (b) Hypereutectic cast iron
 (c) Hypoeutectic cast iron (d) None of the above
11. Solubility of carbon in a ferrite structure at room temperature is _____.
 (a) 0.02% (b) 0.002%
 (c) 0.008% (d) 0.8%
12. Carbon in hypereutectic cast iron is between _____.
 (a) 2% and 4% (b) 4% and 6.675%
 (c) 2% and 6.67% (d) None of the above
13. The alloy of iron and 6.67% carbon appears as _____.
 (a) 100% cementite (b) 100% ledeburite
 (c) 100% austenite (d) Mixture of all above

14. Solubility of carbon in austenite at 1,147°C is _____.
 (a) 0.8% (b) 1.8%
 (c) 2% (d) 4.33%
15. Carbon appears in cast iron in the form of _____.
 (a) Flake (b) Nodular
 (c) Combined (d) Cementite

ANSWERS

1.	d	2.	c	3.	c	4.	d	5.	c	6.	b
7.	d	8.	c	9.	c	10.	a	11.	c	12.	b
13.	a	14.	c	15.	a						

13

chapter

Isothermal and Continuous Cooling Transformation Diagrams

INTRODUCTION

The properties of steel are mainly dependent upon microconstituents or phases present in the structure. Austenite is unstable below 723°C and it undergoes phase transformation into pearlite, bainite or martensite. In the beginning, austenite is transformed into α -iron but this iron is unable to hold Fe_3C in solid solution. The Fe_3C , which is held in the ferrite, is diffused out as free cementite. This requires heat energy and sufficient time. If sufficient heat and time are not allowed, the process of Fe_3C diffusion is decreased and in some cases, altogether arrested. So austenite undergoes transformation depending upon temperature and time. The relationship between structure and rate of cooling (time taken to decompose) can be studied for given steel with the help of a set of isothermal austenite transformation curves, which are popularly known as Time–Temperature–Transformation diagram or TTT diagram. In this diagram, the temperature is plotted on the vertical axis and time is plotted on a logarithmic scale along the horizontal axis. This curve is also known as S curve, C curve or isothermal curve.

13.1 CONSTRUCTION OF TTT DIAGRAM

For eutectoid composition of steel, TTT diagram can be constructed as follows.

Obtain a large number of relatively small specimens, cut from the same bar of given steel sample (composition should not change). The samples are made as thin as possible to bring in the temperature changes uniformly throughout the section. Place the samples in a molten salt bath (brine solution) and heat the eutectoid steel to a temperature above 723°C (Ac_3). Specimens are kept in the molten salt bath for long enough to form complete austenite. Time is an important factor in dissolving the Fe_3C in solid solution.

Withdraw the specimens from the molten salt bath and quickly transfer into another bath which is at a temperature lower than 723°C . For example, bath temperature is maintained at 700°C . Samples are held for varying lengths of time to transfer austenite into pearlite before being quenched to room

temperature. Pearlite is the result of isothermal heat treatment and its amount depends upon the time permitted for isothermal reaction to continue. Specimens are held in the bath for varying periods of time, which may vary from 1 s to as long as several hours. More time given to a sample to react isothermally, the more pearlite is formed. Isothermal reaction stops by quenching in cold water or ice to get untransformed austenite into martensite. Martensite is the result of water quenching of the specimen after the isothermal heat treatment (see Figure 13.1).

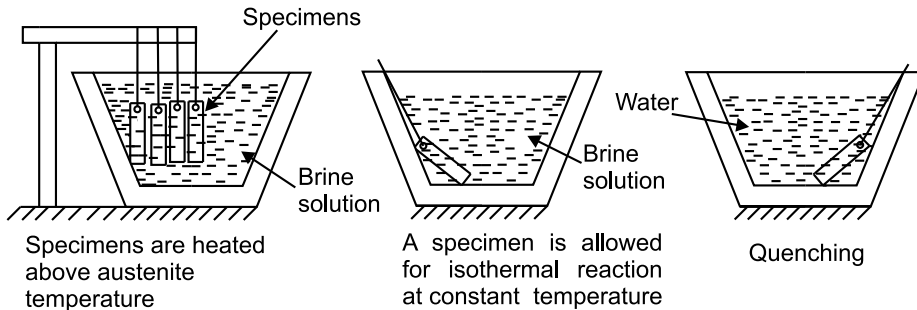


Fig. 13.1 Isothermal heat treatment arrangement

Observe the microstructure of the specimens under the microscope. It shows both the pearlite and martensite. Based on the structure, predict the amount of pearlite in specimens. When a large numbers of specimens which isothermally react at 700°C for varying time periods are metallographically observed, the result is the reaction or S curve as shown in Figure 13.2. S curve is plotted with time on the horizontal axis and pearlite percent on the vertical axis.

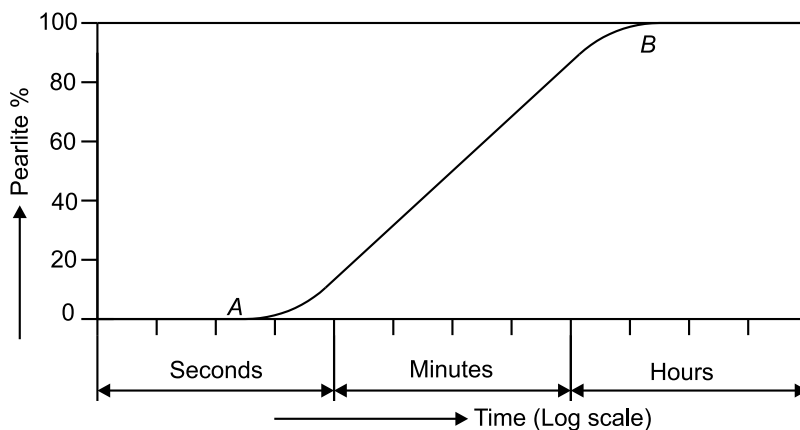


Fig. 13.2 S curve for eutectoid steel for a given temperature of 700°C

Similarly, a number of S curves are constructed over the whole temperature range of austenite instability for eutectoid steel. For example, isothermal reaction curves are constructed for temperatures 750°C , 700°C , 650°C , 600°C , 550°C , 500°C , 450°C , 400°C , 350°C , 300°C , etc. When data are obtained from a series of isothermal reaction curves over the whole temperature range of austenite instability for a given eutectoid steel, a TTT diagram can be constructed as summarized in Figure 13.3.

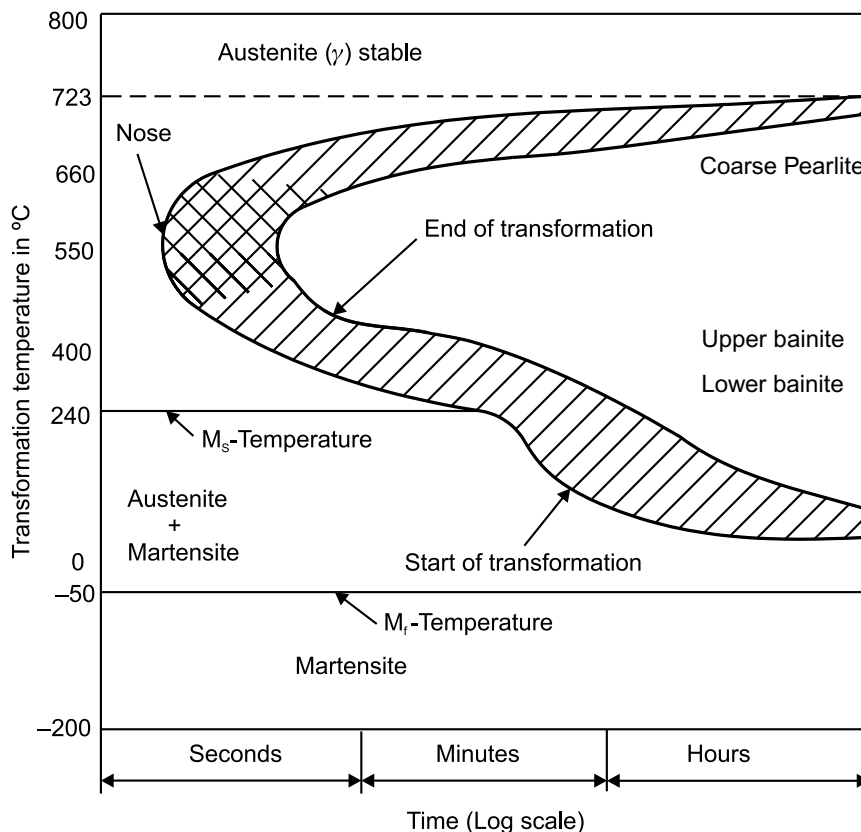


Fig. 13.3 Time, temperature and transformation for eutectoid steel

Austenite is stable above 723°C and below this temperature it is unstable, i.e., it can transform into pearlite, bainite or martensite. Transformation at temperature approximately between 723°C to 550°C results in the characteristics of microstructure of pearlite. The transformation within this range takes place by nucleation and growth of cementite and ferrite respectively. The ferrite formed at slightly below the 723°C is coarse structure due to high temperature and long time is available for diffusing Fe_3C . However, as the temperature is reduced, i.e., just above the nose of the curve, the pearlite becomes fine pearlite.

At temperature between 550°C and 240°C, the transformation product is bainite. Austenite decomposes into ferrite and cementite. Below the nose temperature, bainite looks feathery and above this temperature, it is dark acicular. These are called as upper bainite and lower bainite respectively.

Below 240°C, the austenite transformed is martensite. Martensite is an acicular, supersaturated interstitial solid solution of iron and carbon. At the foot of TTT diagram, there are two lines M_s and M_f at temperatures 240°C and -50°C respectively. M_s represents the temperature at which formation of martensite starts. M_f is the temperature at which the formation of martensite finishes during the cooling of austenite.

13.2 EFFECT OF COOLING RATE ON TTT DIAGRAM

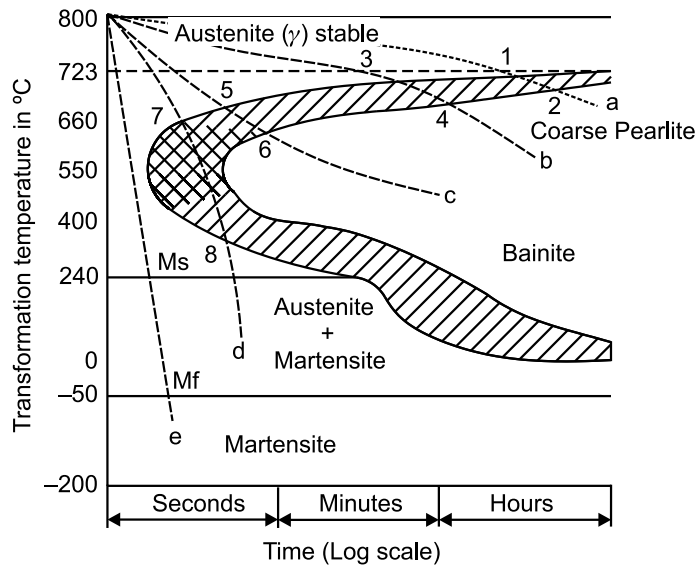


Fig. 13.4 Effect of cooling curve on TTT diagram

Figure 13.4 shows the effect of cooling rate on the formation of different reaction products in eutectoid steel. Austenite transforming into pearlite, bainite and martensite with different cooling rates is an example of this.

When a metal is heated above 723°C, held for a suitable time and cooled very slowly, it cools as per the curve A (becomes annealing) as shown in figure. A transformation starts at point 1, ends at 2 and the product is coarse pearlite with a low hardness and high ductility. This process is known as annealing. Cooling curve B involves a faster cooling rate than curve A and it becomes normalizing heat treatment. In curve B, the austenite transformation starts at point 3 with the formation of coarse pearlite and ends with fine pearlite at point 4. Curve C is a result of further increase in cooling rate. The transformation of austenite is a mixture of pearlite and bainite. It is typical air quench. Hardness of this structure is higher than the structure obtained in the annealing process. Curve D represents the intermediate cooling rate and some amount of austenite starts to transfer as fine pearlite between points 7 and 8. The residue austenite will transform into martensite when cooled at M_s line. Final structure consists of a mixture of pearlite and martensite.

When the cooling curve (E) touches the nose of the TTT diagram, then this curve is called critical rate of cooling curve as shown in Figure 13.5. If the curve touches the nose of the TTT diagram and has enough time, austenite transfers into fine bainite. If the curves miss the nose of the diagram, austenite is directly transferred into martensite. When the material is dipped in oil or water, the substance remains austenite until it reaches the M_s line and changes to martensite between M_s and M_f lines.

13.2.1 Definitions

13.2.1.1 Bainite

Bainite is an isothermal transformation product and is produced on isothermal transformation at a temperature between 550°C and 240°C. It consists of an aggregate of ferrite and cementite ($\alpha + \text{Fe}_3\text{C}$).

13.2.1.2 Martensite

Martensite is formed by transformation of austenite below the M_s temperature. It is an interstitial solid solution of carbon in α -iron and has a BCC lattice structure and is a product of quenching.

13.3 CONTINUOUS COOLING TRANSFORMATION (CCT) CURVE

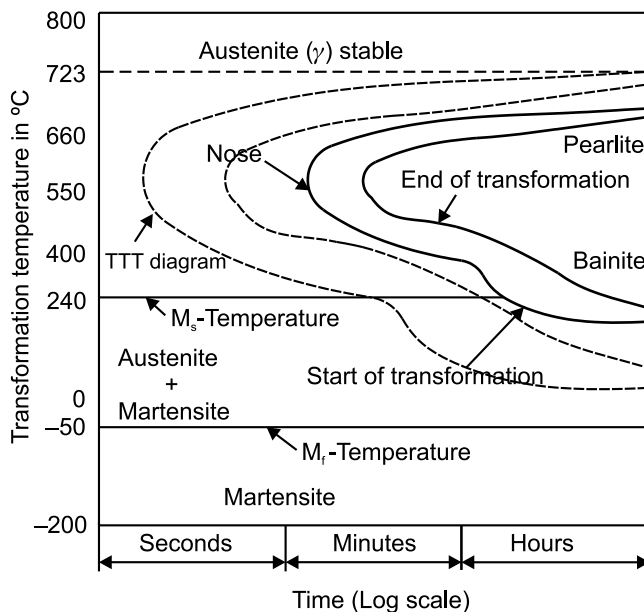


Fig. 13.5 Continuous cooling curve for eutectoid steel

The TTT diagrams hold good for isothermal transformation of austenite. It has limited application because in most of the heat treatment processes, the transformation of austenite takes place at continuous cooling and not at constant temperature or isothermal transformation. When the steel is cooled continuously, the TTT curve shifts to the right and downwards.

To construct a continuous cooling diagram of eutectoid steel, a large number of samples are heated above 723°C to get a complete austenite structure. From this temperature, specimens are cooled at a constant cooling rate of some definite temperature and then quenched in water. The specimens are studied for their microstructure and the time of start and end of pearlite are determined. By repeating

the process, different sets of start and end points of pearlite are obtained. On joining the start and end points, two curves, similar to those of TTT diagram, are obtained as shown in Figure 13.5. This diagram gives the end product of pearlite, bainite and martensite at different cooling rates and at different temperatures. This diagram is widely useful in heat treatment process.

13.4 EFFECT OF CARBON CONTENT AND ALLOYING ELEMENTS

The TTT curves explained are those of 0.8% C steel (eutectoid steel). The change in carbon content above or below this and the addition of alloying elements tend to displace the curves. A reduction in carbon content moves the curve to the left and an increase in carbon content (and alloying elements) tends to move the curve to the right as shown in Figure 13.6(a) to (c).

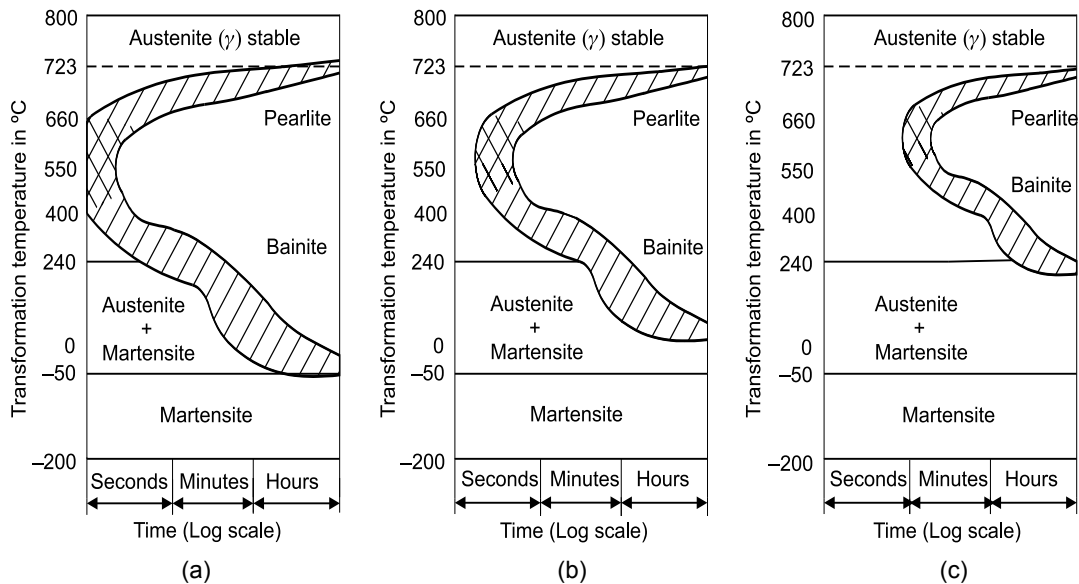


Fig. 13.6 Effect of carbon on TTT diagram: (a) Low carbon steel, (b) eutectoid steel and (c) high carbon steel

As the carbon content decreases, the nose of the curve moves left. At lower carbon content, austenite transformation results in more ferrite than Fe_3C . When the content of carbon decreases in solid solution, the energy and time required for precipitating of Fe_3C also decreases. At 0.01% carbon steel, complete structure is ferrite and no precipitated Fe_3C is visible. Ferrite is soft and does not respond to heat treatment, and the time available for quenching decreases so that the critical cooling rate required for producing a totally martensitic structure will be greater. Hence, this indicates the need for drastic water quench for plain carbon steels.

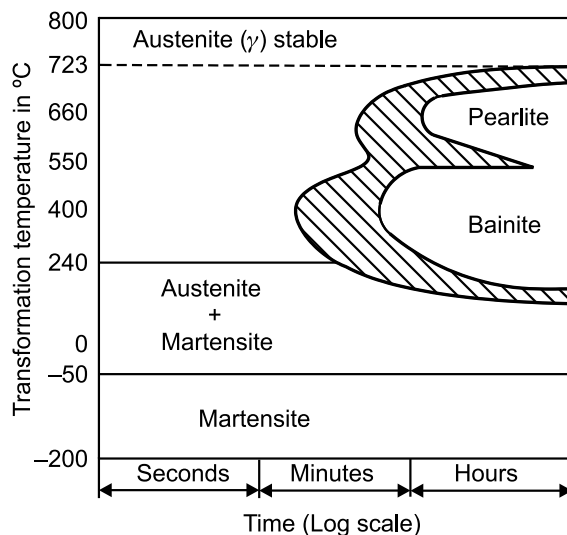


Fig. 13.7 Effect of alloying elements on TTT diagram

On the other hand, an increase in carbon content or the addition of alloys will shift the nose of the curves to the right (see Figure 13.6(b) and (c)). This tends to increase the time required for quenching, the hardness and the depth of hardening. Addition of carbon and alloying elements helps to precipitate Fe_3C more and more. The TTT curve for a low alloy steel is shown in Figure 13.7. This needs a reduced rate of cooling to produce a martensitic structure. This makes it possible to oil-quench (or even to air harden) a suitable steel and obtain a hard martensitic structure throughout.

EXERCISES

1. What is a TTT curve? Explain with a neat sketch the TTT curve for the eutectoid steel. What information can be gathered from this?
2. Neatly sketch Time-Temp-Transformation diagram for eutectoid steel and explain various stages of reactions.
3. Draw the TTT curve for 0.8% C and superimpose cooling curve on it. Mention the cooling curves used for annealing and normalizing.
4. Draw the TTT diagram for eutectoid steel. Superimpose cooling curves on the diagram and explain how to obtain various nonequilibrium phases of iron and carbon.
5. Draw the TTT diagram for eutectoid steel and show the cooling path to produce coarse pearlite, fine pearlite, lower bainite and martensite structures.
6. With a neat sketch explain clearly the TTT diagram. Indicate its usefulness to the materials engineer in practice.
7. Describe how TTT curves are useful in the heat treatment processes of steel.
8. What is critical cooling rate as applied to TTT curve? What type of transformation of phase takes place for steel when cooled at a rate higher than the critical cooling rate?

9. Explain the effect of alloying elements like carbon and chromium briefly on the shape of the TTT diagram and the hardenability of the steel.
10. Sketch and compare TTT and CCT diagrams.

OBJECTIVE -TYPE QUESTIONS

1. Austenite is unstable below _____.
 (a) 550°C (b) 700°C
 (c) 723°C (d) 900°C
2. Transformation of austenite into pearlite depends upon _____.
 (a) Only temperature (b) Only time
 (c) Both temperature and time (d) None of the above
3. Pearlite is the result of _____.
 (a) Quenching (b) Air cooling
 (c) Isothermal reaction (d) None of the above
4. Martensite is the
 (a) Interstitial solid solution of iron and carbon
 (b) Substitutional solid solution of iron and carbon
 (c) Reacted compound
 (d) None of the above
5. When austenite is cooled very slowly and the end product will be _____.
 (a) Martensite (b) Bainite
 (c) Pearlite (d) All of the above
6. When austenite quenched in water, the end product will be _____.
 (a) Bainite (b) Ferrite
 (c) Pearlite (d) Martensite
7. Austenite transfers into martensite below _____.
 (a) 550°C (b) 723°C
 (c) 240°C (d) -50°C
8. End product of isothermal transformation between the temperature 550°C and 240°C is known as _____.
 (a) Pearlite (b) Bainite
 (c) Cementite (d) Martensite
9. Bainite is an aggregate of _____.
 (a) Ferrite and cementite (b) Ferrite and austenite
 (c) Ferrite and martensite (d) None of the above
10. When carbon percent decrease from 0.8%, the nose of the curve moves _____.
 (a) Downward (b) Upward
 (c) Towards right (d) Towards left
11. Quenched 0.1% carbon steel shows _____.
 (a) Ferrite structure (b) Martensite structure
 (c) Bainite structure (d) All above

166 | Isothermal and Continuous Cooling Transformation Diagrams

12. S curve refers to _____.
(a) Percent pearlite versus time (b) Martensite versus time
(c) Ferrite versus time (d) Bainite versus time
13. Addition of alloying elements to steel will _____.
(a) Shift the nose of the curve to right
(b) Shift the nose of the curve to left
(c) Shift the nose of the curve down
(d) None of the above
14. TTT diagram is used for _____.
(a) Melting of alloys
(b) Heat treatment
(c) Constructing phase diagram
(d) None of the above
15. CCT diagram refers to _____.
(a) Continues cooling transformation
(b) Continuous heating and cooling transformation
(c) Continuous holding at predefined temperature
(d) None of the above

ANSWERS

1.	c	2.	c	3.	c	4.	a	5.	c	6.	d
7.	c	8.	b	9.	a	10.	d	11.	a	12.	a
13.	a	14.	b	15.	a						

chapter 14

Heat Treatment

INTRODUCTION

Most of the engineering properties of metals and alloys are related to their structure. Varying the relative properties of microconstituents can change the mechanical properties. In practice, change in mechanical properties can be achieved by a process called heat treatment. Heat treatment can be defined as a heating and cooling operation applied to metals and alloys in solid state so as to obtain the desired properties.

The heat treatment is an important process in the final fabrication of many engineering components. Almost all metals and alloys respond to some form of heat treatment. Practically, all steels respond to one or more types of heat treatment. The strength of nonferrous alloys namely Al, Cu, Ni, Mg, etc. can be strengthened to various degrees by using the heat treatment technique.

14.1 HEAT TREATMENT PURPOSES

The heat treatment can be undertaken for the following purposes:

1. Improvement in ductility
2. Relieving internal stress
3. Refinement of grain
4. Increasing the hardness
5. Improvement in machinability
6. Alteration in magnetic and electrical properties
7. Improvement in toughness

A number of factors are to be considered when heat treating a metal or an alloy. These are known as heat treatment process variables and they are discussed in the following subsections.

14.1.1 Temperature up to Which the Metal or Alloy Is Heated

The heat treatment temperature is governed mainly by the chemical composition of the alloy, prior heat treatment, if any, and the ultimate properties desired. Heat treatment temperature for steels can be determined with the help of iron–carbon diagram. The rate of heating is also important in heat treatment operations. It depends on the size, shape of the object and the thermal conductivity of the alloy. The larger the objects, the lower is the rate of heating. It avoids development of internal stresses due to thermal gradient and ensures homogeneity of the structure.

14.1.2 Length of Time the Metal or Alloy Is Held at This Temperature (Holding Time)

For an object of variable thickness, the holding time is determined on the basis of the thickest section. Holding time is generally provided at a rate of 2–3 minutes per millimetre of the section thickness. Heat treatment temperature and holding time are somewhat related. Increasing the rate of heat treatment temperature reduces the holding time. Similarly, lowering of heat treatment temperature results in increase of holding time.

14.1.3 Rate of Cooling

The mode of cooling as well as the rate of cooling is governed by those factors which control the heating mode and the rate. Objects with heavy section, complicated shapes and variable section thickness are cooled slowly. The size, shape, distribution and relative properties of microconstituents can be controlled over a wide range of varying cooling rates. By increasing the cooling rates beyond the limits, the structure produced will be nonequilibrium products like martensite developed by sudden quenching.

14.1.4 Quenching Media

Quenching is the rapid cooling of a metal or an alloy from a suitable elevated temperature. This is usually accomplished by immersing in water, oil or in a brine used. Commonly used quenching media is air, water, oil and brine. The choices of quenching medium depend upon the type of steel being treated and the resultant properties desired.

14.2 HEAT TREATMENT OF STEEL

The object of heat treatment is to make the steel suitable for some specific application. Steel is an important engineering material as it can be given a wide range of mechanical properties by heat treatment. Heat treatment can alter the properties of steel by changing the size and shapes of the grains, and by altering the microconstituents. The shape of the grains can be altered by heating the steel to a temperature above that of recrystallization and the duration of heating and the rate of cooling.

Heat treatment process can be broadly classified into following:

1. Treatment that produces equilibrium condition
2. Treatment that produces nonequilibrium condition

14.2.1 Treatments that Produce Equilibrium Condition

When steel is heated to a temperature up to 500°C, small residual stresses will be relieved to a small extent to cause only a slight reduction in hardness and strength. On reaching 500°C, recrystallization takes place producing new small grains. If heating is continued, the grains become enlarged and ductility will be increased. If temperature is high enough to produce the austenite structure and if cooling rate is low enough, new grains that relieve stress will be produced. The mechanical properties of steel at the end of heat treatment will depend upon the carbon content, the heat treatment temperature, the holding time and the cooling rate. The principal heat treatments in this group are stress relieving, annealing, normalizing, etc.

14.2.1.1 Annealing

Annealing can be defined as heating and holding the material at a suitable temperature following by cooling at a suitable rate to get softness, to improve its strength and to remove stress.

The purposes of annealing are specified as follows:

1. To improve mechanical properties
2. To improve machinability
3. To restore ductility, particularly after the steel has been subjected to cold working
4. To remove or minimize segregation of the essential constituents of steel
5. To alter the microstructure to make it suitable for hardening
6. To relieve the internal stresses

Depending upon specific purposes, annealing can be classified as follows:

14.2.1.1.1 Recrystallization or Stress-relieving Annealing

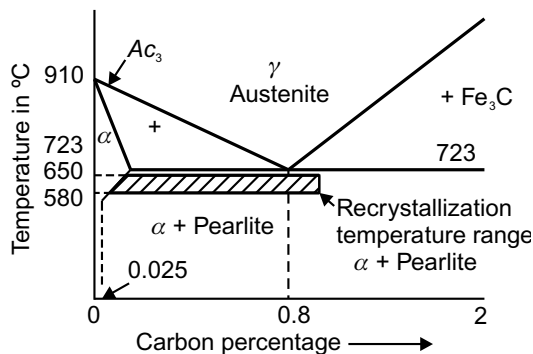


Fig. 14.1 Fe-Fe₃C diagram for recrystallization annealing

This process is used to relieve internal stress which develops during different operations like welding, solidification of casting, machining, etc. The process of recrystallization annealing consists of heating steel uniformly to a temperature 50°C–80°C below 723°C as indicated in Figure 14.1; and holding at this temperature for sufficient time followed by slow cooling. Uniform cooling is most important as nonuniform cooling results in the development of internal stress. Recrystallization or stress-relieving annealing is widely used for annealing steel wires, sheets, etc. Recrystallization annealing is used for both ferrous and nonferrous metals and alloys.

14.2.1.1.2 Process Annealing

Process annealing is usually carried out to remove the effects of cold working and to soften the steel. Process of annealing consists of heating steel uniformly to a temperature of 650°C–723°C (see Figure 14.2) and holding at that temperature for sufficient time, followed by slow cooling. This process is very useful for mild steel, low carbon steel for removing cold working effects.

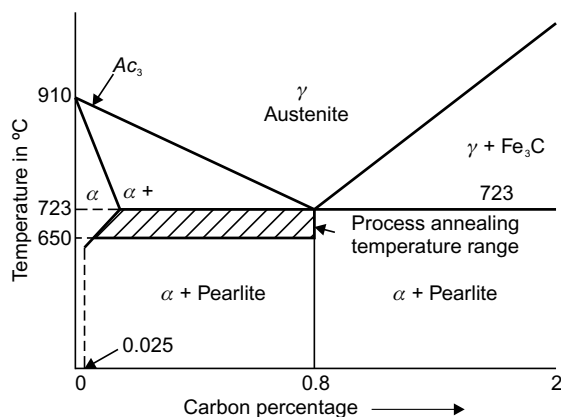


Fig. 14.2 Fe-Fe₃C diagram for process annealing

14.2.1.1.3 Spheroidal Annealing

In spheroidal annealing, graphite with iron in the granular form is produced. The prolonged heating causes the cementite to coalesce into spheres, completely destroying the pearlitic formation. The actual structure is a matrix of ferrite with Fe₃C in the form of spheroidal globules. The heat treatment that follows after machining should be done easily. This process is usually applied to high carbon steel which is difficult to machine. The process consists of heating steel between 650°C to 723°C (see Figure 14.3), holding at this temperature and then cooling very slowly. The rate of cooling in furnace is 25°C–30°C per hour.

