NEHRU COLLEGE OF ENGINEERING AND RESEARCH CENTRE
(NAAC Accredited)
(Approved by AICTE, Affiliated to APJ Abdul Kalam Technological University, Kerala)

DEPARTMENT OF MECHATRONICS ENGINEERING

COURSE MATERIAL

ME 210 METALLURGY AND MATERIALS ENGINEERING

VISION OF THE INSTITUTION
To mould true citizens who are millennium leaders and catalysts of change through excellence in education.
MISSION OF THE INSTITUTION
NCERC is committed to transform itself into a center of excellence in Learning and Research in Engineering and Frontier Technology and to impart quality education to mould technically competent citizens with moral integrity, social commitment and ethical values. We intend to facilitate our students to assimilate the latest technological know-how and to imbibe discipline, culture and spiritually, and to mould them in to technological giants, dedicated research scientists and intellectual leaders of the country who can spread the beams of light and happiness among the poor and the underprivileged.

ABOUT DEPARTMENT

- Established in: 2013
- Course offered: B.Tech Mechatronics Engineering
- Approved by AICTE New Delhi and Accredited by NAAC
- Affiliated to the University of Dr. A P J Abdul Kalam Technological University.

DEPARTMENT VISION

To develop professionally ethical and socially responsible Mechatronics engineers to serve the humanity through quality professional education.

DEPARTMENT MISSION

1) The department is committed to impart the right blend of knowledge and quality education to create professionally ethical and socially responsible graduates.

2) The department is committed to impart the awareness to meet the current challenges in technology.

3) Establish state-of-the-art laboratories to promote practical knowledge of mechatronics to meet the needs of the society

PROGRAMME EDUCATIONAL OBJECTIVES

I. Graduates shall have the ability to work in multidisciplinary environment with good professional and commitment.

II. Graduates shall have the ability to solve the complex engineering problems by applying electrical, mechanical, electronics and computer knowledge and engage in lifelong learning in their profession.

III. Graduates shall have the ability to lead and contribute in a team with entrepreneur skills, professional, social and ethical responsibilities.

IV. Graduates shall have ability to acquire scientific and engineering fundamentals necessary for higher studies and research.

PROGRAM OUTCOME (PO'S)

Engineering Graduates will be able to:

PO 1. Engineering knowledge: Apply the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of complex engineering problems.

PO 2. Problem analysis: Identify, formulate, review research literature, and analyze complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences, and engineering sciences.

PO 3. Design/development of solutions: Design solutions for complex engineering problems and design system components or processes that meet the specified needs with appropriate consideration for the public health and safety, and the cultural, societal, and environmental considerations.

PO 4. Conduct investigations of complex problems: Use research-based knowledge and research methods including design of experiments, analysis and interpretation of data, and synthesis of the information to provide valid conclusions.

PO 5. Modern tool usage: Create, select, and apply appropriate techniques, resources, and modern engineering and IT tools including prediction and modeling to complex engineering activities with an understanding of the limitations.

PO 6. The engineer and society: Apply reasoning informed by the contextual knowledge to assess societal, health, safety, legal and cultural issues and the consequent responsibilities relevant to the professional engineering practice.

PO 7. Environment and sustainability: Understand the impact of the professional engineering solutions in societal and environmental contexts, and demonstrate the knowledge of, and need for sustainable development.

PO 8. Ethics: Apply ethical principles and commit to professional ethics and responsibilities and norms of the engineering practice.

PO 9. Individual and team work: Function effectively as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings.

PO 10. Communication: Communicate effectively on complex engineering activities with the engineering community and with society at large, such as, being able to comprehend and write effective reports and design documentation, make effective presentations, and give and receive clear instructions.

PO 11. Project management and finance: Demonstrate knowledge and understanding of the engineering and management principles and apply these to one’s own work, as a member and leader in a team, to manage projects and in multidisciplinary environments.

PO 12. Life-long learning: Recognize the need for, and have the preparation and ability to engage in independent and life-long learning in the broadest context of technological change.

PROGRAM SPECIFIC OUTCOME(PSO’S)

PSO 1: Design and develop Mechatronics systems to solve the complex engineering problem by integrating electronics, mechanical and control systems.

PSO 2: Apply the engineering knowledge to conduct investigations of complex engineering problem related to instrumentation, control, automation, robotics and provide solutions.

COURSE OUTCOME

After the completion of the course the student will be able to

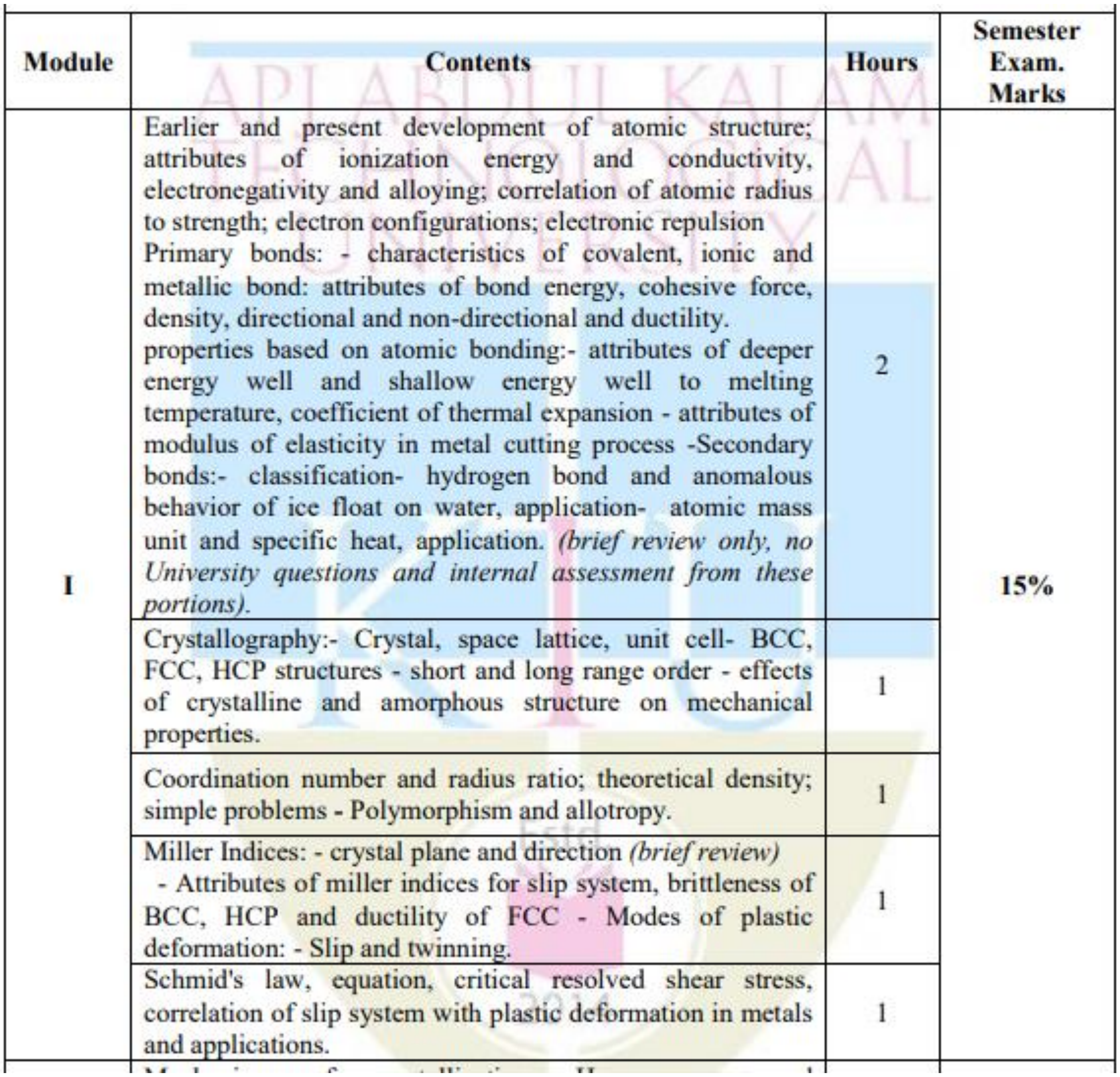
CO 1	Understand fundamental science relevant to materials
CO 2	Acquire knowledge on physical concepts of atomic radius, atomic structure, chemical bonds, crystalline and non-crystalline materials and defects of crystal structures, grain size, strengthening mechanisms, heat treatment of metals with mechanical properties and changes in structure
CO 3	Describe the behavior of materials in engineering applications and select the materials for various engineering applications.
CO 4	Understand the causes behind metal failure and deformation
CO 5	Determine properties of unknown materials and develop an awareness to apply this knowledge in material design.
CO 6	Acquire knowledge on the modern engineering materials

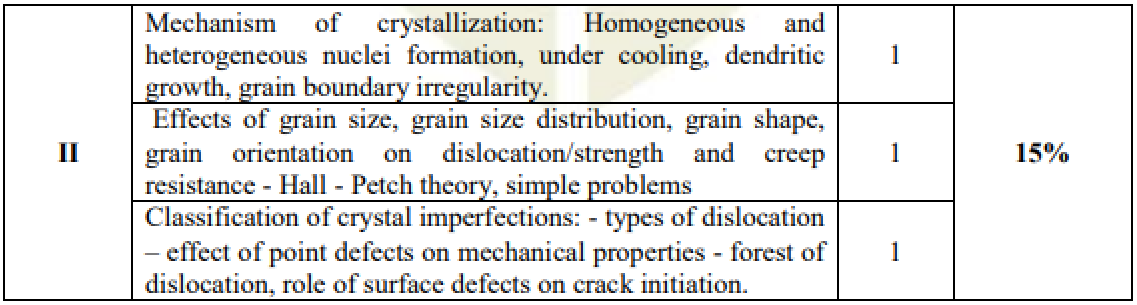
CO VS PO'S AND PSO'S MAPPING

CO	PO1	PO2	PO 3	PO 4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12	PS0 1	PSO 2
CO 1	3	2	-	-	-	-	-	-	-	-	-	-	2	-
CO 2	3	2	-	-	-	-	-	-	-	-	-	-	-	-
CO 3	3	-	-	-	-	-	-	-	-	-	-	3	2	-
CO 4	3	-	-	-	-	-	-	-	-	-	-	-	2	-
CO 5	3	-	-	-	-	-	-	-	-	-	-	-	-	-
CO 6	3	-	-	-	-	-	-	-	-	-	-	-	2	-

Note: H-Highly correlated=3, M-Medium correlated=2, L-Less correlated=1

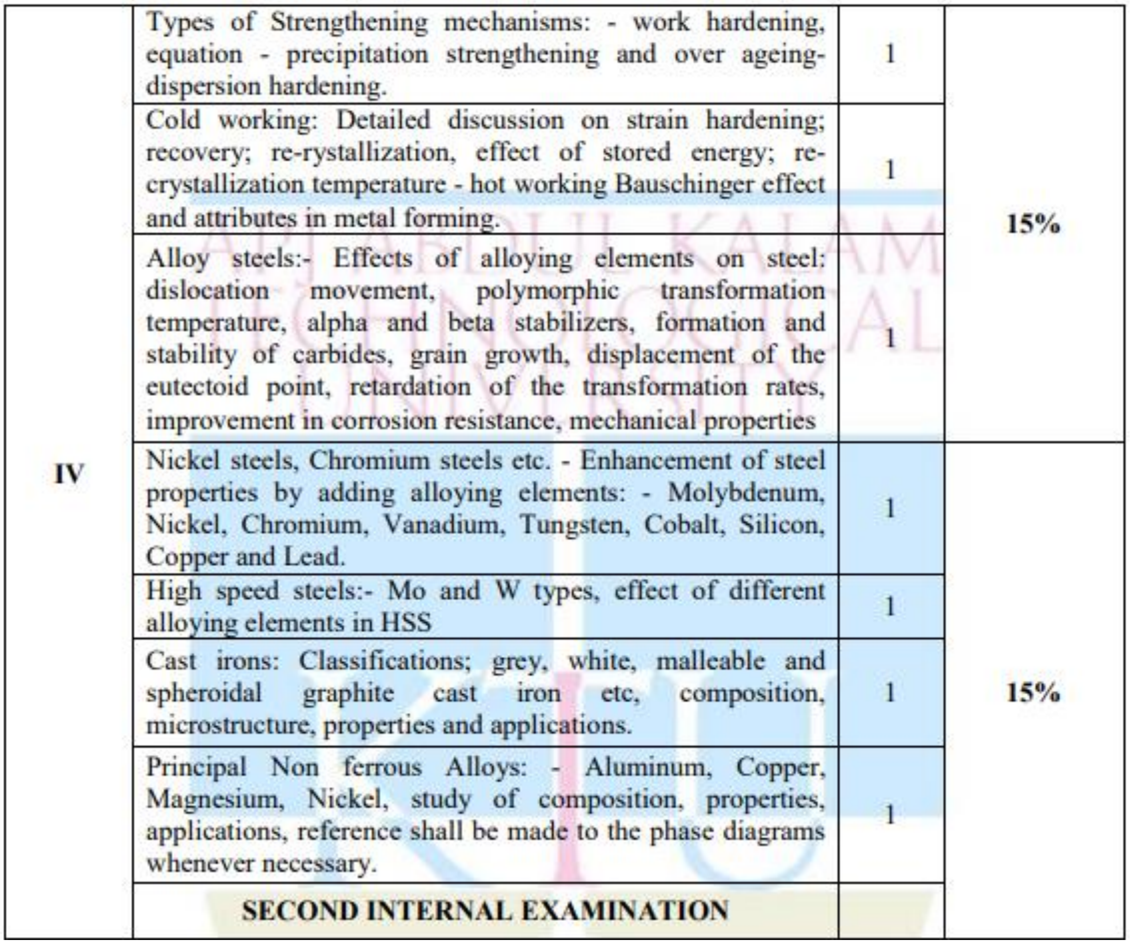
SYLLABUS



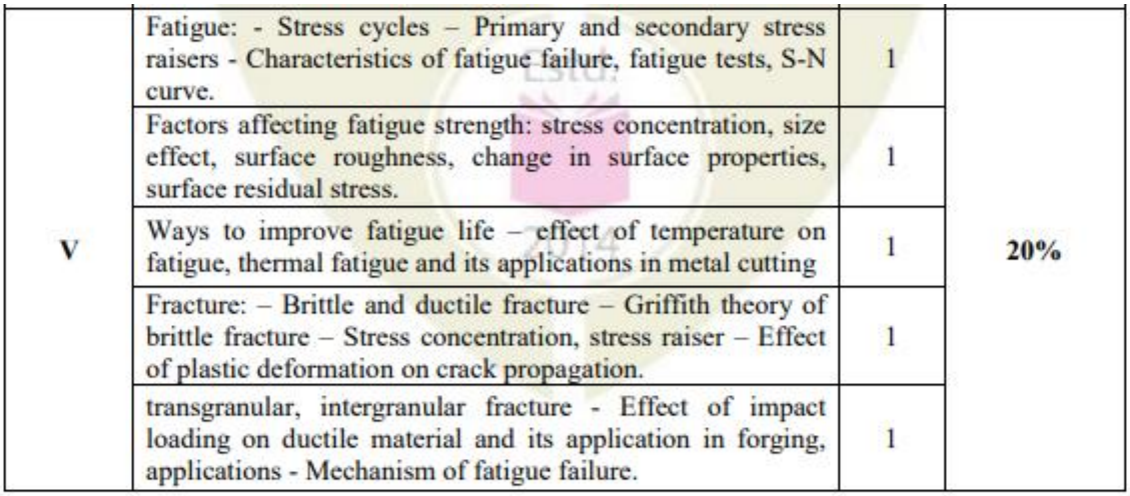


Module	Contents	Hours	Semester Exam. Marks
I	Earlier and present development of atomic structure; attributes of ionization energy and conductivity, electronegativity and alloying; correlation of atomic radius to strength; electron configurations; electronic repulsion Primary bonds: - characteristics of covalent, ionic and metallic bond: attributes of bond energy, cohesive force, density, directional and non-directional and ductility. properties based on atomic bonding:- attributes of deeper energy well and shallow energy well to melting temperature, coefficient of thermal expansion - attributes of modulus of elasticity in metal cutting process -Secondary bonds:- classification- hydrogen bond and anomalous behavior of ice float on water, application- atomic mass unit and specific heat, application. *(brief review only, no University questions and internal assessment from these portions).*	2	15%
	Crystallography:- Crystal, space lattice, unit cell- BCC, FCC, HCP structures - short and long range order - effects of crystalline and amorphous structure on mechanical properties.	1	
	Coordination number and radius ratio; theoretical density; simple problems - Polymorphism and allotropy.	1	
	Miller Indices: - crystal plane and direction *(brief review)* - Attributes of miller indices for slip system, brittleness of BCC, HCP and ductility of FCC - Modes of plastic deformation: - Slip and twinning.	1	
	Schmid's law, equation, critical resolved shear stress, correlation of slip system with plastic deformation in metals and applications.	1	
II	Mechanism of crystallization: Homogeneous and heterogeneous nuclei formation, under cooling, dendritic growth, grain boundary irregularity.	1	15%
	Effects of grain size, grain size distribution, grain shape, grain orientation on dislocation/strength and creep resistance - Hall - Petch theory, simple problems	1	
	Classification of crystal imperfections: - types of dislocation – effect of point defects on mechanical properties - forest of dislocation, role of surface defects on crack initiation.	1	

	Burgers vector –dislocation source, significance of Frank Read source in metals deformation - Correlation of dislocation density with strength and nano concept, applications.	1	
	Significance high and low angle grain boundaries on dislocation – driving force for grain growth and applications during heat treatment.	1	
	Polishing and etching to determine the microstructure and grain size.	1	
	Fundamentals and crystal structure determination by X – ray diffraction, simple problems –SEM and TEM.	1	
	Diffusion in solids, Fick's laws, mechanisms, applications of diffusion in mechanical engineering, simple problems.	1	
	FIRST INTERNAL EXAMINATION		
III	Phase diagrams: - Limitations of pure metals and need of alloying - classification of alloys, solid solutions, Hume Rothery`s rule - equilibrium diagram of common types of binary systems: five types.	2	**15%**
	Coring - lever rule and Gibb`s phase rule - Reactions: - monotectic, eutectic, eutectoid, peritectic, peritectoid.	1	
	Detailed discussion on Iron-Carbon equilibrium diagram with microstructure and properties changes in austenite, ledeburite, ferrite, cementite, special features of martensite transformation, bainite, spheroidite etc.	1	
	Heat treatment: - Definition and necessity – TTT for a eutectoid iron–carbon alloy, CCT diagram, applications - annealing, normalizing, hardening, spheroidizing.	1	
	Tempering:- austermpering, martempering and ausforming - Comparative study on ductility and strength with structure of pearlite, bainite, spherodite, martensite, tempered martensite and ausforming.	1	
	Hardenability, Jominy end quench test, applications- Surface hardening methods:- no change in surface composition methods :- Flame, induction, laser and electron beam hardening processes- change in surface composition methods :carburizing and Nitriding; applications.	2	



IV	Types of Strengthening mechanisms: - work hardening, equation - precipitation strengthening and over ageing-dispersion hardening.	1	15%
	Cold working: Detailed discussion on strain hardening; recovery; re-rystallization, effect of stored energy; re-crystallization temperature - hot working Bauschinger effect and attributes in metal forming.	1	
	Alloy steels:- Effects of alloying elements on steel: dislocation movement, polymorphic transformation temperature, alpha and beta stabilizers, formation and stability of carbides, grain growth, displacement of the eutectoid point, retardation of the transformation rates, improvement in corrosion resistance, mechanical properties	1	
	Nickel steels, Chromium steels etc. - Enhancement of steel properties by adding alloying elements: - Molybdenum, Nickel, Chromium, Vanadium, Tungsten, Cobalt, Silicon, Copper and Lead.	1	15%
	High speed steels:- Mo and W types, effect of different alloying elements in HSS	1	
	Cast irons: Classifications; grey, white, malleable and spheroidal graphite cast iron etc, composition, microstructure, properties and applications.	1	
	Principal Non ferrous Alloys: - Aluminum, Copper, Magnesium, Nickel, study of composition, properties, applications, reference shall be made to the phase diagrams whenever necessary.	1	
	SECOND INTERNAL EXAMINATION		



V	Fatigue: - Stress cycles – Primary and secondary stress raisers - Characteristics of fatigue failure, fatigue tests, S-N curve.	1	20%
	Factors affecting fatigue strength: stress concentration, size effect, surface roughness, change in surface properties, surface residual stress.	1	
	Ways to improve fatigue life – effect of temperature on fatigue, thermal fatigue and its applications in metal cutting	1	
	Fracture: – Brittle and ductile fracture – Griffith theory of brittle fracture – Stress concentration, stress raiser – Effect of plastic deformation on crack propagation.	1	
	transgranular, intergranular fracture - Effect of impact loading on ductile material and its application in forging, applications - Mechanism of fatigue failure.	1	

	Structural features of fatigue: - crack initiation, growth, propagation - Fracture toughness (definition only) - Ductile to brittle transition temperature (DBTT) in steels and structural changes during DBTT, applications.	1	
V1	Creep: - Creep curves – creep tests - Structural change:- deformation by slip, sub-grain formation, grain boundary sliding	1	**20%**
	Mechanism of creep deformation - threshold for creep, prevention against creep - Super plasticity: need and applications	1	
	Composites:- Need of development of composites - geometrical and spatial Characteristics of particles – classification - fiber phase: - characteristics, classifications - matrix phase:- functions – only need and characteristics of PMC, MMC, and CMC – applications of composites: aircraft applications, aerospace equipment and instrument structure, industrial applications of composites, marine applications, composites in the sporting goods industry, composite biomaterials..	2	
	Modern engineering materials: - only fundamentals, need, properties and applications of, intermetallics, maraging steel, super alloys, Titanium – introduction to nuclear materials, smart materials and bio materials.	2	
	Ceramics:-coordination number and radius ratios- AX, A_mX_p, $A_mB_mX_p$ type structures – applications.	1	

Question Paper Pattern

Total marks: 100, Time: 3 hrs
The question paper should consist of three parts

Part A
4 questions uniformly covering modules I and II. Each question carries 10 marks
Students will have to answer any three questions out of 4 (3X10 marks =30 marks)

Part B
4 questions uniformly covering modules III and IV. Each question carries 10 marks
Students will have to answer any three questions out of 4 (3X10 marks =30 marks)

Part C
6 questions uniformly covering modules V and VI. Each question carries 10 marks
Students will have to answer any four questions out of 6 (4X10 marks =40 marks)

Note: In all parts, each question can have a maximum of four sub questions, if needed.

QUESTION BANK

MODULE I				
Q:NO:	**QUESTIONS**	**CO**	**KL**	**PG NO:**
1.	Discuss about BCC structure	CO1	K2	15
2.	Discuss about FCC structure	CO1	K2	17
3.	Find the co-ordination number of HCP	CO1	K1	20
4.	Discuss about the Effect of Crystalline and Amorphous Structure on Mechanical Properties	CO1	K2	21
5.	What is Polymorphism and Allotropy	CO1	K1	22
6.	Discuss about Plastic deformation by Slip:	CO1	K2	26
7.	Comparison between Slip and Twinning	CO1	K1	27
8.	Derive Schmid's Equation and Critical Resolved Shear Stress	CO1	K6	28
9	Explain about Schmid's Law	CO1	K2	28
10.	Explain about Correlation of Slip System with Plastic Deformation in Metals and Applications	CO1	K2	29
MODULE II				
1.	Discuss about Mechanism of crystallization	CO2	K2	30
2.	Explain the Effect of Grain Parameters on Strength (Dislocations) and Creep Resistance	CO2	K2	34
3.	Explain Hall petch theory	CO2	K2	35
4.	Classification of crystal imperfections	CO2	K2	36
5.	Explain the Effect of point imperfections on mechanical properties	CO2	K2	38
6.	Discuss about Types of Dislocations	CO2	K2	38

7.	What are Surface defects	CO2	K1	40
8.	What is the Role of Surface Defects on Crack Initiation	CO2	K1	41
9.	Explain about Burgers vector	CO2	K2	41
10.	Driving Force for Grain Growth and Applications during Heat Treatment	CO2	K1	45
MODULE III				
1.	Classification of Alloys	CO3	K2	58
2.	What is Substitutional solid solution	CO3	K1	59
3.	Discuss about Hume rothery's rules	CO3	K2	60
4.	Explain about Eutectic system	CO3	K2	62
5.	Sketch and explain Peritectic equililibrium diagram	CO3	K2	64
6.	Discuss about Peritectoid reaction	CO3	K2	65
7.	Discuss about Gibb's phase rule	CO3	K2	67
8.	Sketch and explain Iron-carbon equilibrium diagram	CO3	K2	
9.	Explain about Invariant reactions	CO3	K2	74
10.	Sketch and explain TTT Diagram for Eutectoid Steel	CO3	K1	77
MODULE IV				
1	What do you meant by Precipitation Hardening and Overaging	CO4	K1	94
2	Detailed Discussion on Strain Hardening	CO4	K2	96
3	Explain about Recovery, Recrystallization and Grain Growth	CO4	K2	97
4	Differences between Hot working and Cold working	CO4	K2	99

5	Discuss about Bauschinger Effect and Attributes in Metal Forming	CO4	K2	100
6	Explain about the Effect of Alloying Elements	CO4	K2	101
7	Discuss about High speed steels	CO4	K2	103
8	Discuss about Gray cast iron	CO4	K2	105
9	Discuss about White cast iron	CO4	K2	107
10	Discuss about Aluminum and its Alloys	CO4	K2	109
MODULE V				
1	Explain about Stress cycles	CO5	K2	113
2	What are the Characteristics of Fatigue Failure	CO5	K1	114
3	Sketch and explain S-N curve	CO5	K2	116
4	Discuss about the Factors affecting Fatigue Strength	CO5	K2	117
5	What are the ways to improve Fatigue Life	CO5	K2	120
6	Discuss about the Application of Thermal Fatigue on Metal Cutting	CO5	K2	120
7	Differentiate Brittle and Ductile Fracture	CO5	K1	121
8	Explain about Griffith’s Theory of Brittle Fracture	CO5	K2	122
9	Discuss about the Effect of Plastic Deformation on Crack Propagation	CO5	K2	122
10	Explain about the Mechanism of Fatigue Failure	CO5	K2	125
MODULE VI				
1	What is Creep Test	CO6	K1	129

2	Discuss about Mechanism Of Creep Deformation	CO6	K2	131
3	Explain the Applications Of Superplasticity	CO6	K2	133
4	Classification Of Composites Based On Fiber Phase	CO6	K6	134
5	Classification Of Composites Based on Matrix Phases	CO6	K6	136
6	Discuss about the Applications Of Composites	CO6	K2	138
7	Explain about Modern Engineering Materials	CO6	K2	139
8	Discuss about Super Alloys	CO6	K2	140
9	Discuss about Shape Memory Alloys	CO6	K2	141
10	What is Coordination Number And Radius Ratio	CO6	K1	142

APPENDIX 1

CONTENT BEYOND THE SYLLABUS

S:NO;	TOPIC	
1	Practical Aspects of Metallurgical Thermodynamics	134

MODULE 1

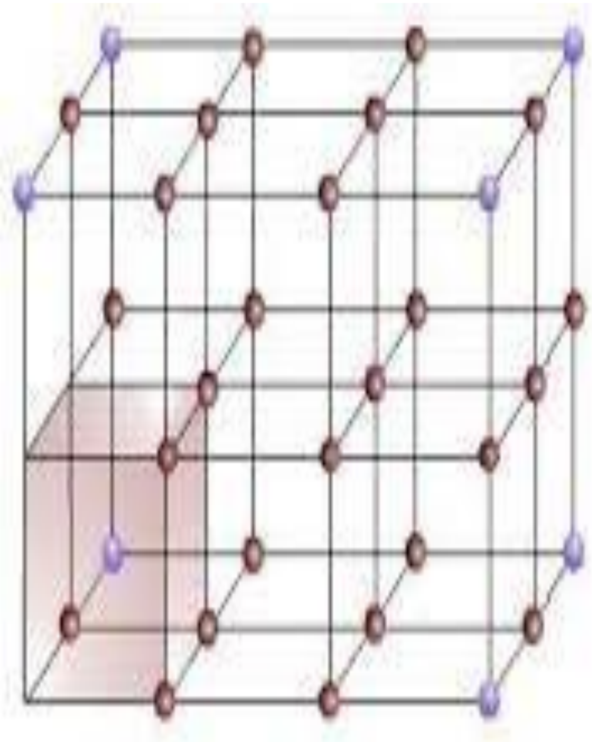
CRYSTALLOGRAPHY

Crystal

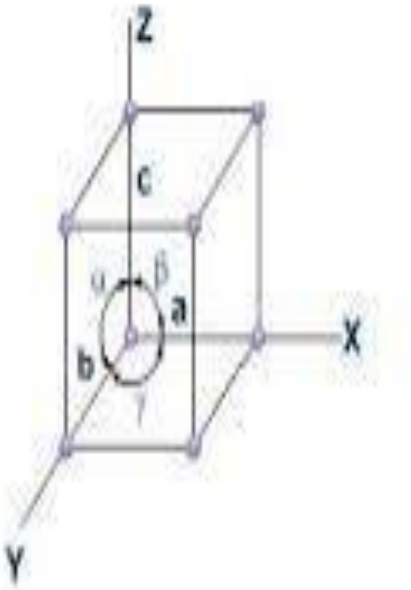
A crystal or a crystalline material is defined as a solid in which the atoms are arranged in a repetitive or periodic manner over large atomic distances. It means that long range order exists in a crystal. Metals, most ceramics and some polymers are crystalline materials.

Space Lattice

A space lattice or crystal lattice is a three dimensional network of lines. The intersections of these lines form a three dimensional array of points. Atoms are thought to be occupying these lattice points.



Representation of space lattice and unit cell



Representation of dimensions of a unit cell

BCC, FCC and HCP Structures (Metallic Crystal Structures)

Most of the metals fall into three crystal structures *viz.*

(i) Body centered cubic (BCC): Cr,Mo,W,α Fe
(ii) Face centered cubic(FCC): Al,Cu,Ag, Ni, γ Fe
(iii) Hexagonal close packed (HCP): Ti, Cd, Zn, Mg

The crystal structure is characterized by:

(a) **Lattice parameters** (a,b,c,α,β,γ)

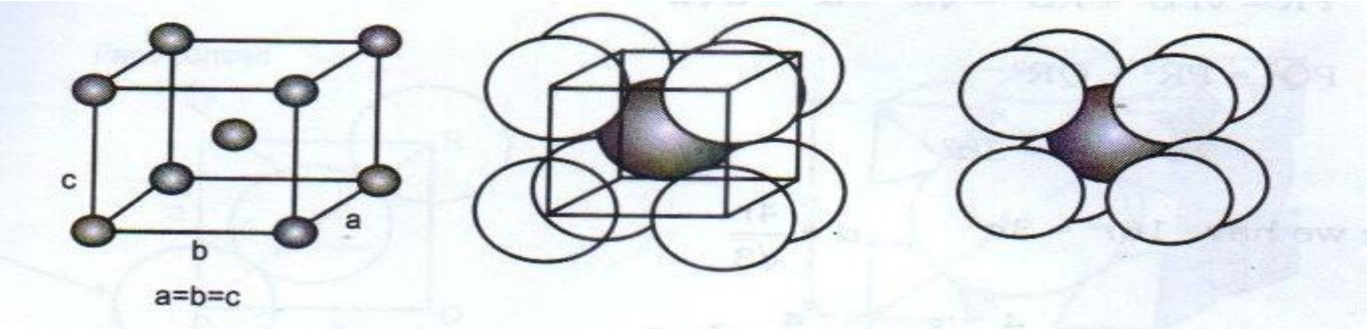
(b) **Number of atoms/unit cell (n):** $n = \frac{Nc}{8} + \frac{Nf}{2} + N_b$ where Nc- number of corner atoms, Nf- number of face centered atoms, Nb- number of body centered atoms.

(c) **Coordination number (N):** number of nearest neighbor atoms surrounding any particular atom.

(d) Atomic packing factor (APF): Fraction of volume occupied by atoms in the unit cell volume

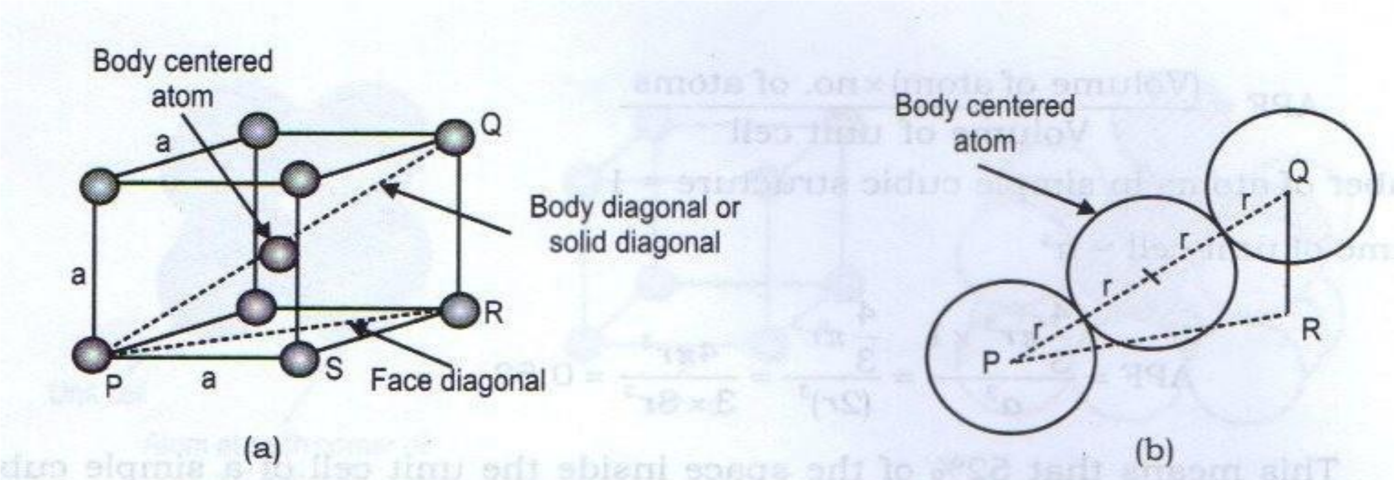
$$APF = \frac{volume\ of\ atoms \in unit\ cell}{volume\ of\ unit\ cell}$$

<u>Body Centered Cubic (BCC)</u>



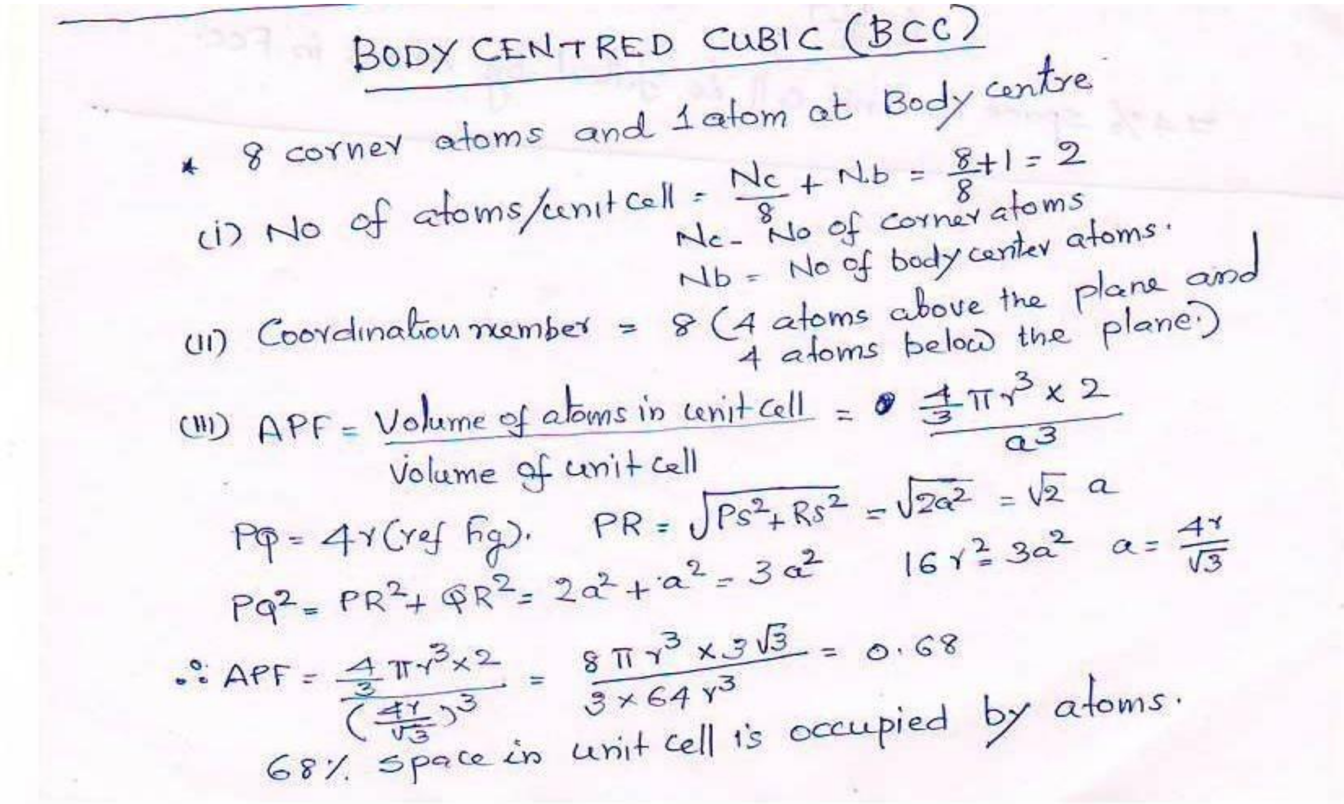
(a) Unit cell with lattice parameters
(b) Representation of unit cell
(c) atoms in unit cell

Figure 2.10 *Body centerd cubic unit cell*



(a) (b)

Figure 2.11 *Structure of BCC crystal*



BODY CENTRED CUBIC (BCC)

8 corner atoms and 1 atom at Body centre

(i) No of atoms/unit cell = $\frac{N_c}{8} + N_b = \frac{8}{8} + 1 = 2$

N_c - No of corner atoms

N_b = No of body center atoms.