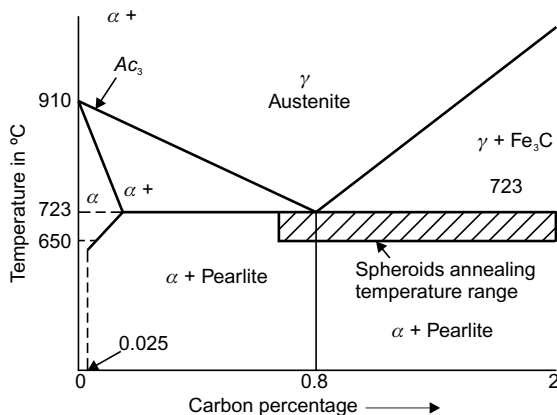


Fig. 14.3 Fe-Fe₃C diagram for spheroids annealing

In medium and high carbon steels, the spherodized structure has the lowest hardness, strength and wear resistance, but has the best machinability, toughness and ductility.

14.2.1.1.4 Diffusion Annealing

In this process, steel is heated uniformly and the component is held at a temperature between 1,000°C and 1,200°C and then cooled very slowly in order to remove the heterogeneity in composition of heavy castings. During this, the homogeneous structures appear. Diffusion annealing process is followed by full annealing (see Figure 14.4).

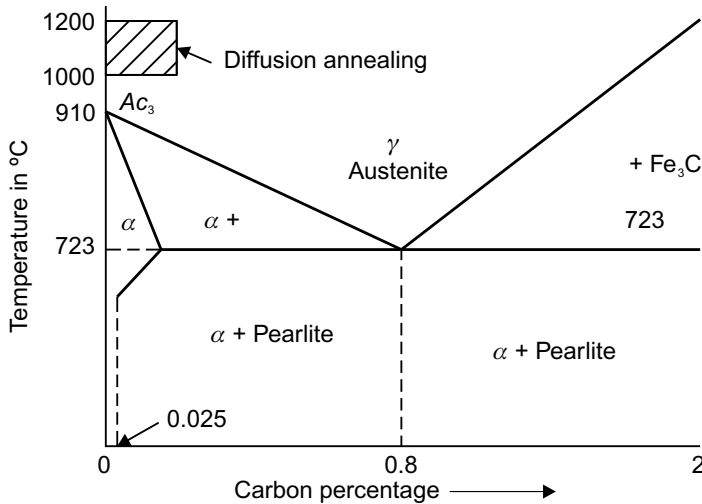


Fig. 14.4 Fe-Fe₃C diagram for diffusion annealing

Depending on specific heating temperature, annealing can be classified into three types (see Figure 14.5):

1. Full annealing
2. Partial annealing
3. Sub-critical annealing

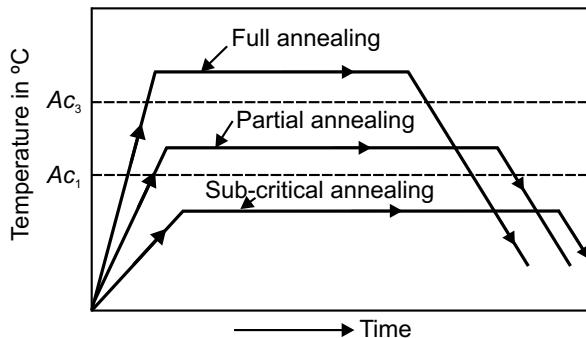


Fig. 14.5 Types of annealing based on heat treatment temperature

Full annealing consists of heating the steel component to about 50°C – 75°C above the A_3 temperature, holding it for a sufficient length of time, say 1 hour for every 25 mm of thickness, and cooling the same in the furnace. The steel is cooled very slowly from the annealing temperature. This process is specifically adopted for steel castings and steel ingots. The coarse structure produced during solidification breaks down to much smaller size and the structure as a whole becomes more homogeneous in chemical composition. The steel becomes more easily machinable and increases in ductility. The hardness is also considerably reduced. Also, full annealing process removes all structural imperfections by complete recrystallization.

Process annealing is the recrystallization of cold worked steel by heating between A_{c3} and A_{c1} temperature, the exact temperature being governed by the amount of cold working, composition, grain size and the time held at the given temperature. This is usually adapted to mild and low carbon steels. In mild and low carbon steels, the ferrite constitutes more than 75% of the grains and these deformed grains are re-oriented by process annealing. Most of the stresses produced in the material during cold working will be relieved. Partial annealing process refines the grain in steel bar. It consists of heating the steel uniformly to temperature between 723°C and 650°C for sufficient time followed by slow cooling.

Sub-critical annealing is used to remove the internal stresses in a steel casting. It consists of heating steel uniformly to temperature below 723°C and holding at that temperature for sufficient time and followed by slow cooling.

14.2.1.1.5 Normalizing

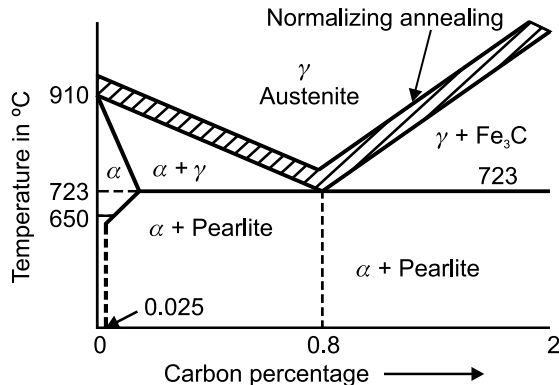


Fig. 14.6 Fe-Fe₃C diagram for spheroids normalization

The normalizing is a process of heating steel about 40°C – 50°C above the A_3 temperature, ‘soaked’ for a specified period of time, depending upon the size and section thickness, and then allowed to cool in still air. The normal rate of cooling in air is about 50°C – 80°C per minute, depending upon the section, size and air conditions. This cooling rate is fast enough to produce a sorbite structure in steel which results in increased tensile strength and yield point. Free cooling will produce a finer structure than that produced by annealing. After normalizing, the microstructure obtained will be pearlite (see Figure 14.6). The normalizing of low carbon steels is usually done for stress relief, grain size refinement and for improvement in toughness, tensile strength and ductility. Normalized steels are generally stronger and harder than annealed steels.

14.2.2 Treatments that Produce Nonequilibrium Condition

Certain applications demand high hardness values so that the components may be successfully used for heavy-duty purposes. High hardness values can be obtained by a process known as hardening process. Steel is heated to produce austenite structure held at that temperature and then quenched in water. The high hardness developed by this process is due to the transformation of austenite at considerable low temperature known as martensite and this metal is known as nonequilibrium condition. The properties produced by this method depends on the carbon content of the steel, temperature, holding time and quenching media. To produce a change in properties, sufficient carbon must be retained in solid solution after quenching to produce the necessary lattice distortion. If the carbon is less than 0.15%, there will be no appreciable change in the properties after quenching. However, as the carbon content is increased, there will be a corresponding increase in the hardness and strength as a result of quenching due to the formation of martensite. An example for the treatment that produces nonequilibrium condition is hardening of steel.

14.2.2.1 Hardening of Steels

Certain applications demand high hardness value so that the components may be successfully used for heavy-duty purpose. High hardness values can be obtained by a process known as hardening process.

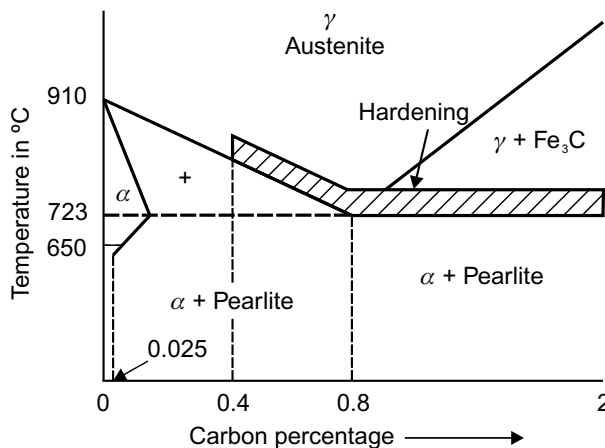


Fig. 14.7 Fe-Fe₃C diagram for spheroids hardening process

When steels are heated above the A_3 temperature and drastically quenched in water, maximum hardness is obtained. The structure so obtained is called martensite. The hardness obtained depends upon the composition of the steel. When the carbon content of the steel is 0.80%, the maximum hardness obtained is 66 Rockwell C. When the carbon content is increased to more than 0.80%, the maximum hardness obtained remains the same, i.e., 66 Rockwell C. When the carbon content is decreased, the maximum hardness that is obtained gradually decreases and with mild steels it is highly impossible to get a superficial surface hardness of about 40 Rockwell C, however drastic the quenching may be. Also, faster the cooling, greater is the hardness; and, slower the cooling, lower is the hardness. The structures obtained with different rates of cooling will differ fundamentally with respect to appearance under the metallurgical microscope as well as in physical properties like tensile strength, yield point, hardness, etc. (see Figure 14.7)

If steel is cooled at a certain minimum rate, called the 'critical rate', all the austenite will be transformed into martensite and thus produces maximum hardness. If the cooling rate is slightly lower than the critical rate, troostite will be formed. If the cooling rate is still lower but is higher than the critical rate, it will allow pearlite formation and sorbite is formed.

The products of decomposition between pearlite and martensite are often termed as bainite. This means that sorbite, troostite and acicular troostite are the same as bainite.

Water and oil are the most common quenching mediums adopted in heat treatment. Some of the alloy steels are hardened by simply cooling in the air. Such steels are known as air-hardening steels. The quenching medium used depends upon the specification and the section of the steel. Plain carbon steels are usually water hardened. Such steels are called water-hardening steels. Most of the low and high alloy steels are oil hardened. Such steels are known as oil-hardening steels. Air-hardening steels are few and their heat treatment has to be carefully handled. When thick piece is heated and quenched, only outside will be martensite and core will be of pearlite. The condition of the surface of the steel also affects hardening. The presence of oil, grease, scale, etc. reduces the cooling rate of the metal than the treated surface which may lead to incomplete hardening.

To produce high hardness, sufficient carbon must be retained in solid solution after quenching to produce necessary lattice changes. Hypoeutectoid steels are heated to about 30°C – 50°C above the upper critical temperature, where as hyper-eutectoid steels are heated to about 30°C – 50°C above the lower critical temperature. Duration of heating depends upon the thickness of material. The steel components are cooled at a certain minimum rate called critical cooling rate.

In the hardening process, steel is heated to produce an austenite structure held at that temperature and then quenched in water or oil. The high hardness developed is due to the transformation of austenite at considerable low temperature into nonequilibrium product known as martensite.

14.2.2.2 Tempering

Steels are hardened by heating them above the critical temperature and quenching in water or oil. The quenching process brings about great stresses in the hardened steels. Hardening treatment develops maximum hardness, excellent wear resistance and high strength in steels. At the same time, it affects properties such as ductility, impact strength, etc. because of internal stresses developed by quenching. A process which consists of heating hardened steel below the lower critical temperature followed by air cooling is known as tempering which reduces internal stresses and degree of brittleness.

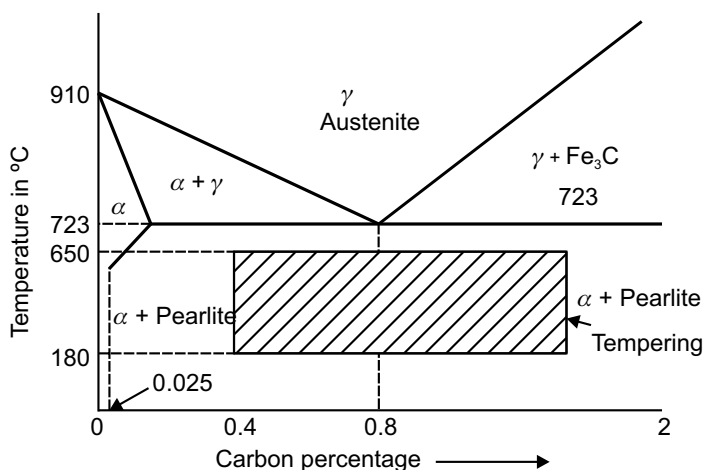


Fig. 14.8 Fe-Fe₃C diagram for tempering process

The tempering temperature is determined by the specification of steel and the final hardness and toughness desired. The tempering temperature depends on the properties required, but it is between 180°C–550°C, and duration of heating depends upon the thickness of the materials. The tempering temperature below 220°C relieves the hardening stress, but at the tempering temperature above 220°C, the martensite structure transfers into a fine pearlite structure (see Figure 14.8).

By the tempering operation, the following changes occur:

1. The quenching stresses are mostly relieved.
2. The hardness in the piece is equalized, as far as possible.
3. The hardness is reduced to the desired extent and the toughness proportionately restored.

For tempering, the hardened steel is again heated in a furnace or in heavy oil or in molten salts and held long enough for the heat to penetrate to the centre. For most steels, cooling after the tempering operations is of little consequence and in practice the cooling after tempering is usually done in the air.

14.3 MARTEMPERING (INTERRUPTED QUENCHING)

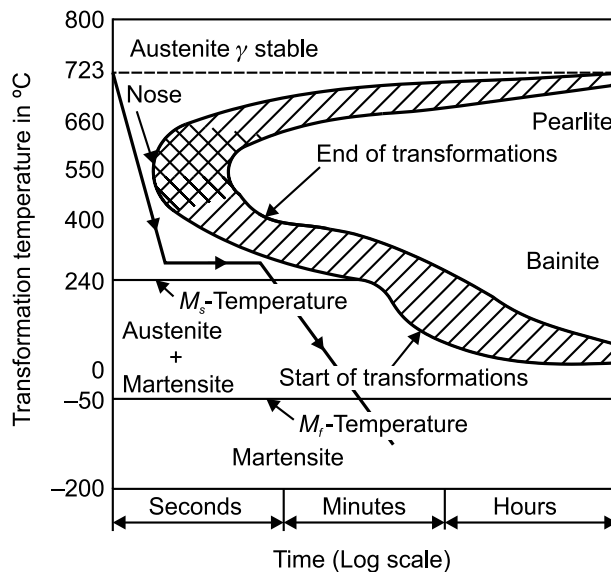


Fig. 14.9 Martempering process for eutectoid steel

In martempering, the steel is heated above the austenitic temperature and held at that temperature till the entire component becomes austenite. In this process, the steel is quenched rapidly past the knee or nose of the transformation curve to avoid pearlite formation by immersing in oil or salt bath maintained at temperatures (intermediate T_i) slightly above the M_s temperature. Steel is heated at this temperature for a short period of time. Cooling is then continued at a slow rate through the martensite range to ambient temperatures so that the surface and the centre of the steel may transform more or

less simultaneously thus avoiding quenching cracks. During the cooling, austenite is transferred to martensite and at same time, a maximum of residual stresses are reduced by a slight expansion of steel in transferring austenite to martensite. Slower cooling is possible at these temperatures because the pearlite forms very slowly while the martensite forms directly with the drop in the temperature (see Figure 14.9).

This process is more complicated from the production viewpoint as the cooling rate must be shifted from a quench to a 'hold' and then to a slow cooling rate. As with the earlier direct quench, martensite is the product and this must be tempered to secure toughness. The main advantage of martempering is that the formation of quenching cracks is minimized due to interrupted quenching.

14.4 AUSTEMPERING (ISOTHERMAL TRANSFORMATION)

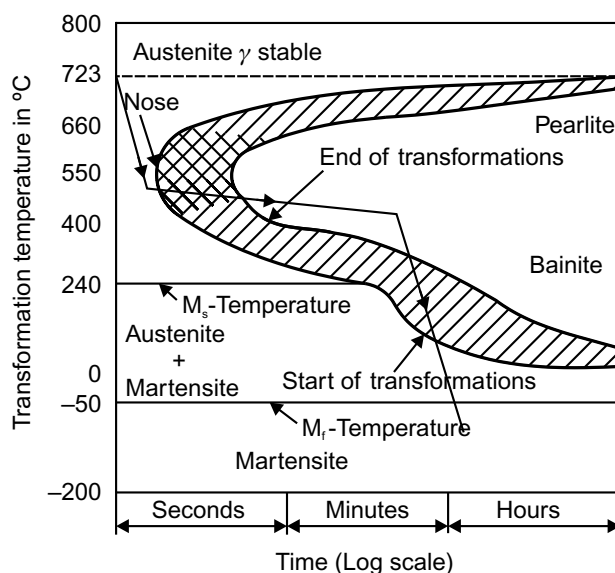


Fig. 14.10 Austempering process for eutectoid steel

In austempering process, the steel component is heated slightly above the austenitic temperature till the entire component becomes austenite. The steel parts from the austenite temperature are quenched to a temperature (intermediate T_i) above the M_s temperature by dropping them in an oil bath maintained at 350°C–400°C. The components are held at the same temperature long enough to see that the austenite transforms isothermally to the intermediate phase called bainite. The holding time should be long enough so that the cooling curve passes the C curve as shown in Figure 14.10. Slow cooling to room temperature and presence of bainite in the microstructure improve the toughness of steels to a great extent. All quenching cracks are reduced in steel component and austempered steel has equal hardness and tensile strength.

14.5 HARDENABILITY

Hardenability can be defined as the ability to harden the metal and it determines the depth and distribution of hardness induced by quenching. Steel, so quenched, will be hardened throughout. This property of steels of acquiring hardness throughout the section by means of heat treatment is known as hardenability. Hardness is a measure of resistance to plastic deformation; while hardenability is the ease with which the hardness may be attained.

In any steel, maximum hardness is obtained only when 100% martensite is formed. Thus, the steel is said to possess good hardenability when it is possible to get uniform hardness all through its section thickness upon quenching. However, in practice, the hardness values decrease along the cross section as we go away from the quenched end.

14.5.1 Jominy End-Quench Tests

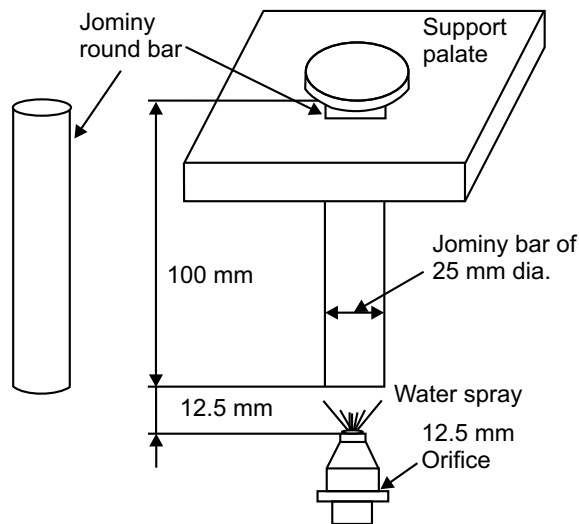


Fig. 14.11 Jominy end-quench for eutectoid steel

When steel is quenched, the cooling rate decreases from the surface to the interior and the hardness is highest at the surface and lowest in the central portion. There is a standard test called the Jominy end-quench test to determine the hardenability of steel. In this test, a round bar of a specified size is heated to form austenite and is then end quenched with water stream of specified flow rate and pressure as shown in Figure 14.11. Hardness values along the cooling rate gradient are determined on a Rockwell hardness tester and the hardenability curve is plotted. The quenched end is cooled very fast and, therefore, has the maximum possible hardness for the particular carbon content of the specimen. Hence, it follows that the surface of the bar is hardened so that on the surface martensite structure is obtained. The hardness will decrease towards the centre of the section. The centre will remain soft and ductile. Every variety of steel, depending upon its composition, has got its own critical cooling rate. Since the steel behind the quenched surface is cooled at a slower rate, its hardness is less than the maximum possible hardness for the particular steel being tested.

14.6 SURFACE HARDENING

Many components like gear, camshafts and piston pins require a very hard wearing surface to withstand the constant wear in service conditions and at the same time, a tough core which will withstand the shock loads. The treatments given to steels to achieve this are called surface heat treatments. This combination of widely differing properties can be combined in a single piece of steel by surface hardening.

The classification of surface heat treatments is as follows:

1. Method in which the whole component is heated
2. Methods in which only the surface of the component is heated

14.6.1 Method in which Whole Component Is Heated

In this method, the hardness of the surface is improved by diffusing interstitial elements like carbon, nitrogen or both into the surface of steel components by heating the whole component. Only on heat treating, the surface of the component will respond to the treatment depending on its diffusing elements chosen. Diffusion treatment can be classified as follows:

1. Case hardening
2. Nitriding
3. Cyaniding

14.6.1.1 Case Hardening

In case hardening process, steel made with a carbon content of about 0.15% is used for carburizing to increase the carbon content of the steel surface. Hence, case hardening is carried out in two steps, carburizing and heat treatment. Carburizing is divided into three categories according to carbon material used.

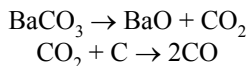
The steels for case hardening are usually made of 0.18% carbon maximum, fine grained mild steel or usually 0.15% carbon steel with 3% nickel. Nickel–chromium or other specifications of low-alloy steels are also used for special components like gears, splines and shafts, whatever may be the composition, and the carbon content rarely exceeds 0.20%.

14.6.1.1.1 Solid Carburizing

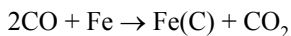
In solid carburizing process, mild steels and low-alloy steels of high tensile strength but with low carbon content are used. This method of carburizing is also known as pack carburizing. Here, the steel component to be heat treated is packed with 80% granular coal and 20% barium carbonate and heated at 930°C in a furnace for a specific period of time which depends on case depth required. Even ordinary charcoal mixed with BaCO₃ serves the purpose. But, it is preferable to purchase patented carburizing compounds from reputed firms for this purpose.

During the process of carburizing, the BaCO₃ splits up. At high temperature, the following reactions take place:

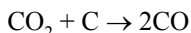
BaCO₃ decomposes and to give CO to steel surface.



Carbon reacts on surface of steel



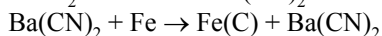
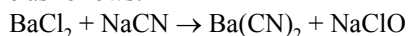
The carbon dioxide formed in step in this reaction reacts with the carbon in the coal.



Generally, carburizing time varies from 4 to 8 hours and case depth obtained varies from 1 to 3 mm.

14.6.1.1.2 Liquid Carburizing

In solid carburizing, time is excessively long and uniform depth of penetration by the carbon is not always assured. Hence, the alternative process of liquid carburizing is adopted. It is also known as salt bath carburizing. In this process, carburizing occurs through molten cyanide. The bath contains NaCN or KCN and BaCl_2 , which acts as a catalyst. Low-carbon steels are heated between 900°C and 910°C and reactions in cyanide bath are as follows:

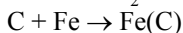
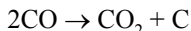


In this heating, time is short and the clean hardened layer is up to 3 mm thickness.

14.6.1.1.3 Gas Carburizing

This is the most widely used method of carburizing. The gaseous hydrocarbons most widely used in gas carburizing are natural gas (methane), town gas and any other gas containing CO and hydrocarbons which decompose at red heat and deposit the carbon on the surface of the steel. The thickness of the case formed depends upon the rate of flow of the gases into the retorts and also upon the temperature. It is carried out in a closed-type furnace. These furnaces are gas fired or heated electrically and the temperature varies from 900°C to 950°C . A mixer of propane or methane with air is injected to hot chamber to form a gas. The approximate compositions of this gas are N_2 —40%, H_2 —7.5%, CO—20%, water vapour—7.5% and O_2 —balanced.

Carburizing occurs mainly due to conversion of CO to CO_2 . That is,



In gas carburizing, the overall time taken for the whole cycle including packing, charging, etc. is very much shorter. More uniform results with regard to case depth are obtained.

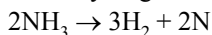
14.6.1.1.4 Heat Treatment

Carburizing doesn't harden steel. It adds carbon to outer layers of steel. Hence the object of heat treatment is to produce a harden case. Carburized steel is heated above upper critical temperature, held for suitable time and then quenched in oil or water. A brittle martensite is formed on the outer surface and leaves core as a soft surface.

The toughening of the core is accomplished by heating to about 850°C – 875°C , holding or soaking for a sufficient time and quenching in water or oil. The quenching medium used depends upon the composition of the steel. On account of the low carbon content of the core, it is only toughened by this treatment. The steel is then reheated to about 775°C and again quenched in water or oil. By this quenching, the eutectoid composition of the case is properly hardened, and the grain size of the case will become fine. Though the case gets hardened even during the first quenching operation, the structure will be coarse due to the high quenching temperature of 850°C – 875°C . Hence, the hardening operation is repeated at 775°C in order to get a fine grain size. After that, the steel is tempered at about 170°C to relieve the quenching stress caused by the hardening operation. In both the toughening and hardening operations, the quenching medium, whether water or oil, should be properly agitated in order to ensure uniform toughening and hardening.

14.6.1.2 Nitriding

Nitriding can be defined as a surface hardening in which the special alloy steel is heated in the atmosphere of gaseous nitrogen. The process consists of heating the finished machined articles in a closed container into which the ammonia gas is forced under pressure at a temperature of about 450°C–540°C. The ammonia gets dissociated into nitrogen and hydrogen. The nitrogen then combines with the surface layer of steel to form complex nitrogen compounds with iron and other elements present in the steel. Nitriding is carried out in a ferritic region, i.e., NH_3 gas is passed into the furnace at 550°C where it dissociates into nitrogen and hydrogen.



Nitrogen is readily absorbed by the surface of steel. The treatment time varies from 90 to 110 hours. After nitriding, the steel components are allowed to cool or quenched. But nitriding is done on finished articles. Nitriding is a very costly process and is resorted to for the following purposes:

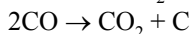
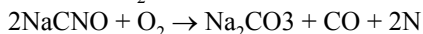
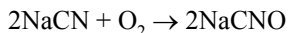
1. To get a really super-hard wearing surface
2. To resist corrosion
3. Where resistance to softening of the hardened surface at elevated temperatures is desired, as in the case of parts used for steam turbines, aircraft engines, etc.

The hardness obtained in nitriding is the highest that can be obtained in all the known methods of heat treating steel.

14.6.1.3 Cyaniding

This is a process of introducing both nitrogen and carbon on the surface of low-carbon steel components. It is carried in a liquid bath of solid cyanide (NaCN). Here the steels are heated up to about 800°C in a molten sodium cyanide bath for a period of 30 min to 3 hours depending upon the thickness required. At this temperature, sodium cyanide dissociates to give carbon and nitrogen in the atomic form, which goes in to the surface of the steel component.

The basic reactions in the bath are as follows:



Quenching completes the formation of hard, wear-resistant case with a relatively soft core. The cyanide bath consists of 30% NaCN , 40% NaCO and 30% NaCl . A case depth of up to 2.5 mm is obtained.

14.6.2 Method in which Only Surface of Component is Heated

In this method, only the surface of steel components are heated to temperatures above the upper critical temperature and is suddenly quenched to get martensite on the surface which gives higher hardness. The following two methods employ local heating:

1. Flame hardening
2. Induction hardening

14.6.2.1 Flame Hardening

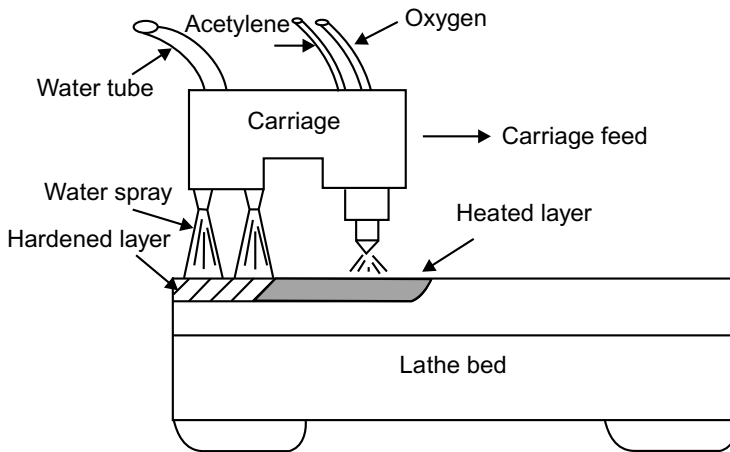


Fig. 14.12 Flame hardening process for lathe bed

It is the simplest form of surface hardening treatment. Localized surface hardening can also be achieved in medium high carbon steel and by rapid local heating and quenching. Figure 14.12 shows the principle of flame hardening. A carriage, i.e., heating and quenching unit, moves over the work piece so that surface is rapidly heated by an oxy-acetylene flame. The same unit carries water-quenching spray. Thus, the surface of work piece is heated and quenched before its core can rise to the hardening temperature. This process is known as flame hardening treatment.

14.6.2.2 Induction Hardening Process

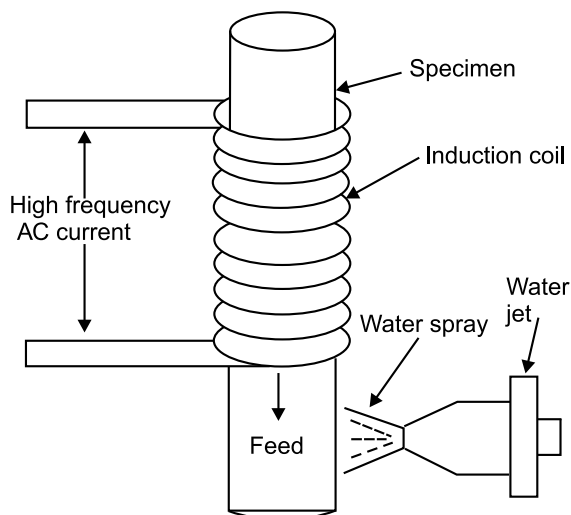


Fig. 14.13 Induction hardening process for small shaft

Figure 14.13 shows the induction hardening of steel shaft. Induction hardening process may be used for local surface heat treatment. Generally it is used to surface harden the crank shafts, gears, etc. In this process, heating of the component is achieved by electromagnetic induction. Induction coil is connected to a high frequency AC current, which induces high frequency, eddy current in the component causing it to become hot. When the hardening temperature has been reached, water spray quenches the component. The induction coil can be made from copper tube, which also carries quenching water. In induction hardening process, the component is heated usually for a few seconds. Due to quenching, a martensite structure is formed which makes the outer surface hard and wear resistant. Here a very close control can be exercised on the depth of hardness required which is one of the major advantages of this process over flame hardening.

14.7 HEAT TREATMENT OF NONFERROUS METALS

Heat treatment is being applied not only in ferrous metals and alloys but also in case of many non-ferrous metals and alloys (Al, Cu, etc.). Changes are caused in the mechanical properties by heat treatment process.

The purposes of heat treating nonferrous metals are as follows:

1. To improve strength and hardness
2. Improve the ductility
3. Improve the machinability

Nonferrous metals and alloys are generally subjected to following types of heat treatments:

1. Precipitation hardening
2. Annealing heat treatment

14.7.1 Precipitation Hardening (Age Hardening)

The phenomenon of hardening is found in nonferrous alloys like aluminium and copper. By controlling the precipitant from the solid solution, we can achieve varying properties for such alloys. The heat treatment process to achieve this consists of the following:

1. Solution treatment
2. Ageing treatment (precipitation treatment)

14.7.1.1 Solution Treatment

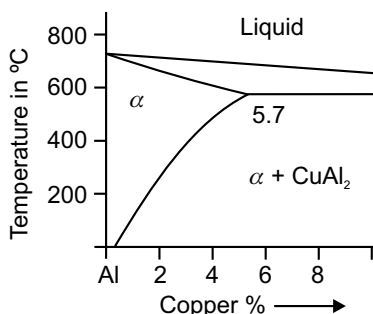


Fig. 14.14 Aluminium portion of Al-4%Cu phase diagram

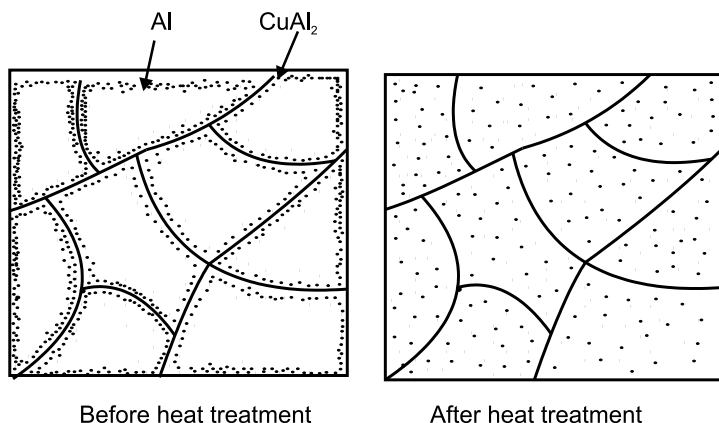


Fig. 14.15 Solution heat treatment for Al-4%Cu alloy

The aim of solution heat treatment is to distribute the solute atoms uniformly in the solvent atoms to achieve uniform cast structure to improve corrosion resistance and casting ductility. When Al-3%Cu alloy is heated above a certain temperature, the Cu in the alloy goes into what is known as solid solution and the alloy exists in the form of single α -phase. This operation is called solution treatment. At this point, the alloy is soft and malleable. Slow cooling of the alloy will cause formation of relatively coarse particles of CuAl_2 phase. In the solution treatment, the components of Al-Cu alloys are heated to about 530°C in a heat treatment furnace and are soaked for a predetermined length of time. Then the components are quenched in an oil or water bath at about 60°C – 80°C . On such rapid cooling, there is not enough time for the diffusion of copper atoms to form the precipitate particles. Therefore, a supersaturated solid solution is obtained at room temperature. Solid solution in this nonequilibrium state is called supersaturated solid solution (see Figures 14.14 and 14.15).

14.7.1.2 Ageing Treatment

Strengthening by the precipitation of fine particles of a second phase from a supersaturated solid solution is called precipitation or age hardening. This heat treatment would be used to increase the strength and hardness of a part by precipitating second phase. Solubility of one metal in the other decreases with decreasing temperature and supersaturated with respect to the solute at lower temperatures. Then the solute atoms are precipitated from the matrix and reacts with the matrix atoms in the form of precipitate particles.

The precipitation hardening mechanism in Al-3%Cu alloys may be illustrated by the phase diagram of Al-Cu system. When an Al-3%Cu alloy is heated to above 548°C , all CuAl_2 particles are dissolved and the alloy exists in the form of single-phase solid solution (α -phase). Slow cooling of the alloy will cause formation of relatively coarse particles of CuAl_2 intermetallic phase. Precipitation from supersaturated solid solution occurs in several steps. The Cu atoms are segregated into plane clusters. These clusters are called Guinier-Preston zones (G-P zones). This phase is coherent with the matrix. This phase provides maximum hardening and it is called artificial ageing. It usually takes a time of several hours to one day. When the ageing is conducted at the room temperature, it is called natural ageing. Natural ageing takes several days or more. The ageing process done at room temperature is often called natural ageing, which takes a prolonged period of time in terms of several days. However, ageing at higher temperatures of 100°C – 200°C accelerates the precipitation process and the time required is reduced considerably.

14.7.2 Annealing

Annealing is a heat treatment procedure involving heating the nonferrous alloy and holding it at a certain temperature (annealing temperature), followed by controlled cooling for reducing hardness, improving machinability, facilitating cold working, producing a desired microstructure or obtaining the desired mechanical, physical or other properties. When applied to nonferrous alloys, the term annealing implies a heat treatment designed to soften an age-hardened alloy. Annealing results in relief of internal stresses, softening, chemical homogenizing and transformation of the grain in structure into a more stable state.

EXERCISES

1. Define heat treatment and explain its objective.
2. Explain the term heat treatment and write its advantages.
3. Discuss the process, temperature range, microstructure of products and applications of stress-relieving annealing.
4. Using Fe–C diagram, explain the following heat treatment processes:
(i) Full annealing (ii) Normalizing
5. What is meant by normalizing? Write its applications.
6. Explain the purpose of diffusion annealing and spheroids annealing. Mention clearly the differences between them.
7. Using the relevant portion of the iron–iron carbide equilibrium diagram and the TTT diagram, explain the ‘normalizing’ heat treatment of a plain carbon steel containing 1% carbon. What changes in properties and microstructure do you expect due to the heat treatment?
8. With the help of schematic TTT diagram and superimposed cooling curves, explain the heat treatment ranges represented on the relevant portion of the iron–carbon equilibrium diagram.
9. Process annealing and (i)/(ii) quench hardening and clearly state the process, changes in microstructure and changes in properties due to the process.
10. Write short notes on (i) Annealing and (ii) Induction hardening, hardness and hardenability.
11. Explain in detail the case hardening of steel.
12. Define hardenability. Explain with a neat sketch the Jominy end-quench test and discuss the effect of alloying elements on the hardenability of steel.
13. With neat sketches differentiate between martempering and austempering.
14. Explain the process of martempering and state its advantages over the conventional hardening process.
15. When do you prefer case hardening of steel? State different methods of case hardening and explain any one of them in detail.
16. Explain (i) Annealing and (ii) Austempering
17. Explain clearly the mechanism of precipitation hardening treatment. Why it is used and for which type of alloys?

18. Explain the following:

(i) Normalizing	(ii) Annealing
(iii) Hardening	(iv) Tempering.
19. What is precipitation hardening? Describe precipitation hardening with respect to duraluminium (Al–4.5%Cu alloy) with the help of aluminium-rich aluminium–copper phase diagram.
20. What is the purpose of case hardening? Classify the methods of case hardening and describe briefly any two of them.
21. Differentiate cyaniding and induction hardening process clearly.
22. Discuss the process of liquid carburizing. What is the basic principle underlying this surface hardening method?
23. Using an example, describe the principle and application of precipitation hardening method.
24. Explain the following heat treatment processes:

(i) Annealing	(ii) Carburizing
(iii) Tempering	(iv) Induction hardening
25. Using the relevant portion of the iron–iron carbide equilibrium diagram and TTT diagram, explain the ‘normalizing’ heat treatment of a plain carbon steel containing 1% carbon. What changes in properties and microstructure do you expect due to the heat treatment?
26. What are the different quenching media used in the hardening process of steel? What is the difference made by using these.
27. Why does tempering cause decrease in strength and hardness of steel.
28. Explain any two case-hardening techniques briefly.
29. What is critical cooling rate as per applied TTT curve? What type of transformation of phase takes place for steel when cooled at a rate higher than critical cooling rate?
30. What is the engineering purpose of tempering the hardened steel?
31. Write brief notes on surface hardening methods for steel containing 0.35% carbon.
32. Explain the process of flame hardening.
33. Explain the nitriding process of surface hardening with the specific advantages of the process.

OBJECTIVE -TYPE QUESTIONS

1. Microconstituent of the metal can be changed by _____.
 - (a) Forming
 - (b) Cold working
 - (c) Heating and cooling
 - (d) Painting
2. Large metal components can be heated _____.
 - (a) Slowly
 - (b) Rapidly
 - (c) Rate of heating does not affect the heat treating components
 - (d) None of the above

186 | Heat Treatment

3. Heat treatment holding time is determined on the basis of _____.
 - (a) Quantity of components
 - (b) Size of the component
 - (c) Thickness of the section
 - (d) All of the above
4. The objective of heat treatment of steel is to _____.
 - (a) Make steel suitable for some application
 - (b) Make steel suitable for melting
 - (c) Make steel suitable for forming
 - (d) All of the above
5. Example of treatment that produces equilibrium condition is _____.
 - (a) Hardening
 - (b) Martempering
 - (c) Austempering
 - (d) Annealing
6. Treatment that produces nonequilibrium condition is _____.
 - (a) Hardening
 - (b) Recrystallize annealing
 - (c) Tempering
 - (d) Diffusion annealing
7. Annealing can be defined as _____.
 - (a) Heating and holding at a suitable temperature following slow cooling
 - (b) Heating and holding at a suitable temperature following quenching
 - (c) Heating and holding at a suitable temperature following air cooling
 - (d) None of the above
8. The recrystallization annealing consists of heating steel to a temperature _____.
 - (a) 50°C – 80°C to below 723°C
 - (b) 50 – 80°C to above 723°C
 - (c) At 723°C
 - (d) At 900°C
9. Spheroidal annealing is used for _____.
 - (a) Low carbon steel
 - (b) Medium carbon steel
 - (c) Medium and high carbon steel
 - (d) Low and medium carbon steel
10. Low carbon steel responds for _____.
 - (a) Hardening process
 - (b) Normalizing process
 - (c) Annealing process
 - (d) All of the above
11. End product of nonequilibrium heat treatment is _____.
 - (a) Martensite
 - (b) Bainite
 - (c) Ferrite
 - (d) Pearlite
12. Carburization is a process to introduce _____.
 - (a) Boron atoms to steel
 - (b) Nitrogen atoms to steel
 - (c) Hydrogen atoms to steel
 - (d) Carbon atoms to steel
13. In the case of hardening, _____.
 - (a) Full component will respond for heat treatment
 - (b) Only core of the component will respond for heat treatment

- (c) Surface of the component will respond for heat treatment
 (d) Both surface and core will respond for heat treatment
14. Nitriding process is used for.
 (a) Low carbon steel (b) Medium carbon steel
 (c) High carbon steel (d) Alloy steel
15. Flame hardening process is used for _____.
 (a) Large objects (b) Small objects
 (c) Cast irons (d) All of the above

ANSWERS

1.	c	2.	a	3.	c	4.	a	5.	d	6.	a
7.	a	8.	a	9.	c	10.	c	11.	a	12.	d
13.	c	14.	d	15.	d						

Composite Materials

INTRODUCTION

Historically, there is enough evidence of composite materials in the literature, and in the earliest of times, composite materials consisting of two equally essential component parts have been employed for building and construction. In the olden days, bricks were made up of clay and reinforced with straw. This is an example of world's oldest engineering material. However, even before that, birds were using mud strengthened with straw for building their nests.

A composite material is a structural material and it is defined as 'the material system consisting of two or more microconstituents insoluble in each other and differing in form and material composition'. They are different from alloys and are generally made by mixing dissimilar materials together to work as a single mechanical unit. The constituents are combined at macroscopic level and are not soluble in each other. One of the phases is discontinuous, stiffer and stronger and is called the reinforcement phase; and the one in which it is embedded is continuous and is called the matrix.

The composites are widely used in many structural applications where the mechanical performances are of prime importance. The composites are made up of two basic constituents called matrix and reinforcements and these are classified into two categories depending on the type, geometry and orientation of the reinforcement phase as shown in Figure 15.1.

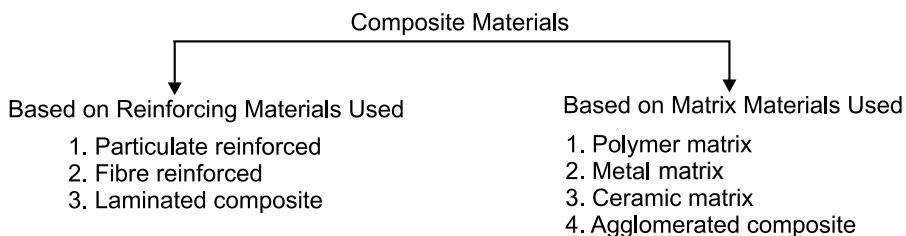


Fig. 15.1 General way of classification of composite materials

15.1 PARTICULATE REINFORCED COMPOSITES

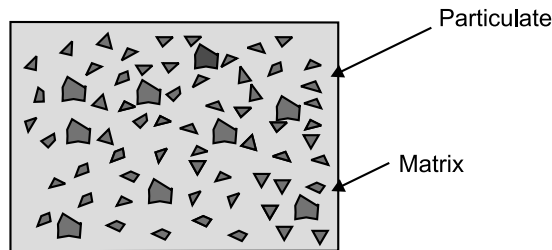


Fig. 15.2 Particulate composite

The particulate composite consists of particles of various sizes and shapes randomly dispersed within the matrix (see Figure 15.2). The particles are 1 μm or less in size and the volume concentration is in between 20% and 40%. Typical examples include use of metallic particles in metallic matrices (lead particles in copper alloys to improve machinability), nonmetallic particles in metallic matrices (silicon carbide particles in aluminium to improve high temperature properties), nonmetallic particles in a nonmetallic matrices (brittle polymer reinforced with rubber) and metallic reinforcement in nonmetallic matrices (aluminium particles in rubber used in rockets). These are usually isotropic and are added randomly. Particulate composite have advantages such as improved strength, increased operating temperature, low density and improved wear resistance.

15.2 FIBRE REINFORCED COMPOSITES

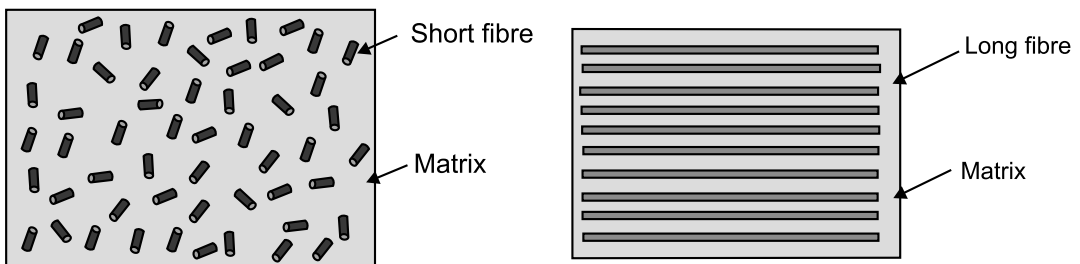


Fig. 15.3 Fibre reinforced composites

The fibre reinforced composites consist of matrices reinforced by discontinuous (short fibre) or continuous (long) fibre (see Figure 15.3). In any case, the second phase is in the form of fibres with the length many times larger than their diameter. A discontinuous fibre composite consists of short fibre in matrices and it can be oriented in one direction or randomly. These fibres are anisotropic. Carbon nanotube reinforced epoxy composite is the best example for short fibre reinforced composites. Continuous fibre composites are reinforced by long continuous fibres. These fibres can be oriented in several directions like right angles to each other, parallel to each other and inclined to any direction with each other. Matrix materials used for fibre reinforced composites are polymers (cotton thread reinforced rubber in tyre to improve strength), metals (carbon fibre reinforced aluminium composites to improve strength), ceramics (ceramic fibre – reinforced silicon carbide composite for high

temperature application), etc. Usually, fibre reinforcement results in high strength and high modulus combined with low thermal expansion and low density.

15.3 LAMINATED COMPOSITE MATERIAL

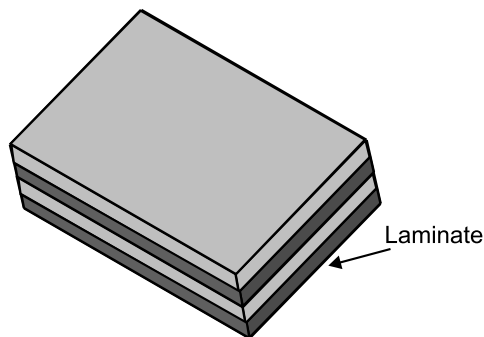


Fig. 15.4 Laminated composites

The laminated composite is made up of two or more laminates or layers bounded together at single or different orientations as in Figure 15.4. Unidirectional composite consists of more than two layers which are stacked in one direction. Carbon layer bonded epoxy composite is example for unidirectional composite. Laminates or layers can be of various thickness and they are stacked on top of each other at various angles to form a multidirectional laminate. It consists of layers of at least two different materials that are bonded together. These are called hybrid composite. Examples for multidirectional composites are bimaterial laminates of two different metals with different coefficient of thermal expansion, plywood, etc. These composites have high strength, low density and high corrosive resistance.

15.4 POLYMER MATRIX COMPOSITES

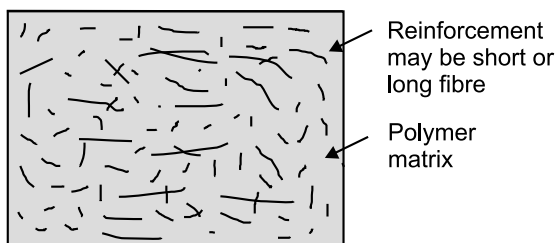


Fig. 15.5 Polymer matrix composite

The polymer matrix composite consists of a polymer (epoxy, polyester, urethane) reinforced by short or long fibre with glass, carbon, Kevlar or boron (see Figure 15.5). The most advanced composites are polymer composites. These are mainly used in low temperature applications. Polymer composites

are of low cost and high strength and are easy to fabricate principles. An example for short fibre reinforced polymer composite is carbon nanotube reinforced epoxy composite, and an example for long fibre reinforced composite is cotton thread reinforced rubber. Polymer composites have low density and are corrosion resistant, ductile and formable.

15.5 METAL MATRIX COMPOSITE

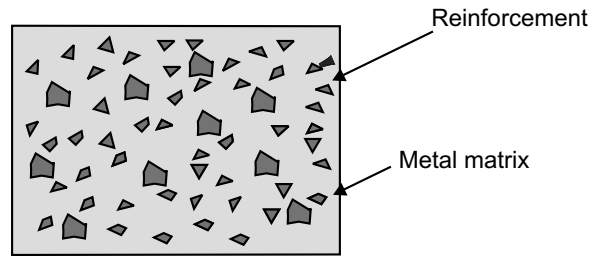


Fig. 15.6 Metal matrix composite

A metal matrix composite consists of metal reinforced with particulates or fibres (Figure 15.6). Examples of metals used as matrices are aluminium, magnesium and titanium. The particulate used are carbides, nitrides and borides. The fibres used are carbon, steel and ceramic. Particulates or fibres are mainly reinforced to increase elastic stiffness, strength and can be decreased thermal expansion, thermal conductivity, etc. Metal matrix composites have higher service temperature and are insensitive to moisture, better wear and fatigue resistance.

15.6 CERAMIC MATRIX COMPOSITES

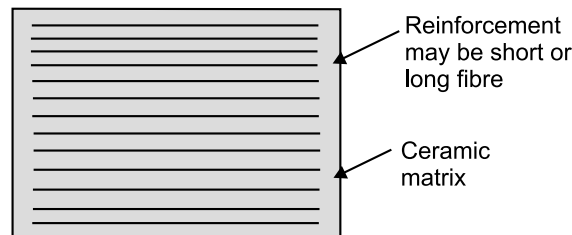


Fig. 15.7 Ceramic composites

A ceramic matrix composite consists of ceramic matrices. Examples of ceramic matrix material used are aluminium oxide, glass ceramic, silicon carbide and silicon nitride. These matrices are reinforced with ceramic fibres as shown in Figure 15.7. Typical fibres include carbon, silicon carbide and steel. Ceramic matrix composites are mainly reinforced to increase their properties to suit the needs of operating at elevated temperature as furnace parts, boiler furnace components, etc. These are best suited for high temperature applications. The advantages include higher temperature resistant without reducing its rigidity, high wear resistance and low thermal expansion.

15.7 AGGLOMERATED COMPOSITE MATERIAL

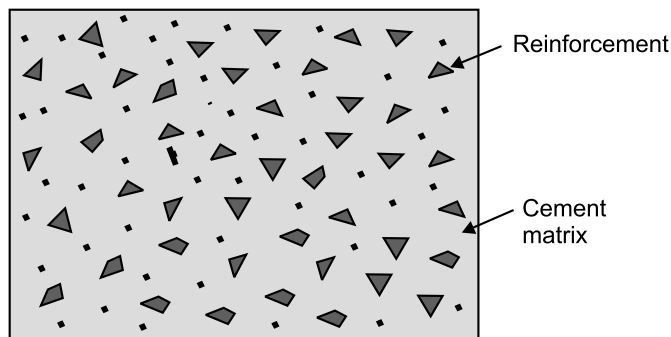


Fig. 15.8 Agglomerated composites

The oldest composites are agglomerated composites. Macroscopic particles such as sand, gravel and ceramic powder are called as agglomerated particles. These composites consist of sand and gravel, and a combination of sand and ceramics are reinforced by particulate or fibre (see Figure 15.8). In this reinforced constituent, materials may be organic or inorganic, hand metallic or nonmetallic. Some examples of agglomerated composites are concrete (iron rod reinforced cement composite), grinding wheel (epoxy bonded silicon carbide), etc. These composites have strength and are wear resistant to abrasion.

15.8 MANUFACTURING METHODS FOR COMPOSITE MATERIALS

The composite manufacturing process is one of the most important steps in the application of composite materials. Fabrication technology should be selected based on the type of matrix material, volume fraction type and reinforcement, melting temperature of the matrix, volume of composite casting, design of component, applications of the composites, etc. Few fabrication methods for different composites are described in the following.

15.9 MANUFACTURING METHOD FOR PARTICULATE REINFORCED COMPOSITES

Particulate reinforced metal matrix composites can be manufactured by any one of the following methods.

15.9.1 Liquid-state Methods

15.9.1.1 Stir Casting (Melting and Casting)

Fabrication methods for particulate reinforced composites can be varied. One method for manufacturing particulate reinforced metal matrix composite is stir casting. In this method, discontinuous reinforcement is stirred into molten metal, which is allowed to solidify. An example for stair casting composite is silicon carbide reinforced aluminium composite. This method is also known as vertex or stirrer method as shown in Figure 15.9.

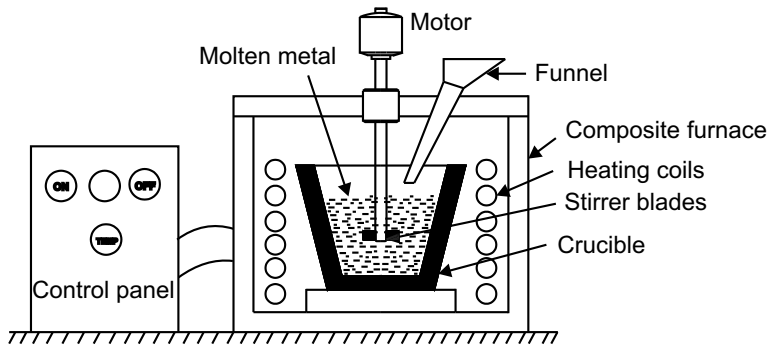


Fig. 15.9 Stir casting method for manufacturing metal matrix composites

The process consists of stirrer, crucible, heating element, funnel and furnace for heating metal. A weighed quantity of base metal is melted in a crucible during the process. Temperature of the molten metal should be 60°C – 70°C above the melting temperature of the metal. Stirrer containing aluminium oxide-coated stainless steel impeller is inserted. It can rotate up to 500 rpm by stirrer motor.

The heated dispersions or particles are added to the vortex through the nozzle of the powder feeder. Stirring is continued for about 3–5 minutes. After stirring the liquid, the molten metal is transferred into a mould. The melt particle slurry can be made into casting by any one of the following methods.

Sand Casting: Sands may be prepared for moulding by mixing the ingredients (sand, clay, water and other such materials) by hand. The fundamentals of mould making are simple and expert hand moulding requires much skill and practice. After some time, the sand mould was prepared by machines in mass production. Two main routes are used for bonding the sand moulds. The green sand mould technique consists of mixtures of sand, clay and moisture and the dry sand mould techniques consists of sand and synthetic binders cured thermally or chemically. The sand cores used for forming the inside shape of hollow parts of the casting are made using dry sand components. Composite molten liquid is introduced into the mould cavity through the gating system and allowed for solidification.

Die Casting: Die casting is the production of casting in permanent metal moulds in which metal fills the mould cavity under gravity or pressure. Permanent moulds are made into half; they may be designed with a vertical parting line. Gravity mould casting are much thicker in cross section than pressure die casting, as gravity alone does not provide enough pressure to force molten metal into the metal moulds in section much thinner than 3–6 mm. High pressure die casting is the most widely used, representing about 50% of all light alloy matrix composites casting production.

Squeeze Casting: A squeeze casting method is adopted for manufacturing metal matrix composites which require little or no finishing operations. Squeeze casting, also known as liquid metal forging, is a combination of casting and forging process. The composite melt slurry is poured into the bottom half of the pre-heated die. As the metal starts solidifying, the upper half closes the die and applies pressure during the solidification process. The amount of pressure thus applied is significantly less than that used in forging, and parts of complicated shape can be produced. The porosity is low and the mechanical properties are improved.

15.9.1.2 Injection of Particles through Gas Stream into Melt

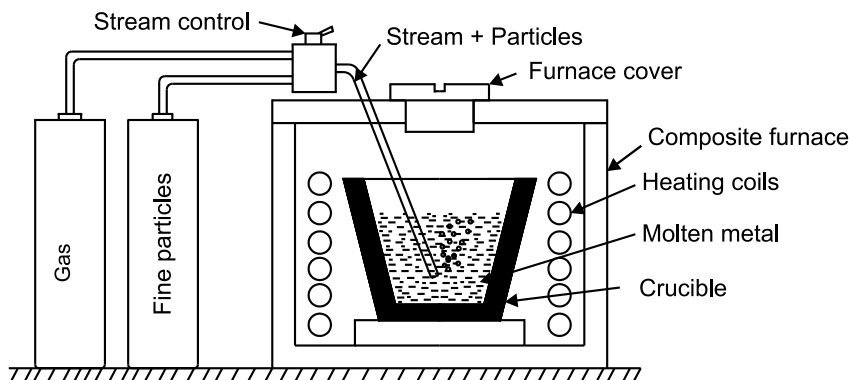


Fig. 15.10 Injection of particles for manufacturing metal matrix composites

It involves the melting of metals to a super heated condition and injects the pre-heated particulates through gas stream. Several attempts have been made to make aluminium graphite composite by introducing graphite particles in an aluminium matrix. Composites have been prepared by injecting the nickel-coated graphite powder through an inert gas stream (see Figure 15.10). Fine particles are forced into liquid metal by inert helium at high velocity. The particles are suspended in the liquid metal due to the fluidity.

15.9.1.3 Spray Deposition

Spray deposition involves the atomization of molten metal and the spray is collected on a substrate to form billets for subsequent forging. The process is a rapid solidification, because the metal experiences a rapid transition through the liquid to the solid at the room temperature. This results in a fine grain and precipitated structure.

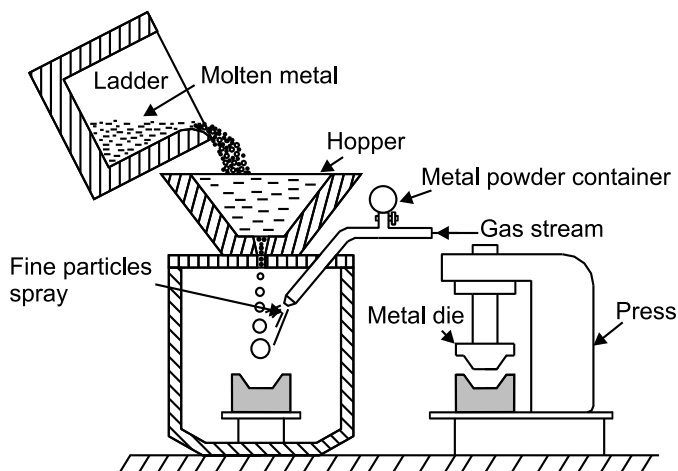
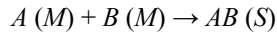


Fig. 15.11 Spray deposition method for manufacturing metal matrix composites

Spray deposition has been developed mainly for aluminium, steel and nickel matrix composites. The alloy to be sprayed is melted by induction heating in a crucible. The crucible is pressurized and the metal is ejected through nozzle in an atomizer. The production of composites by spray deposition can be accomplished by introducing the particulate into the standard spray deposition. Careful control of the metal and particulate feeding condition is required to get a uniform distribution of particulate within a metal. The atomized stream of metal is then collected on a metal die placed inside the container. The collected composite metal in a semi-solid condition is pressed using a forging process. Atomized powder that is not deposited is separated from the exhaust gas and collected and recycled. The shape of the final product depends upon on the atomized condition and the shape of the metal die cavity (see Figure 15.11). Silicon carbide reinforced aluminium composite can be produced in this method.

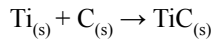
15.9.1.4 In Situ Fabrication Technique (Reaction Technique)

Systems for in situ production of reinforcements could be designed on the basis of thermodynamic and kinetic studies. A reacting constituent A may be in solution in a molten alloy M and the other constituent B may be introduced as solid particle which may also dissolve in M and react as



There will be formation of compound AB in molten metal M .