(ii) Coordination number = 8 (4 atoms above the plane and 4 atoms below the plane.)

(iii) APF = $\frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r^3 \times 2}{a^3}$

$PQ = 4r$ (ref fig). $PR = \sqrt{PS^2 + RS^2} = \sqrt{2a^2} = \sqrt{2}\,a$

$PQ^2 = PR^2 + QR^2 = 2a^2 + a^2 = 3a^2$ $\quad 16r^2 = 3a^2 \quad a = \frac{4r}{\sqrt{3}}$

$\therefore \text{APF} = \frac{\frac{4}{3}\pi r^3 \times 2}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{8\pi r^3 \times 3\sqrt{3}}{3 \times 64 r^3} = 0.68$

68% space in unit cell is occupied by atoms.

Face Centered Cubic (FCC)

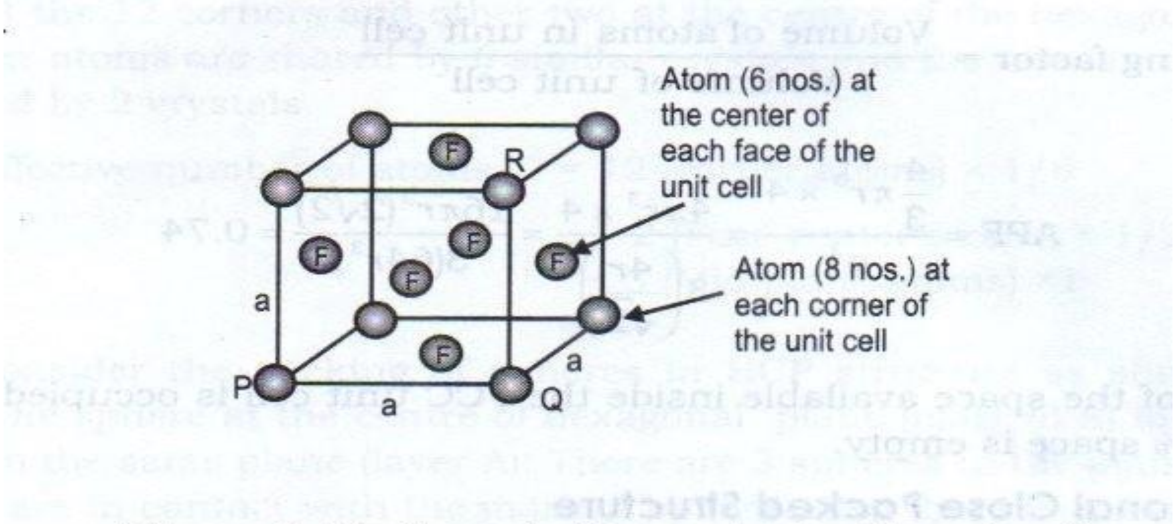
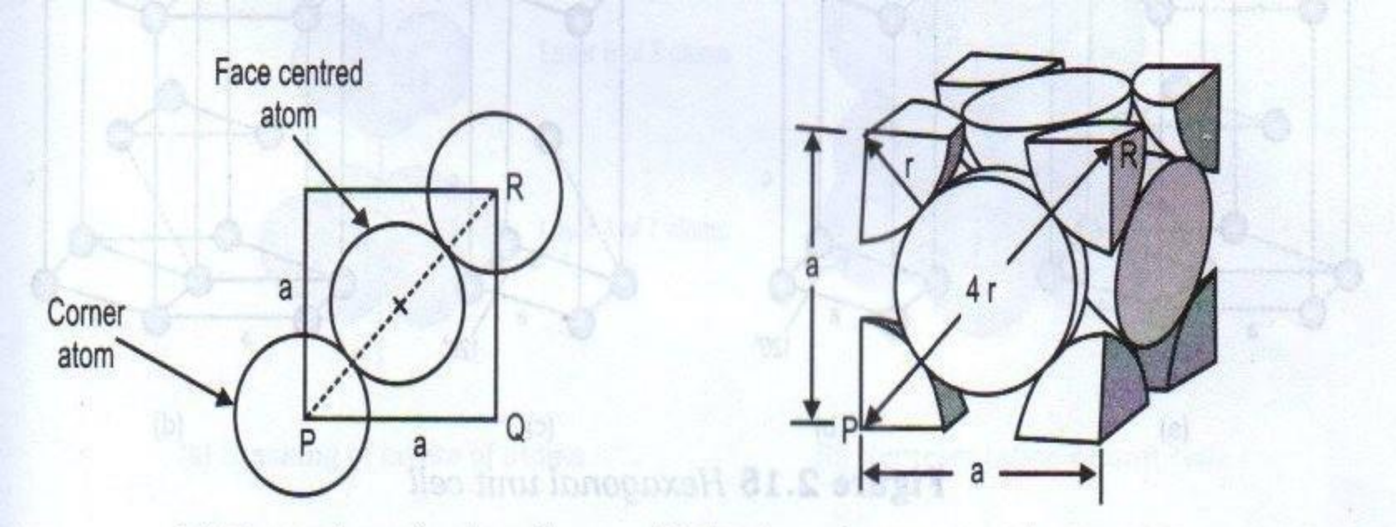


Figure 2.13 *Atoms in face centred cubic unit cells*



(a) Front view of unit cell (b) Portion of atoms inside the FCC unit cell

Figure 2.14 *Structure of FCC crystal*

FACE CENTRED CUBIC (FCC)

- 8 atoms at corners and 6atoms at face centres.

(i) No of atoms/unit cell = $\frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 4$ N_f: No of atoms at face ce

(ii) Coordination number = 12 (6 in the same plane + 3 each in planes above and below)

(iii) $APF = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r^3 \times 4}{a^3}$

Ref Fig.

From $\triangle PQR$ $PR^2 = PQ^2 + QR^2$ $PR = 4r$

$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$a = \frac{4r}{\sqrt{2}}$$

$$\therefore APF = \frac{\frac{4}{3}\pi r^3 \times 4}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{16\pi r^3 \times 2\sqrt{2}}{3 \times 64 r^3} = 0.74.$$

74% space in unit cell is filled by atoms in FCC.

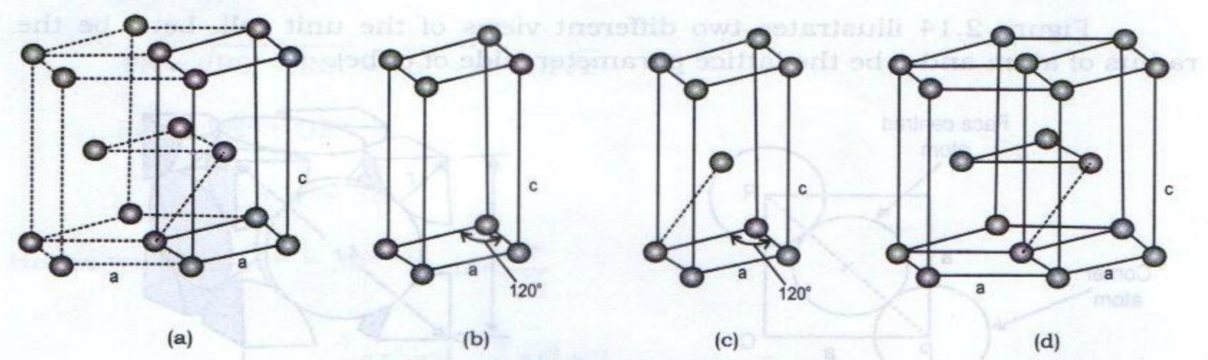
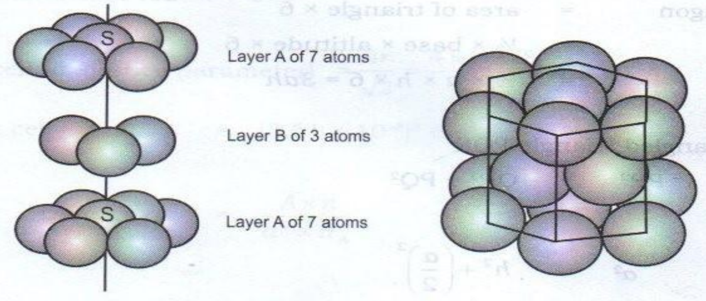
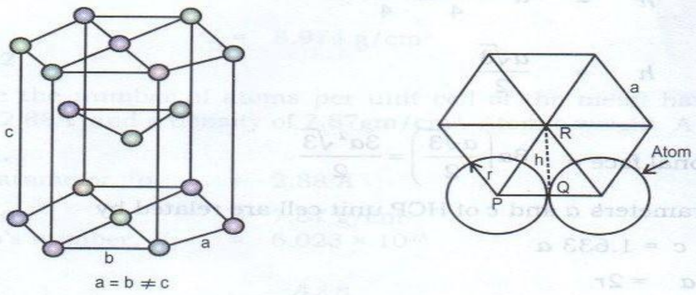


Figure 2.15 *Hexagonal unit cell*

Hexagonal Close Packed (HCP)

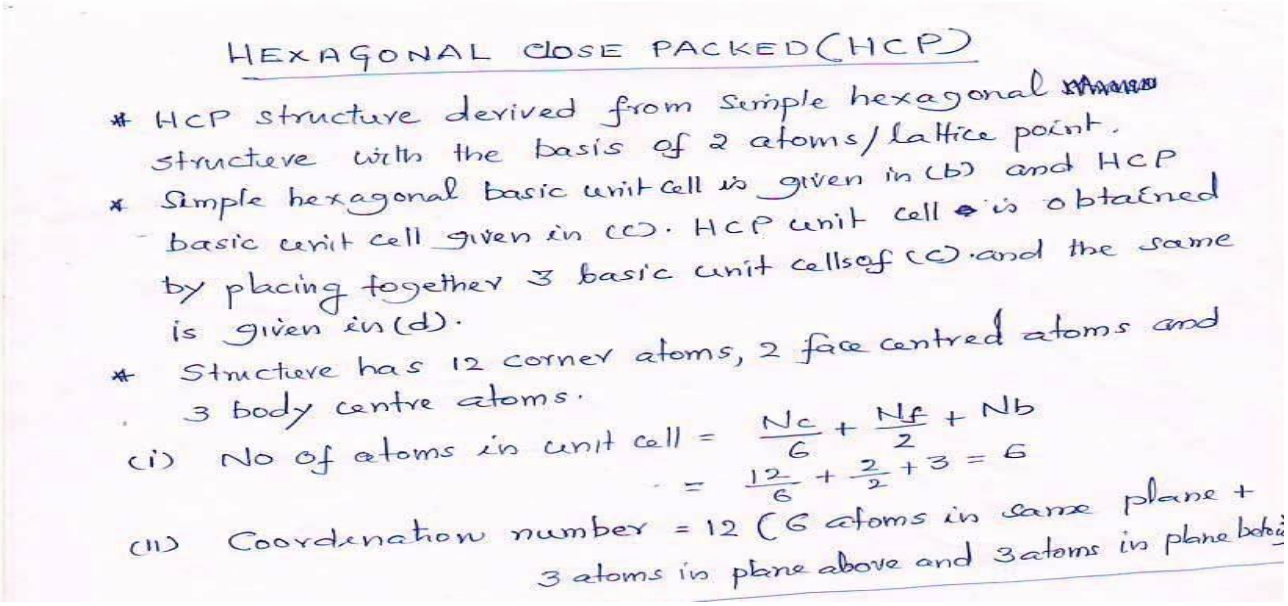


(a) Stacking of layers of atoms (b) Representation of unit cell



(c) Unit cell with lattice parameters (d) Hexagonal plane

Figure 2.16 *APF for HCP structure*



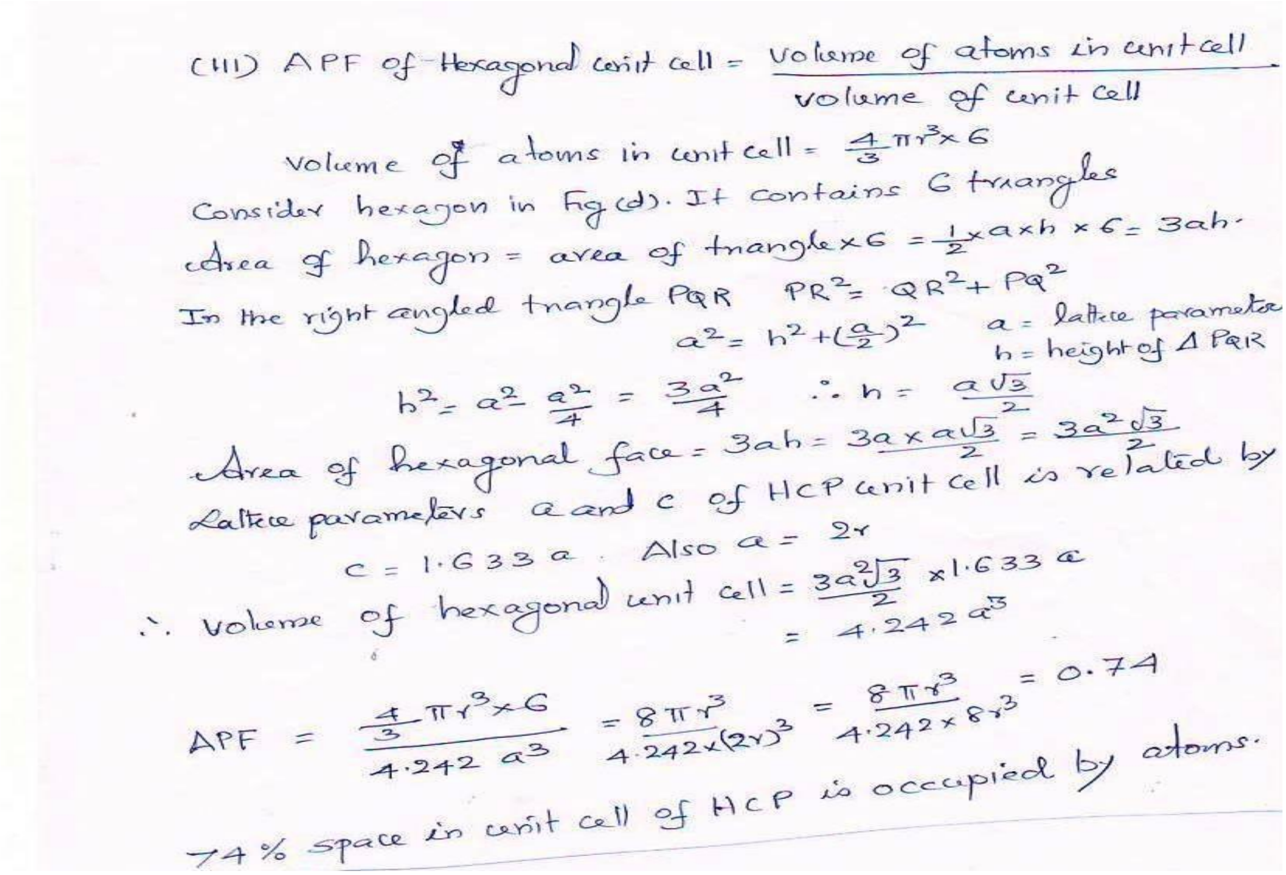
HEXAGONAL CLOSE PACKED (HCP)

- HCP structure derived from simple hexagonal structure with the basis of 2 atoms/lattice point.
- Simple hexagonal basic unit cell is given in (b) and HCP basic unit cell given in (c). HCP unit cell is obtained by placing together 3 basic unit cells of (c) and the same is given in (d).
- Structure has 12 corner atoms, 2 face centred atoms and 3 body centre atoms.

(i) No of atoms in unit cell = $\frac{N_c}{6} + \frac{N_f}{2} + N_b$

$= \frac{12}{6} + \frac{2}{2} + 3 = 6$

(ii) Coordination number = 12 (6 atoms in same plane + 3 atoms in plane above and 3 atoms in plane bel



(iii) APF of Hexagonal unit cell = $\frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}$

volume of atoms in unit cell = $\frac{4}{3}\pi r^3 \times 6$

Consider hexagon in Fig (d). It contains 6 triangles

Area of hexagon = area of triangle × 6 = $\frac{1}{2} \times a \times h \times 6 = 3ah$.

In the right angled triangle PQR $PR^2 = QR^2 + PQ^2$

$a^2 = h^2 + (\frac{a}{2})^2$

a = lattice parameter

h = height of Δ PQR

$h^2 = a^2 - \frac{a^2}{4} = \frac{3a^2}{4}$ ∴ $h = \frac{a\sqrt{3}}{2}$

Area of hexagonal face = $3ah = 3a \times \frac{a\sqrt{3}}{2} = \frac{3a^2\sqrt{3}}{2}$

Lattice parameters a and c of HCP unit cell is related by

$c = 1.633a$. Also $a = 2r$

∴ volume of hexagonal unit cell = $\frac{3a^2\sqrt{3}}{2} \times 1.633a$

$= 4.242a^3$

$$APF = \frac{\frac{4}{3}\pi r^3 \times 6}{4.242a^3} = \frac{8\pi r^3}{4.242 \times (2r)^3} = \frac{8\pi r^3}{4.242 \times 8r^3} = 0.74$$

74% space in unit cell of HCP is occupied by atoms.

Long and Short Range Order

Long range order exists in crystalline materials. It means that atoms are arranged in regular repetitive pattern in all three dimensions over long atomic distances. When regular, repetitive pattern is absent and the overall arrangement is random, the structure is called amorphous. However, regular atomic arrangement may exist over few atomic distances. Hence amorphous materials is said to have short range order.

Effect of Crystalline and Amorphous Structure on Mechanical Properties

As a result of long range order, crystalline materials are solids with good rigidity. They have sharp, well defined melting points. They have a particular geometric structure. They are symmetrical which is clear from the fact that their appearance does not change if they are rotated about an axis. The bond strength between atoms, molecules and ions are same.

Crystalline materials are generally poly crystalline (containing large number of grains) Mechanical properties are anisotropic, that is properties are different in different directions. Breaking (cleavage) of crystalline materials occur along specific directions on particular planes (cleavage planes).

Amorphous materials have short range order at best or a purely random order. Liquids, gases and some solids are amorphous. They lack rigidity of crystalline materials. Amorphous solids melt over a range of temperature. They are unsymmetrical. Bond strength between atoms varies. Mechanical properties are isotropic (same properties in different directions). They break along random planes and directions.

1.1.7 Coordination Number and Radius Ratio

In ionic compounds (NaCl, CsCl, ZnS etc) or ceramic materials (MgO, WC etc) there are two types of ions. Metallic ions (Na, Mg etc.) are positively charged and are called cations. Non metallic ions (Cl, O etc) are negatively charged and are called anions. The ratio of radii of cation and anion is called radius ratio.

c
r
a
Radius ratio= r
radius of anion
radius of cation

In general, non-metallic ions (anions) are larger in size. Hence radius ratio is less than one. Each cation likes to have as many anion neighbors as possible. Likewise, anion is surrounded by many cations. Coordination number refers to nearest neighboring atoms. Hence there is a close relation between radius ratio and coordination number. In fact coordination number can be predicted from the calculated radius ratio for various ionic compounds as given below:

.

Radius Ratio	**Coordination number**	**Example**
< 0.155	2	
0.155 - 0.225	3	Ba_2CO_3
0.225 - 0.414	4	ZnS, CuCl
0.414 - 0.732	6	NaCl, MgO
0.732 - 1.000	8	CsCl, NH_4Br

1.1.8 Theoretical Density

Avogadro's hypothesis states that one gram molecule of any substance contains $6.023 x\ 10^{23}$ molecules or atoms, referred to as Avogadro's number. Therefore weight of NA molecules or atoms is equal to 'A' gram where N_A is Avogadro's number and A is atomic weight of substance.

Mass of one molecule or atom= $\frac{A}{N_A}$ gm

Mass of a unit cell having 'n' number of molecules or atoms= $\frac{A}{N_A} x\, n$ gm

Mass of one unit cell= volume of one unit cell x density (ρ) =a^3 x ρ in the case of cubic unit cell

Equating a^3 x ρ = $\frac{A}{N_A} x\, n$ or ρ■$\frac{AXn}{a^{3x} N_A}$

P can be termed as theoretical density of the substance.

Polymorphism and Allotropy

If a material exists in more than one crystal structure, the phenomenon is known as polymorphism. Polymorphism is observed in all materials (metals, non-metals, compounds etc.). Ceramic materials like silica and zirconia are polymorphic. Polymorphism seen in pure elements is called allotropy. Pure iron has 3 allotropic forms; α, γ and ∂. Refer Figure.

Carbon is another element exhibiting allotropy. Diamond and graphite are two allotropic forms of carbon. Both have very different properties. Diamond is very hard and insulating while graphite is soft and conducting. Titanium exists in HCP structure up to 880^0 C and then changes to BCC.

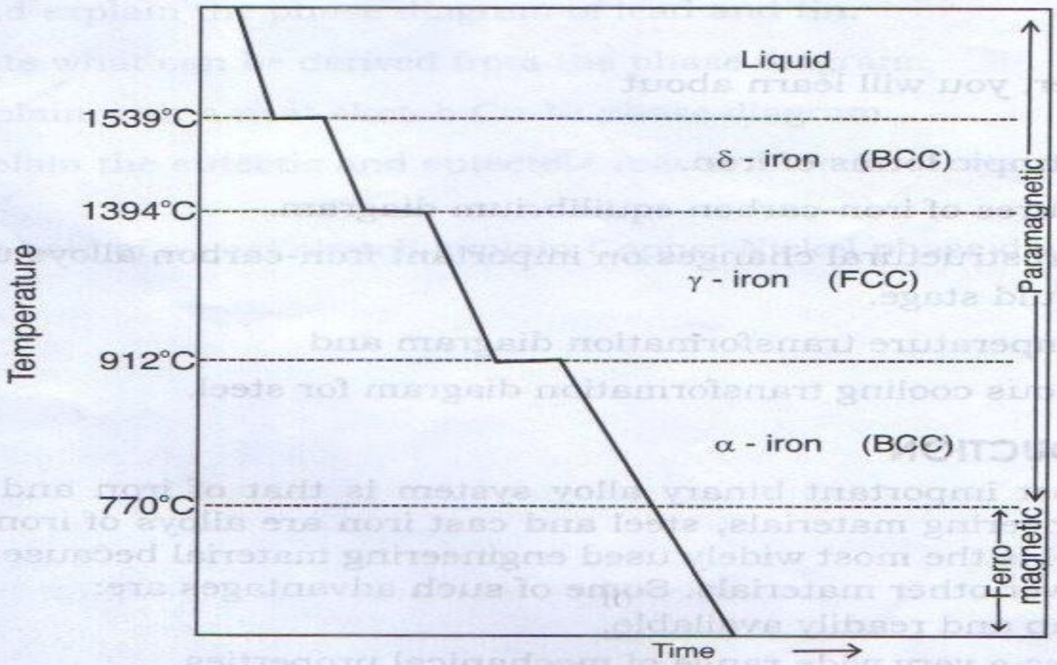


Figure 7.1 *Allotropes of iron*

MILLER INDICES AND PLASTIC DEFORMATION

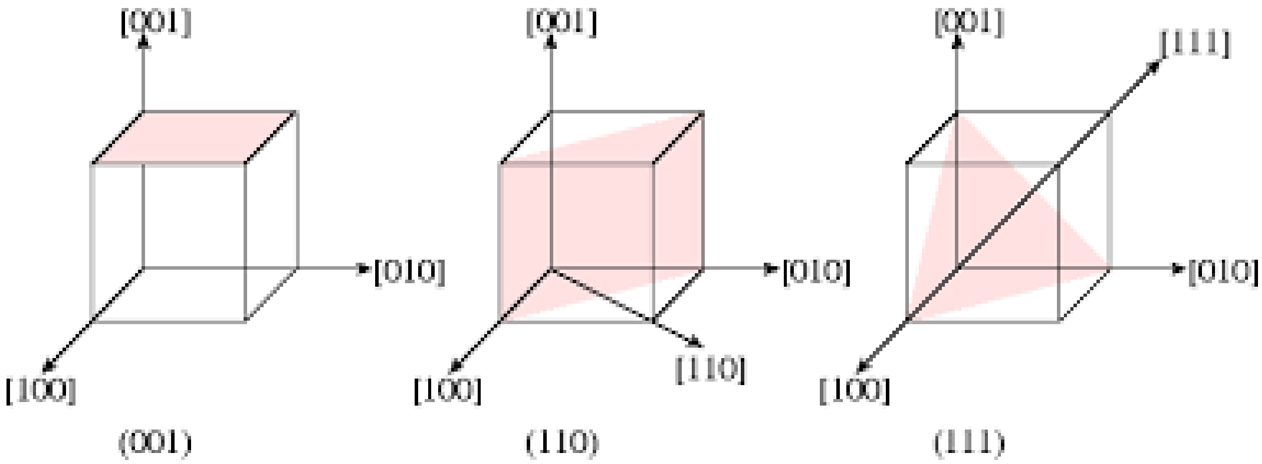
It is necessary to designate crystallographic planes and directions in a unit cell. Miller indices refer to a three digit notation system used for this purpose for cubic structures. In the case of hexagonal crystal structures, a four digit system, called Miller-Bravais indices, are used to indicate planes and directions. A right hand coordinate system using three axes is used for determining Miller indices.

Miller Indices for Directions of Cubic Structure

A crystallographic direction is defined as a line vector between two points. Procedure for determining the Miller indices of a direction are given below:

1. Determine coordinates of two points (head point and tail point).
2. Subtract coordinates of tail point from head point.
3. Multiply or divide the subtracted numbers by a common factor to obtain smallest integers.
4. Enclose the indices in square brackets [hkl].

Miller indices for some important directions are given below:



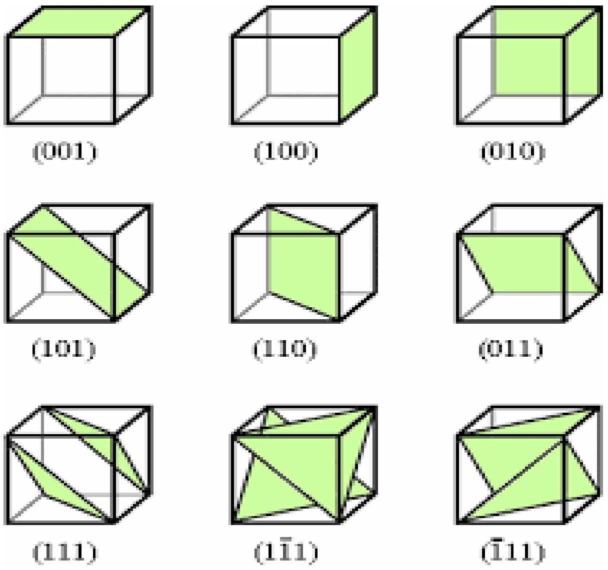
A family of equivalent directions is indicated by enclosing the indices within angle brackets.
For example <100> = □ $1\bar{0}0$□ ,□ 100□ ,□̄ 010□ ,□ 010□̄ ,□ 001□ ,□ 001□ directions

Miller Indices for Planes of Cubic Structure

The stepwise procedure is outlined below:

1. Find the intercepts of the points at which planes intercept x, y and z axes. Express the intercepts in terms of lattice parameters.
2. Take the reciprocals of these intercepts. A parallel intercept (∞) has reciprocal as zero.
3. Change the reciprocals to smallest integers.
4. Enclose the indices within parentheses (hkl)

Some important planes of cubic unit cell are shown in the sketches below:



Family of planes are denoted by enclosing the indices in braces {100}

Miller –Bravais Indices for Hexagonal Structure

Planes and directions in hexagonal crystals are defined using 4 axes (a_1, a_2, a_3 and c axes). Hence there will be four digits in the indices (h, k, I, l). Among these, third digit i= -(h+k) always.

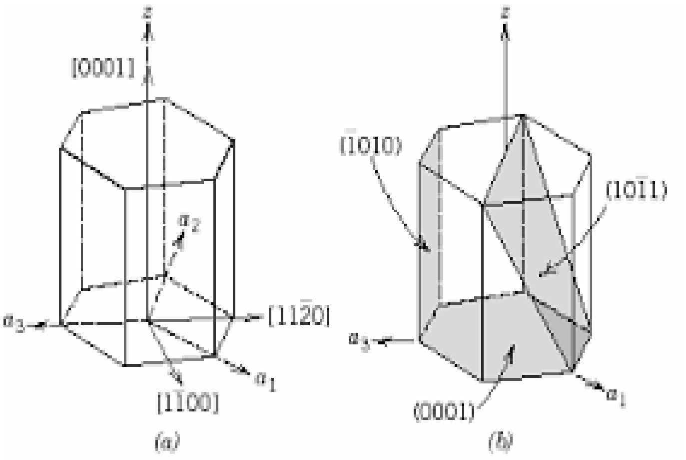


Fig (a) shows directions and Fig (b) indicates planes of hexagonal unit cell.

Attributes of Miller Indices for Slip System

Slip is the most important mechanism for plastic deformation of metals and alloys. In slip, atoms move relative to each other resulting in permanent deformation. Slip occurs on specific crystallographic planes in specific directions. The important characteristic of slip planes and slip directions is that they are the most close packed with atoms. Combination of a slip plane with a slip direction is called slip system. Slip planes and slip directions are denoted by Miller indices only. Hence Miller indices play a very important role in slip system.

Brittleness of BCC, HCP and Ductility of FCC

Materials which undergo extensive plastic deformation before breakage due to stresses are called ductile. Materials which break suddenly with little or no plastic deformation are called brittle. The behavior of ductility or brittleness can be explained on the basis of available slip systems.

In FCC metals,{111} planes and <110> directions are the most closely packed. There are 4 such planes and 3 directions in each plane. Therefore FCC has 12 (4x3) possible slip systems. Slip can occur in any of these slip systems. Hence slip and resulting plastic deformation can occur easily in FCC. FCC materials are therefore ductile.

In BCC structure <111> directions are densely packed with atoms. However there are no planes having very high atomic density like {111} planes. {110} planes are preferred slip planes, but the stress required to start slip in these planes is much higher than in FCC. Hence BCC materials are less ductile though number of slip systems is arguably 12 or more.

In HCP structure, basal plane {0001} is closely packed like {111} plane of direction 2 0 FCC (3 nos) has high atomic density. Hence HCP has only 3 slip systems (one plane x 3direcions). As a result HCP metals are normally brittle.

These findings are summarized in the table given below

Crystal structure	Slip plane	Slip direction	No of slip systems
FCC	{111} - 4 planes	<110> 3 on each plane	12
BCC	No close packed plane {110}	<111> -3 nos	High critical shear stress
HCP	{0001} – 1 plane	<11$\bar{2}$0> 3 nos	3

It may be noted that slip in other planes and directions (less common slip systems) is possible when temperature or stress is increased to high values.

Modes of Plastic Deformation

Mechanisms of plastic deformation: Yielding implies atoms moving to new equilibrium positions and forming new bonds. Atoms cannot return to original position. Deformation is thus inelastic or irrecoverable and is called plastic deformation. There are two mechanisms/methods for plastic deformation 1) Slip and 2) Twinning. Slip is the main mechanism.

Plastic deformation by Slip:

Most metals are weak in shear than in tension and compression. Hence yielding always occurs by shear forces. Even tensile or compressive stresses have resolved shear stress.

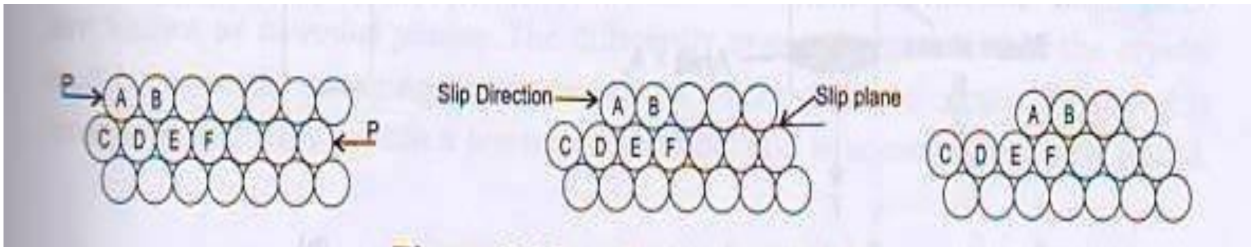


Figure 3.13 *Mechanism of slip*

Under the action of the shear force P, atom A in the slip plane moves from the valley between C and D to the valley between E and F atoms. All these are equilibrium positions. Hence atom A cannot return back and displacement is permanent.

Some atoms slipping past other atoms on certain plane and on certain direction is called as SLIP. The relevant plane is Slip Plane and relevant direction is Slip Direction. Slip plane and slip direction are always close packed with respect to atoms. A slip plane together with a slip direction is referred to as a slip system.

Plastic deformation by Twinning

Twinning occurs only in certain materials. It is also a mode of plastic deformation like slip. On applying shear stress on these materials, atoms in certain regions move such that the orientation of the lattice changes to form a mirror image of the original lattice. This phenomenon is called twinning. The region is called twinned region.