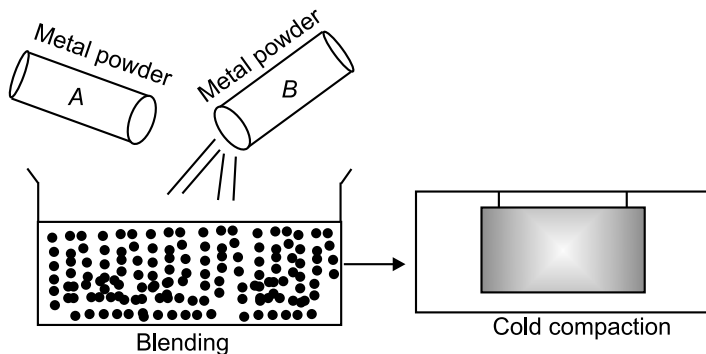
The reaction process involves heating the metal M along with the reacting constituent A . The constituent B may be in gas, solid or liquid form and is introduced into the molten metal. The constituent B reacts with A and is converted into compound of AB . The basic advantage of this process is the self-generation of energy which avoids costly equipments. Very high temperature is reached in many combustion synthesis reactions and volatile impurities are evaporated at these temperatures producing high purity products. An example for composite produced by reaction technique is titanium carbide reinforced steel matrix composite. Carbon and titanium are heated in an inert atmosphere along with steel. At higher temperatures ($> 1,450^\circ\text{C}$), the reaction is established between titanium and carbon and is given by



Precipitated TiC is dispersed in the matrix of the steel as hard carbide and improves mechanical and wear properties.

15.9.2 Solid-state Methods

15.9.2.1 Powder Metallurgy Method



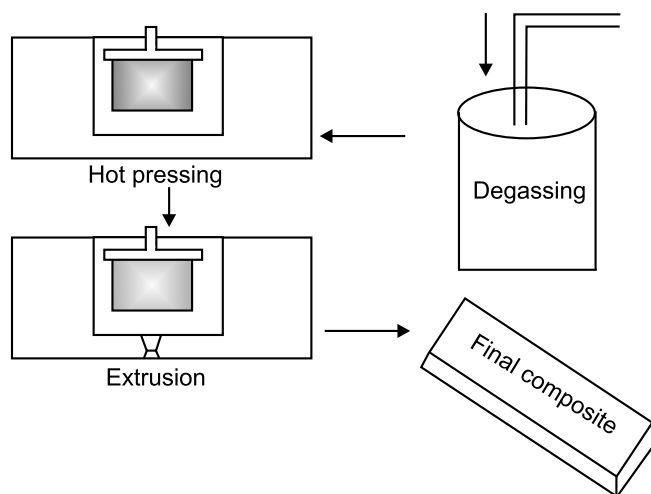


Fig. 15.12 Powder metallurgy method for manufacturing metal matrix composites

The metal matrix composites can be manufactured by powder metallurgy technique. In this technique, the metal powders are mixed with reinforced fibre or particles and compacted to desired shape and sintered to the required temperature to attain the strength and then finished. It involves mixing of powdered metal and discontinuous reinforcement which are then bonded through a process of compaction, degassing, heating and compacting. Composites are produced in their final form by pressing metal powder into the desired shape, usually in a metal mould, and then heating the compacted powder, either concurrently or subsequently for a period of time at a temperature below the melting point of the major constituent. Solid phase processes invariably involve the blending of rapidly solidified powder with particulates, using a number of steps as shown in Figure 15.12.

Powder metallurgy roots are currently employed on an industrial scale to produce iron-based TiC metal matrix composites marketed under a number of trade names. Seilstofer (Germany) have recently produced TiC ALLOY (trade name) composites consisting typically 40 vol.% TiC in a heat treatable steel alloy matrix by hot iso-static pressing. In addition, materials containing 45–50 vol.% TiC embedded in high alloy steel matrix are available from Thyssen (Germany) under the trade name FERRO-TITANIT.

The powder metallurgy method has some potential benefits in obtaining near-net-shape products but the capital investment is still high compared to conventional and other emerging techniques. It also has several limitations for the homogeneity of the material including density and intricate shape casting.

15.9.2.2 Diffusion Bonding

Layers of metal foil are sandwiched with long fibres, and then pressed through to form a matrix. It is a solid-state fabrication method, in which matrix in the form of foils and dispersed phases in the form of layers of long fibres are stacked in a particular order and then pressed at elevated temperature. The finished laminate composite material has a multilayer structure. Diffusion bonding processes are of two types—roll bonding and wire or fibre bonding. In the roll bonding, two different metal sheets are rolled resulting in the formation of a laminated composite material. This material is heated to

the desired temperature (above the recrystallization temperature) for diffusing the atoms from one metal sheet to the other. Wire or fibre bonding is process of combined continuous ceramic fibres and metallic wires followed by sintering in solid state and pressing at elevated temperature. In contrast to the liquid-state fabrication of metal matrix composites, diffusion bonding method allows obtaining materials containing up to 50% of dispersed phase.

15.10 MANUFACTURING OF FIBRE-REINFORCED POLYMER MATRIX COMPOSITES

The most widely used composites are polymer matrix composites. These composites consist of a polymer matrix reinforced by thin fibres. The properties of the finished product are closely related to the manufacturing method. Fibre-reinforced composites may be produced either in open mould or in closed mould processes.

15.10.1 Open Mould Process

Open moulding processes are those where the part being manufactured is prepared in open atmosphere. The composite part is prepared by mixing resin and fibre followed by compaction with or without heat. Examples for open mould presses are hand lay-up, pressure bag, vacuum bag, autoclave, filament winding and pultrusion.

15.10.1.1 Hand Lay-up Process

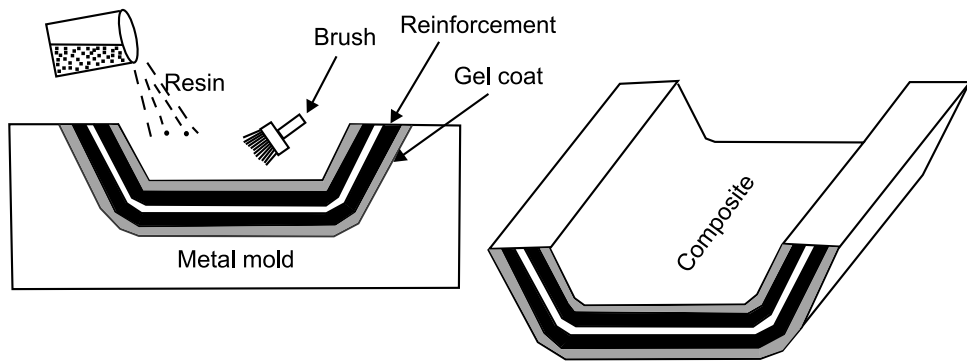


Fig. 15.13 Hand lay-up method for manufacturing polymer matrix composites

This is the simplest and widely used process. In this process, first apply the gel coat on the surface of the mould cavity. It helps in easy withdrawal (avoid the breakage) of the composite materials. Next, apply a layer of resin on the gel coat and brush it. The fibre is trimmed and laid down over a mould where it is formed to the desired shape and followed by another layer of the resin on the fibre surface. This process is continued till the required thickness is attained and pressed hydraulically or manually. Allow sufficient time for drying and remove the component. This process of hand lay-up gives maximum design flexibility with minimum investment on equipment at room temperature. Polyesters and epoxies are most common matrix material. Figure 15.13 shows hand lay-up method for producing polymer matrix composite.

15.10.1.2 Vacuum Bag Process

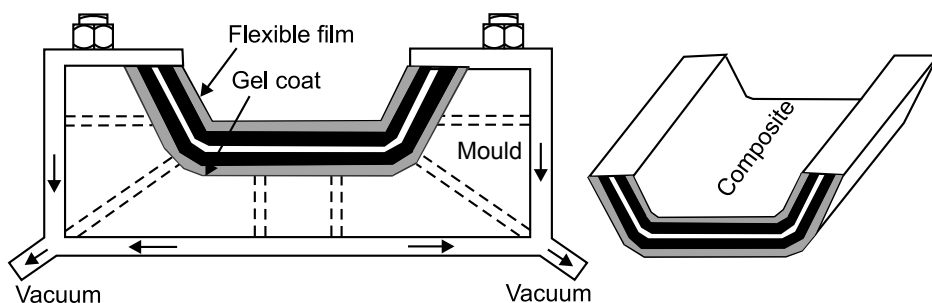


Fig. 15.14 Vacuum bag method for manufacturing polymer matrix composites

In the vacuum bag process, apply the gel coat on the surface of the mould cavity. This gel coat helps in easy withdrawal of the composite part. Next, apply a thin layer of the resin on the gel coat surface in turns and place the fibre material. Apply another layer of the resin and brush it. This process is continued till the required thickness is attained. Place the flexible film over the resin surface in turns and apply the vacuum. A vacuum is applied to the bag to remove air and volatile products. Vacuum pulls air and excess resin from the cavity, compacted the part by vacuum and serves as a barrier when the assembly is placed in an autoclave for curing under heat and pressure. Allow sufficient time for drying and remove the component (see Figure 15.14).

15.10.1.3 Pressure Bag Method

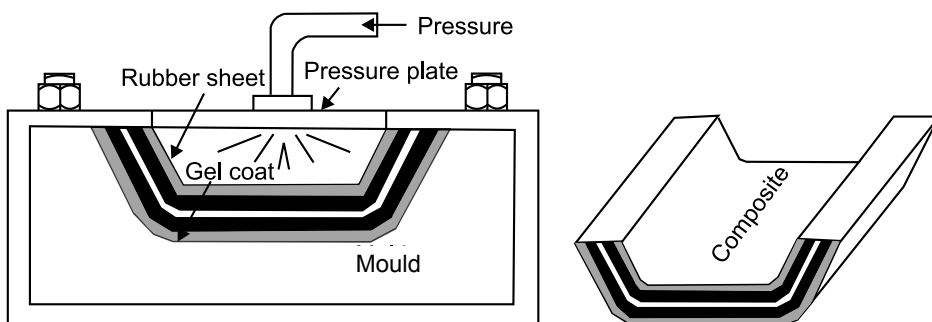


Fig. 15.15 Pressure bag method for manufacturing polymer matrix composites

The pressure bag process is used when a low-pressure moulding process is advantageous. In this process, place the laminate on the surface of the cavity. This helps easy withdrawal of the component. Fibre reinforcement fabric or mat is laid by hand into a mould and resins are pired on the fibre and brushed. This process is continued till the required thickness is attained. On the laminate, apply resin in turns and place the fibre materials. Cover the cavity and apply the pressure by air blower. The part is then cured under heat and pressure. Allow sufficient time for drying and remove the component (see Figure 15.15).

15.10.1.4 Autoclave Process

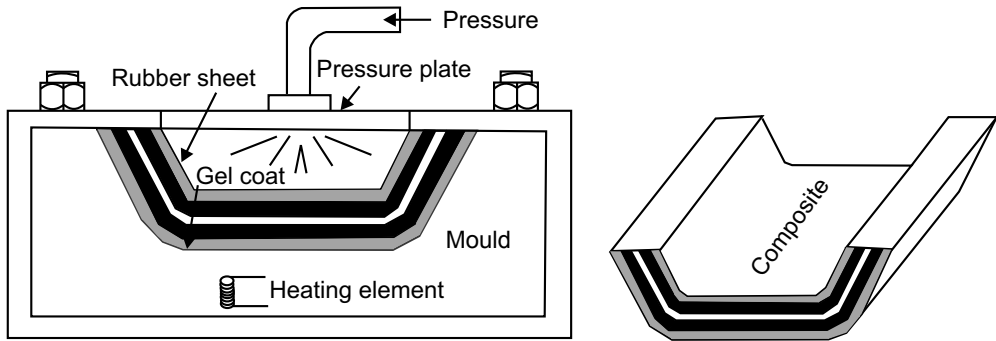


Fig. 15.16 Autoclave method for manufacturing polymer matrix composites

The autoclave process is an improvement over the pressure bag process. Most parts made by hand lay-up or automated-type lay-up must be cured by a combination of heat, pressure, vacuum and inert atmosphere. To achieve proper cure, the part is placed into an autoclave equipment to achieve void-free composite component. Usually, an inert atmosphere is provided inside the autoclave through the introduction of nitrogen or carbon dioxide. The speciality of this process is to apply heat at the desired temperature and cool to room temperature at high pressure (see Figure 15.16).

15.10.1.5 Filament-winding Method

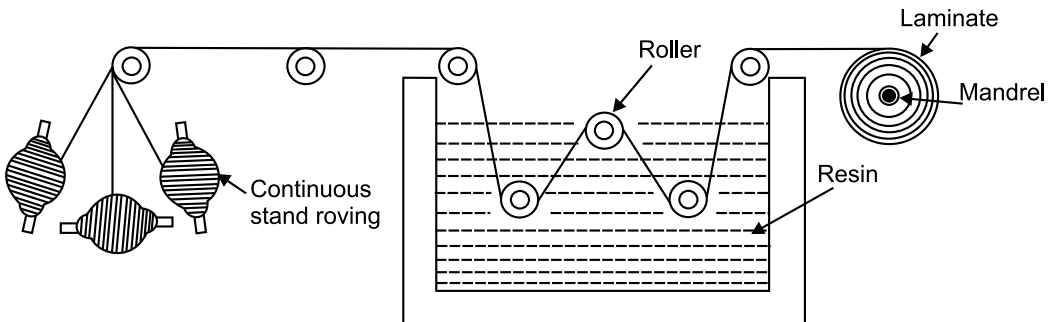


Fig. 15.17 Filament-winding method for manufacturing polymer matrix composites

The filament-winding process consists of feeding reinforcement filament through a resin bath and winding it on a mandrel (see Figure 15.17). Continuous fibre reinforcement materials are drawn through a container of resin mixture and formed onto a rotating mandrel to achieve the desired shape. The wound filaments are taken out and placed in predetermined pattern to give the required shape and size after pressure is applied hydraulically on the required layer placed in the cavity and the part is cured in an oven. This process gives an efficient control over the orientation and uniformity of fibre and resin.

15.10.1.6 Pultrusion Process

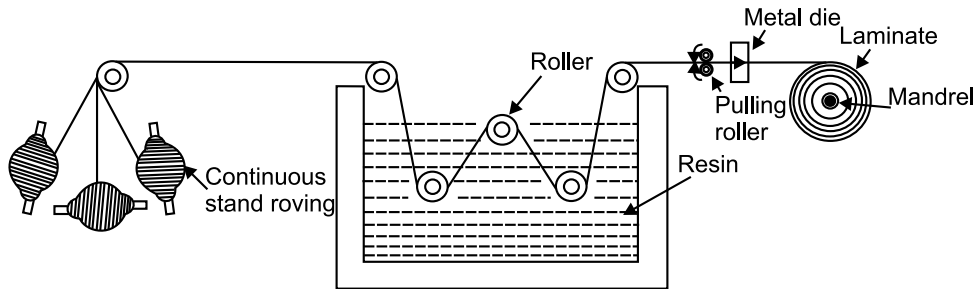


Fig. 15.18 Pultrusion method for manufacturing polymer matrix composites

In the pultrusion process, continuous roving strands are pulled from a resin bath through a metallic die and wound on a mandrel. The coated strands are then passed through a heated die where curing occurs. Allow time for drying a fabricated part. Sometimes, reinforcements are drawn through a die by maintaining the resin ratio. The continuous cured part, usually a rod or similar shaped object, is then cut to the desired length. Parts having constant cross section area are fabricated by pultrusion method (see Figure 15.18).

15.10.2 Closed Mould Process

In the closed moulding process, resin and fibres are mixed manually or automatically and heated to the desired temperature followed by injecting into metallic die cavity. An example for closed mould process is injection moulding process.

15.10.2.1 Injection Moulding Process

In the injection mould process, matrix and reinforcement are mixed and the blend is fed into a metallic mould. These mixtures are heated before or after injecting into the mould. Depending upon the matrix material and heating, injection moulding process is of two types: (1) Thermoplastic moulding and (2) Thermoset moulding.

Thermoplastic Moulding:

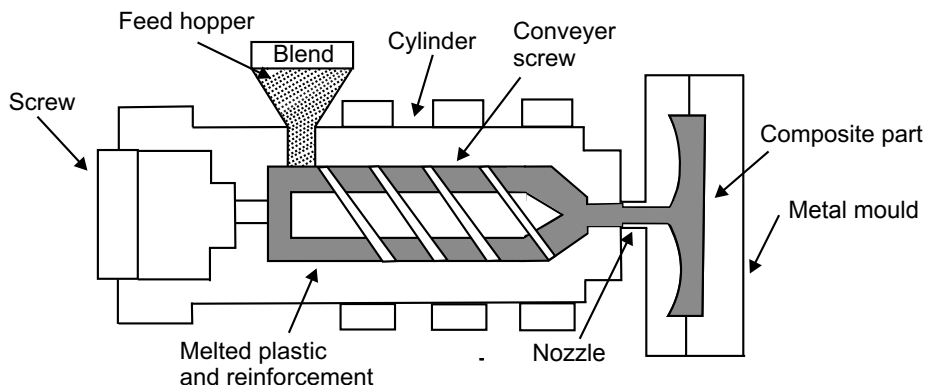


Fig. 15.19 Thermoplastic moulding method for manufacturing polymer matrix composites

In thermoplastic process, resin reinforced blends are fed through a hopper and these materials are carried to injection chamber through screw conveyer. The melted blend is injected into a heated mould where the part is formed (see Figure 15.19). This process is often fully automated. This process requires only heat and pressure to form the finished part and then cooled to room temperature. Unlike the thermosets, the thermoplastics can usually be reheated and reformed into another shape, if desired.

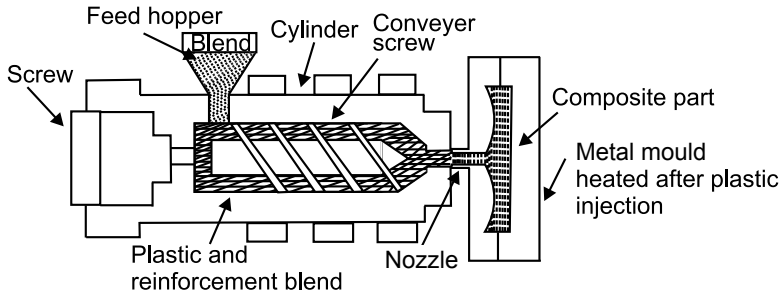


Fig. 15.20 Thermosets moulding method for manufacturing polymer matrix composites

Thermosets Moulding: The thermoset resins require the addition of a curing agent or hardener and impregnation onto a reinforcing material, followed by a curing to produce a finished part (see Figure 15.20). This process is often fully automated and the thermoplastic granules are fed via a hopper into a screw conveyer. This material is carried to injection chamber by screw conveyer and then injected under high pressure in to injection mould. The moulds are heated and once cured, the part cannot be changed or reformed, except for finishing.

15.11 MANUFACTURE OF LAMINATED COMPOSITE

The laminated composite can be manufactured by the following method:

15.11.1 Solid-state Bonding of Composite

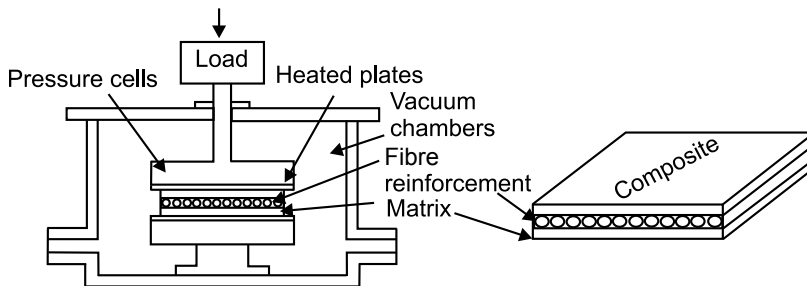


Fig. 15.21 Solid-state bonding of laminated composites

In the solid-state bonding, composites in the form of sheets are inserted in between the reinforcement fibre and this metal fibre, which are placed in between the hot plates. Hot plates are interconnected to pressure transducer. Metal and reinforcement are heated by a hot plate and the load is applied by

hydraulic press. Due to the load and temperature, the metal and fibre are combined and get converted into solid-state bonding (see Figure 15.21).

15.12 MECHANICAL BEHAVIOURS OF A COMPOSITE MATERIAL

The mechanical behaviour of composites mainly depends upon the reinforcement and the base matrix. Composite properties can be predicated on the basis of the properties of fibre and matrix. This can be obtained by mechanical behaviour of composite materials. For suitable structural application, it is necessary to select a specific material such that the composite should have increased stiffness and strength. These properties can be theoretically obtained by understanding the micromechanics of composites. The most common approach for the study of micromechanical theory is mechanics of material approach. The property of a lamina can be mathematically derived by studying the properties of fibre and matrix.

The mechanical study of a composite structure is more complex than that of a metal structure. Unlike metals, composite materials are not isotropic and their properties are not the same in all directions. Here, for understanding the study of fibres, lamina composite is taken up. The study of other types (particulate) of composites can be taken up similarly. The simplest way to model the behaviour of a composite containing continuous, aligned fibre is to treat it as if it were composed of two slabs bonded together, one of the matrix and other of the reinforcement, with the relative thickness of the latter in proportion to the volume fraction of the fibre.

Example The elastic modulus of a fibre composite must be determined in terms of properties and relative volume of fibres and matrix.

Elastic modulus is a function of E_f , V_f , v_f , E_m , V_m and v_m .

$$C_{ij} = C_{ij}(E_f, V_f, v_f, E_m, V_m, v_m)$$

where E_f is the Young's modulus of the fibre, V_f is the volume fraction of the fibre = Volume of fibre/total volume of composite, E_m is Young's modulus of the matrix, V_m is the volume fraction of matrix, v_f is the Poisson's ratio for the fibre and v_m is the Poisson's ratio for the matrix.

Similarly, the strength is also function of X_{ij} :

$$X_{ij} = X_{ij}(X_{if}, V_f X_{im}, V_m)$$

where X_{im} is the composite strength and X_{if} is the fibre strength.

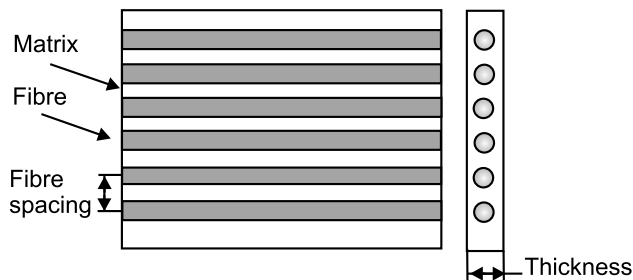


Fig. 15.22 Long fibre arrangement in the matrix

For the study of micromechanics, the representative volume is the smaller region over which the stress and strain are macroscopically uniform. Generally, single fibre is considered in the representative volume element. Figure 15.22 shows the typical representative of long fibre arrangement in the matrix. For the study of micromechanics, the representative volume is the smaller region over which the stress and strain are microscopically uniform. Generally, single fibre is constant in the representation.

15.12.1 Determination of E_1 (Longitudinal Direction or Iso-strain Condition)

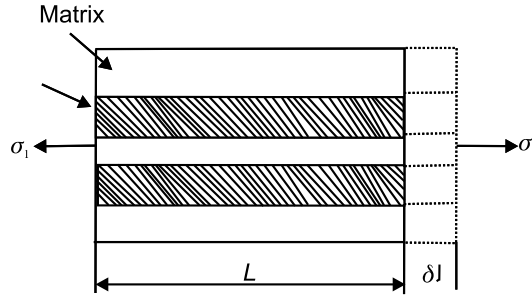


Fig. 15.23 Fibre and matrix under iso-strain condition

The modulus of the composite in direction of 1 is tensile strain $e_1 = \frac{\delta l}{L}$.

Assume that e_1 appears for both fibre and matrix as per longitudinal direction as shown in Figure 15.23. Let both constituents (fibre and matrix) behave elastically because of combined form.

The stress are

$$\begin{aligned}\sigma_f &= e_1 E_f \\ \sigma_m &= e_1 E_m\end{aligned}\quad (1)$$

where e_1 is the strain $= \frac{\delta l}{L}$, E_f is the Young's modulus of the fibre, E_m is Young's modulus of the matrix, σ_f is the stress developed in the fibre and σ_m is the stress developed in the matrix.

The resultant force on the element of composite is given by

$$\begin{aligned}P &= \sigma_f A_f + \sigma_m A_m \\ &= \sigma_1 A\end{aligned}\quad (2)$$

where A_f is the area of cross section of the fibre, A_m is the area of cross section of the matrix, σ_1 is the average stress that acts on a cross section of the composite and A is the cross section area of composite material.

Substituting Equation (1) in Equation (2)

$$\begin{aligned}\sigma_1 A &= \sigma_f A_f + \sigma_m A_m \\ E_1 e_1 A &= E_f e_f A_f + E_m e_m A_m \\ E_1 &= \left(\frac{E_f e_f A_f}{e_1 A} + \frac{E_m e_m A_m}{e_1 A} \right), \quad \therefore e_f = e_m = e_1 \\ E_1 &= \frac{E_f A_f}{A} + \frac{E_m A_m}{A},\end{aligned}\quad (3)$$

but volume fraction of fibre and matrix is $V_f = \frac{A_f}{A}$, $V_m = \frac{A_m}{A}$, Equation (3) becomes

$E_1 = E_f V_f + E_m V_m$ which is known as the rule of mixture for Young's modulus in direction of fibre or iso-strain condition.

Problem 15.1

A continuous and aligned glass reinforced composite consists of 40% volume of glass fibre having modulus of elasticity 69×10^3 MPa and 60% volume polyester resin with modulus of elasticity 3.4×10^3 MPa.

204 | Composite Materials

1. Compute the modulus of elasticity of the composite in the direction of fibre.
2. If cross sectional area is 258 mm^2 and a stress of 48.3 MPa is applied in the longitudinal direction, compute the load carried by fibre and matrix.

Solution

Volume of fibre, $V_f = 0.4$

Volume of matrix, $V_m = 0.6$

Young's modulus of fibre, $E_f = 69 \times 10^3 \text{ MPa}$

Young's modulus of matrix, $E_m = 3.4 \times 10^3 \text{ MPa}$

1. Modulus of elasticity of the composite in the direction of fibre is

$$E_1 = E_f V_f + E_m V_m$$

$$E_1 = (69 \times 10^3)0.4 + (3.4 \times 10^3)0.6$$

$$E_1 = 27,600 + 2,040 = 29,640 \text{ MPa or } 29.64 \times 10^3 \text{ MPa}$$

2. Cross sectional area $A = 258 \text{ mm}^2$

Stress in E_1 direction $\sigma_1 = 48.3 \text{ MPa}$

For iso-strain (strain in the direction of fibre), $e_1 = e_f = e_m$

$$E_1 = \frac{\sigma_1}{e_1} \text{ or } e_1 = \frac{\sigma_1}{E_1} = \frac{48.3}{29.64 \times 10^3} = 1.6296 \times 10^{-3} \text{ MPa.}$$

Also,

$$E_f = \frac{\sigma_f}{e_f}$$

or

$$\begin{aligned} \sigma_f &= E_f \times e_f \\ &= (69 \times 10^3) \times (1.6296 \times 10^{-3}) \end{aligned}$$

$$\sigma_f = 112.43 \text{ MPa.}$$

However, $V_f = \frac{A_f}{A}$ or $A_f = V_f A = 0.4 \times 258 = 103.2 \text{ mm}^2$

Load on fibre $= \sigma_f \times A_f = 112.43 \times 103.2$

$$= 11,602.77 \text{ MPa.}$$

15.12.2 Determination of Young's Modulus in the Direction of E_2 (Transverse Direction or Iso-stress Condition)

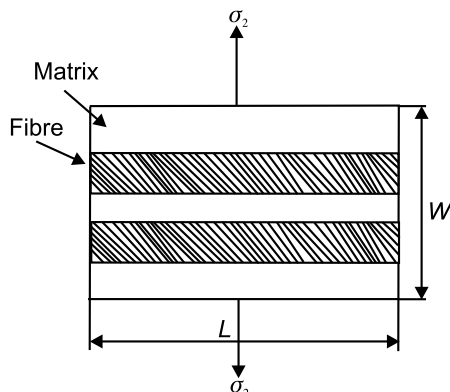


Fig. 15.24 Fibre and matrix under iso-stress condition

The Young's modulus E_2 in transverse direction is to be determined in the mechanics of material approach.

The strain in the fibre and matrix are

$$e_f = \frac{\sigma_2}{E_f}, \quad e_m = \frac{\sigma_2}{E_m} \quad (1)$$

The transverse dimension over which, on the average, E_f acts is approximately $V_f w$ as shown in Figure 15.24.

Here V_f = volume fraction of the fibre, W = width of the metal, whereas e_m acts as $V_m w$, where V_m = volume fraction of matrix and w = width of the composite.

Therefore, total transverse deformation is

$$\begin{aligned} e_2 w &= V_f w e_f + V_m w e_m \\ e_2 &= V_f e_f + V_m e_m \end{aligned} \quad (2)$$

Substituting Equation (1) in Equation (2)

$$\begin{aligned} e_2 &= V_f x = \frac{\sigma_2}{E_f}, \quad V_m x = \frac{\sigma_2}{E_m} \\ e_2 &= \left(\frac{V_f}{E_f} + \frac{V_m}{E_m} \right) \sigma_2 \end{aligned} \quad (3)$$

Also, Young's modulus in the transverse direction is

$$E_2 = \frac{\sigma_2}{e_2} \quad (4)$$

Substituting Equation (3) in Equation (4)

$$E_2 = \frac{\sigma_2}{\sigma_2 \left(\frac{V_f}{E_f} + \frac{V_m}{E_m} \right)} = \frac{1}{\left(\frac{V_f}{E_f} + \frac{V_m}{E_m} \right)}$$

$$E_2 = \frac{E_f E_m}{(E_m V_f + V_m E_f)} \quad E_2 \text{ is the Young's modulus in transverse direction as indicated in Figure 15.24.}$$

Problem 15.2

Calculate the Young's modulus of composite in the direction 2 (iso-stress condition), if its fibre reinforced plastic composite is to have a Young's modulus of fibre 50 GPa and modulus of matrix 72.4 GPa. Composite is made up of volume of fibre 35% and volume of matrix 65%.