Table: Comparison between Slip and Twinning

Slip	Twinning
Involves sliding movement of atoms	Involves displacing movement of atoms
Crystal orientation before and after slip same	Orientation of twinned region different. Forms mirror image.
Atomic movements in steps of inter atomic spacing	Atomic movements only in fractions of inter atomic spacing
Slip appears as thin lines under microscope	Twinning appears as bands
Slip occurs at lower stresses	Twinning requires higher stresses
Critical shear stress to be exceeded for starting slip	No such minimum value
Observed in all lattices	Mostly observed in HCP
Slip lines can be odd or even	Always even (in pairs)

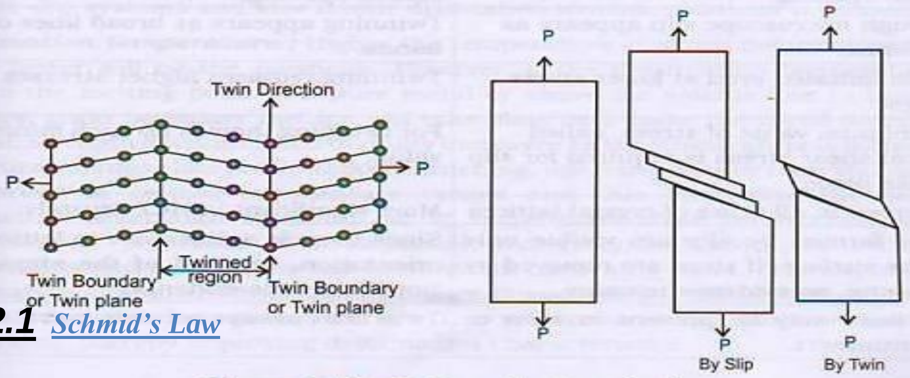


Figure 3.15 *Deformation by twinning*

1.2.1 Schmid's Law

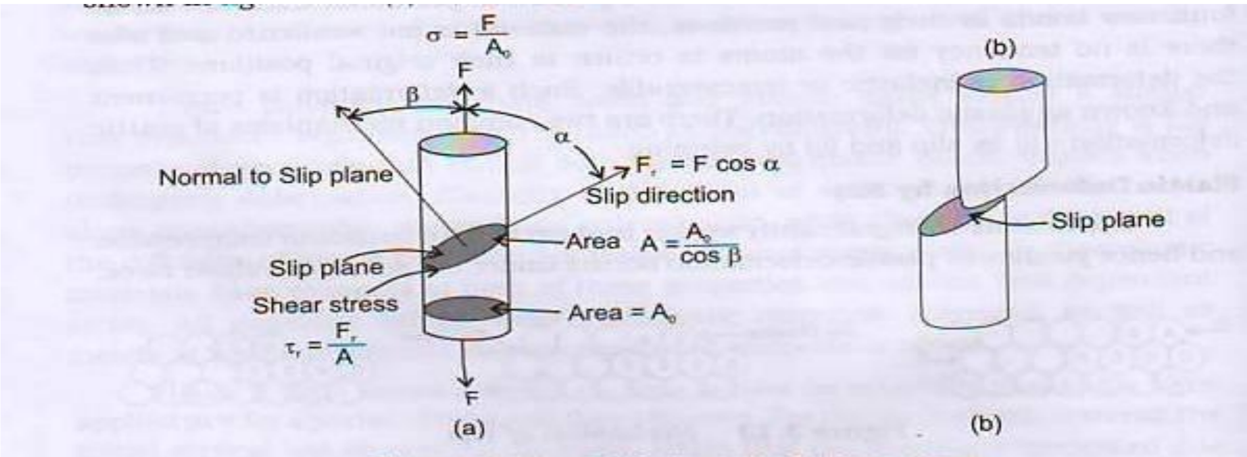
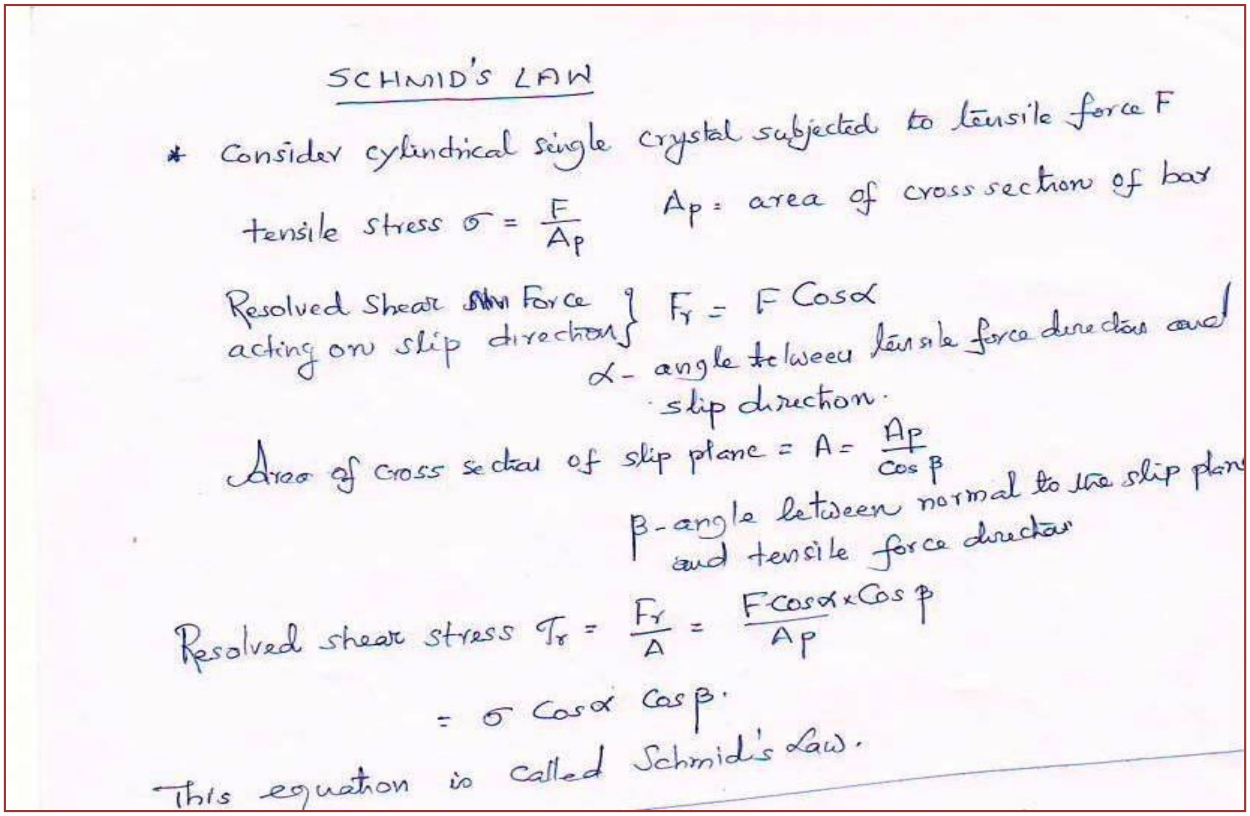


Figure 3.14 *Critical resolved shear stress*



SCHMID'S LAW

* Consider cylindrical single crystal subjected to tensile force F

tensile stress $\sigma = \frac{F}{A_p}$ A_p: area of cross section of bar

Resolved Shear ~~Str~~ Force acting on slip direction } $F_r = F \cos\alpha$

α - angle between tensile force direction and slip direction.

Area of cross section of slip plane = $A = \frac{A_p}{\cos\beta}$

β - angle between normal to the slip plane and tensile force direction

Resolved shear stress $\tau_r = \frac{F_r}{A} = \frac{F\cos\alpha \times \cos\beta}{A_p}$

$= \sigma \cos\alpha \cos\beta$.

This equation is called Schmid's Law.

Schmid's Equation and Critical Resolved Shear Stress

Resolved shear stress $\tau_r = \sigma \cos\alpha \cos\beta$ (where σ= tensile stress, α= angle between tensile load axis and slip direction, β= angle between tensile load axis and normal to slip plane) is also called Schmid's Equation. τr is highest when $\alpha=\beta=0$ and it is zero when α or $\beta=90^0$.

It should be noted that there is a **critical resolved shear stress (τ_{crss})** which has to be exceeded for starting slip. It means that slip will occur only when the applied shear stress calculated as per Schmid's equation exceeds the critical resolved shear stress of the material ($\tau_r > \tau_{crss}$).

Correlation of Slip System with Plastic Deformation in Metals and Applications

Slip plane is the plane with most densely packed atoms. Slip direction is the direction which is most closely packed with atoms (in the slip plane). Slip system refers to combination of a particular slip plane and slip direction. Slip systems depend on crystal structure of material. For example FCC has 12 slip systems whereas HCP has only 3 slip systems.
Critical shear stress refers to the minimum shear stress required to initiate slip on an active slip system. It is a property of the material. It varies from material to material. Even in a specific material, its value varies with slip system.Applied stress is usually tensile. Its resolved shear stress component is given by Schmid's equation, *viz.* $\tau_r = \sigma \, \mathrm{Cos}\alpha \, \mathrm{Cos}\beta$. It is clear from the equation that value of resolved shear stress depends on value of applied stress (σ) and orientation of slip system (α and β.

Suppose that stress is gradually applied to a material. For the given direction of the applied stress, some slip systems will be favorably oriented for slip. Slip will take place on these slip systems when applied (resolved) shear stress reaches the value of critical resolved shear stress of the material for these slip systems.

In a polycrystalline material, grains (crystals) are oriented at random in all possible directions. Therefore in such a material, slip will start simultaneously in many crystals having favorably oriented slip systems. However the progress of slip in one crystal will be influenced by slip in adjacent crystals as grain boundaries are to be maintained continuous. This imposes some constraints causing increase in strength of material and elongation of grains.

MODULE 2

MECHANISM OF CRYSTALLIZATION

Crystallization is also called solidification. It is the transformation from liquid state to solid state. It is essentially a nucleation and growth process. In liquid state, atoms do not have any definite arrangement. As the temperature of the liquid is coming down, a stage is reached where group of atoms cluster together forming embryos. The temperature at which these embryos (solid) form and coexist with the liquid is known as freezing point.

Undercooling

At the freezing point, the volume free energy of the solid is lower than that of liquid. The difference in energy is known as latent heat of fusion. But energy is needed to create a solid surface from liquid. This energy is called surface free energy. During formation of solid nuclei, volume free energy is negative and surface free energy is positive. Stable nuclei can be formed only when net free energy change becomes negative. A plot of free energy change with respect to radius of nuclei (assuming spherical shape of nuclei) for any particular temperature is given in figure.

Figure

It can be seen that net free energy starts decreasing only when the nuclei attain a critical radius (r*). Nuclei of radii smaller than r* tend to re-dissolve in the liquid and those larger than r* tend to grow. It is also known that critical radius r* goes on decreasing as the temperature is lowered below the freezing point. In pure metals solidifying by homogeneous nucleation, significant **under cooling (cooling below freezing point)** is necessary to obtain stable nuclei which can grow.

Homogeneous Nucleation

In homogenous nucleation nuclei (grown embryos) form from within the liquid itself. This type of nucleation is difficult and needs significant under cooling to form stable nuclei. The nuclei are formed throughout the liquid. These nuclei release latent heat of fusion and the temperature is raised to freezing point. At the same time, heat is being continuously lost to surrounding and solidification proceeds by growth of these nuclei. Under very rapid heat transfer conditions, under cooling may persist and fresh nuclei can form which also grow.

Heterogeneous Nucleation

Some impurities act as nuclei. Such nucleation is called heterogeneous nucleation. This type of nucleation can occur with little or no under cooling. The impurities may be present without intentional addition (e.g. impurity nuclei present on mold walls). Grain refiners can also be added intentionally to the melt (e.g.Ti and B additions to Al alloys). Grain refiners form large number of solid nuclei throughout the liquid.

Dendritic Growth

Nuclei actually grow in certain preferred directions. This gives rise to a characteristic tree like structure called **dendrite**. The dendrite arms grow and thicken in three dimensions. Finally the liquid in between the dendrites also solidifies. The outer arms grow until they make contact with a neighboring dendrite. Each dendrite becomes one grain. The area along which the grains meet is known as grain boundary. The grains look alike. But their crystallographic orientations are different. Orientations change randomly.

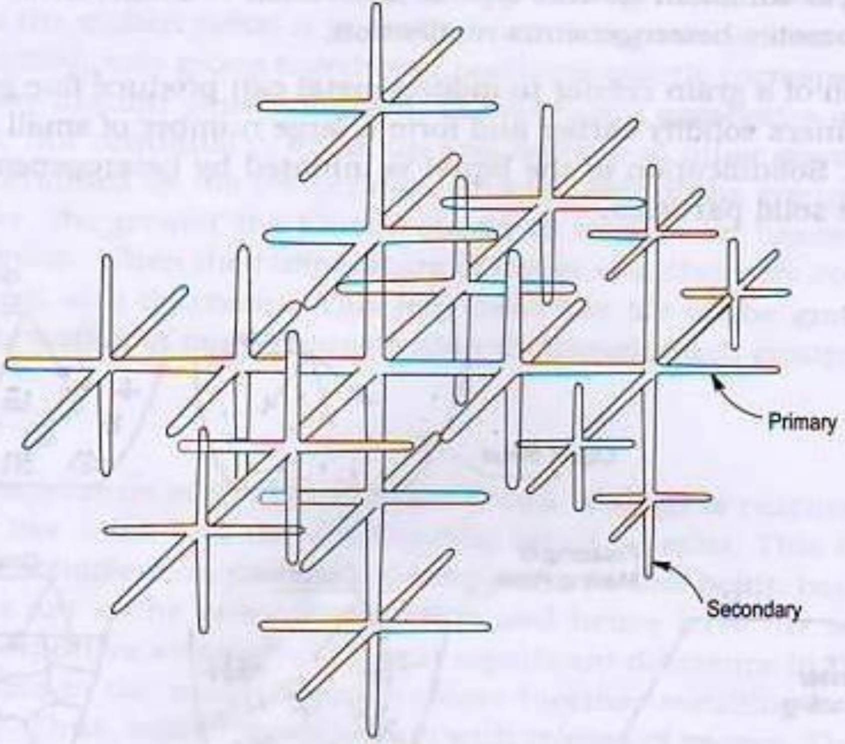


Figure 3.2 *Dendritic crystal*

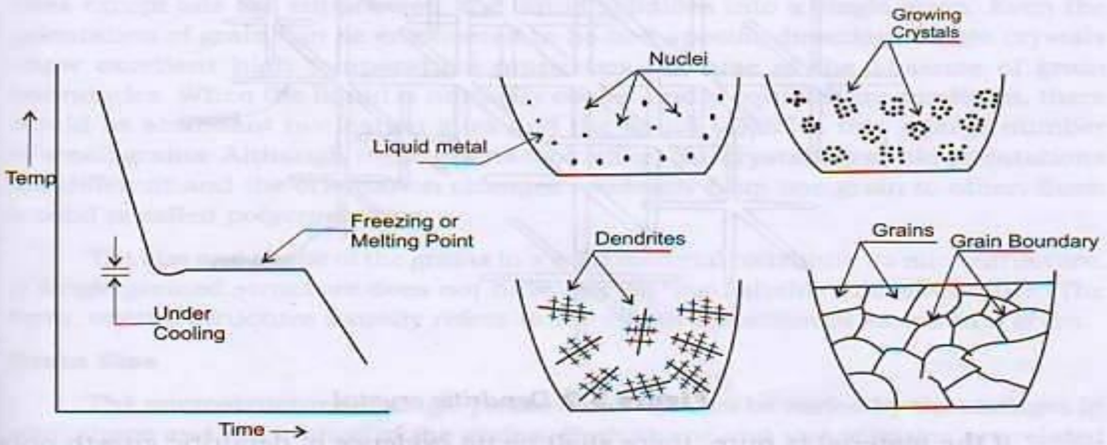


Figure 3.1 *Solidification Process*

Grain Boundary Irregularity

Randomly formed nuclei have different crystallographic orientations. These nuclei grow maintaining the orientations. As they grow, the outer arms of the dendrites meet similar arms of neighboring grains. Then further outward growth becomes impossible and solidification is completed. Because of crystal formation as explained above, grains are of irregular polyhedron shape, even though for analytical purposes, grains are treated as spherical and grain diameters are specified. Inside one grain, orientation of atoms is nearly identical. But atomic orientations of adjoining grains will be different. Area along which the grains meet is called grain boundary. It is a region of high atomic mismatch without any orderly arrangement of atoms. Grain boundaries are also therefore irregular shaped.

Effect of Grain Parameters on Strength (Dislocations) and Creep Resistance

Grain Size

Number of grains after solidification depends on number of nuclei formed. If all nuclei except one are suppressed, liquid solidifies into a single grain called a single crystal. Single crystals exhibit excellent high temperature properties and creep strength because of absence of grain boundaries. Under normal conditions, there are large numbers of nuclei and hence the solidified structure is poly crystalline. Small number of nuclei results in large (coarse) grain size. Large number of nuclei leads to fine grains. At normal temperatures, grain boundaries are stronger than grains whereas at elevated temperatures, grain boundaries are weaker than grains. Hence fine grains provide high strength at normal temperatures because grain boundaries hinder dislocation motion. However coarse grains give higher creep resistance than fine grains since creep is a high temperature phenomenon. It may be noted that grain size can also be controlled by thermo-mechanical treatments (plastic deformation combined with annealing) apart from solidification processes described above.

Grain Size Distribution

A material yields at its weakest portion. It is established that materials having low values of mean grain size have better strength compared to large mean grain size. However there could be considerable variations in grain size distribution even though the mean grain sizes remain the same. It is clear that portions where maximum grain size exists, will be the weakest. It has been established that for given mean grain size, samples with relatively broad size distributions, and, hence, relatively large populations of larger-than-average grains, were softer than those with narrow grain size distributions at the same grain size. Hence it is evident that grain size distribution can affect strength and creep resistance though its effect is highly significant.

Grain Shape

A grain is called equiaxed when it is having same dimensions along the three axes. A spherical grain is therefore equiaxed. Other commonly observed grain shapes are columnar, plate like or dendritic. Generally there are three zones in a large ingot mold as shown in figure. Because of the large number of nuclei present near the mold wall, the first zone near the mold wall contains fine equiaxed grains. Since fresh nuclei are not formed, the grains of the first zone tend to grow in certain preferred directions resulting in columnar grains observed in second zone. Fresh nucleation starts at the centre due to a phenomenon called constitutional under cooling (under cooling due to variation in composition of liquid and solid.

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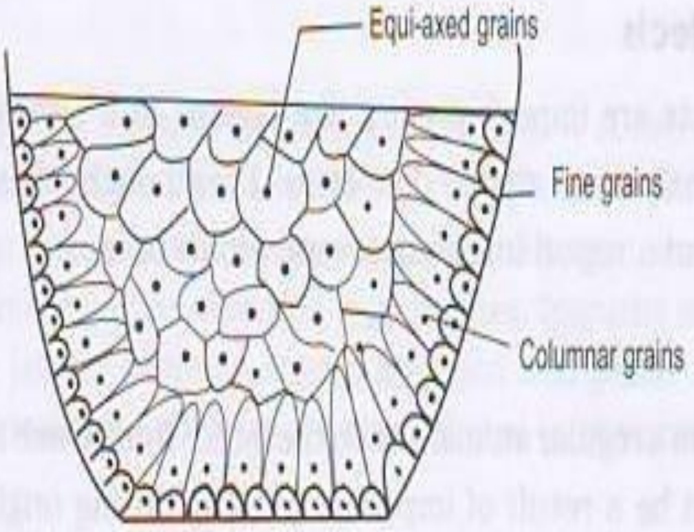


Figure 3.3 *Grain growth on solidification*

The tensile strength and flow stress are found to be not affected by grain shape. But elongation and elastic modulus are found to be influenced by grain shape. Elongation is more in longitudinal direction.

Grain Orientation

In sinle crystals, ultimate tensile strength shows a clear orientation dependency, where samples tested parallel to the shear plane reaches higher values compared to samples tested perpendicular to the shear plane. However the grains are randomly oriented in a polycrystalline material. There will be a number of crystals favorably for the dislocations to glide. Thus for big enough polycrystalline samples, the orientation is not a factor and the strength and creep resistance depend only on the average grain size.

Hall Petch Theory

Hall Petch theory (equation) was proposed by E.O Hall and N.J Petch. It gives a general relation between yield stress (flow stress) and grain size of a material.

$$\sigma_0 = \sigma_i + \frac{k}{\sqrt{D}}$$

Where σ_0 = yield stress (stress needed to start plastic deformation), σ_i and k are constants for the material and D is the mean grain size (average grain diameter).

The equation is not valid for extremely large and extremely fine grains. It is valid for grains as small as 50nm.

CLASSIFICATION OF CRYSTAL IMPERFECTIONS

Most engineering materials are poly crystalline. Perfectly periodic and repeated arrangement of atoms is absent. Many interruptions called crystal imperfections or defects exist. Their volume may be as small as 0.01%. But they greatly influence mechanical, chemical and electrical properties (structure sensitive properties). There is no effect on structure insensitive properties like-density.

Crystal imperfections can be classified as given below:

1. Point Defects or Zero dimensional Defects
   (i) Vacancy
   (ii) Self Interstitial or Interstitialcy
   (iii) Substitutional Impurity
   (iv) Interstitial Impurity
   (v) Frenkel Defect
   (vi) Schottsky Defect
2. Line Defects or One Dimensional Defects
   (i) Edge Dislocation
   (ii) Screw Dislocation
3. Surface Defects or Two Dimensional Defects
   (i) Grain Boundaries
   (ii) Tilt Boundaries
   (iii) Twin Boundaries
   (iv) Stacking Faults
4. Volume Defects or Three Dimensional Defects

Point Defects

These are point like regions containing defects. Different types of point defects are:

a) Vacancy : Atoms are missing from regular site. Vacancy forms during solidification or high temperature exposure. Higher the temperature more is the number of vacancies.

b) Interstitials : An atom squeezing into space between normal lattice positions is called interstitial. If interstitial atom is same as normal atom, it is called self- interstitial. Distortion or energy is higher for interstitial than vacancy. Hence number of interstitials is negligible compared to vacancies.

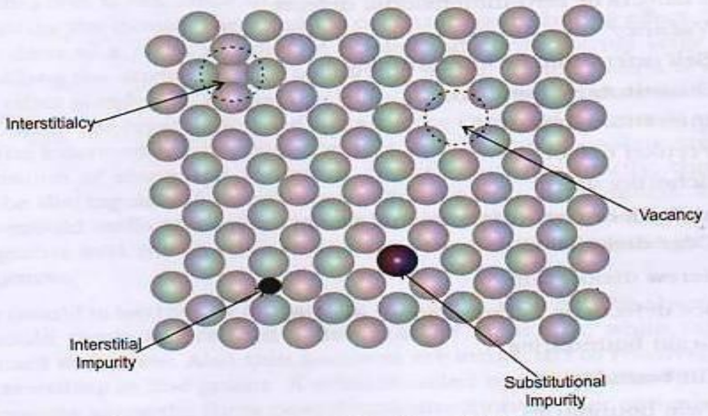


Figure 3.4 *Point imperfections*

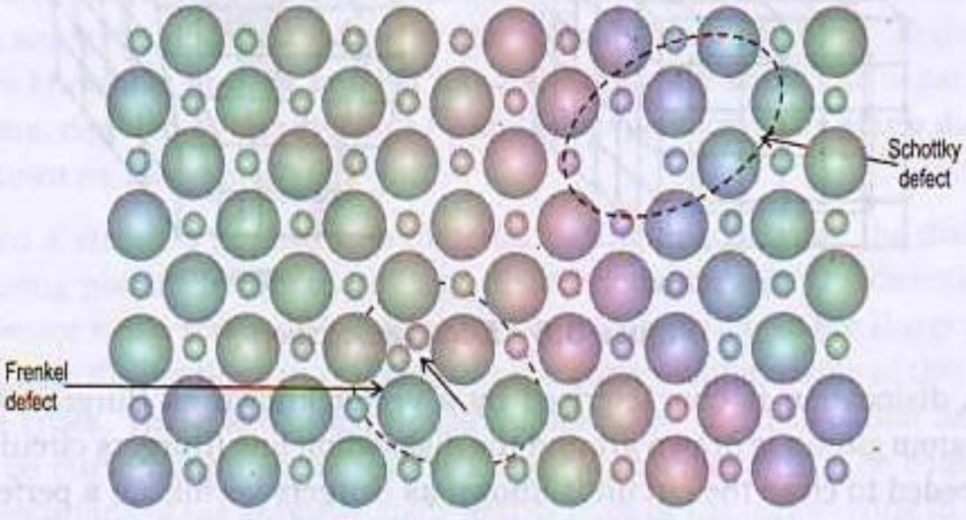


Figure 3.5 *Point imperfections*

Effect of point imperfections on mechanical properties

Point defects can be intrinsic defects (occurring in pure metals) or extrinsic defects (caused by solute or impurity atoms) . Vacancy and interstitialcy (self interstitial) are intrinsic defects. Interstitialcy is a high energy defect and is uncommon. Most pronounced effect of vacancies is in solid state diffusion. Rate of diffusion is a function of concentration of vacancies.

Impurities or solutes are extrinsic defects. The difference between the two is that solutes are intentionally added foreign atoms. These extrinsic defects affect almost all engineering properties. In semi conductors such as silicon and germanium, the solutes are added to control electrical properties. It is called doping. Two types of dopants are used for silicon (4 valence electrons) *viz.* (i) solutes like boron having 3 valence electrons (acceptors) and (ii) solutes like phosphorous with 5 valence electrons (donors). In both cases conductivity is significantly increased.

In structural materials, addition of solute elements increases strength and hardness by solid - solution hardening mechanism. Solute atoms are either bigger or smaller than the parent atoms. In both cases, crystal lattice is distorted to fit the solute atoms. These distortions impede the movement of dislocations and thereby the strength is increased. The distortions are significantly larger for interstial solutes compared to substitutional solutes. Therefore interstitial solutes are more effective strengtheners (E.g steels containing carbon as interstitial solute in iron).

Another type of hardening (strengthening) is through tetragonal distortion. It is found that crystal lattice of steels containing more than few tenths of carbon gets distorted into a body centered tetragonal (BCT) structure instead of BCC when cooled rapidly. This distortion is caused by carbon atoms and the structure is called martensite (Hardest phase)

.

Types of Dislocations

Dislocation is the most important line defect. It is a disturbed region between perfect parts of a crystal. It is responsible for plastic deformation. There are two types of dislocations.

(a) Edge Dislocations**:** These are formed by extra partial plane in a crystal. A disturbed region is seen around edge of incomplete plane. There are two types of edge dislocations (i) Positive : Extra plane is on the top half of the crystal and (ii) Negative: Extra plane on the bottom half of crystal.

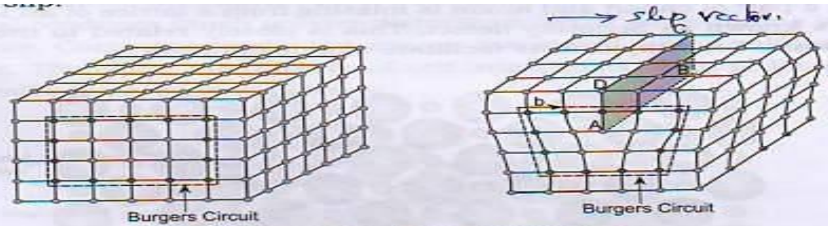


Figure 3.6 *Edge Dislocation*

AB represents edge dislocation line. Plane ABCD is slip plane. Slip occurs in the direction of slip vector. Dislocation is characterized by burgers vector. A Burger's circuit is drawn through specific atomic distances. Circuit closes in perfect crystal. Circuit does not close in crystals with dislocation. The vector needed to close the circuit is burger's vector. In edge dislocation burger's vector is perpendicular to dislocation line. Edge dislocation moves in the direction of burger's vector.

<u>(b)</u> <u>Screw Dislocation :</u> Ref fig. When shear stress is applied, upper part of crystal to the right of PS(dislocation line) is slipped relative to the lower part. PS is parallel to slip vector or burgers vector.

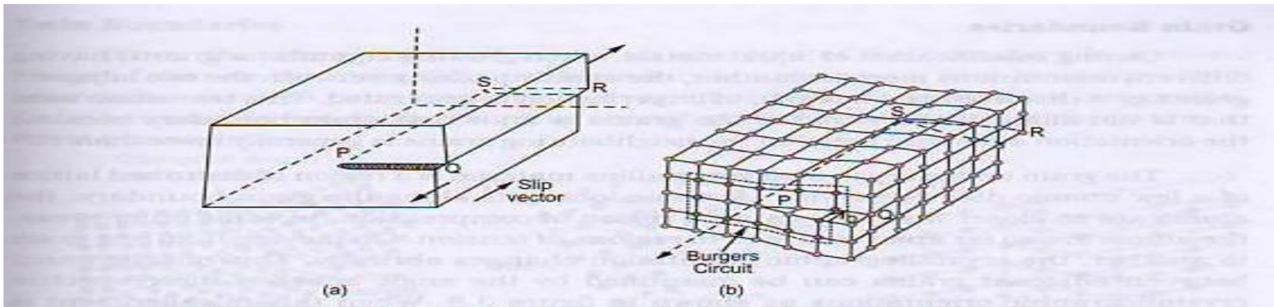


Figure 3.7 *Schematic representation of screw dislocation*

Name 'screw' comes from spiral or helical path of dislocation. Right handed spiral is known as positive screw and left handed spiral indicates negative screw dislocation. Screw dislocation move perpendicular to burgers vector.

Dislocations in real crystals are mixed type with edge and screw component

Forest of Dislocations

A collection of dislocations passing through active slip plane forms a dislocation forest. Dislocation forest arrest movement of other individual dislocations just like a forest of trees creating difficulty in movement. When moving dislocations cut through dislocation forest, jogs are produced. These jogs create additional barriers for dislocation motion.

Surface Defects

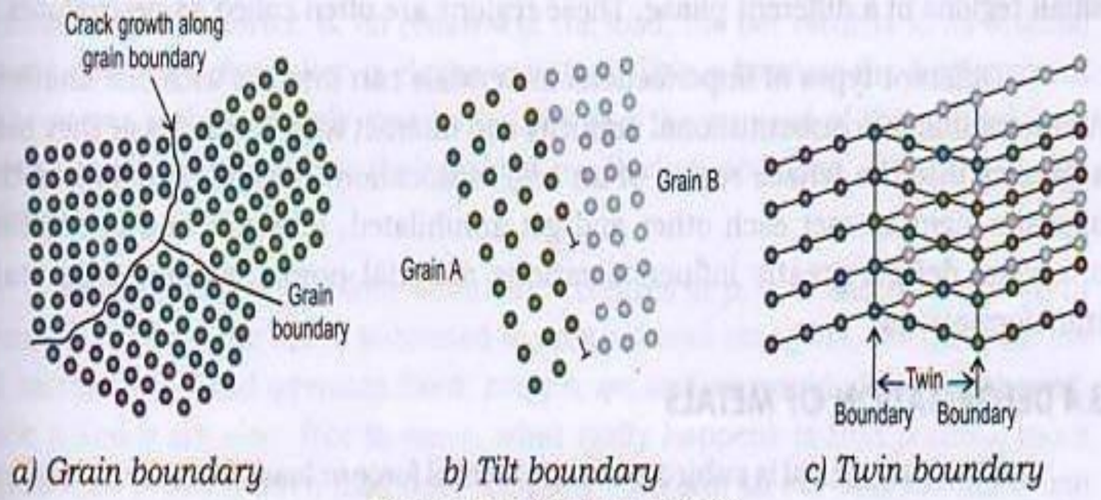
These are two dimensional defects. Surface defects occur due to change in stacking of atomic planes.

(a) Grain boundaries: They form during solidification. They are boundaries between grains. They are of few atomic diameters wide. There is high orientation difference between grains (more than 10 degrees)

(b) Tilt boundaries and twist boundaries: Small angle grain boundaries (less than 10 degrees) form during plastic deformation. Tilt boundaries are created by edge dislocations of same sign arranging one above the other. Twist boundaries –low angle boundaries formed by screw dislocations.

(c) Twin boundaries: In twin boundaries atomic arrangement on one side of boundary is mirror Image of that on the other side- They form during plastic deformation or annealing.

(d) Stacking faults: They generally occur in close packed structures like FCC and HCP. Stacking sequence in FCC is ABC ABC ABC and that in HCP is AB AB AB. Suppose the stacking sequence in FCC changes to ABC AB ABC or that in HCP changes to AB AB ABC AB. These are called stacking fault defects.



a) Grain boundary b) Tilt boundary c) Twin boundary

Figure 3.9 *Surface defects*

Role of Surface Defects on Crack Initiation

The atoms near the grain boundaries have non-equilibrium surroundings and are at higher energy levels. Likewise, atoms at the surface are also under the same situation. The surface is usually rough and contains many notches. These notches initiate cracks. The cracks propagate along the grain boundaries leading to intergranular fracture. Refer Fig (a) given above depicting crack growth.

Surface defects are particularly important for fatigue crack initiation. Fatigue is failure under repeated cyclic loading. The failure involves two parts; namely crack initiation and crack propagation. Cracks invariably initiates from surface defects which act as stress raisers. An important contributor for crack initiation is persistent slip bands (PSB) formed by dislocations. PSB could be above surface (extrusion) or below the surface (intrusion).

Burgers Vector

Burgers vector, named after the Dutch physicist, Jan Burgers, is a vector denoted by b which represents the lattice distortion produced by a dislocation (edge type or screw type) in the crystal lattice. In order to determine the burgers vector an atom by atom circuit is drawn with fixed atomic distances (PQMN). This circuit is called Burgers circuit. Burgers circuit for an edge dislocation is represented in top figure and that for a screw dislocation In given at bottom. In a perfect crystal without dislocation the circuit closes. But when dislocation is present, the circuit does not close. The vector needed to close the circuit from the end point to start point is called Burgers vector. It can be seen that in an edge dislocation, burgers vector is perpendicular to dislocation line and in a screw dislocation, burgers vector is parallel to dislocation line.

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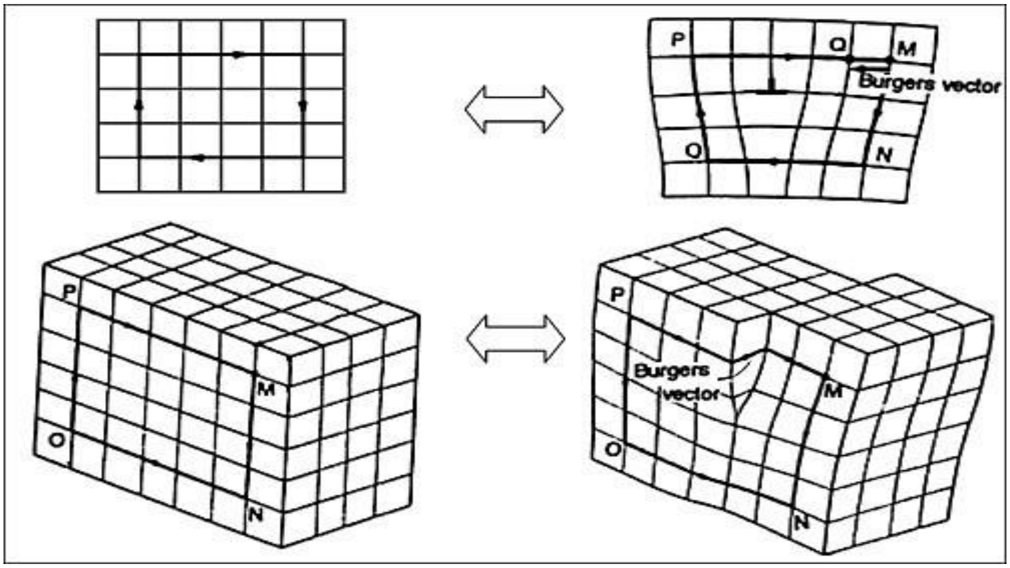
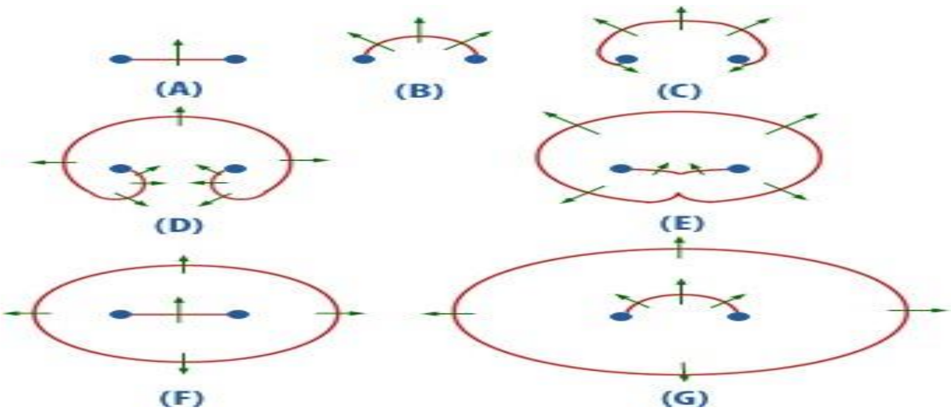


Dislocation Sources

A large number of dislocations are necessary for plastic deformation (slip). These dislocations come from different sources. One source is solidification itself. There is an equilibrium concentration of vacancies, generated during solidification. But these are grossly insufficient for significant plastic deformation. Other sources are condensation of vacancies, cross slip and high angle grain boundaries. However the most important source for dislocations is Frank Read source.