Solution

Young's modulus of fibre $E_f = 50$ GPa

Young's modulus of matrix $E_m = 72.4$ GPa

Volume of fibre $V_f = 0.35$

Volume of matrix $V_m = 0.65$

$$E_2 = \frac{E_f E_m}{(E_m V_f + V_m E_f)}$$

$$E_2 = \frac{72.4 \times 50}{(50 \times 0.35) + (72.4 \times 0.65)} = \frac{3620}{64.56} = 56.07 \text{ GPa}$$

15.12.3 Determination of Poisson's Ratio V_{12}

Poisson's ratio ν_{12} is obtained, which is similar to the analogy of E_1 . Poisson's ratio is defined as

$$\nu_{12} = \frac{e_2}{e_1} = \frac{\text{Lateral strain}}{\text{Longitudinal strain}}$$

Let us consider stress state $\sigma_1 = \sigma$ and all other stresses as zero.

The deformation δw is given by

$$\delta w = -w e_2 = -w \frac{e_2}{e_1} (e_1) = -w \nu_{12} e_1 \quad (5)$$

Also, $\delta w = \delta_m w + \delta_f w$

Similarly, transverse Young's modulus E_2 , deformation $\delta_m w$ and $\delta_f w$ are approximately

$$\delta_m w = -w V_m \nu_m e_1 \text{ and } \delta_f w = -w V_f \nu_f e_1 \quad (6)$$

Substitute Equation (6) in Equation (5).

Therefore,

$$\delta w = \delta_m w + \delta_f w$$

$$-w \nu_{12} e_1 = -w V_m \nu_m e_1 - w V_f \nu_f e_1$$

$$\nu_{12} = V_m \nu_m + V_f \nu_f$$

The above equation gives the Poisson's ratio for the composite.

15.12.4 Determination of G_{12} (Shear Modulus)

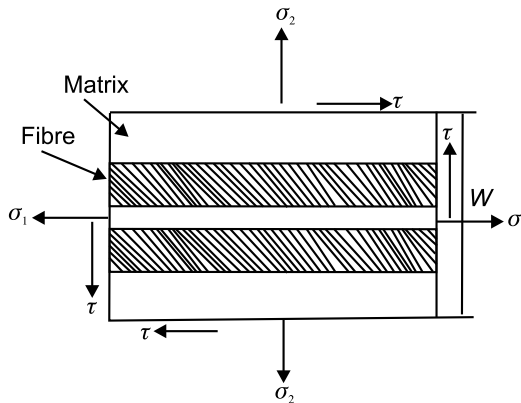


Fig. 15.26 Fibre and matrix under shear load

For determination of G_{12} , assume that the shear stress on the fibre and the matrix are the same as seen in Figure 15.26.

By the basic assumption,

$\gamma_m = \frac{\tau}{G_m}$, $\gamma_f = \frac{\tau}{G_f}$ where τ is the shear stress, G_m is the shear modulus of the matrix, γ_m is the shear strain for matrix and γ_f is the shear strain for fibre.

The total shearing deformation of fibre and matrix can be given as

$$\delta = \delta_m + \delta_f \quad (7)$$

Also, $\delta_m = V_m w \gamma_m$ and $\delta_f = V_f w \gamma_f$, therefore Equation (7) becomes

$$\gamma w = V_m w \gamma_m + V_f w \gamma_f$$

$$\gamma = V_m \gamma_m + V_f \gamma_f$$

$$\frac{\tau}{G_{12}} = V_m \frac{\tau}{G_m} + V_f \frac{\tau}{G_f}$$

$$G_{12} = \frac{1}{\frac{V_m}{G_m} + \frac{V_f}{G_f}}$$

$$G_{12} = \frac{G_m G_f}{V_m G_f + G_m V_f}$$

The above equation gives shear modulus for the composite.

15.13 PROPERTIES OF COMPOSITE MATERIALS

The following are the properties of composite materials:

1. The composite materials are lightweight, which is the most significant property, in comparison with the conventional materials.
2. The property of any composite material depends largely on the material chosen for reinforcement. Generally, the material improves a specific property, for example, graphite improves the bearing effect, silicon carbide improves toughness, etc.
3. The properties can be improved are high longitudinal and transverse strength at normal and elevated temperatures.
4. Good electrical and thermal conductivity, excellent anti-friction, machinability, high tensile strength toughness, corrosion resistance, etc.

15.14 ADVANTAGES OF COMPOSITES

The following are the advantages of composites:

1. They possess a combination of mechanical, chemical, structural, electrical, optical and other desired properties.
2. They are lightweight materials possessing higher specific strength and specific modulus than the conventional materials.
3. Power by weight ratio in aeroplanes is approximately 5 with the conventional materials while it is about 16 with composites. This will require prime mover of reduced power resulting in fuel economy or more pay-load carrying capacity. Alternately, it helps in weight reduction.

4. Composites can be moulded to any shape and size and according to any desired specification.
5. They possess excellent anti-chemical and anti-corrosion properties.
6. Making, repairing and fabricating of composites are easier than the metals and RCC.
7. Assembling and de-assembling of components is easy and quick.
8. Efficient utilization of materials may be done. The fibres may be oriented in such a way so as to provide greatest strength and stiffness in the desired direction.
9. Seepage and weathering problems are negligible.
10. Composites may be designed to obtain aesthetic appearance.

15.15 LIMITATIONS OF COMPOSITES

The following are the limitations of composites:

1. They have low flash and fire points.
2. They may develop undesired biological effects seen in polymers.
3. Polymeric composites are not suitable for high temperature applications.
4. Cost of composites is still higher than many conventional materials.
5. On prolonged exposure to sunlight, the colours of composites generally fade out.

15.16 APPLICATIONS

Nowadays, composites are used almost everywhere. Some important fields of applications are as follows:

1. Space vehicles and satellites
2. Aircraft
3. Rockets
4. Automobiles
5. Pressure vessels and heat exchangers
6. Sports, music and amusements
7. Building constructions
8. Machine components
9. Electronic and computer components.

Some notable applications where composites have been used are given in the following:

1. The roof of Montreal Olympic stadium was built with Kevlar fabric reinforced composite.
2. The air-conditioned, Nagar Mahapalika's underground market of London is fully made of composites.
3. Boeing 747 contains 929 m² surface areas made of composites.
4. Fighter plane F-18 has about 10% structure made of graphite-epoxy (Gr-Ep) composite those results in a weight saving of about 25%.
5. Moon landing mission Apollo 15, 16 and 17 had tubular drill bore stem made of boron-epoxy (B-Ep) composite.
6. Turbine and engine shafts, discs and bearings are made of carbon fibre composites.
7. Satellites employ composites to work in the temperature range of -160°C to $+95^{\circ}\text{C}$.
8. Voyager spacecraft used 3.7 m diameter Gr-Ep flight antenna.

9. Commercial acoustic guitars are made of graphite-epoxy composites.
10. Natural gas vehicle fuel cylinder and fibre reinforced aluminium pistons are used in Toyota cars.
11. Printed circuit boards, switchgears, body of computers, etc. are made of composites.
12. G-10 is a laminated thermosetting glass fibre composite used in magnets and cryostats as a high strength material where metals are unsuitable.
13. Carbon fibre reinforced composites are used in biomedical applications such as total hip replacement and fracture fixation.

EXERCISES

1. What is a composite material? What are its advantages and disadvantages?
2. Explain the term 'composite materials' with examples. State their applications.
3. How are composites classified? What are its advantages and limitations?
4. Explain clearly the three types of composites with examples.
5. Explain the following composite materials with examples:
 - (i) Agglomerated materials
 - (ii) Reinforced materials
6. Differentiate between particulates, long fibres and short fibres. Give an example for different types of composite materials.
7. Define volume fraction of a fibre in composite material.
8. Describe briefly the different methods of obtaining metal-matrix composites.
9. What important factors influence the successful production of metal matrix composites? Explain clearly.
10. What are fibre reinforced plastics? Give at least four examples.
11. List the different methods of manufacturing fibre reinforced plastic. Explain any two of them.
12. Describe the steps involved in the manufacture of fibre reinforced plastic composites. Give the applications of fibre reinforced plastics in practice.
13. Explain the open mould and closed mould processes of manufacturing fibre reinforced plastic products. Give two examples in each case.
14. Clearly explain the production of fibre reinforced plastic composites. What precautions are to be taken during their production?
15. Give four examples for laminated composite materials used in everyday life.
16. Differentiate between thermosetting and thermoplastic polymers.
17. What are the different types of composite materials? Describe any one of the production methods of composite using neat sketches.
18. Give the important differences between metal matrix composites and fibre reinforced plastics.
19. Explain the advantages and limitations of composite materials in practice.
20. Derive an expression for the elastic modulus of a composite in terms of moduli and volume fractions of its components in iso-strain condition.

210 | Composite Materials

21. Derive the rule of mixtures for calculating Young's modulus of a fibre plastic matrix composites in the direction of the fibres.
22. Derive an expression for the Young's modulus and density of a composite in terms of weight fractions or volume fractions and Young's moduli. Use regular nomenclatures.
23. Derive an expression for the fraction load carried by the fibre as a function of Young's moduli, volume fraction of the matrix for iso-strain conditions.
24. Derive an expression for the fraction load carried by the fibre in terms of Young's moduli, volume fraction of the matrix for iso-stress condition.
25. Derive the rule of mixtures for calculating Young's modulus of a fibre plastic matrix composites in the direction of the fibres.
26. What are the advantages and limitations of composite materials?
27. Write briefly on various applications of metal composites in an industry.
28. Discuss the advantages of a composite material over a single-phase material. Give examples of composite materials.
29. Calculate the volume fraction of fibres, if its fibre reinforced plastic composite is to have a longitudinal Young's modulus of 50 GPa. Given the Young's moduli of the fibre and epoxy resin matrix as 72.4 GPa and 3.4 GPa respectively. What is the fraction of the load carried by the fibres in longitudinal loading? Assume iso-strain conditions.
30. Calculate the tensile strength of a GFRP composite of $V_f = 0.7$, when loaded in tension along the direction of fibres, given in the following data:

Material	Young's Modulus, GPa	Tensile Strength, MPa
Glass fibre	69.0	3450.0
Polyester resin	2.1	55.0

Assume iso-strain condition.

31. A composite material is made by using 10% by volume of Kevlar fibre and 90% epoxy matrix. If the Young's modulus of Kevlar is 130 GPa and epoxy is 4 GPa, calculate
 - (i) Young's modulus of the composite material in the fibre direction
 - (ii) Young's modulus of the composite material in the transverse direction
 - (iii) Fraction of load carried by the fibres.
32. A tensile load of 500 N is applied to epoxy-glass fibre composite. If the cross section of the composite is 1 mm^2 and the volume of the fibre is 30%, calculate the stress in the glass fibre when
 - (i) The load axis is parallel to the fibre and
 - (ii) The load axis is perpendicular to the fibre.Take the values of Young's modulus for the glass fibre as 86 GPa and for the matrix as 3.38 GPa.

OBJECTIVE -TYPE QUESTIONS

1. Composite is _____.
 - (a) Oldest engineering materials
 - (b) New engineering materials
 - (c) Modern engineering materials
 - (d) All of the above

2. Composite is made up of _____.
 - (a) Two basic constituents called matrix and reinforcements
 - (b) Two or more micro-constituents insoluble in each other
 - (c) Two or more dissimilar materials putting together to work
 - (d) All of the above
3. In particulate composite, the particle size varies _____.
 - (a) In microns
 - (b) In millimetres
 - (c) In centimetres
 - (d) All of the above
4. Second phase in the form of fibre with length many times larger than their diameter is called _____.
 - (a) Laminated composite
 - (b) Agglomerated composites
 - (c) Fibre composites
 - (d) Particulate composite
5. Plywood is an example for _____.
 - (a) Fibre reinforced plastic
 - (b) Laminated composite
 - (c) Particulate composite
 - (d) None of the above
6. In fibre reinforced plastic, the matrix will be _____.
 - (a) Polymer
 - (b) Cement
 - (c) Wood
 - (d) Metal
7. Chopped glass fibre reinforced resin composite is an example for _____.
 - (a) Particulate composite
 - (b) Laminated composite
 - (c) Fibre reinforced plastic composite
 - (d) None of the above
8. For ceramics, matrix is reinforced with _____.
 - (a) Natural fibre
 - (b) Glass fibre
 - (c) Carbides
 - (d) All of the above
9. In in-situ composite fabrication technique, _____.
 - (a) Reinforcements are dispersed by adding to the molten metal
 - (b) Reinforcements are dispersed by reactions
 - (c) Reinforcements are dispersed by bonding
 - (d) None of the above
10. Powder metallurgy technique is used for preparing _____.
 - (a) Metal matrix composite
 - (b) Ceramic matrix composite
 - (c) Polymer matrix composite
 - (d) All of the above
11. Fibre reinforced composites are _____.
 - (a) Highly corrosive
 - (b) Heavy
 - (c) Lightweight
 - (d) All of the above
12. Fibre reinforced plastic composites _____.
 - (a) Increase the weight of the plane
 - (b) Reduce the weight of the plane
 - (c) Are not affected in terms of weight
 - (d) None of the above
13. In solid-state bonding of composite, _____.
 - (a) Metal and reinforcement are heated by hot plate and loaded by press
 - (b) Metal and reinforcement are loaded by only press
 - (c) Metal and reinforcements are heated
 - (d) All of the above

212 | Composite Materials

14. Fibre reinforced plastic composites are of _____.
- (a) Low flash point (b) Low density
(c) High cost (d) All of the above
15. The properties of any composite depend on the _____.
- (a) Matrix (b) Reinforcement
(c) Methods of manufacturing (d) Size and shape of the composite

ANSWERS

1.	d	2.	d	3.	a	4.	c	5.	b	6.	a
7.	c	8.	c	9.	b	10.	a	11.	c	12.	b
13.	a	14.	d	15.	b						

chapter 16

Properties of Ferrous and Non-ferrous Materials

INTRODUCTION

The metallic materials are one of the most important elements that are used for industrial applications in our everyday lives. The properties of metals and alloys have to be understood before using them. Properties of metals describe the different characteristics of metals when subjected to forces or load. This is used by mechanical engineers to calculate different conditions of metals and it is especially important to people building structures or vehicles or machines. Metals and alloys are safe for humans during their operation in the structures or machines.

The metallic materials can be classified into two main groups ferrous and nonferrous. The ferrous materials are iron based with other constituents. Metals other than iron are called nonferrous materials. The major nonferrous materials are copper, aluminium, magnesium, nickel, tin, lead and zinc.

16.1 FERROUS METALS

The widely used engineering metals in the industry are ferrous metals and their alloys. The metals in which the chief constituent is iron are ferrous metals. In addition to iron, the ferrous metals contain carbon, nickel, phosphors and manganese.

The various ferrous metals used in engineering are discussed in the following subsections.

16.1.1 STEELS

Steel is an iron-based alloy with carbon content less than 1.8% and contains other elements. Increasing percentage of carbon adds to the strength and hardness in steel and they are classified according to the carbon and alloying elements which are discussed in the following.

16.1.1.1 Plain Carbon Steels

Plain carbon steel includes those steels in which the properties mainly result from the existence of carbon. Additional elements such as manganese, silicon, phosphorous and sulphur may be present in relatively small amounts but do not add to the the mechanical properties of the steel. In plain carbon steel, carbon may vary from 0.08% to 1.55%.

Plain carbon steels are classified into three types according to the percentage of carbon.

Mild Steel:

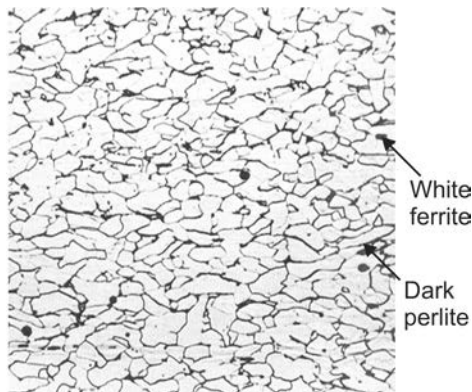


Fig 16.1 Shows microstructure of low carbon (mild) steel

Steels in which the carbon content ranges from 0.08% to 0.35% are known as mild steels. The microstructure consists of ferrite and small quantity of perlite as shown in Figure 16.1. It is soft, highly ductile and tough. These steels do not respond to hardening and have good machineability and weldability. Mild steel is mainly used in automobiles, structural fabrication, wires, rivets, nuts, bolts, sheets, tubes and shafts railway axle.

Medium Carbon Steel:

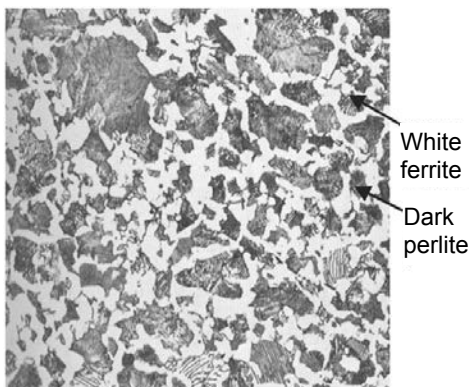


Fig 16.2 Shows microstructure of medium carbon steel

The steels in which the carbon content ranges from 0.35% to 0.55% are called medium carbon steels. The microstructure consists of pearlite and ferrite as indicated in Figure 16.2. It is harder, stronger and less ductile than mild steel. They are used in various steel sections, rail steel, springs, wire ropes and hammer.

High Carbon Steel:

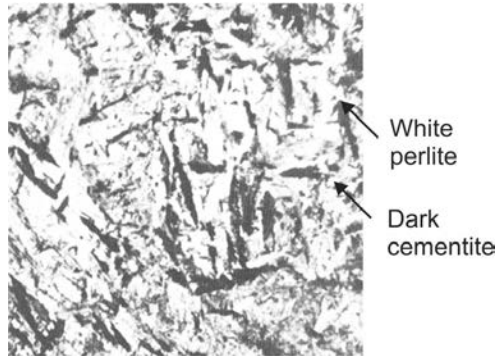


Fig 16.3 Shows microstructure of high carbon steel

The steels in which the carbon content ranges from 0.55% to 1.55% are known as high carbon steel. Hardness and strength are increased by increasing the carbon content. Microstructure consists of cementite and pearlite. They are hardest, strongest and low ductile as indicated in Figure 16.3. High carbon is responsible for hardening, and the mechanical properties can be altered by heat treatment. High carbon steels are used for knives, razors, metal-cutting tools, hacksaw blades, hand files, forging dies and drills bits.

The chemical analyses of some commercial plain carbon steel along with other elements are given in Table 16.1.

Table 16.1 Shows Typical Analysis of Some Commonly used Commercial Steels

Types of Steel	C%	Mn%	Si%	S%	P%
Wrought Iron	0.05	0.05	0.07	0.01	0.01
Mild Steel					
(i) Rivet Steel	0.05	0.30	0.07	0.04	0.04
(ii) Structural Steel	0.20	0.08	0.12	0.05	0.05
(iii) Free Cutting Steel	0.13	0.45	0.03	0.12	0.10
(iv) Railway Axle	0.35	0.80	0.20	0.04	0.04
Medium Carbon Steel					
(i) Rail Steel	0.38	1.00	0.08	0.06	0.05
(ii) Railway Spring Steel	0.50	0.85	0.10	0.05	0.05
High Carbon Steel					
(i) Chisel Steel	0.75	0.50	0.08	0.05	0.05
(ii) Carbon Tool Steel	1.30	0.32	0.15	0.02	0.02
(iii) Saws, Razor	1.40	0.50	0.10	0.30	0.05
(iv) Saws for Cutting Steel	1.55	0.40	0.15	0.02	0.02

16.1.4.2 Alloy Steels

In the alloy steels, the presence of other elements like manganese, nickel, chromium, etc. along with the carbon improve the mechanical properties, even though carbon still plays a major part in maintaining the superiority of the steels. The alloying elements are added in steels to achieve one or more of the following properties.

1. Increase resistance to corrosion
2. Improve machinability
3. Increase resistance to abrasion
4. Increase high temperature properties

On the basis of the total alloy content, the alloy steels may be classified as low alloy steels and high alloy steels.

The alloy steels in which, generally, the alloying elements are less than 10% are called low alloy steels. The importance of low alloy steels is that the alloying elements like chromium, manganese, nickel, vanadium and boron permit much wider range of physical and mechanical properties. Some alloy steels possess a very high tensile strength, which is impossible with plain carbon steel. Low alloy steels are mainly used as machine components in railway, ship, aeroplane, automobile and other engineering industries. If the alloying elements constitute more than 10%, they are called high alloy steels. The high alloy steels are mainly used as cutting tools, blades, razors and wear-resistant parts in industry.

Some common alloy steels are discussed in the following subsections.

Manganese Steel: Manganese is one of the principal alloying elements using along with steel. Plain carbon contains small trace of manganese ranging from 0.05% to 0.85% and it improves strength and ductility. The use of 1.5%–2% manganese in low alloy steel further increases the strength in heat-treated condition. Manganese which amounts between 2% and 10% along with carbon is responsible for brittleness in steel. If the manganese content is increased to 11%–16% along with 1%–1.5% carbon, the alloy produced is hard and wear resistant. This material is known as Hadfield austenitic manganese steel. Manganese steels are used extensively for frogs and switches in railroad, rock crusher and dredge buckets in mining.

Nickel Steel: Nickel is one of the important alloying elements alloyed with steel. Small quantity of nickel helps to improve the toughness and impact resistance. Nickel content of 1.5%–6% produces much finer grain size than other elements and increases the elastic limit, hardness and tensile strength of steel. The low carbon and 3.5% nickel are used for carburizing as it develops hardness on the surface and toughens the core. Nickel content of 8%–22% improves corrosion resistance and provides additional strength and hardness to steel without affecting the ductility. These steels are used for bolts, gears, axles, nuts and various machine arts. Nickel steel containing 36% nickel is called Invar steel. It is mainly used for measuring instruments.

Chromium Steel: Chromium is also one of the principal alloying elements in steel. Chromium exists in steel predominantly as carbide which provides hardness and also increases the elastic limit and tensile strength without affecting the ductility. The low carbon chromium steels are suitable for carburizing and produce very hard, wear-resistant alloys and are used for springs, gears, bolts and nuts. Addition of chromium to plain carbon steel improves the hardenability, strength and wear resistance; and both

nickel and chromium improve the ductility of steel. It is mainly used in surgical instruments, files, ball and roller bearings, gears and springs.

Stainless Steel: The proper combination of chromium and nickel will improve some properties of carbon steel. The addition of nickel confirms the increased strength, surface hardness while the depth of hardness is increased by the addition of chromium. Nickel and chromium steel are also called as stainless steel and are classified as follows:

Martensitic Stainless Steel: Martensitic steels typically contain 11.5 to 18 percent chromium and upto 1.2 percent carbon with 1 to 1.2 percent nickel. They are hardenable by heat treatment, have modest corrosion resistance and are employed in surgical instruments, wrenches and turbines. These steels can cold work. They are also used for making springs, steam turbine plates and ball bearings.

Ferritic Stainless Steel: Standard ferritic steels contain 10.5 to 27 percent chromium and are nickel-free; because of their low carbon content (less than 0.2 percent), they are not hardenable by heat treatment. They are resistant to corrosion and have great strength. They are used for household steels, surgical instruments, chemical industries and automobile.

Austenitic Stainless Steel: Austenitic steel which contain 16 to 26 percent chromium and up to 35 percent nickel, usually have the highest corrosion resistance. They are not hardenable by heat treatment and are nonmagnetic. Typical applications include aircraft and the dairy, food-processing industries, household equipment, heat exchangers and dairy equipment..

High-speed Steel: High-speed steels are high-alloyed steel containing large amounts of tungsten, chromium, vanadium and cobalt. They are withstand high temperature without losing hardness under high cutting speeds. The tools made up of high speed steels can be run at high speeds as compared to tools made up of carbon steels. Drills, milling cutters, tool for lathe are the example for high speed steel.

Tungsten High-speed Steel: Tungsten is commonly used as alloying elements in high alloy steels. It varies from 1%–20% in the form of ferrite and also carbide. It helps retain hardness and sharp cutting edges at high temperatures. It precipitates as tungsten carbide by reacting with carbon available in the molten steel. One of the most important tool steels is high tungsten alloy called high-speed steel. It has the ability of the steel to maintain a sharp cutting edge even at a red hot condition and used in high-speed machining operations.

16.1.2 Pig Iron

Pig iron is produced in a blast furnace by smelting iron ore with coke and limestone. It is the first product in the process of converting iron into a useful metal. The product of blast furnace has the following composition (approximately): C 3% to 4 %, Si 1% to 3%, Mn 0.1% to 1.5%, P 0.3% to 1.7% and the balance iron. The final composition depends upon the type of ore used. Pig iron is the raw material for all iron and steel products.

16.1.3 Wrought Iron

Wrought iron is a mechanical mixture of very pure iron and silicate slag and its chemical composition is carbon 0.02%–0.03%, slag 0.05%–1.5%, silicon 0.02%–0.1%, manganese 0.02%–0.4% and the balance iron. Wrought iron is never cast and all the shapes are obtained by hammering, pressing and forging due to high ductility. Cold working can increase the ultimate strength of wrought iron. It also possesses a high resistance to corrosion. Wrought iron is used as sheets, bars, rivets, etc. in the fabrication process.

16.1.4 Cast Iron

An alloy of iron that contains 2%–4% carbon along with varying amounts of silicon and manganese and traces of impurities such as sulphur and phosphorus is called cast iron. It is made by reducing iron ore in a blast furnace. The liquid iron is cast into crude ingots called pig iron, and the pigs are subsequently remelted along with scrap and the alloying elements in cupola furnaces and recast into moulds for producing a variety of products. Commercially, cast irons have the carbon range between 2.2% and 4.3%. All cast irons are low in terms of ductility and hence, cannot be rolled. The fluidity of cast iron is very good, and therefore can be cast into any complicated shapes. Cast irons have high compressive strength.

According to the shapes of the free carbon available in the microstructure, the cast irons are classified into four types which are discussed in the following subsections.

16.1.4.1 Gray Cast Iron

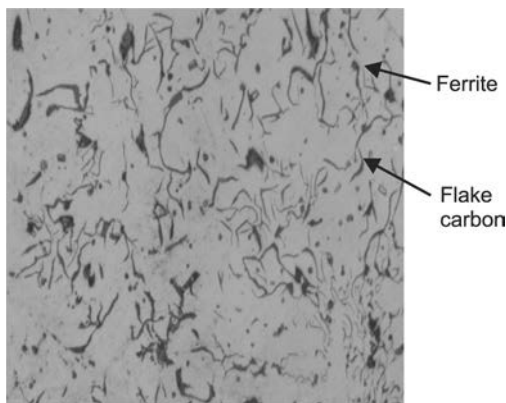


Fig 16.4 Shows microstructure of gray cast iron

Gray cast iron basically is an alloy of iron and carbon. It contains 2.5%–3.8% carbon, 1.1%–2.8% silicon, 0.4%–1% manganese, 0.15% phosphorous and 0.10% sulphur. Microstructure consists of ferrite and flake graphite as shown in Figure 16.4. It can be cast into any shape in a sand mould, and it possesses the lowest melting point of the ferrous alloys. It provides excellent casting quality for producing simple and complex shapes. It has high resistance to wear, high compressive strength and high vibration damping capacity. Gray cast iron is mainly used for water pipes, manhole covers, IC engine blocks, piston rings and machine components.

16.1.4.2 White Cast Iron

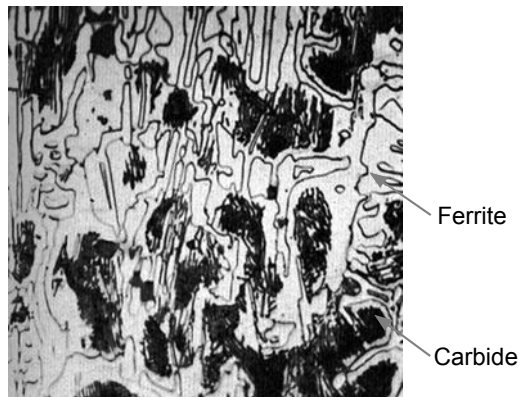


Fig 16.5 Shows microstructure of white cast iron

White cast iron derives its name from the fact that its freshly broken surface shows a bright white fracture. This is because, the carbon present in them is in combined form as cementite and perlite. Carbon is chemically bonded with the iron as iron carbide. White cast iron contains 1.8%–3.6% carbon, 0.5%–2% silicon, 0.2%–0.8% manganese, 0.18% phosphorus and 0.10% sulphur. Microstructure consists of iron carbide along with perlite as shown in Figure 16.5. It has excellent abrasive wear resistance and brittleness. It can be cast only in sand moulding and is mainly used for producing malleable cast iron and wear-resistance component machine component.

16.1.4.3 Malleable Cast Iron

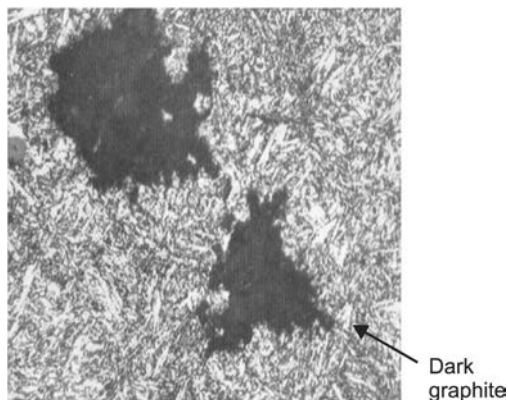


Fig 16.6 Shows microstructure of malleable cast iron

Malleable cast iron is obtained from hard and brittle white iron through controlled heat conversion (malleabilisation) process. It is having all the carbon in the free form in irregular shapes as shown in Figure 16.6. Malleable cast iron contains 2.3% carbon, 0.6%–1.3% silicon, 0.2%–0.6% manganese and 0.15% phosphorous. Microstructure consists of dark graphite in a ferrite matrix as shown in Figure 16.6. Malleable cast iron possesses high yield strength and high Young's modulus and it possesses good wear resistance. It is mainly used for railroad, agricultural implements and conveyor chain links.