Significance of Frank Read Source in Metal Deformation



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Frank –Read source is a scheme of generating dislocations from existing dislocations itself. Consider a segment of dislocation shown in (A) lying in slip plane. The dislocation is anchored at the two ends. Suppose a shear force acts on the slip plane. Dislocation bulges out as given in (B). The loop continues to expand under increasing shear stress as given in (C). When the loop reaches stage (D), segments are approaching to meet. The position after the segments meet is shown in (E). There is a new dislocation loop. The dislocation line segment is left intact (shown at center of loop). The process continues [(Figures (F) and (G)] and more dislocations are formed from the same dislocation source. The Frank-Read source can operate continuously and produce a large number of dislocation loops.

It has been observed that dislocation (total length of dislocation lines per unit volume) increases by two to six orders of magnitude depending on amount of cold working (cold deformation). This is almost entirely due to Frank Read source of dislocations by which large number of dislocations is generated from a single dislocation segment. As long as the dislocations move out and disappear at the surface, the production continues. When the dislocations loops get piled up at obstacles such as grain boundaries, back stresses develop and source gradually dies out. It should be noted that deformation happens when dislocations move and hence the more the number of dislocations moving, the larger will be the deformation.

Correlation pf dislocation density with strength and nano concept

Dislocation density is defined as the total length of dislocation lines per unit volume or the number of dislocation lines that move across a unit cross section area. Usual unit is mm^{-2}. Cold working increases dislocation density many fold. Dislocation density of an annealed material is 10^4 to 10^6 mm^{-2} while a cold worked material has a dislocation density of 10^8 to 10^{10} mm^{-2}.

Purity of metal determines initial dislocation density. Strength of a material is inversely related to mobility of dislocations and ductility (amount of plastic deformation) is directly related to mobility of dislocations. Even though cold working increases dislocation density, dislocations movement is hindered due to various barriers formed by the interaction of these dislocations. Therefore cold working increases strength at the expense of ductility.

In nanomaterials also, the yield strength is determined by the mobility of dislocations through the crystal. Nanomaterial is considered as polycrystalline materials with very small grain size. Accordingly the initial strength of nanomaterial is quite high in line with Hall Petch concept. However additional strengthening by strain hardening is relatively small because dislocation density does not increase as in conventional materials.

Significance of High and Low angle Grain Boundaries on Dislocations

Grain boundaries disrupt the motion of dislocations through the material. Low angle grain boundaries have a misorientation (orientation difference) of less than 10^0. Generally they are composed of an array of dislocations and their properties and structure are a function of the misorientation. In the case of high angle grain boundaries having a misorientation of more than 10^0 , properties are independent of misorientation.

Low angle grain boundaries may be a tilt boundary or a twist boundary. Tilt boundaries are formed by an array of edge dislocations where as twist boundaries are created by an array of screw dislocations. If dislocations remain isolated and distinct, the boundaries continue to be low angle type. Low angle boundaries form sub grains within the main grain. When deformation happens, dislocation density will increase. At a sufficiently large deformation, low angle boundaries break down and they convert into high angle grain boundaries. Thus sub-grains become individual, separate grains.

High angle grain boundaries are more disordered and have open structure. They are very effective in retarding motion of dislocations resulting in grain boundary strengthening.

Driving Force for Grain Growth and Applications during Heat Treatment

Grain growth is the increase in the size of grains of a material at high temperature. It occurs after completion of recovery and recrystallization stages during annealing operation. Larger grains have lower free energy compared to smaller grains. Grain boundaries are regions of high energy. When grain boundaries become lesser as in grain growth, energy is greatly reduced. In fact, the lowest energy state of a material is a single crystal. This is the driving force for grain growth.

Rigidity of the lattice opposes this driving force. As temperature increases, the rigidity gets reduced. Hence grain growth is more rapid at high temperatures. At any given temperature, there is a maximum grain size where the two opposing forces are in equilibrium.

Grain growth is an undesirable phenomenon. It should be suppressed. Some of the precautions to be taken during heat treatment to restrict grain growth are given below.

1. **Prior deformation:** Higher cold deformation leads to more nucleation and consequently finer grain size. These fine grains will be more resistant to grain growth.
2. **Time at temperature:** More the time at elevated temperature, the higher will be the grain growth. Hence the time should be kept to minimum needed for achieving the required temperature at the core (center) portion of the job.
3. **Heat treatment temperature:** Temperature should be held to the minimum required for achieving the heat treatment purpose. Lower the temperature, lower is the grain growth.
4. **Insoluble impurities:** Fine insoluble impurities help in the prevention of grain growth.

POLISHING AND ETCHING TO DETERMINE MICROSTRUCTURE AND GRAIN SIZE

Metallography is the study of microstructure of metals and alloys using microscopes. Optical metallography deals with microstructure obtained by optical microscope with magnification up to 2000X. Microstructure reveals structure of grains, grain size, microphases etc. For obtaining microstructure, a small sample of material (specimen) has to be prepared.

1.Selecting and cutting Specimen

Specimen has to be representative of the material under study. Smaller specimens have to be mounted on Bakelite or plastic.

2. Rough Grinding:

The purpose is to make the surface absolutely flat. File, rotating grinding wheel or motor driven emery belt is used. Avoid specimen heating. After rough grinding, specimen is washed and dried.

3. Intermediate and Fine Grinding :

For intermediate grinding, specimen is rubbed against a series of emery papers designated as 220,320,400 and 600 grit. For fine grinding, emery papers 1/0, 2/0, 3/0 and 4/0 are used.

4.Polishing :

Fine grinding leaves the specimen surface with very small parallel grooves from last emery paper. Polishing removes these grooves. A rotating cloth pad (a rotating wheel covered with suitable cloth or chamois leather) is used for polishing. The pad is impregnated with a polishing powder or paste. Distilled water is continuously applied to the wheel which moves in low speed.

Specimen is moved in a direction opposite to the wheel rotation. Specimen is also given a rotating motion. For iron and steels, 2 stage polishing using diamond powder and alumina powder is used. The first polishing is done with polishing agents containing particles of about 6 microns. For final polishing the particle size used is 0.5-1 micron. For non-ferrous alloys magnesia (MgO) is used. For copper alloys a polishing paste called Brasso is sometimes used. After polishing the surface should be perfect shining (mirror like) and fully scratch free.

Important precautions during specimen preparation

1. Specimen is not heated up during cutting and grinding
2. Deep scratches cannot be removed by polishing. These are to be removed by step by step grinding.
3. Apply light pressure only during grinding and polishing.
4. Too long polishing makes the specimen surface rippled.

5. Etching

Etching involves application of chemical solutions (etchants) to the surface of specimen to obtain clear microstructure. It serves two main functions (a) To remove a flawed or amorphous layer produced by polishing and (b) preferentially stain or dissolve one or more phases to clearly reveal microstructure. This happens because of differences in chemical composition and grain orientations. Grain boundaries are attacked more by etchants. Porosity, inclusions etc can be viewed before etching.

Light etch removes flawed layer and reveal grains. Deep etch removes or stains some regions in the structure. Ref Figure. Before etching, specimen is washed in running water, swabbed with cotton wool dipped in soap solution, again washed in running water and then dried. Better cleanliness is obtained by dipping the surface in boiling alcohol for about 2 minutes.

The specimen is now etched by dipping the surface into the etchant and agitating foe required time. Etching for few seconds is sufficient for plain carbon steels and brasses. Etching for several minutes is needed for stainless steels.

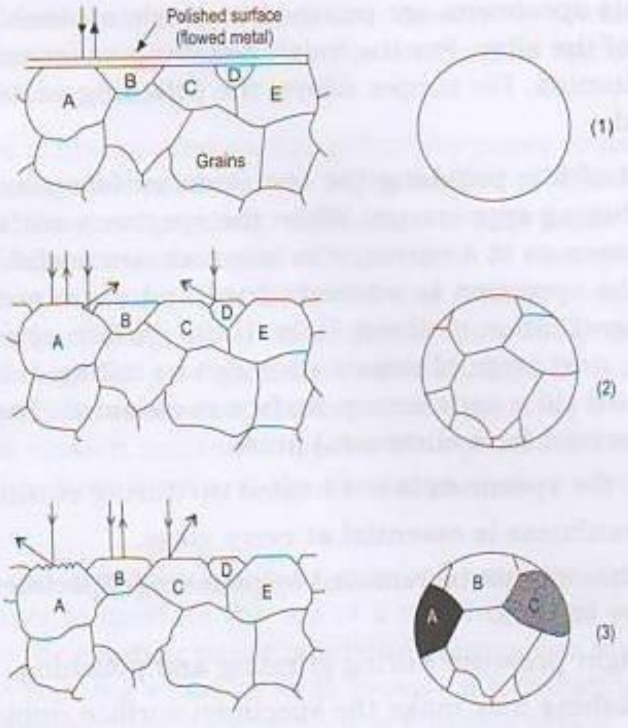


Figure 2.19 *Specimen under microscopic study (1) after grinding and polishing (2) after light etching (3) after deep etching*

After etching, the specimen is washed in running water and dried. During etching, the surface becomes uniformly dull. If the etching is not successful, the specimen has to be re-polished and re-etched. The specimen surface has to be viewed without delay after etching to avoid oxidation and contamination of the surface. Typical microstructures obtained after polishing, light etching and deep etching are illustrated in the figure.

Table: Common Etchants

Etchant Name	**Composition**	**Use**	**Etching time**
Nital	2% HNO_3 + 98% methyl alcohol	General etchant for all ferrous alloys	30-60 s
Picral	5% picric acid +95% methyl alcohol	High carbon steels, Cast iron	10-30 s
Acid ammonium persulphate	10 g ammonium persulphate+10 ml HCl + 80 ml water	Stainless steels	10-30 inutes

Grain Size Determination by Comparison with Standard Chart

Grain size influences mechanical properties to a considerable extent. Grain size is usually determined by the standard method proposed by American Society for Testing Materials (ASTM). The grain size is specified by an index called ASTM grain size number. Specimen is viewed using optical microscope at a magnification of 100X. It is compared with standard chart having different ASTM grain size numbers. Matching grain size number is identified. Larger grain size number corresponds to finer grains.
$N= 2^{(n-1)}$ where N= Number of grains per square inch and n= ASTM Grain size number.

FUNDAMENTALS AND CRYSTAL STRUCTURE DETERMINATION BY X-RAY DIFFRACTION

Fundamentals (Bragg's Law)

When a beam of electromagnetic waves such as X-rays is directed towards a two dimensional grating, waves undergo diffraction. For efficient diffraction, spacing of grating must be approximately equal to the wavelength of the rays. This principle is used for determining crystal structure by X-ray diffraction technique. Periodic array of atoms can be considered as a grating system. Wave length of low voltage X-rays are of the same order as the inter atomic spacing (2-3 A^0).

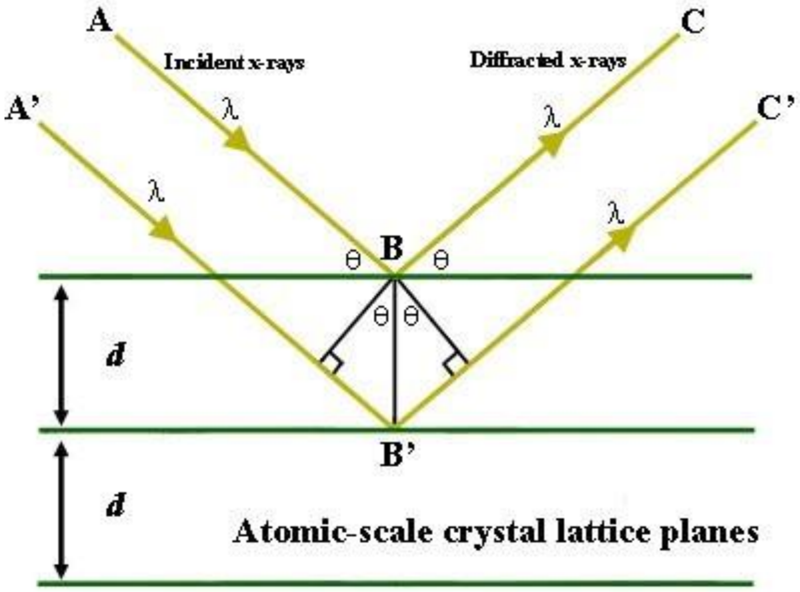


Figure shows a set of parallel planes in a crystal. When a monochromatic (single wave length λ) beam of X rays is incident at an angle θ to the atomic planes. X-rays are diffracted from parallel planes such that angle of incidence equals angle of diffraction. Let us consider diffraction from two parallel planes. Inter

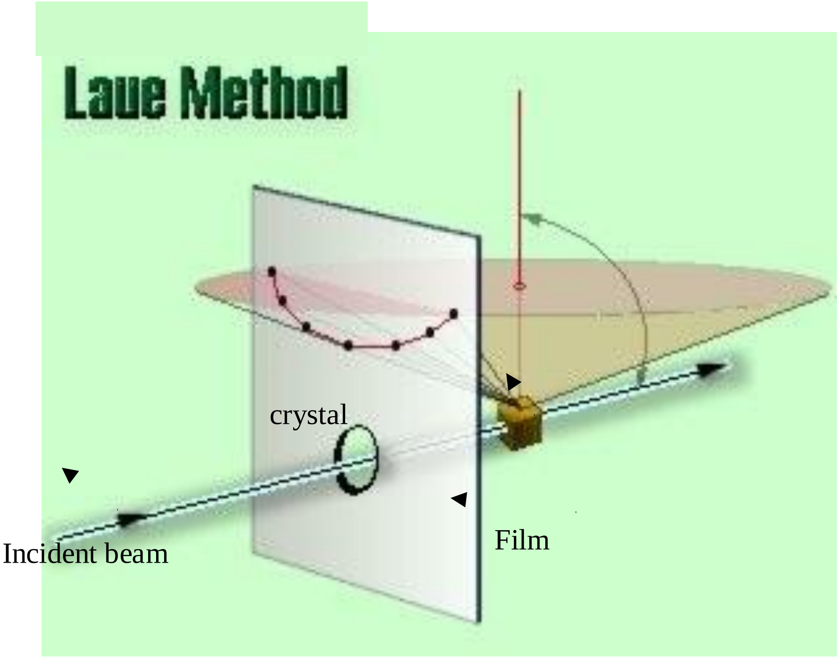
atomic distance between the two planes is denoted by *d*. If the diffracted rays are not in phase, destructive interference occurs. When they are in phase constructive interference happens.
Path difference= dsinθ + dsinθ =2dsinθ
When 2dsinθ equals nλ, constructive interference and reinforcement of the diffracted rays occurs. Here n=1,2,3 called order of diffraction. The equation **nλ=2dsinθ** is called Bragg's Law. The diffracted rays which have undergone constructive interference leave the crystal as a narrow beam. It is capable of making sharp images on a photographic plate or film. Usually first order diffraction is taken (n=1). In this case Bragg's law takes the form **λ=2dsinθ.**

Crystal Structure Determination

There are three methods of X-ray diffraction for determination of crystal structure.

(i) Laue Method: θ fixed, λ variable
(ii) Rotating crystal Method: θ varied, λ fixed
(iii) Powder Method: θ varied, λ fixed

1. Laue Method
There are two types of Laue Technique. (a) back reflection method in which beams diffracted back are studied and (b) transmission Laue method in which beams passed through the specimen are studied. Back reflection method is more widely used.



This method is especially valuable for determining crystal orientation. A narrow beam of **white radiation** (x-rays containing numerous wave lengths) strikes the **single crystal** specimen. Diffraction takes place from certain crystallographic planes. The image is obtained on photographic film as a series of spots. The spots are analyzed to obtain the required feature.

2. Rotating Crystal Method

The light (single wave length) impinges on a rotating single crystal specimen. A cylindrical photographic film surrounds the specimen. Rotation brings crystallographic planes into reflecting positions. These reflections are recorded on the film. These are analyzed to determine unknown crystal structure.