16.1.4.4 Nodular Cast Iron or Spheroid Graphite Iron

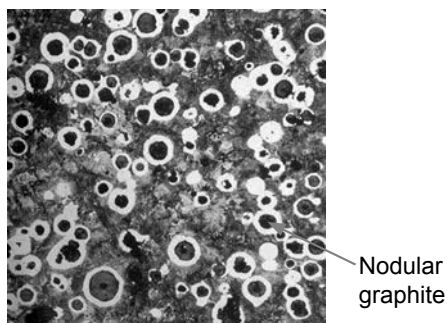


Fig 16.7 Shows microstructure of nodular cast iron

In nodular cast iron, graphite appears as round shape instead of flakes as in gray cast iron. Nodular-shaped graphite is obtained by adding small amounts of magnesium or cerium in the molten gray cast iron. Nodular cast iron contains 3.2%–4.2% carbon, 1.1%–3.5% silicon and 0.3%–0.8% manganese. Figure 16.7 shows the microstructure of nodular cast iron. Microstructure consists of nodules surrounded by ferrite. It is highly ductile and machinable with excellent castability and wear resistance. It is mainly used in internal combustion engine, earth moving machinery, valves and fittings, pipes and flywheels.

16.2 NON-FERROUS METALS AND ALLOYS

Nonferrous metals are those which do not contain iron. Owing to their rare existence, they are more expensive than ferrous metals. Most of the nonferrous metals have high electrical conductivity, low density and high strength-to-weight ratio. The major nonferrous metals used in industry are aluminium, copper, zinc, titanium, etc.

The most important nonferrous metals and alloys are discussed in the following subsections,

16.2.1 Copper and Copper-based Alloys

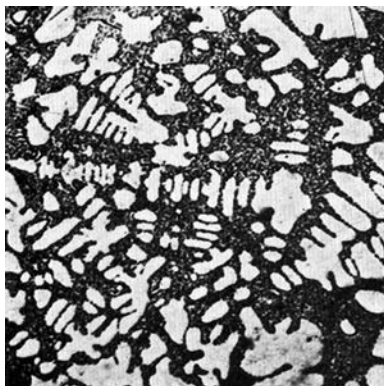


Fig 16.8 Shows microstructure of pure copper

Copper is an important engineering metal. Pure copper is reddish in colour and is available in the earth as pure and as ore as well. It is highly malleable, ductile and is a good conductor of heat and electricity. In pure state, its application lies in the electrical industries because of its high electrical conductivity. It can be combined with other elements to form alloys like brass and bronze. It is widely used in wire and some industrial applications like heat exchanger, bearing, etc. The microstructure of pure copper is shown in Figure 16.8.

16.2.1.1 Brass

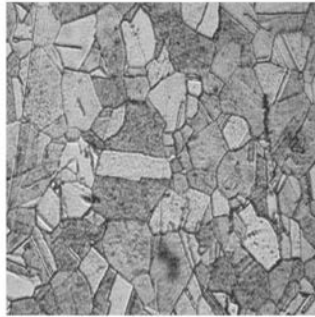


Fig 16.9 Shows microstructure of brass

Brass is an alloy of copper and zinc containing at least 50% copper. It is bright yellow to golden in colour. It is soft and ductile and is stronger than copper. It has good casting properties and is resistant to corrosion. Figure 16.9 shows a microstructure of copper–zinc. It is used for making plumbing fittings, bushes, bearings and pumps.

Table 16.2 Gives Composition, Properties and uses of Various Brasses.

SI No.	Type	Composition	Properties	Uses
1.	Yellow brass	65% Copper 35% Zinc	High Ductility, good strength, high resistant to corrosion.	Plumbing, lamp fixtures, grill works, rivets, tubes
2.	Red brass or Red metal	85% Copper 15% Zinc	Better corrosion then yellow brass, superior to copper to handling water.	Plumbing lines, electrical sockets.
3.	White brass	10% Copper 90% Zinc	Hard and strong	Used for ornamental work
4.	Muntz metal (Alpha and Beta brass)	60% Copper 40% Zinc	More brittle, suitable for hot working	Used for casting condenser tubes, suitable for hot working, rolling, extrusion etc.
5.	Naval brass	69% Copper 30.25% Zinc 0.75% Sn	High strength, high resistance to corrosion	Architectural work, condenser tubes, brazing rods etc.
6.	Leaded yellow brass	67% Copper 29% Zinc 3% Lead 1% Sn	High strength, high resistance to corrosion	Furniture hardware, radiator, light fittings etc.

16.2.1.2 Bronzes

The bronze is an alloy of copper and tin. They have higher strength than copper and can be cast to any shape. They are noncorrosive and wear resistant. The commercial bronzes are made up of copper, tin and aluminium.

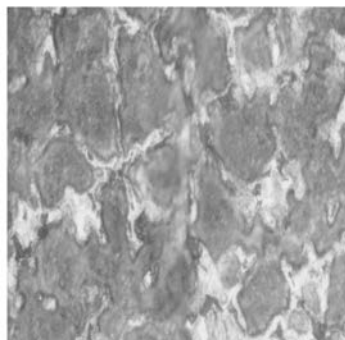


Fig 16.10 Shows microstructure of bronzes

Table 16.3 The following table gives the composition, properties and uses of various bronzes.

Sl No.	Type	Composition	Properties	Uses
1.	Bell metal	82% Copper 18% Tin	Hard and brittle. It posses resonance	Making bells
2.	Gun metal	88% Copper 10% Tin 2% Zinc	Hard, tough and strong. Corrosion resistant to water	Bearings, bolts, nuts, naval applications.
3.	Phosphor bronze	89% Copper 10% Tin 1% Phosphorous	High endurance limit, hard, strong, corrosion resistant to seawater.	Gears, springs, bearings etc.
4.	Speculum metal	67% Copper 33% Tin	High reflective surface after surface finishing	Used for telescope
5.	Silicon bronzes	95% Copper 5% Silicon	Strong, high corrosion resistances	Tanks, presser vessels,
6.	Beryllium bronzes	88% Copper 1.5 Beryllium 0.2% Cobalt	Good fatigue, creep resistance, high electrical conductivity.	Surgical instruments, bolts, etc.
7.	Aluminum bronzes	80% Copper 20% Aluminium	Hard, strong, light, malleable.	Corrosion resistant vessels, blades, bearings etc.

16.2.2 Aluminum and Its Alloys



Fig 16.11 Microstructure of pure aluminium

Aluminium is a white lustrous metal available in the earth as pure and as ore as well. It is highly malleable and ductile and is a good conductor of heat and electricity. Pure aluminium is highly resistant to corrosion and is easily cast to the required shape. It has good machinability and cold and hot working. It is widely used in wire and some industrial applications like heat exchanger. It can be alloyed with copper, zinc, tin and nickel. Figure 16.11 shows microstructure of pure aluminium.

16.2.2.1 Aluminum and Copper Alloys

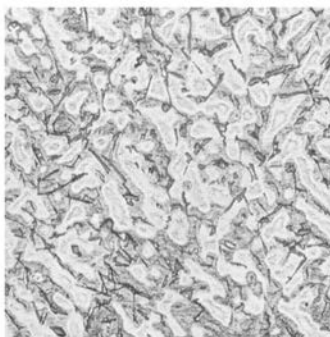


Fig 16.12 Microstructure of aluminium—4% copper alloy

An aluminium-rich copper microstructure is as shown in Figure 16.12. The maximum solubility of copper in aluminium is 5.7 at 548°C and the solubility reduces to 0.2% percent at 0°C. The alloy containing between 2% and 5% copper will have effective age hardening and produces CuAl_2 during heat treatment.

Table 16.4 The following table gives composition, properties and uses of various aluminium alloys.

Sl. No.	Type	Composition	Properties	Uses
1.	Durallunium	94% Aluminum 0.5% Magnesium 4% Copper	Good conductor of heat, high	Air craft, automobile, electrical cable etc.

(Contd)

(Contd)

Sl. No.	Type	Composition	Properties	Uses
		0.5% Iron 0.5% Silicon 0.5% Manganese	strength at high temperature	
2.	Y-alloy	95% Aluminum 2% Nickel 4% Copper 1.5% Magnisium	Good conductor of heat, high strength at high temperature	Piston cylindre, gear box, propeller blades etc.
3.	Aluminum–Silicon–Copper alloys.	90.4% Aluminium 6% Silicon 3% Copper 0.6 Magnisium	High temperature resistances, high strength,	Uses are structural framework, engine arts, overhead cables, refrigeration
4.	Aluminum–zinc alloys	67% Aluminium 31.6% Zinc 2% Magnisium	High tensile strength, stress corrosion resistances	Air craft, radio equipments.
5.	Aluminum—Silicon alloys	% Aluminum 13% Silicom	High tensile strength, stress corrosion resistances	Marine applications, gear boxes, radiators etc.

EXERCISES

- Classify the steels based on carbon percentage and mention two applications for each of them.
- Give any two examples of applications of the following materials:
 - Austenitic stainless steel
 - Low carbon steel
 - High speed steels.
 - High carbon steel
- Write the applications of the following:
 - Stainless steel
 - High carbon steel
 - Aluminium alloys
 - Copper base alloys
- Explain the properties of any two types of cast iron.
- Mention at least three different types of cast irons. How do they differ with respect to composition and structure?
- Give the composition, structure and uses of the following
 - Spheroid graphite iron
 - Malleable cast iron
 - Gray cast iron
- Discuss briefly the structure, properties and uses of gray cast iron, spheroid graphite iron and white iron.
- Draw the microstructure and explain the properties and uses of any two types of cast iron.
- Differentiate between gray cast iron and spheroid graphite iron with reference to their microstructure, composition, properties and applications.

10. Explain the properties of any two types of cast iron.
11. Mention at least three different types of cast iron. How do they differ with respect to composition and structure?
12. Write a note on copper base alloys.
13. Write short notes on Cu–Zn alloys
14. Name at least four important aluminium base alloys. Give composition and their applications.
15. Give the name and composition of two important copper-base alloys used for (i) Bush bearing and (ii) Idols and statues.
16. Explain the following
 - (i) Family of cast iron
 - (ii) Copper and its alloys
 - (iii) Classification of steels
17. Write a note on Al–Si alloys.
18. Discuss the important properties and applications of the following alloys:
 - (i) Gray cast iron
 - (ii) Brasses
 - (iii) Spheroid graphite iron
 - (iv) Al–4% Cu Alloy.
19. Write a brief note on composition, properties and applications of (i) Brasses and (ii) aluminium–silicon alloys. Consider two important types in each:
20. Mention the composition, properties and uses of the following
 - (i) bush bearing
 - (ii) Idols/statues
21. Mention composition, properties and uses of:
 - (i) Stainless steel
 - (ii) High-speed steel
 - (iii) Muntz metal

OBJECTIVE -TYPE QUESTIONS

1. Metals other than iron is called
 - (a) Metallic materials
 - (b) Ferrous metals
 - (c) Non-ferrous metals
 - (d) Metallic compounds
2. Steel is example for
 - (a) Nonmetals
 - (b) Ferrous metals
 - (c) Nonferrous metals
 - (d) Nonmetallic materials
3. In plain carbon steel, carbon varies from
 - (a) 0.008%–1.8%
 - (b) 0.08%–1.55%
 - (c) 0.08%–2%
 - (d) 0.08%–0.8%
4. Low carbon steel will not be respond for hardening treatment because
 - (a) It has low carbon
 - (b) It has high alloying elements
 - (c) It has low alloying elements
 - (d) It has high carbon
5. Chisel is example for
 - (a) Low carbon steel
 - (b) High carbon steel
 - (c) Medium carbon steel
 - (d) All of the above

226 | Properties of Ferrous and Non-ferrous Materials

6. Hardfield austenitic manganese steel contain
 - (a) 11%–16% manganese
 - (b) 2%–6% manganese
 - (c) 8%–10% manganese
 - (d) 2%–4% manganese
7. Martensitic stainless steel contain
 - (a) Carbon, chromium and nickel
 - (b) Carbon, nickel and vanadium
 - (c) Carbon, nickel and manganese
 - (d) Nickel, manganese and chromium
8. High speed steel used as
 - (a) Bearing materials
 - (b) Iron sheets
 - (c) Cutting tools
 - (d) Casting materials
9. Gray cast iron contain
 - (a) Circular graphite
 - (b) Graphite combined with iron
 - (c) Flake graphite
 - (d) All of the above
10. Nodular cast iron contains
 - (a) 2%–3.5% carbon
 - (b) 2%– 6% carbon
 - (c) 4.35%– 6.67% carbon
 - (d) 3.2%– 4.2% carbon
11. Brass is an alloy of
 - (a) Copper and tin
 - (b) Copper and nickel
 - (c) Copper and zinc
 - (d) Copper and aluminium
12. The brass which is used for architectural work is called
 - (a) Yellow brass
 - (b) Red brass
 - (c) White brass
 - (d) Navel brass
13. Gun metal contain
 - (a) More than 80% of copper
 - (b) 50% copper
 - (c) Less than 50% of copper
 - (d) All of the above
14. Aluminum is a
 - (a) Good conductor of heat
 - (b) Good conductor of electricity
 - (c) Highly resistant to corrosion
 - (d) All of the above
15. Y-alloy is used for
 - (a) Piston cylinder in engine
 - (b) Structural framework
 - (c) Radio equipments
 - (d) Marine applications

ANSWERS

1.	c	2.	b	3.	b	4.	a	5.	b	6.	a
7.	a	8.	c	9.	c	10.	d	11.	c	12.	c
13.	a	14	d	15.	a						

chapter 17

Powder Metallurgy

INTRODUCTION

Powder metallurgy is the art of fabrication of metal objects from a powder rather than casting of molten metal or forging at some temperatures. This process becomes economical in producing small components like gears for small machines, carbide-tipped tools for machining, etc. Because this technique is generally adopted to make a tool made of metals like tungsten, melting becomes unsuitable due to the large difference in the melting points of the other elements and hence cannot be alloyed to obtain specific properties.

In the bonding process, the powder particles are first compressed to the desired shape in a mould. The compacted powder is then taken out and heated or sintered to the desired temperature for developing the strength of the part. During sintering, the metal powder remains in the solid state throughout the process. The properties of this solid are similar to cast component of similar composition.

The sequence of operations involved in the powder metallurgy process is shown in the following schematic flowchart (see Figure 17.1).

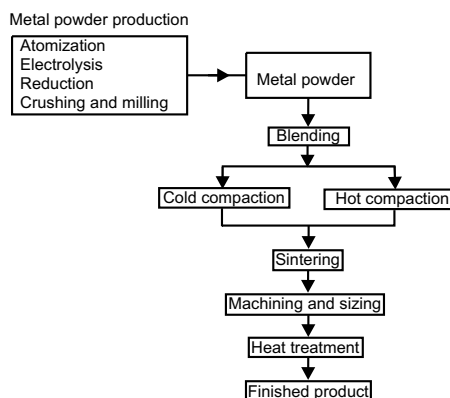


Fig. 17.1 Sequence of operations involved in the powder metallurgy

17.1 METHOD OF PRODUCING POWDERS

All metals cannot be manufactured in a similar way because of their individual physical and chemical characteristics but all metals can be produced in the powder form. The procedure varies widely due to the size and shape of particles obtained from the various processes. The particle size of the powder used for the process varies from 1 to 100 μm . But for most metallurgy processes, particles of range 10–20 μm are used.

Most commonly used methods of manufacturing metallic powders are discussed in the following.

17.1.1 Atomization of Molten Metal

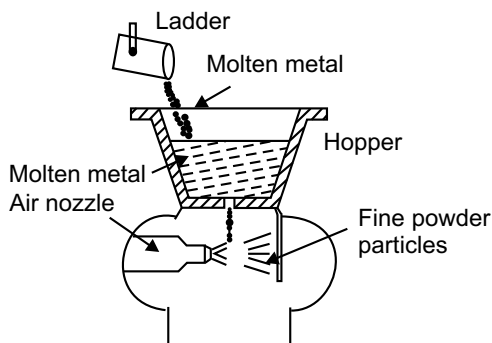


Fig. 17.2 The atomization techniques for producing metal powder

The atomization or metal-spraying techniques are widely used to produce powder from many of the low-temperature metals such as lead, aluminium, zinc and tin. The particles are irregular in shape and are produced in many sizes. The molten metal is forced through a hopper into a stream of air or water as indicated in Figure 17.2, and the liquid metal solidifies into particles of wide ranges of size. The factors which govern the particle size are nozzle size, metal flow rate, temperature and pressure.

17.1.2 Electrodeposition

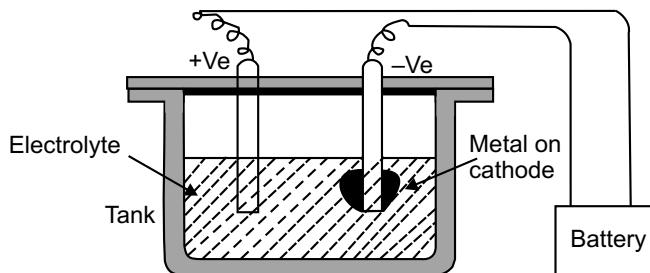


Fig. 17.3 Electroplating of a metal

Electrolytic deposition is a common method of producing the metal powders and this process is similar to electroplating as shown in Figure 17.3. The metal plates are placed in an electrolytic tank with the plate as anode and the other plate as cathode. High ampere current produces the powder deposits on the cathode to the required fineness. The cathode plates are taken out and after drying, the deposit is scrapped. This method is mainly used for manufacturing copper, tin, zinc and iron.

17.1.3 Reduction of a Compound

The reduction method reduces the metal oxides to powders by contact with oxygen at temperature below the melting point. Iron oxide is reduced to sponge iron at a temperature below the melting point of the iron. The sponge iron is crushed and gets powdered. Coke and lime stone are used to provide reducing atmosphere. Tungsten, molybdenum, nickel and cobalt are also produced commercially by this method.

17.1.4 Crushing and Milling

Crushing and milling result in coarse particles and are used mainly for producing magnesium powders. The raw materials are supplied through a hopper and the metals are broken down by the milling process by crushing. Due to the friction and cutting action of the roller at high load, the metal is crushed into a fine powder. Large amount of metallic powder can be obtained by this process. An annealing process is carried out to reduce the work hardening effect.

17.2 BLENDING OF POWDER

The blending of powder is the mixing of metal with lubricants. Various sizes of powder particles are mixed together to change the characteristics such as flowability or density. The ductile metals are combined in an alloy of two or more metals with a lubricant and then pressed or briquetted in a hard steel die. Refractory metals with high melting points are compacted with a paraffin wax. Cemented carbides are formed by bonding the hard, heat-resistant cobalt together with a metal. Also, the lubricants are introduced during the operation to reduce the friction. This results in reducing the wear of roller, cutter, and lowering the pressure required for compaction. Blending can be either wet or dry. Wet blending has an advantage of reducing the dust.

17.3 COMPACTION (COLD AND HOT)

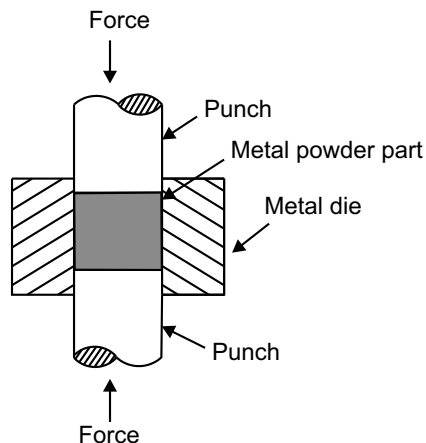


Fig. 17.4 Green compaction of powder

Pressing is the process of converting powder into green compacts with shapes and sizes corrected to the desired accuracy. Powders are pressed to shape in steel dies under pressure to obtain adequate density. First, pour the powder into the die cavity and then apply pressure from both the top and bottom of the die as shown in Figure 17.4. This is called cold compaction. Pressing of metal powder in a die along with heat is called hot compaction. Generally, for high volume parts, carbide die is used. The powder is compressed approximately to one-third of its original volume. The density and hardness increase with the pressure. The pressure can be applied either mechanically or hydraulically.

17.4 PRE-SINTERING AND SINTERING

Pre-sintering is an operation of heating a green compact to a temperature below the final sintering temperature. This operation improves the strength of the compacted part and removes the lubricants.

Heating of powder compacts in a furnace below the melting point of the constituents under a controlled atmosphere is called sintering. In this process, the solid bodies are bonded by atomic forces. At this stage, all the possible final strength and hardness are developed in the finished product. Temperature and time are the important variables governing this process. The temperature used in sintering is usually well below the melting point of the main powder constituent.

Many attempts have been made to combine the pressing and sintering operations. Experiments have demonstrated that the compacted products obtained by this method have improved strength and hardness, greater accuracy and higher densities than the production obtained by the usual methods. Hot pressing is used to some extent in the manufacturing of commercial carbides along with sintering.

17.5 FINISHING OPERATIONS

The powder metallurgy products require close tolerance or sizing for final operation such as coining, machining, etc. Improved dimensional accuracy by cold working operation and better dimensional accuracy with increase in density can be achieved.

The main purpose of the machining process is to reduce the powder product to the required size and shape. Powder metallurgy is to press the metal powder directly to the required shape and size. However, it is difficult to produce certain shapes like grooves, side holes and threads in powder metallurgy. Hence they are generally machined in the same finished sintered block with conventional machining methods like turning, milling and drilling. The coining operation is similar to the sizing except that the sintered part is pressed in the die to reduce the void space.

Infiltration improves the physical properties by eliminating the voids which act as internal notches. In this operation, the metal compact is filled with low melting metal or alloy by capillary action. The iron part to be infiltrated is first made by sintering to about 900°C, and then copper or brass is placed on the part and send through the furnace the second time. The brass melts and the liquid is coated on surface of the porous part producing close to the required 100% density.

17.6 HEAT TREATMENT

All pressed metal parts may be heat treated and the best results are obtained with improved grain structure, better strength and hardness. Also, uniform structure can be obtained by heat treating of the powder metal parts under conventional heat treatment process.

17.7 CHARACTERISTICS OF POWDER AND ITS PARTS

The following are the characteristics of powder and its parts:

1. It is possible to combine the materials that cannot be alloyed by usual methods or cannot be welded and brazed. Lead in copper to form bearing surface, steel in copper to produce a self-brazing alloy and cermets (combination of ceramics with metal) are some of the examples.
2. The density, porosity and compressibility are controlled by distribution and size of the powder particle. Fine particles are used for better density, but it needs higher compacting pressure.
3. Flow rate gives the duration of time required to fill a cavity, and the density of the compacted parts depends upon the working pressure. Higher the density of the product, higher is the working pressure needed.
4. Green strength is the mechanical strength of the compacted part before sintering. During the mass production, low strength compacted powder possesses serious handling problems. Hence the compact should have good mechanical strength.
5. The metal powder should be of good quality. Any impurities in it will affect the briquette and sintering.
6. The cost may vary from a few hundred rupees to several thousand rupees for a small and simple part to a large complicated part respectively.
7. Tolerance as close as 0.01 mm/cm on dimension can be achieved. Sizing can be used to reduce this tolerance to half.
8. Generally, with the addition of iron powder, the powder metal parts are manufactured in the range of 10–25 kg/mm² of tensile strength; and with other additions, it is possible to achieve tensile strength up to 70 kg/mm².

17.8 APPLICATIONS OF SOME POWDER METALLURGY PARTS

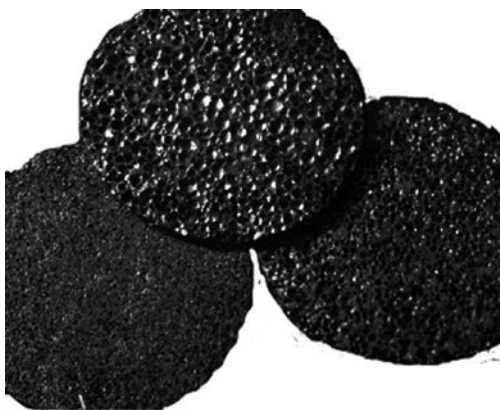


Fig. 17.5 Metal filter produced by powder metallurgy technique

Tungsten carbide particles with cobalt binder is pressed to shape and then sintered at a temperature above the melting point of the matrix material. The metal cobalt binds the particles tougher and gives strength and toughness to the final product. Most bearings are made from copper, tin and graphite

powders. An ideal bearing material is a porous compact. It is useful where positive lubrication is to be done, the parts which supply the lubrication for a life time. The lubricants are feed to shaft surface by capillary action when heat or pressure is applied (see Figure 17.5).



Fig. 17.6 Metal bushes produced by powder metallurgy technique

Brushes for motors are made by mixing copper with graphite to give adequate strength (see Figure 17.6). Tin and lead may also be added in small quantities to improve wear resistances. Gears for automobile, and oil pumps are produced by mixing the iron powder with graphite. Magnetic components are also produced by powder metallurgy. Carbide-tipped tools are manufactured by this method.

Cermets are a combination of ceramics and metal powder being bonded in a similar fashion to that of metal powder mixture. These materials provide high refractoriness, toughness and thermal shock resistance to the metal. The cermets are being used where abrasive resistance, heat resistance and impact strength are required.

17.9 ADVANTAGES OF POWDER METALLURGY COMPONENTS

The use of powder metallurgy parts is rapidly increasing and these can be produced economically when compared to the conventional manufacturing methods. Some of the advantages obtained by this process are as follows:

1. Products like sintered carbides can be produced only in powder metallurgy technique.
2. Porous bearing cannot be produced by any other method or process.
3. Tolerance of the order of 0.01 mm can be obtained.
4. The parts have good dimensional accuracy and excellent finish.
5. Metals, alloys and nonmetals can be mixed in any proportion.
6. Parts with desired porosity can be manufactured.
7. The process is very rapid.

17.10 DISADVANTAGES OF POWDER METALLURGY

Powder metallurgy has some limitations like mechanical equipment, thermal characteristics of powder and economical produces by other manufacturing process. Some of the limitations obtained by this process are as follows:

1. Metal powders are expensive and, in some cases, difficult to store.
2. Not all metals and alloys are suitable for this process.
3. Expensive equipments are required.
4. Die should be highly accurate and should withstand high temperature and pressure.
5. The process is limited for small components because it requires high pressure for pressing.
6. Some shrinkage occurs during sintering process.
7. Difficult to obtain complicated shapes.

EXERCISES

1. What is powder metallurgy technique? Explain the principle involved.
2. Explain the principal steps involved in the process of powder metallurgy components.
3. Write briefly about any two important characteristics of a metal part produced by powder metallurgy methods.
4. Why are conditioning and blending of powders needed? Explain briefly.
5. Explain the physical changes taking place in a powder compact. When it is sintered?
6. Explain the following: (i) Compacting and (ii) Sintering
7. Explain the terms compaction and sintering. What are the changes that take place during the process?
8. Draw a flowchart which summarizes the various processes and operations used in powder metallurgy.
9. List the various methods of powder production in powder metallurgy process. Describe any one in detail.
10. Describe with a neat flowchart the manufacture of a part using powder metallurgy technique.
11. Explain clearly the various operations involved in powder metallurgy technique for producing a spur gear.
12. What factors control the quality of powder metallurgy components? How are they controlled?
13. What are the practical applications of powder metallurgy components? List at least four items produced by powder metallurgy.
14. List the advantages and limitations of powder metallurgy.

OBJECTIVE -TYPE QUESTIONS

1. The powder metallurgy technique is used when _____.
 - (a) Melting becomes unsuitable due to the large difference in melting temperature
 - (b) Making an alloy is not possible due to the large difference in density
 - (c) Machining is not possible after casting
 - (d) All of the above
2. Atomization technique is used for the production of _____.
 - (a) Low temperature melting metals
 - (b) High temperature melting metals
 - (c) High density metals
 - (d) Low density metals

234 | Powder Metallurgy

3. Copper powder can be produced by _____.
 - (a) Reduction method
 - (b) Atomization technique
 - (c) Electrodeposition method
 - (d) Crushing and milling
4. In reduction method, _____.
 - (a) Iron ore gets reduced to metal oxide
 - (b) Tin ore gets reduced to metal oxide
 - (c) Bauxite ore gets reduced to metal oxide
 - (d) Gold ore gets reduced to metal oxide
5. In a crushing and milling process, _____.
 - (a) Metal is crushed into powder
 - (b) Large amount of powder can be obtained
 - (c) Powder obtained is due to friction and cutting action
 - (d) All of the above
6. Flow ability and density of the powder component depend upon _____.
 - (a) Volume of the metal
 - (b) Colour of the metal
 - (c) Size of the powder particles
 - (d) Amount of lubricants
7. The powder is compacted approximately to _____.
 - (a) Half of its original volume
 - (b) One-fifth of its original volume
 - (c) One-third of its original volume
 - (d) One-tenth of its original volume
8. Pre-sintering removes _____.
 - (a) Moisture
 - (b) Lubricants
 - (c) Colour
 - (d) All of the above
9. In the sintering process, _____.
 - (a) Solid bodies are bonded by atomic force
 - (b) Gives all the possible final strength and hardness
 - (c) Heating in a furnace below the melting point of at least one of the constituents
 - (d) All of the above
10. Infiltration technique _____.
 - (a) Improves the density
 - (b) Increases the voids in the solid
 - (c) Reduces the physical properties
 - (d) All of the above
11. An example for powder parts is _____.
 - (a) Metal filter
 - (b) Metal bushes
 - (c) Connecting rod
 - (d) All of the above
12. From the powder metallurgy, _____.
 - (a) Parts of desired porosity cannot be obtained
 - (b) Only different metal powders can be mixed at any proportion
 - (c) Metals and nonmetals can be mixed any proportion
 - (d) All of the above
13. Powder metallurgy process _____.
 - (a) Is an expensive process
 - (b) Is a slow process
 - (c) Is suitable for all metals and alloys
 - (d) Cannot produce porous bearing

14. Powder metallurgy technique can be used for _____.
 (a) Small components (b) Large components
 (c) Both for small and large components (d) All of the above
15. Cermets is a combination of _____.
 (a) Ceramics with nonmetals (b) Ceramics with lubricants
 (c) Ceramics with metals (d) Ceramics with graphite

ANSWERS

1.	a	2.	b	3.	c	4.	a	5.	d	6.	c
7.	c	8.	b	9.	d	10.	a	11.	d	12.	a
13.	a	14	a	15.	c						

chapter 18

Ceramic Materials

INTRODUCTION

The ceramic materials consist of compounds of metallic and nonmetallic elements that exhibit not only useful properties like strength and hardness, high melting temperatures, chemical resistance and low thermal and electrical conductivity, but also display brittleness and sensitivity to flaws. Ceramics include a wide variety of substances such as brick, stone, concrete, glass, abrasives, porcelain enamels, dielectric insulator, nonmetallic materials and high-temperature refractories.

The common ceramic products are made from common naturally occurring minerals such as clay and sand for the pottery, bricks, etc. The clay materials are the end result of a chemical reaction between the constituents of the earth and its environment. They are used as structural materials where there is resistance to high temperature and oxidation, such as in steel and glass manufacture.

Refractories such as carbides, nitrides and oxides (SiO_2 , Al_2O_3 , SiC and MgO) having high melting point and wear resistance are used in extractive metallurgy, cement kilns and glass manufacturing industries as protected lining materials.

18.1 CLASSIFICATION OF CERAMICS

The classification of ceramics is discussed in the following subsections.

18.1.1 Based on Fusing or Melting Temperature

On the basis of fusing or melting temperature, ceramics are classified as follows:

1. Low-temperature refractory
2. High-temperature refractory
3. Super-temperature refractory

The refractory materials whose melting temperatures are between $1,500^\circ\text{C}$ and $1,700^\circ\text{C}$ are called as low-temperature refractory materials. Refractories with melting temperatures between $1,700^\circ\text{C}$ and

2,000°C are considered as high temperature refractory materials. Similarly, materials with melting temperatures more than 2,000°C are considered as super-melting refractories.

18.1.2 Based on Nature of Reaction

On the basis of nature of reaction, ceramics are classified as follows:

1. Acidic refractories
2. Basic refractories
3. Natural refractories

On the basis of reaction in lining for a furnace, the refractories are classified into acidic and basic refractories. Acidic refractories contain acidic oxide in nature and examples for acidic oxides are SiO_2 and Al_2O_3 .

Basic refractories contain basic oxides in nature and examples for basic oxides are MgO , CaO , etc. Basic refractories have high refractoriness (about 1,800°C) and it has poor resistance and high coefficient of thermal expansion. Acidic refractories react with basic slag and basic refractories are attacked by acidic slag. Since acidic refractories are resistant to basic slag, it is used in basic electric and open hearth steel-making furnace.

Neutral refractories are inert to both acid and basic materials. Examples for neutral refractories are carbon, carborundum and chromate.

18.1.3 On the Basis of Chemical Composition of the Refractories

On the basis of chemical composition of refractories, they are classified as follows:

1. Aluminous refractories
2. Siliceous refractories
3. Insulating refractories

Fire clay refractories such as fire bricks, chamotte and aluminous clay are all aluminosilicates. Fire clays contain more silica (50%–80%) and have less alumina. Chamotte denotes refractory clay which is used as the nonplastic constituent of a refractor mixture.

Siliceous is a refractory material containing more than 93% SiO_2 . Refractory materials of this class are made up of fine grained quartz. Silica bricks have high refractoriness (1,700°C), resistance to deformation under load and thermal shock resistance. They are relatively lighter (density 1.8 g/cm³) and are also not deformed under load at high temperature. These are extensively used in roof arches as in open hearth furnaces and reverberatory furnaces. Silica bricks have been used as walls of coke ovens.

Generally, insulators are ceramic materials and they prevent the flow of electric current through them. Insulating refractories are used to prevent heat loss from the furnace by conduction. The raw material used depends on the operating temperature of the furnace. At low temperatures (less than 900°C), insulators like vermiculite and asbestos are normally used.

18.1.4 Based on the Nature of Materials

On the basis of nature of materials, the refractories are classified as follows:

1. Special refractories
2. Pure oxide refractories
3. Nonoxide refractories
4. Glass

Special ceramics are referred to in various parts of the world as technical ceramics, high-temperature ceramics and high-performance ceramics. These may be oxide refractories or nonoxide refractories or graphite. Special refractories are used in aerospace research, rocket designing, nuclear engineering, etc.

Pure oxide refractories, referred to as the pure alumina (corundum) refractories, are usually fabricated by fusion in an electric arc furnace and the melt is poured into suitable moulds. High porous structures are used as furnace insulation. Corundum crucibles are used for melting metals, alkalis, oxides and slag. Beryllia (BeO) refractories are used for making crucibles to melt uranium and thorium. It is extensively used in nuclear engineering as a moderator in view of its low neutron absorption.

Zirconia (ZrO_2) refractories have to be stabilized by the addition of oxides such as CaO and MgO in order to prevent its transformation to another crystalline form. Pure silica or fused silica is used to make laboratory ware such as crucibles and china dishes which are used for acid fusion, but these are attacked by alkaline fluxes. Fused quartz transmits visible and UV radiation and is used as containers for mercury lamps.

Nonoxide refractories include zircon, carbides, nitrides and borides. Zircon has a high melting point of $2,200^\circ\text{C}$, low thermal expansion, good spalling resistance and good resistance to abrasion. It is used as foundry moulds for melting aluminium and in glass-making furnaces. Silicon carbide is made by fusing together SiO_2 and coke in an electric furnace. Refractories formed from SiC , graphite and phosphoric acids are used for making spray nozzles, pumping units, etc.

Borides possess high refractories, hard and good spalling resistance. However, in view of their tendency to get oxidized, they are to be used only under reducing atmospheres. They are mostly used for making cermets. Zirconium boride bonded Cr and Mo, and titanium boride bonded to Mo have excellent resistances to the action of molten metals such as Al, Cu, Sn, etc.



Fig. 18.1 Varieties of glasses

Pure silica that is solidified from the liquid state without crystallization can be called a glass. Glass is a supercooled liquid which appears in a variety of shapes and colours as indicated in Figure 18.1. It is an inorganic product of fusion of one or more oxides of silicon, boron, calcium, magnesium, sodium, etc. The principal ingredient of glass is silica in the form of quartz sand. This may be amorphous or crystalline depending upon the heat treatment.

Glass can be drawn into tubes, rods, blowing, rolling, etc. Optical properties determine the suitability for making of glass for optical system. Similarly, conductivity, dielectric strength and dielectric losses determine the suitability of glass for manufacturing incandescent lamps, radio valves, x-ray tubes, etc.

Glass is not attacked by acids except HF, which converts silica into SiF_4 . The use of glass is based on its transparency and chemical inertness. It is used as window glass in houses and automobiles. Other uses include lenses, tableware, bulbs, chemical apparatus and glass fibre for reinforcement.

18.2 CHARACTERISTICS OF REFRACTORIES

The following are the characteristics of refractories:

1. It should be capable of retaining shape and structure at high temperature.
2. It must be capable of retaining its original form without cracking, splitting or cracking when refractory is suddenly exposed to high temperature.
3. It should not react with slag, molten metal and gases like CO , CO_2 , SO_2 , Cl , and H_2O .
4. It should be resistant to abrasion, wear, impact, etc.

18.3 PROPERTIES OF CERAMIC MATERIALS

The following are the properties of ceramic materials:

1. They have high hardness and are resistant to wear.
2. They have low tensile strength; hence, they generally fail due to stress concentration on cracks.
3. They possess much higher compressive strength.
4. Most of the ceramics possess low fracture strength and fail in a brittle manner.
5. Majority of the ceramic products are highly resistant to all chemicals except hydrofluoric acid and, to some extent, hot caustic solutions.
6. Oxides of ceramics are completely resistant to oxidation even at very high temperatures.
7. Ceramics possess favourable properties at high temperatures and under oxidizing conditions.
8. A number of special glasses have been employed for selective transmission or absorption of particular wavelengths such as infrared and ultraviolet.

18.4 APPLICATION OF CERAMICS

18.4.1 Traditional Ceramics



Fig. 18.2 Traditional chinaware

Traditional ceramic items are almost as old as the human race. After the first crude clay vessels were made, people learned to make them stronger, harder and less permeable to fluids by burning. With this knowledge, many useful ceramic products are produced by using natural clay called brick and tile. Clay-based bricks, strengthened and toughened with fibres such as straw, were among the earliest composite materials. The objects made by ceramics are technically shaped and burnt. Common examples of such traditional ceramic products are brick, tiles, pot and decorating articles. Some of the articles made by clays of pottery, chinaware, porcelain, SiO_2 , Al_2O_3 , glass and cermets are shown in Figure 18.2.

18.4.2 Industrial Ceramics



Fig. 18.3 Various industrial ceramic parts

Varieties of industrial products are available in the market from common floor tile to nuclear fuel pellets as indicated in Figure 18.3. The composition, structure and properties of industrial ceramics, and their processing into both traditional and advanced materials are different with different applications. Products made from whiteware, abrasive ceramics, conductive ceramics and bioceramic materials are the advanced ceramic products. A majority of ceramic products are highly resistant to all chemicals except hydrofluoric acid and, to some extent, hot caustic solutions. Oxides of ceramics are completely resistant to oxidation even at very high temperatures. Magnesia, zirconia, porcelain, graphite, alumina, etc. are resistant to certain molten metals and are thus employed for making crucibles and furnace linings. Ceramics like glass are employed where resistance to attack from acids, bases and salt solutions is required. Glazed porcelain is used for chemical vessels.

18.4.3 Automotive Ceramics



Fig. 18.4 Various parts made by advanced ceramics

Advanced ceramic materials are used to make components for automobiles. Many types of glass have been used for the production of windows. Some advanced ceramics are used for making spark plugs, catalysts and catalyst supports for emission control devices, and sensors of various kinds in automobiles are shown in Figure 8.4.

18.4.4 Tribological Ceramics

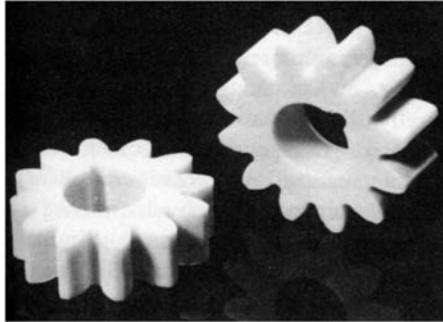


Fig. 18.5 Ceramic gear for oil pump

Ceramic materials are resistant to friction and wear. The most widely used tribological ceramic is coarse-grained alumina oxide (Al_2O_3) in the form small gear in oil pump (see Figure 18.5), wear-resistant parts as cutting blades in sugar industries and wear- and heat-resistance components in furnace. Al_2O_3 is preventing grain pullout in the metal and, thus, prevents damaging of the components.

18.4.5 Conductive Ceramics

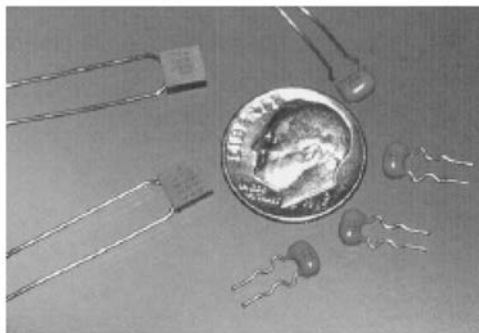


Fig. 18.6 Transistor, resistor and capacitor made by conductive ceramics

Some ceramics, however, are excellent conductors of electricity. Most of these conductors are advanced ceramics, modern materials whose properties are modified through precise control over their fabrication from powders into products. Electronically, conductive ceramics are used as transistors, semiconductors, thermoelectric, storage cells in memory systems and piezoelectric transducers as shown in Figure 18.6.

18.4.6 Nuclear Ceramics

Since ceramics are chemically resistant and because different compositions offer a wide range of neutron capture and scatter characteristics, they are employed in the generation of nuclear power and in the disposal of radioactive nuclear wastes. In nuclear-related applications, ceramics are of major importance. In nuclear power generation, oxide ceramics are used to make uranium and plutonium fuel pellets for both water-cooled and liquid-metal-cooled reactors.

18.4.7 Optical Ceramics

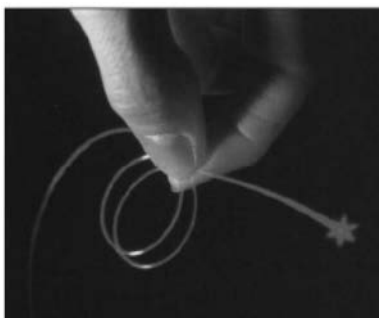


Fig. 18.7 Optical fibre made by ceramics

Advanced industrial materials are developed for use in optical applications. Optical materials derive their utility from their response to infrared, optical and ultraviolet lights. The most obvious optical materials are glasses. Many types of glass have been used for the production of windows and optical lenses. A number of special glasses have been employed for selective transmission or absorption of particular wavelengths such as infrared and ultraviolet. The index of refraction of normal glass can be varied from 1.46 to 2 thereby making them useful for all types of lens. Some of the optical fibres made by ceramics are shown in Figure 18.7.

18.4.8 Pigments

The ceramic colour industry is an old industry. Ceramic pigments or stains are made of oxide of compounds in combination with some special earth elements. Absorption of certain wavelengths of light by these species gives specific colour to the compound. For example, cobalt aluminate (CoAl_2O_4) and cobalt silicate (Co_2SiO_4) are blue; tin-vanadium oxide (known as V-doped SnO_2) and zirconium-vanadium oxide (V-doped ZrO_2) are yellow; cobalt chromite (CoCr_2O_3) and chromium garnet ($2\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$) are green; and chromium hematite (CrFe_2O_3) is black. A true red colour, unavailable in naturally occurring silicate materials, is found in the solid solutions of cadmium sulphide and cadmium selenide (CdS-CdSe).

EXERCISES

1. What are ceramics? Discuss their types and applications.
2. Classify the ceramics and give an example for each type.
3. Explain in detail the special and nonoxide refractories with examples.

4. What is meant by pure oxide refractories? Give examples.
5. Differentiate between pure oxide and nonoxide ceramics.
6. Explain in detail glass and its applications.
7. Write a note on the following:
 - (i) Industrial ceramics
 - (ii) Conductive ceramics
8. Briefly explain the characteristics of ceramics.
9. List the advantages and disadvantages of ceramics.
10. Write a note on traditional ceramics.

OBJECTIVE -TYPE QUESTIONS

1. Clay is a ceramic material and it is an end result of _____.
 - (a) Burning of sand along with air
 - (b) Chemical reaction between constituents of the earth and its environment
 - (c) Mixing of metallic and nonmetallic ceramics
 - (d) All of the above
2. The melting temperature of high temperature ceramics is _____.
 - (a) $800^{\circ}\text{C} - 1,000^{\circ}\text{C}$
 - (b) $1,000^{\circ}\text{C} - 1,500^{\circ}\text{C}$
 - (c) $1,700^{\circ}\text{C} - 2,000^{\circ}\text{C}$
 - (d) Above $2,000^{\circ}\text{C}$
3. Example for acidic refractories is _____.
 - (a) CaO
 - (b) CuAl_2
 - (c) SiC
 - (d) Al_2O_3
4. Basic refractories have _____.
 - (a) High refractories
 - (b) Noncorrosive
 - (c) Low coefficient of thermal expansion
 - (d) Resistant to acidic refractory
5. Siliceous refractory material contains _____.
 - (a) More than 90% Al_2O_3
 - (b) More than 90% CaO
 - (c) More than 90% SiO_2
 - (d) Less than 50% CaO
6. Insulator are ceramic materials and they prevent _____.
 - (a) Flow of heat
 - (b) Flow of electricity
 - (c) Low thermal expansion
 - (d) All of the above
7. Example of nonoxide refractory is _____.
 - (a) Al_2O_3
 - (b) Corundum
 - (c) MgO
 - (d) Carbides
8. Any substance that solidifies from the liquid state without crystallization is called _____.
 - (a) Carbides
 - (b) Nitrides
 - (c) Glass
 - (d) Pigments
9. Principal ingredient of glass is _____.
 - (a) Alumina
 - (b) Silica
 - (c) CaO
 - (d) MgO
10. Ceramics should _____.
 - (a) Retain the shape and structure at high temperature
 - (b) Not react with molten metal, slag and gas in metal melting
 - (c) Have resistance to abrasion
 - (d) All of the above

244 | Ceramic Materials

11. Crude clay vessel is an example for _____.
 (a) Industrial ceramics (b) Nuclear ceramics
 (c) Traditional ceramics (d) Conductive ceramics
12. Magnesia, zirconium, porcelain and graphite can be used as _____.
 (a) Traditional ceramics (b) Industrial ceramics
 (c) Conductive ceramics (d) Optical ceramics
13. Spark plug is an example for _____.
 (a) Advanced ceramics (b) Automobile ceramics
 (c) Wear-resistant ceramics (d) All of the above
14. Electrically conductive ceramics are used as _____.
 (a) Gears (b) Semiconductors
 (c) Bearings (d) All of the above
15. Optical ceramics can be responsive to _____.
 (a) Infrared light (b) Normal light
 (c) Ultraviolet light (d) All of the above

ANSWERS

1.	b	2.	c	3.	d	4.	a	5.	c	6.	d
7.	d	8.	c	9.	b	10.	d	11.	c	12.	b
13.	d	14.	b	15.	d						

Corrosion of Metals and Alloys

INTRODUCTION

Most common metals and their alloys are attacked by ordinary environments such as atmosphere, water or aqueous solutions to form compounds of the metal. Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation. The metal corrosion can be defined as the destructive chemical attack of a metal through interaction with its environment and can result in a loss of function of the component or system. The chemical attack results in the oxidation of the metal and the formation of a corrosion product. Generally, the corrosion products produced are the oxides, hydroxides, hydrated oxides, carbonates and sulphides of the metal. The corrosion product is insoluble in the environment and forms a separate phase on the metal.

19.1 ELECTROCHEMICAL THEORY OF CORROSION

The phenomenon of corrosion can be explained with the help of electrochemical principles called electrochemical theory.

According to this theory, when a metal is exposed to an environment, oxidation of the metal takes place with the loss of electrons and some substances in the environment undergo reduction with the absorption of electrons. These two reactions do not take place at the same spot on the metal surface but on different areas which are not widely separated. The area over which the metal is attacked (oxidation) is called the anode and that at which the reduction takes place is called the cathode. Therefore, an electric current flows between these two areas through the environment thereby producing the corrosion product. The combination of anodic area, cathodic area and the aqueous solution (water vapour adsorbed over the metal surface) constitutes a galvanic cell over the metal surface. More the number of galvanic cells formed, more is the corrosion and vice versa.

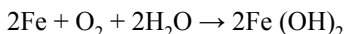
The formation of anodic and cathodic areas is due to the inequalities in the amounts of oxygen reaching different parts of the metal surface. This is called 'differential aeration'. The aerated areas become cathodes, and the non-oxygenated areas become anodes and suffer corrosion. Seawater layer is another example of differential aeration.

The classical example of corrosion is rusting of iron. When iron rusts, its oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is formed by the electrochemical reaction between iron, water and oxygen. During this reaction, iron (Fe) at the surface of a component undergoes a number of simple changes. According to the electrochemical theory, the following reactions are involved:

$\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}$ (anodic reaction), $+2\text{e}$ electrons the iron atom can lose some electrons and become a positively charged ion. This allows it to bond to other groups of atoms that are negatively charged like water (H_2O) and oxygen (O_2) from the atmosphere.

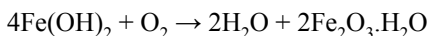


Negatively charged material can be combining with iron and develops iron hydroxide.



Iron + Water with oxygen $\rightarrow$ Iron hydroxide

Further, oxygen dissolves quite readily in water and further reacts with iron hydroxide.



Iron hydroxide + Oxygen $\rightarrow$ Water + Hydrated iron oxide (brown rust)

The brown rust which is precipitated as a result of secondary reactions is porous and encourages further corrosion.

19.2 GALVANIC CELL

The galvanic corrosion occurs when two different metals electrically contact each other and are immersed in an electrolyte. For galvanic corrosion to occur, an electrically conductive path and an ionically conductive path are necessary. Corrosion occurs when two dissimilar metals are placed in contact with each other in the presence of an electrolyte, such as salt water, forming a galvanic cell and produce some electromotive force (EMF). The potential difference which exists between the two electrodes because of cell reaction with the open circuit is called electromotive force or EMF of the cell and is expressed in volts. The EMF of such a cell is, therefore, directly proportional to the intensity of chemical reaction taking place in it.

Working of a galvanic cell is illustrated with the help of Daniel cell in Figure 19.1.

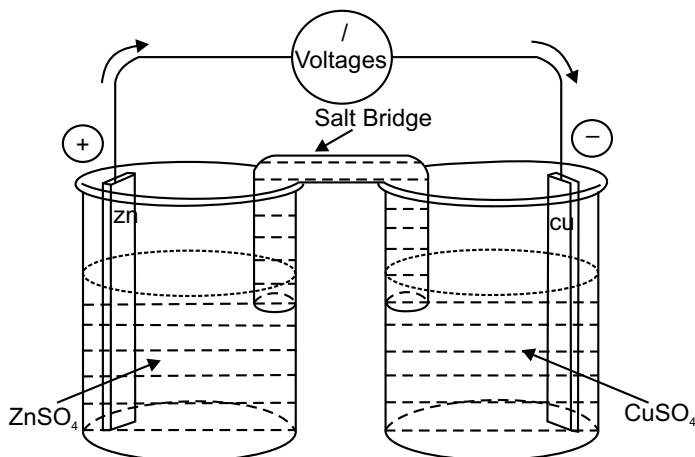
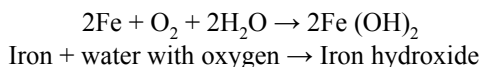


Fig. 19.1 Galvanic cell or Daniel cell

Please insert as given below



Daniel cell consists of two electrodes—zinc electrode dipped in zinc sulphate solution and copper electrode dipped in copper sulphate solution. Internally, the two electrolytic solutions are connected with the help of a salt bridge or a porous membrane and externally they are connected to a voltmeter. The cell may be represented as



This cell produces electricity energy because of the following:

1. The zinc metal passes into the solution as metal ions liberating electrons as $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$. Hence, at the Zn electrode, oxidation takes place. The electrode where oxidation takes place is called oxidation electrode or anode.
2. Copper ions (Cu^{+2}) of copper sulphate solutions absorb electrons to form metallic copper as $\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$. Thus, reduction takes place at the copper electrode. Therefore, the electrode at which reduction takes place is called reduction electrode or cathode.

Hence, the movement of electrons produces a definite amount of energy which is measured in terms of volts as EMF of the cell. A galvanic cell, therefore, is made up of two half-cells known as oxidation half-cell and reduction half-cell. Correspondingly, the reactions taking place at each electrode are termed as ‘half-cell reactions’.

Galvanic corrosion is often utilized in sacrificial anodes. For example, zinc is often used as a sacrificial anode for steel structures, such as in pipelines or docked naval ships. Galvanic corrosion is of major interest in the marine industry and also anywhere where water is in contact with pipes or metal structures. A galvanic cell can also be formed if the same metal is exposed to two different concentrations of electrolyte. The resulting electrochemical potential then develops an electric current that electrolytically dissolves the less noble material.

19.3 ELECTRODE POTENTIAL

In an electrochemical cell, each electrode is in contact with the electrolytic solution. Each electrode sets up a potential corresponding to oxidation and reduction reactions at the surface of separation of the metal and the solution. This potential is known as ‘electrode potential’.

If the potential developed is because of oxidation, then it is said to be ‘oxidation potential’ whereas the reduction potential is the electrode potential developed at the cathode because of reduction.

The single electrode potential is the difference in potential between the electrode and electrolytic solution. There is not a reliable method known for determining the absolute potential of a single electrode. However, it can be measured indirectly by coupling the electrode whose single electrode potential is to be measured with a reference electrode and measuring the EMF of a resulting cell with the help of a potentiometer. The choice of a reference electrode in a particular situation depends on the nature of the substance in solution. The following are the two types of reference electrodes:

1. Primary reference electrode
2. Secondary reference electrode

19.3.1 Primary Reference Electrode

Hydrogen electrode is used as the primary reference electrode. A simple type of standard hydrogen electrode (SHE) is shown in Figure 19.2.

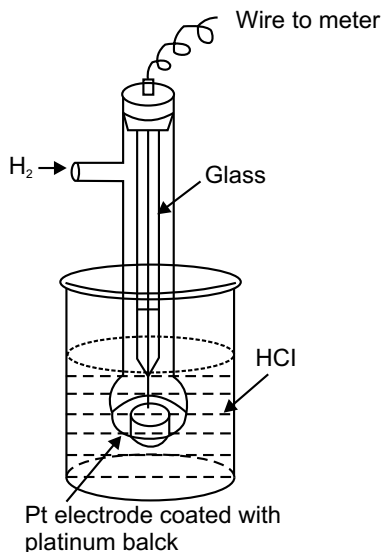
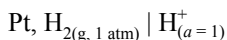


Fig. 19.2 Standard hydrogen electrode

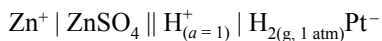
Hydrogen gas at 1 atm pressure in contact with solution of hydrogen ions constitutes a hydrogen electrode and can be represented as follows:



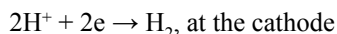
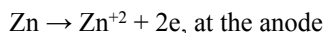
A rectangular piece of platinum foil, which is platinized, is connected to a piece of platinum wire sealed in a glass tube. A glass jacket encloses the tube carrying the platinum foil. The jacket is closed at the top and open and widened at the bottom. A side tube attached to the jacket admits hydrogen at normal atmospheric pressure which escapes through two holes made in the widened part of the jacket at a level mid-way between the platinum foil. The whole apparatus stands in a beaker containing HCl solution having effective concentration of hydrogen ions equal to 1 g H⁺ per litre, i.e., activity is equal to unity.

This particular electrode is known as standard hydrogen electrode (SHE), because both hydrogen gas and hydrogen ions are present in their standard states. The SHE is arbitrarily assigned a potential of 'zero' volt at all temperatures. All other potentials expressed on this basis are referred to as the potentials on the hydrogen scale.

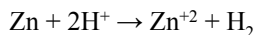
The half-cell whose potential (single electrode potential) is desired is combined with this SHE to form a complete cell whose potential is determined potentiometrically. Complete cell could be represented as follows:



The half-cell reactions are



The overall reaction is



The EMF of the cell measured potentiometrically can be written as follows:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{anode}} + E_{\text{cathode}} \\ &= E_{\text{Zn|ZnSO}_4} + E_{\text{SHE}} \\ &= E_{\text{Zn|ZnSO}_4} + \text{Zero} \end{aligned}$$

Therefore, $E_{\text{Zn|ZnSO}_4} = E_{\text{cell observed}} = 0.763 \text{ V}$

19.3.2 Secondary Reference Electrode

Owing to the difficulties involved in maintaining the purity and pressure of hydrogen gas and the unit activity of hydrogen ions in solution, the use and setting of SHE is not always convenient in practice. Therefore, several secondary or subsidiary reference electrodes are used. The most commonly used is the calomel electrode.

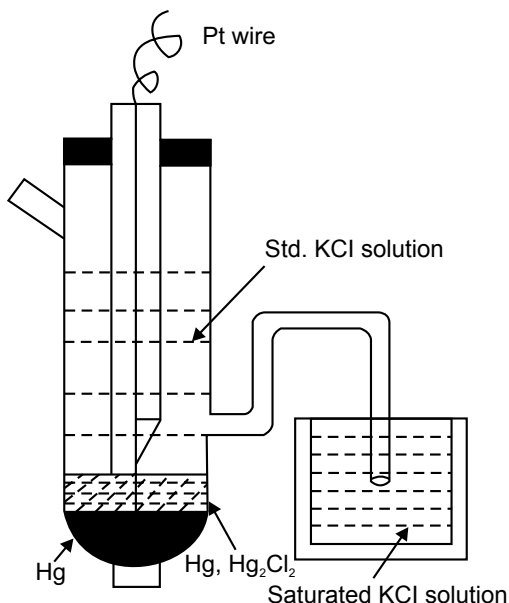
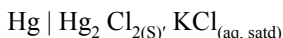
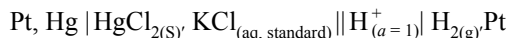


Fig. 19.3 Calomel electrode

The calomel electrode consists of a glass tube having a side tube on each side as shown in Figure 19.3. A layer of mercury is covered with a paste of mercurous chloride and mercury. The rest of the vessel is filled with a standard solution of potassium chloride. A platinum electrode is dipped in mercury to make the electrical contacts. This set up forms a half cell. Connection with another half-cell can be made using the side tube and it can be represented as follows:

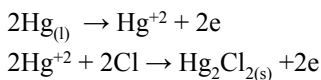


This saturated calomel electrode has an EMF of -0.2415 V at 25°C . For the measurement of the potential of standard calomel electrode, the half-cell is connected to a SHE as follows:

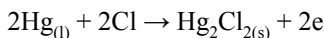


Depending on the half-cell whose electrode potential is to be determined, calomel electrode can be used as an anode or a cathode.

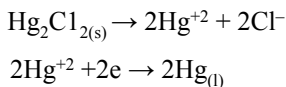
If the calomel electrode acts as anode, the following is the reaction:



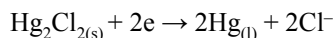
The overall reaction is



With the result, the concentration of chloride ions in solution decreases. If the calomel electrode acts as a cathode, the reaction is as follows:



The overall reaction is



Thus, the concentration of chloride ions increases. Therefore, the calomel electrode is ‘reversible’ with respect to chloride ions. With the help of reference electrodes, therefore, the electrode potential of the half-cell under consideration can be evaluated with the help of potentiometric technique.

19.4 STANDARD ELECTRODE POTENTIAL AND ELECTROCHEMICAL SERIES

If the concentration of the ions is unity and the temperature is 25°C, the potential of the electrode is termed as the ‘standard electrode potential’ (E°). The magnitude of the standard electrode potential of an electrode determined the tendency of the electrode reaction (half-cell reaction). The standard electrode potentials are measured using an SHE and hence, they are referred to as the potentials on the hydrogen scale.

The arrangement of elements in the decreasing order of their standard electrode potentials is called electrochemical series or galvanic series. It predicts the reactivity of elements and their behaviour with respect to other elements. Following is the small list of elements in the electrochemical series based on the reduction potentials.

Electrode system	Half-cell reaction	E° , V
Pt, F_2/F^-	$\text{F}_2 + 2\text{e} \rightarrow 2\text{F}^-$	+3.0600
Cl_2/Cl^-	$\text{Cl}_2 + 2\text{e} \rightarrow 2\text{Cl}^-$	+1.3595
Ag/Ag^+	$\text{Ag}^+ + \text{e} \rightarrow \text{Ag}$	+0.7990
Cu/Cu^+	$\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}$	+0.3370
H_2/H^+	$2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$	+0.0000
Fe/Fe^{2+}	$\text{Fe}^{2+} + 2\text{e} \rightarrow \text{Fe}$	-0.4400
Zn/Zn^{2+}	$\text{Zn}^{2+} + 2\text{e} \rightarrow \text{Zn}$	-0.7618
Li/Li^+	$\text{Li}^+ + \text{e} \rightarrow \text{Li}$	-03.405

Thus, fluorine has the maximum positive value hence it has the maximum tendency to accept electrons to undergo reduction. On the other hand, lower the standard potentials, lesser is the tendency of the half-cell reaction to take place in the direction of reduction. Hence, lithium has the maximum tendency to lose electrons and get oxidized to Li^+ ions.

The latest convention adopted by IUPAC International Union of Pure and Applied Chemistry for the values of electrode potentials is as follows:

1. If the electrode reaction, when connected to the SHE, involves reduction (i.e., consumption of electrons), the electrode potential is given a positive sign. Thus, when the copper electrode dipped in a solution of copper salt is connected with a SHE, reduction occurs at the copper electrode as $\text{Cu}^{+2} + 2\text{e} \rightarrow \text{Cu}$. Accordingly, its reduction potential is positive which has got the value of +0.3370 V.
2. If the electrode reaction, when connected to SHE, involves oxidation (i.e., liberation of electrons), the electrode potential is given a negative sign. Thus, the zinc electrode dipped in zinc sulphate solution undergoes oxidation when connected with a SHE as $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}$. Hence, the potential developed due to this process is given a negative sign and it has got the value of -0.7618 V.

19.5 TYPES OF CORROSION

Corrosion can be classified as follows based on the method of corrosion:

1. Uniform corrosion
2. Galvanic corrosion
3. Pitting corrosion
4. Stress corrosion

19.5.1 Uniform Corrosion

If the destruction of the metal is uniform throughout the metal surface, then it is called uniform or general corrosion. This type of corrosion is not common. It is encountered when the metal is acted upon by the action of strong alkalis or strong acids. In such cases, the destruction of the metal takes place at a constant rate.

19.5.2 Galvanic Corrosion

Galvanic corrosion occurs when two or more dissimilar metals in electrical contact are placed in an electrolyte. This results from the existence of a potential difference between the metals, which causes a flow of current between them. The EMF series and galvanic series have been used to predict the galvanic corrosion tendency of various metals. More active metals undergo oxidation and become the anode while the less active metal or the more noble metal acts as the cathode. Therefore, more active metal corrodes whereas the less active metal remains unaffected. Atmospheric humidity or water generally acts as electrolytes. Some common examples of galvanic corrosion are Pb–Sb solder around a copper wire, steel propeller shaft with bronze bearings, steel pipes in connection with copper for plumbing and steel screws in brass marine hardware.

Therefore, the easiest way to combat this corrosion is to select those metals which are close together as possible in the EMF series.

19.5.3 Pitting Corrosion

Pitting corrosion is a form of extremely localized attack, the rate of attack being greater at some areas than at others. Pitting is the most destructive form of corrosion. Pitting corrosion results in the

252 | Corrosion of Metals and Alloys

formation of pin holes, pits and cavities in the metal. The cavities or pinholes penetrate deep into the metal thus destroying the pipes or vessels of various types.

Pitting is usually the result of a breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathode areas. This generates corrosion current thereby forming the product as a localized area, anode. Continuous processes lead the destruction by the formation of pits.

Schematic representation of pitting corrosion is shown in Figure 19.4.

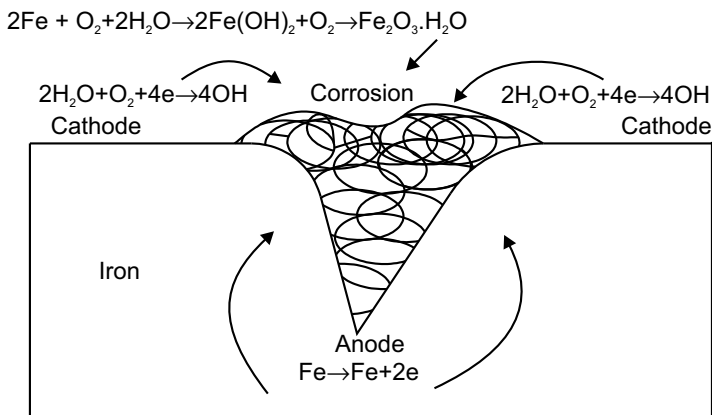
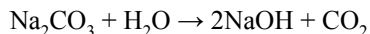


Fig. 19.4 Pitting corrosion on iron surface

19.5.4 Stress Corrosion

Stress corrosion or stress cracking is the combined effect of static tensile strength and the corrosive environment on a metal. The corrosive environment is generally alkalis, nitrates, ammonia and acids. This type of corrosion is seen in fabricated articles and at points where the stresses are more. Stresses are usually caused by heavy working like rolling, drawing or insufficient annealing. A typical example of stress corrosion is caustic embrittlement.

Caustic embrittlement is nothing but the breakdown of material in the presence of caustic alkalis. Usually it takes place in boilers made of mild steel and operating at high temperatures. Boiler water contains small quantities of sodium carbonate which is added during softening. Under high pressure and at higher temperature, it breaks up to give sodium hydroxide and carbon dioxide as follows:



This decomposition makes the boiler water alkaline. Alkali thus liberated attacks the boiler material at stressed parts like rivets and joints, making the metal brittle in nature. Continuous attack, thus, breaks the metal or the material. Hence it is called 'caustic embrittlement'. It can be prevented by adding sodium sulphate, tannin or lignin to the boiler water.

19.6 PREVENTION AND CONTROL OF CORROSION

Corrosion causes a loss in strength and decrease in ductility of a metal. Different methods are used for protecting the material against different types of corrosion. The following methods are commonly used:

1. Protection by proper design and selection of the metal
2. Modifying the environment
3. Change the metal potential
4. Protective coatings (metallic and organic)
5. Metal passivation

19.6.1 Proper Design and Selection of Metals

A proper selection of the material for any particular corrosive environment and a sound engineering design are the best means of controlling and, even, preventing corrosion.

The selection of the material plays an important role. The selected metal must be such that the corresponding environment has very little effect. For example, mild steel which will be attacked by a strong alkali should be avoided; two elements with a larger difference in their electrode potentials must be avoided to combat galvanic corrosion; materials with a larger stress should be avoided and sometimes alloys may be used.

The most effective and economical way of reducing losses due to corrosion starts at the design stage. A good design prevents the presence of inhomogeneities in the same metal. A good geometrical design avoids the formation of cracks, sharp corners, contact with absorbant materials and also avoids galvanic corrosion.

19.6.2 Change of Environment

In some cases, corrosion can be effectively controlled by changing the corrosive environment. The following are the common methods employed for the purpose:

1. Removal of corrosive constituent
2. Use of inhibitors
3. Change of operating variables

Removal of the corrosive constituent can effectively prevent corrosion. A few examples are removal of moisture from air by dehumidification using silica gel (in closed spaces); lowering of the relative humidity of air by increasing the temperature by 6° – 7°C in storage area; removal of oxygen from water from the environment by saturation with inert gas like nitrogen or by adding oxygen scavengers like hydrazine or sodium sulphite; removal of the acid from water by neutralization; removal of chloride ions from the environment to prevent pitting and stress corrosion cracking; removal of solid/dust particles from the environment by filtration and removal of salts from water by ion-exchangers.

Inhibitors are substances which are added in small quantities to corrosive environment to lower the corrosion rate. It reduces corrosion by acting as a barrier by forming an adsorbed layer in the cathodic or anodic process. The inhibitors are mostly used in the closed system. By changing the operating variables like temperature, velocity and pH, the electrolyte can reduce corrosion in many cases. Lowering of temperature and decrease in the velocity result in the decrease of corrosion.

19.6.3 Change of Metal Potential

In most of the cases, corrosion can be prevented by changing the electrode potential of the metal. Two common methods are (1) cathodic protection and (2) anodic protection.

19.6.3.1 Cathodic Protection

The cathodic protection is defined as the reduction or prevention of corrosion by making an anode into a cathode in the cell. The following are the two methods of applying cathodic protection to metallic structures:

1. Sacrificial anode method
2. Impressed current method

In each method, a direct current supply is made available for the protection of metal structures. The choice of the method to be used depends upon a number of economic and technical considerations.

In the sacrificial anode method, the metallic structure is made cathode by connecting it with the galvanic anodes which are more active than the metal structure to be protected. Thus, the structure will be protected by the sacrificing nature of the anode material. Since the potential is developed between them, no external power supply is needed.

In the impressed current method, the metallic structure to be protected is made cathode with the use of impressed current by connecting the negative terminal of the external power supply source and the positive terminal to an inert anode. The inert anode can be made of scrap steel, graphite or platinum group metals. Underground pipelines, underground cables, chemical equipments and steel structure exposed to seawaters are some of the typical examples of cathodic protection.

19.6.3.2 Anodic Protection

On the basis of theories of corrosion, all metals which have become anodes cannot undergo destruction at all potentials. The anodic protection is based on the fact that under certain range of potential, a metal or alloy becomes passive, resulting in the lowering or prevention of corrosion. Therefore, in this method, the metal to be protected is impressed with the positive current itself from an external source to bring the electrode potential to the passive range.

19.6.4 Protective Coatings

Corrosion of metals which occur due to chemical or electrochemical reaction of the environment can be prevented by separating the metal from the environment. The protective coatings can either be metallic or nonmetallic (organic). Both metallic and nonmetallic coatings should have the following characteristics:

1. Good resistance to corrosion
2. Perfect adherence to the underlying metal
3. Continuous so as to cover the metal surface completely

19.6.5 Passivation

The passivation is a reaction in which a layer of oxide deposits on the metal to make it passive in the form of hard nonreflective surface film that inhibits further corrosion. Aluminium naturally forms a corrosion-resistant film oxide and it prevents further oxidation when the metal is exposed to atmosphere. There are three ways to artificially passivate the corroded alloys—alclading, chromate coating and anodizing. Alclading is the process of metallurgically bonding a thin layer of pure aluminium to the metal. Chromate coating on the metal is a common way of passivating not only aluminium, but also zinc, cadmium, copper, silver, magnesium and tin alloys. Anodizing forms a thick oxide coating. This finish is more robust than the other processes and also provides good electrical insulation.

19.7 METALLIC COATINGS

Protection of metals from corrosion by using metal coatings has been in practice for over centuries. The coating of metal objects with noble metals has been in practice for at least four centuries. The metallic coatings are more durable, are more decorative and have better shielding against corrosion than the nonmetallic coatings.

The usual metallic coatings are of zinc, tin, nickel, aluminium and chromium. Lead and copper are also sometimes used. Different metallic coatings are also being used depending upon the end-use of such materials. Electroplating is the technique that is usually used for coating the metals.

Electroplating is an art of plating a metal over a metal with the help of electricity, and it is carried out in an electrolytic bath. In this method, the freshly cleaned base metal, which is to be protected, is made as the cathode in a bath of suitable electrolyte. In many cases, anodes of the metal being deposited are used. Generally, the plating solution consists of an electrolyte of the metal itself to be deposited together with additives to increase the conductivity. Sometimes, dyes are added to impart colour to the coating and to bring out the brightness of the coating. In many cases, conditions like the pH, by adding buffers, and temperature are to be maintained. The nature of the deposit depends upon the current density, bath composition, the temperature and the presence of other additives.

The article to be plated is first treated with organic solvent like CCl_4 to remove oils and greases. It is then made free from surface scales like oxides by treating with dilute acids like HCl or H_2SO_4 . Finally, it is washed and dried before it is plated. Examples of electroplating are discussed in the following.

19.7.1 Nickel Plating

In a nickel plating bath, nickel sulphate is the electrolytic solution providing the metal ion, boric acid is used to serve as a buffer to maintain the pH of the solution, ammonium chloride is added to increase the conductivity of the bath and addition of nickel chloride assists the solution of the anode. After the deposition is over within specific ranges of current density and temperature, the deposited metal is then subjected to mechanical polishing to give the required polish and shining and to enhance its decorative value. Nickel is far more extensively applied in electroplating than any other metal. It is more resistant to atmospheric corrosion than other metals except noble metals such as gold and platinum.

19.7.2 Chromium Plating

The chromium plating is usually done for its appearance but it also makes very good wear-resistant and hard surface materials. When chromium plating is done for appearance and corrosive resistance, it is usual to plate the material first with copper or nickel and then with chromium. A thin plating of chromium is by itself porous and does not prevent corrosion. The plating bath consists of 20%–30% chromic acid and a small amount of sulphuric acid and water. If a polished chromium surface is needed, the surface must be polished.

19.7.3 Silver Plating

The principal use of silver plating is for the tablewares because of its pleasing appearance and its resistance to attack by most foods (except those containing sulphur which tarnishes silver). An application of silver plating, which is considered important, during World War II was on airplane

engine bearings. Silver is applied to the interior of wave guides and on electrical contacts. Silver plating is done from solutions made by dissolving silver cyanide in a potassium cyanide solution. Brighteners such as carbon disulphide are added to form bright deposits.

19.7.4 Cadmium Plating

On aircraft parts, cadmium plating is generally done than any other plating. Steel parts are cadmium plated to improve the corrosion resistance. Parts made of copper and its alloys are cadmium plated to reduce the electrical potential between these parts and the adjacent steel or aluminium parts. The aluminium parts are seldom cadmium plated. The plating solution consists of sodium cyanide, cadmium oxide and caustic soda dissolved in water at the room temperature. A brightener like glue or molasses is added to brighten the plated surface. After the completion of the plating operation, the parts are removed and cleaned with warm water. Then the parts are dipped in chromic acid solution to remove the alkali from the surface (and also to passivate the cadmium) and are finally rinsed with water. Cadmium is much like zinc and also furnishes galvanic protection for steel.

19.7.5 Gold Plating

The most expensive application of gold plating is on jewellery. It furnishes a pleasing yellow colour which is resistant to tarnish. The deposit of alloys of gold produces different colours. Green gold with silver, rose gold with copper and white gold with nickel are some of the examples. Most of these coloured gold coatings contain about 85% gold. Gold plating is established using a dilute solution of gold cyanide.

19.8 ORGANIC PROTECTIVE COATINGS

Protection of metallic and wooden structure from corrosion is achieved by organic protective coatings like paints and varnishes. The protecting material is applied by brushing, spraying or dipping. The organic coatings are used also for the decorative purposes. The organic protective coating on the material not only offers a smooth surface, but also forms an impervious and adherent film thus giving protection from deterioration of the surface by corrosion. Varnishes are nothing but solutions of certain gums or resins in alcohol and linseed oil. Lacquers are transparent varnishes made from various resins.

19.9 DISADVANTAGES OF CORROSION

The following are the some of the disadvantages of corrosion:

1. Losses of metal leading to reduction in strength, and structural failure or breakdown.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g., bridges, cars and aircraft).
3. Loss of time in availability of industrial equipment during servicing of parts.
4. Reduced value of goods due to corrosion appearance.
5. Contamination of fluids in vessels and pipes by corrosion affects the human health and environment.
6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings.

7. Loss of important surface properties of a metallic component by corrosion leads to more wear and tear of the machine component.

EXERCISES

1. Define corrosion and explain its disadvantages.
2. Explain the electrochemical theory of corrosion with an example.
3. What is meant by hydrated iron oxide (brown rust)? Explain in detail the chemical reaction of iron.
4. With a neat sketch explain the working of galvanic (Daniel cell) cell.
5. Explain the mechanism of the process of corrosion by chemical reaction.
6. With a neat sketch explain hydrogen electrode.
7. What is meant by electrode potential? Explain the secondary reference electrode using calomel electrode.
8. Classify corrosion and explain any one type in detail.
9. What are the requirements for corrosion by galvanic action?
10. What is the cause of caustic embrittlement?
11. Explain pitting and stress corrosion in detail.
12. Indicate the four methods that may be used to prevent corrosion.
13. Name some corrosive-resistant metals and alloys.
14. Describe in detail the cathodic and anodic protection of metals.
15. Write a note on metallic coatings.
16. Explain the following:

(i) Nickel plating	(ii) Chromium plating
(iii) Silver plating	(iv) Cadmium plating

OBJECTIVE -TYPE QUESTIONS

1. Metal corrosion is _____.
 - (a) Erosion of the metal
 - (b) Chemical reaction of the metal with other metals
 - (c) Destructive chemical attack of the metal
 - (d) Wear of the metal
2. During corrosion, the area over which the metal is attached (oxidized) is called _____.
 - (a) Cathode
 - (b) Anode
 - (c) Neutral metal
 - (d) None of the above
3. Brown rust is the result of _____.
 - (a) Iron reacting with water
 - (b) Iron reacting with oxygen
 - (c) Iron reacting with both water and oxygen
 - (d) All of the above

258 | Corrosion of Metals and Alloys

4. In a galvanic cell, the reaction taking place at each electrode is called as _____.
(a) Oxidation half-cell (b) Reduction half-cell
(c) Half-cell reactions (d) All of the above
5. Oxidation potential is a _____.
(a) Potential developed due to the oxidation of metal
(b) Potential developed due to the reduction of metal
(c) Potential developed both in the oxidation and reduction of metal
(d) None of the above
6. Hydrogen electrode is a _____.
(a) Secondary reference electrode
(b) Primary reference electrode
(c) Reference electrode used to measure oxidation
(d) Reference electrode used to measure corrosion
7. Calomel electrode is an example for _____.
(a) Primary electrode (b) Secondary electrode
(c) Galvanic cell (d) Reduction half-cell reduction
8. Galvanic corrosion occurs due to _____.
(a) Two or more dissimilar metals in electrical contact
(b) Two or more dissimilar metals in atmospheric contact
(c) Two or more dissimilar metals in water contact
(d) All of the above
9. Corrosion due to static tensile strength and corrosive environment is called _____.
(a) Pit corrosion (b) Stress corrosion
(c) Galvanic corrosion (d) Uniform corrosion
10. Caustic embrittlement is a _____.
(a) Braking of metals in the presence of caustic alkalis
(b) Braking of metals in the presence of sodium sulphate
(c) Braking of metals in the presence of tannin
(d) Braking of metals in the presence of salt

ANSWERS

1.	c	2.	b	3.	c	4.	c	5.	a	6.	b
7.	b	8.	a	9.	b	10.	a				

Index

A

acidic refractories, 237
activation energy, 56
age hardening, 183
ageing treatment, 183
aircraft engines, 180
allotropic modification, 147
alloy steels, 216
alpha iron, 147–148
alumina, 240
aluminous refractories, 237
aluminum bronzes, 222
aluminum–silicon alloys, 224
aluminum–zinc alloys, 224
amorphous, 13
angle of contact, 116
Angstrom, 15
angular momentum quantum number, 5
anisotropic, 189
annealing, 101, 161, 169
annealing twin, 47, 73
antimony–bismuth, 133
argon, 6
array of atoms, 14
Arrhenius equation, 56
artificial ageing, 183
atomic mass number, 2
atomic number, 2
atomic radius, 17
atomic weight, 2
atoms, 13, 122
attractive force, 89
austenite, 150, 158, 160
 structure, 169
austenitic stainless steels, 217
autoclave process, 199
automobile bodies, 147
automotive ceramics, 240
azimuthal quantum number, 5

B

bainite, 160, 162
bakelite, 13
basic refractories, 237
Bauschinger effect, 80
bearing alloys, 139
bell metal, 222
beryllium, 6
beryllium bronzes, 222
binary alloy, 142
binary diagram, 133
body-centred cubic, 17
Bohr's theory, 4
Boltzmann constant, 56
boron, 125, 190
brass, 123
Bravais lattices, 15
brick, 240
brittle fracture, 88, 90–91
brittle material, 91
bronzes, 222
Burgers vector, 43

C

cadmium plating, 256
calcium, 6
camshafts, 59
carbon, 3, 52, 178
carbon nanotube, 189
carbon steel, 52
carburization, 52
case hardening, 178
cast iron, 147, 153, 218
caustic embrittlement, 252
cellulose, 13
cementite, 150
ceramic, 13
 matrix of, 191
ceramic materials, 237

cermets, 240
 chemical affinity factor, 124
 chemical bond, 7
 chemical vessels, 240
 chinaware, 240
 chlorine, 3
 chromium plating, 255
 chromium steels, 216
 civil structures, 147
 coarse-grained steels, 101
 coefficient of diffusion, 54
 cohesive forces, 89
 coining, 230
 cold working effects, 170
 columnar crystal, 119
 composite melt slurry, 193
 concentration gradient, 50, 53
 conductive ceramics, 241
 conventional strain, 63
 conveyers chain, 219
 coordination number, 17
 copper, 123, 220
 alloys of, 170
 copper-based alloys, 220
 corrosion, 245
 prevention and control of, 252–253
 corrosive environment, 109
 Cottrell and Hull theory, 107
 covalent bonds, 7
 crack nucleation, 88
 crack propagation, 88
 craze propagation, 91
 crank shafts, 182
 creep curve, 94
 creep fracture, 98
 creep limit, 98
 creep rupture strength, 98
 creep strength, 101
 critical cooling rate, 174
 critical radius, 118
 critical resolved shear stress, 71
 critical shear stress, 71
 crushing and milling, 229
 crystal growth, 47
 crystal imperfections, 39
 crystal lattice, 14

crystal structure factor, 124
 crystal systems, 15
 crystalline solids, 13
 crystallization, 78
 crystallographer, 25
 crystallography, 13
 crystals, 114
 Curi temperature, 148
 cyaniding, 180

D

Daniel cell, 246
 Debye–Scherrer method, 33
 defects, 39
 deformation, 63
 delta iron, 147
 dendrite growth, 118
 density packing factor, 17
 die casting, 193
 differential aeration, 245
 diffusion annealing, 171
 diffusivity, 55
 dislocation density, 78
 ductility, 77
 dyes, 8

E

edge defect, 39
 edge dislocation, 72
 elastic action, 63
 elastic deformation, 65
 elastic limit, 67, 88
 elastic strain energy, 91
 elastic strength, 68
 electrochemical theory, 245
 electrode potential, 247–250
 electrolytic deposition, 228
 electromagnetic radiation, 4
 electromotive force, 246
 electron configuration, 3
 electronic defects, 42
 electrostatic attraction, 7
 embryo, 114

endurance limit (EL), 108
 energy barrier, 56
 epoxies, 197
 epoxy composite, 189, 190
 equiaxed grain, 117, 119
 equilibrium diagram, 135
 eutecic mixture, 136, 154
 eutectic reaction, 139, 151
 eutectoid reaction, 151
 eutectoid transformation, 150

F

face-centred cubic, 17
 fatigue behaviour, 105
 fatigue fracture, 104
 fatigue life, 108
 fatigue strength, 108
 ferrite, 149, 150
 ferritic stainless steels, 217
 fibre-reinforced composites, 189
 filament-winding method, 199
 fine pearlite, 160
 flame hardening, 181
 flywheels, 220
 fracture strength, 76
 Frenkel defect, 42
 full annealing, 171

G

galvanic cell, 245
 galvanic corrosion, 246, 251
 gas carburizing, 179
 gaseous nitrogen, 180
 gating system, 193
 Gaussian error function, 55
 gear, 59
 gold plating, 256
 grain boundaries, 101
 grain boundary diffusion, 52–53
 grain boundary imperfection, 45
 grain growth, 117
 granular coal, 178
 graphite, 10, 153, 240

gray cast iron, 153
 Guinier-Preston zones, 183
 gun metal, 222

H

half-cell reactions, 247
 hand lay-up process, 197
 hard creep, 95
 hardenability, 177
 hardening stress, 175
 helium, 6
 heterogeneous nucleation, 114, 116
 hexagonal close-packed, 17
 hexagonal lattice, 28
 hexagonal planes, 22
 high alloys steels, 216
 high carbon steels, 151, 251
 high-speed steels, 217
 high-performance ceramics, 238
 homogenization, 50
 Hook's law, 65
 hot creep, 96
 Hume theory, 124
 hydrogen scale, 250
 hypereutectic cast iron, 153
 hypoeutectic cast iron, 148, 153–154
 hypoeutectoid steel, 151

I

ideal crystals, 39
 imperfections, 39
 impurity defect, 40
 induction hardening process, 181
 industrial ceramics, 240
 inert gas stream, 194
 infiltration, 230
 injection moulding process, 200
 inoculants, 117
 insulating refractories, 237
 insulators, 237
 interatomic attractions, 7
 interface energy, 116
 interfacial angles, 14

intermediate phases, 125
 internal combustion engine, 220
 internal stress, 167
 interplanar spacing, 34
 interstitial defect, 39, 41
 interstitial diffusion mechanism, 52
 interstitial solid solution, 123–124
 ion vacancy, 42
 ionic bond, 7
 iron, 125
 iron–carbon diagram, 168
 irregular loading, 106
 isothermal curve, 158
 isothermal heat treatment, 158
 isothermal transformation, 151
 isotones, 3
 isotope, 3

L

laminated composite, 190
 lattice constants, 14
 lattice parameters, 14
 low alloy steel, 216
 leaded yellow brass, 221
 ledeburite, 150, 154
 lithium chloride, 8
 low carbon steel, 170
 lower yield point, 74
 low-temperature refractory, 236

M

machinability, 167
 machining, 230
 magnesia, 240
 magnesium, 6
 magnetic iron, 147
 malleability, 77
 malleable cast iron, 219
 manganese steel, 216
 manhole covers, 218
 martensite, 159, 162
 martensitic stainless steels, 217
 Maxwell–Boltzmann distribution law, 56
 mechanical twin, 47

medium carbon steels, 151
 metal matrix composites, 196
 metal powder, 196
 metallic bond, 9
 metallic coatings, 255–256
 metallurgy, 125
 methane, 10
 microconstituents, 167, 188
 mild steel, 170, 214
 Miller indices, 25
 modulus of elasticity, 65
 modulus of resilience, 68
 molecular weight, 2
 Muntz metal, 221

N

natural ageing, 183
 natural refractories, 237
 naval brass, 221
 neck formation, 87
 negligible deformation, 88
 neutron, 1
 nickel plating, 255
 nickel steels, 216
 nitriding, 180
 nitrogen, 125, 178
 nodular cast iron, 220
 non-linear elastic properties, 69
 nonoxide refractories, 237–238
 normalizing, 101
 notch sensitivity, 81
 nuclear ceramics, 242
 nucleating agents, 119
 nucleation, 114, 128
 nuclei crystallizes, 114

O

offset method, 75
 oil-hardening steels, 174
 open mould, 197
 optical ceramics, 242
 optical extensometer, 101
 organic protective coatings, 256
 oxidation potential, 247

oxide refractories, 238
oxy-acetylene flame, 181

P

packing factor, 17
paint, 8
paraffin, 10
partial annealing, 171
particulates, 191
passivation, 254
Pauli's exclusion principle, 6
pearlite, 150–154
percent elongation, 77
peritectic reaction, 140, 151
peritectic temperature, 140
peritectoid reaction, 141
phosphar bronze, 222
pig iron, 217
pigments, 242
piston pins, 59
piston rings, 218
pitting corrosion, 251–252
plain carbon steel, 214
Plank's constant, 4
plastic deformation, 43, 63
plywood, 190
point imperfections, 40
Poisson's ratio, 64
polycrystalline, 33
polycrystals, 98
polymer matrix composite, 190
polymers, 109
porcelain, 240
positive free energy, 115
pottery, 240
precipitation hardening, 182
pre-sintering, 230
pressure bag, 198
primary reference electrode, 248–249
principle quantum number, 4

Q

quantum numbers, 3
quenching media, 168

R

real crystals, 39
recrystallization, 124, 169
red brass, 221
red metal, 221
reinforcement, 188
repulsive force, 89
resilience, 68, 70
rotating crystal method, 33
rubber, 69
rusting of iron, 246

S

Schottky defect, 42
screw dislocation, 43, 45
secondary quantum number, 5
secondary reference electrode, 249–250
self-diffusion, 52
self-nucleation, 114
silica bricks, 237
silica gel, 253
siliceous refractories, 237
silicon bronzes, 222
silver, 20
silver plating, 255
solid solubility, 125
solid solution, 122, 136
solidification, 193
solute, 122
sorbite, 174
space lattice, 14
special refractories, 237
speculum metal, 222
spheroid graphite iron, 220
spheroidal annealing, 170
spin quantum number, 4, 5
spray deposition, 194–195
squeeze casting, 193
stable nucleus, 117
stacking fault, 47
stainless steels, 217
standard electrode potential, 250
steady loads, 104
steady-state condition, 54
steam turbines, 180

steel, 147, 151, 168
 steel shaft, 182
 stiffness, 66
 stir casting, 192
 strain energy, 68
 strain hardening, 95
 stress corrosion, 252
 stress relaxation, 100
 stress-relieving, 169
 sub-critical annealing, 171–172
 substitutional impurity, 41
 substitutional solid solution, 123
 supersaturated solid solution, 183
 surface distortion, 45

T

technical ceramics, 238
 tempering, 174
 tensile axis, 74
 ternary phase diagram, 142
 theoretical density, 19
 theoretical shear stress, 72
 thermal hysteresis, 155
 thermosets moulding, 201
 tin, 72
 traditional ceramic, 240
 transient creep, 95–96
 treatment of steel, 168
 triaxiality, 81
 tribological ceramics, 241
 true stress, 64
 tungsten high speed steel, 217
 twin boundaries, 45
 twin boundary imperfection, 46
 twin region, 73
 twinning, 70
 twinning deformation, 73
 twinning plane, 73

U

ultimate tensile strength, 66–67, 76
 unary diagram, 133
 under-cools, 114
 uniform corrosion, 251
 unit cell, 14
 unsteady state, 54

V

vacancy defect, 40
 vacant lattice, 51
 vacuum bag process, 198
 valency electrons, 9
 van der Waals forces, 9
 vectors, 14
 vertex, 192
 vibration energy, 51
 viscous creep, 95–96
 volume diffusion, 52
 volume imperfections, 47

W

water-hardening steels, 174
 wave mechanics, 4
 wear resistance, 123
 wear-resistant, 180
 white brass, 221
 white cast iron, 153, 219
 whiteware, 240
 Wood's theory, 107
 work hardening, 110
 wrought iron, 218

X

X-ray, 9, 30

Y

y-alloy, 224
 yellow brass, 221
 yield point phenomenon, 74
 yield strength, 66, 75–76
 yielding, 74–81
 Young's modulus, 65

Z

zero-dimensional imperfections, 40
 zinc, 109, 123
 zinc oxide, 42
 zirconia, 240