3. Powder Method

This is the most commonly used diffraction technique for crystal structure determination. The specimen is in the form of fine powder in a plastic/glass tube or solid polycrystalline thin wire having several hundred grains. Specimen is in the shape of cylinder of about 0.5 mm. λ is constant since monochromatic beam is used. Θ is variable because of the presence of large number of grains. The camera called Debye-Scherrer camera consists of a cylindrical cassette with a photographic film positioned around the periphery. Specimen is kept at the center of cassette. X-ray beam enters through a small hole. The diffracted rays will lie along the surface of a cone that makes an angle of 2θ around the x-ray beam direction. These rays are caught on the photographic plate. These are observed as a series of lines of varying curvature. Each crystal type has a characteristic pattern of lines in the film.From the spacing of the lines and the known dimensions of camera, 2θ angles can be calculated by using the formula $2\theta = \frac{S}{2R}$ where S= distance of image from center and R= radius of the camera

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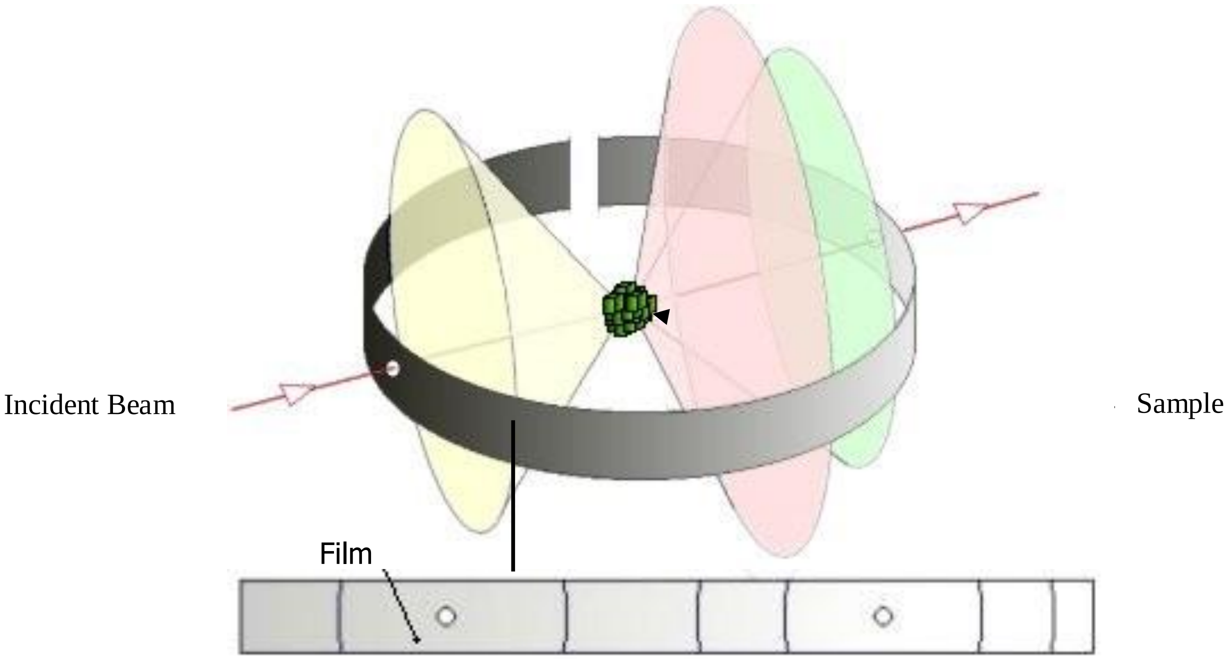
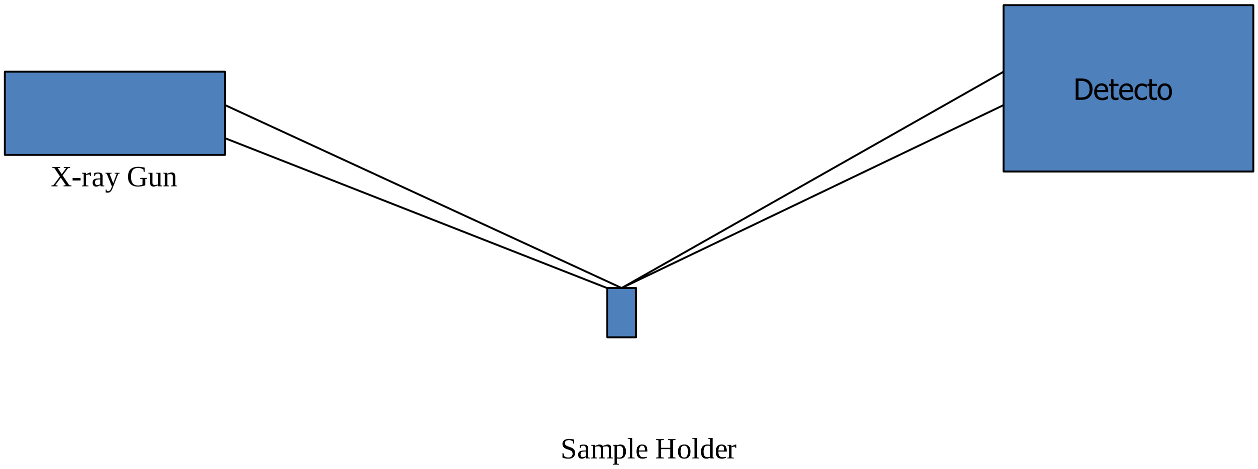


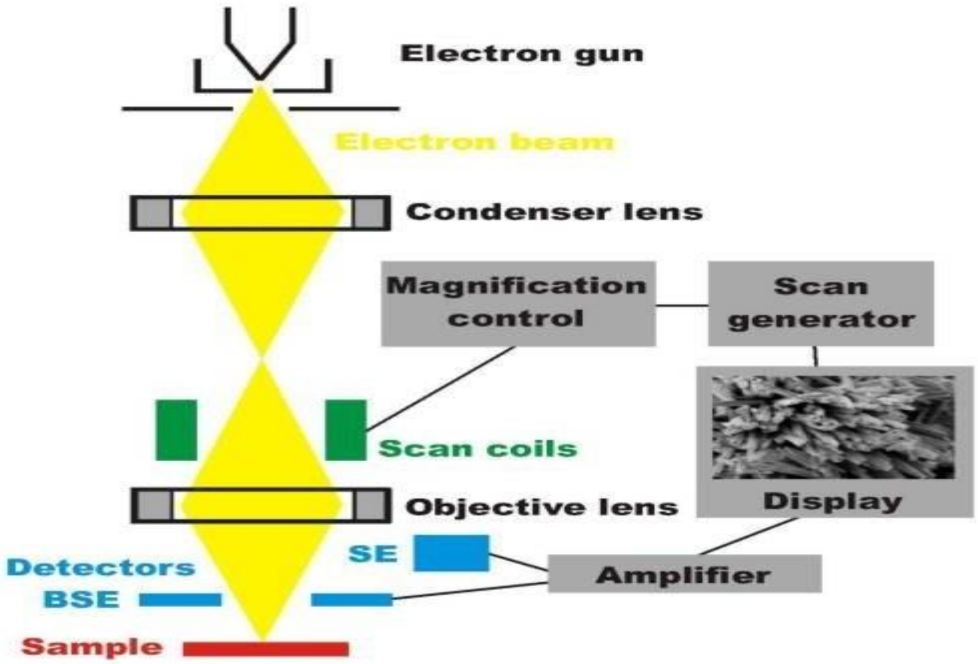
4. Modern X-ray Diffractometer



In modern crystal analysis, an X-ray diffractometer is used . Detector records the angle and intensity of the diffracted beam automatically and plots the intensity (I) against 2θ values. Such a plot is shown in figure below. Using these data for crystals, crystal structures can be determined. As an example we know that for cubic crystals, $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ where d_{hkl} is interplanar spacing. If this is inserted in Bragg equation, the equation becomes $\lambda = \frac{2a\sin\theta}{\sqrt{h^2+k^2+l^2}}$. From this lattice constant *a* can be calculated.

The data can also be used to determine whether a cubic crystal is simple cubic, BCC or FCC. Unknown complex structures can be identified by comparing θ and intensity of diffractions from unknown structure with published data (JCPDS) all known compounds and phases.

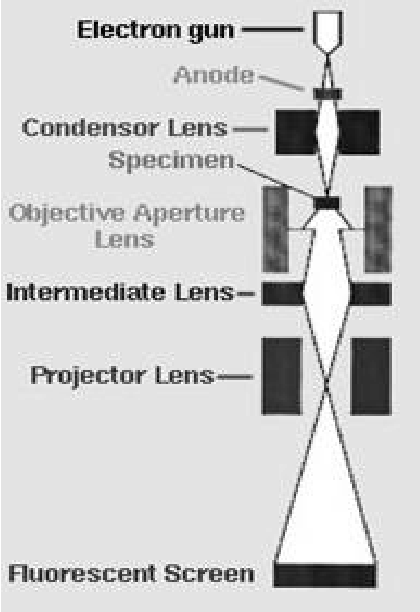
SEM (Scanning Electron Microscope



A schematic diagram of SEM is shown in figure. Electrons from the gun are accelerated and focused as a thin beam. The beam impinges on the specimen. Secondary electrons are emitted or scattered back from the specimen. This electron current is measured and displayed as intensity on a monitor. The display gives the surface features of the specimen. Specimen surface may or may not be polished. But the surface must be conductive. A thin conductive film has to be given for non conductive materials. Magnification up to 50,000 is possible. Depth of field is much higher than TEM. The following analyses are possible using SEM.

1. Topography: Surface features, texture
2. Morphology: Shape and size of phases and particles
3. Composition: Relative amounts of various elements and components through EDAX (Energy Dispersive analysis of X-rays) accessory.
4. Crystallography: Arrangement of atoms through diffraction techniques.

TEM(Transmission Electron Microscope)



In metallurgical research, it becomes often necessary to examine microstructures at very high magnifications. In electron microscopes, magnifications from 2000X to 200,000X are possible. Electron beams are used to resolve structures in this microscope. Magnetic lens are used to focus the electron beams. General arrangement is schematically shown in the figure.

The microscope consists of an electron gun. Vacuum is necessary for the travel of electron beam. The electrons coming out of the cathode are accelerated by the anode to form an electron beam in the gun. The electron beam strikes the specimen. Some electrons are scattered, some are absorbed and balance electrons are transmitted (passed through the specimen. TEM uses the transmitted beam for forming the image on a fluorescent screen.

In order to make the electrons to pass through the specimen, very thin (100-2000μm) metal films are to be used as specimen. Such specimens are prepared by techniques like ion bombardment, electro polishing etc.. If this is not feasible, the surface of the specimen is copied on a transparent plastic film. Such a film is called a replica.TEM can only provide surface features.

DIFFUSION IN SOLIDS

Diffusion means material transport (mass flow) by atomic motion. Atoms migrate stepwise from lattice site to lattice site. Diffusion is very important for a number of manufacturing processes. Classification of Diffusion Processes is given below:

1. Self diffusion: Diffusion of atoms of pure metal through the solid medium is termed as self diffusion.
2. Inter diffusion: It occurs in alloys. Atoms of one element diffuse into another.
3. Surface diffusion: It is the diffusion through surface. Atoms at surface have lesser bonds. Atoms diffuse easily.
4. Grain boundary diffusion: Atoms at grain boundaries are loosely bonded. Hence diffusion is easier.
5. Volume Diffusion: Bulk movement of atoms through solid.

Fick's Laws

1.Fick's First Law for Steady State Diffusion

_Rate of mass transfer is important in diffusion. It is expressed as Diffusion flux J which gives the mass M or number of atoms N diffusing through a unit cross sectional area per unit time. J=Mass/ Area x time = M/At where A- cross section area through which diffusion takes place and elapsed time. 1

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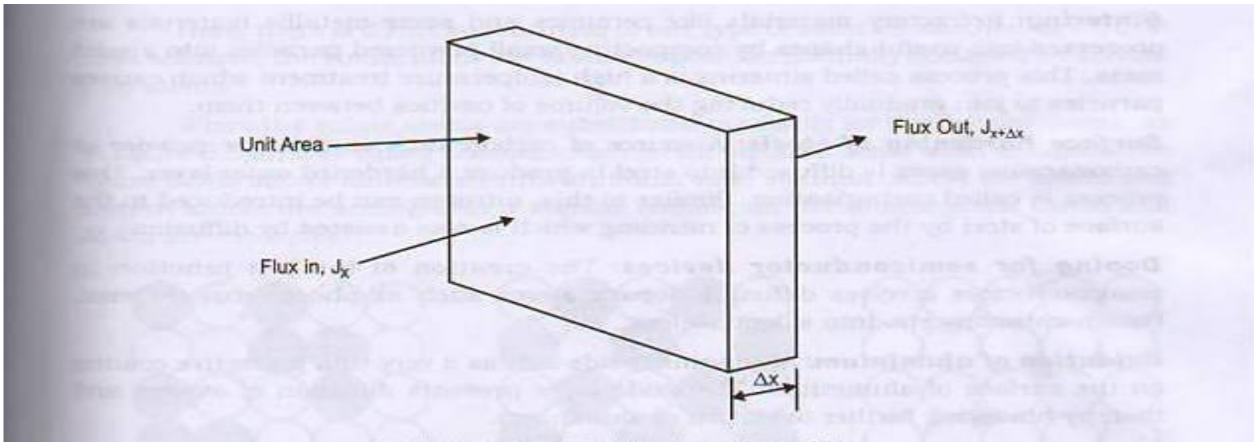

Figure 5.4 *Diffusion through a plate*

Consider an elemental volume of length Δx along diffusion direction and having unit cross section area.

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Two conditions are to be satisfied for diffusion of atoms (a) empty neighboring sites (b) sufficient energy to break bonds

1. **Vacancy diffusion:** It involves interchange of a normal atom and a vacancy. As a result, a new vacancy is created to which another atom can move. Hence diffusion can be considered to be due to movement of vacancies. Sufficient vacancies must exist in material to for this to happen. Large concentration of vacancies is present at elevated temperatures. Hence higher the temperature, more the diffusion. Self diffusion and inter diffusion can occur by this mechanism.

2. **Interstitial diffusion:** It involves migration of atoms from one interstitial position to another empty neighboring interstitial position. It is seen in inter-diffusion. It occurs more easily than vacancy diffusion. It is due to 2 reasons (a) atom size is smaller (b) more interstitials are present than vacancies

3. **Interstialcy diffusion**: An atom at the interstitial position forces a normal atom to an interstitial position

4.**Direct interchange diffusion:** It may involve 2 or more atoms. All atoms exchange their positions. If 4 atoms are involved, it is known as Zener ring

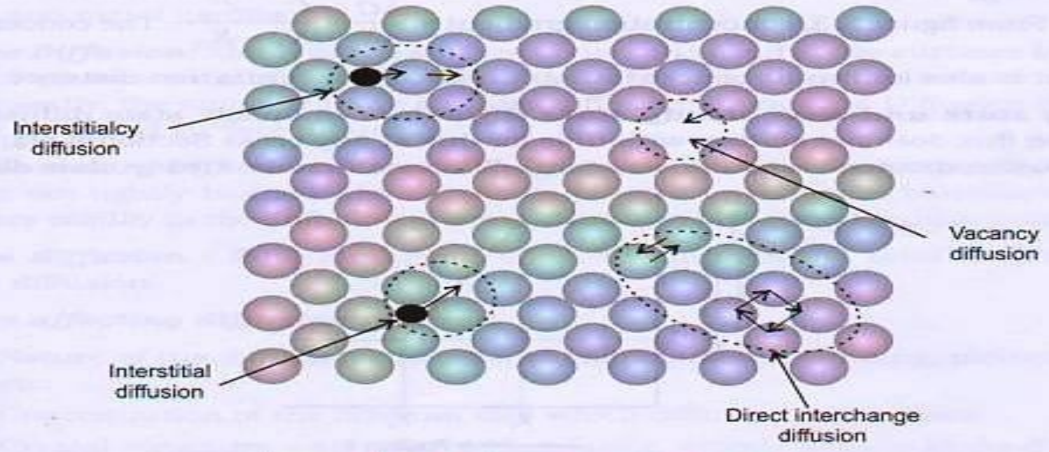

Figure 5.2 *Mechanisms of diffusion*

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Applications of Diffusion in Mechanical Engineering

Diffusion processes are very important in processing and use of materials at high temperatures. Few important applications in mechanical engineering where diffusion plays a major role are given below:

1. Melting and casting (especially in solidification) of metals and alloys.
2. Sintering: Compaction of metal or ceramic powders into solid products by high temperature treatment.
3. Surface hardening of steels: Introducing C and N into the surface of steels in carburization and nitriding processes at high temperature.
4. Doping of semi conductors: Introducing dopants like P, As, B. Sb etc, into silicon wafer to create p-n junctions.
5. Oxidation of aluminum: Aluminum oxide readily forms as a film (coating) over an aluminum surface. This coating prevents further diffusion of oxygen.
6. Beverage bottles:PET (polyethylene terephthalate) bottles are used for storing carbonated beverages. These bottles minimize diffusion of CO_2 . Thus fizz is maintained for more time.

MODULE 3

Limitations of Pure Metals and Need of Alloying

Pure metals have the following limitations:

1. Poor properties: Generally pure metals are not strong enough for engineering applications where stresses have to be withstood. Combination of low strength with high ductility results in easy plastic deformation and consequent change in size and shape. This makes the component useless.
2. High cost: Pure metals are very costly because of the need for extensive refining steps.
3. Lack of availability (scarcity)

These limitations are overcome by alloying. Pure metals are mixed or alloyed with other metals to form alloys. Yield strength, tensile strength, hardness and creep resistance of pure metals are improved by alloying. At the same time, ductility and electrical conductivity are reduced. For example, pure silver can be made stronger and harder when some copper is added to it which also reduces the cost.

Classification of Alloys

Almost all metallic materials in use today are in the form of alloys. These are formed by melting two or more metals together. Alloys can be classified into three types namely solid solution alloy, multi-phase alloy and inter-metallic compound.

If X and Y are two component metals, solid solution will form if the strength of X-Y bond is intermediate between strengths of X-X and Y-Y bonds. Sold solution has a single crystal structure .In the unit cell, both metal atoms are present. An example is Cu-Ni system.

A multi phase mixture is formed if X-Y bond is weaker than X-X and Y-Y bonds. The liquid alloy solidifies into two distinct and separate phases. One phase will be richer in X and the other richer in Y. Sn-Pb alloy is an example.

An inter-metallic compound is formed when X-Y bond is stronger than X-X and Y-Y bonds. An example is Fe_3C in iron-carbon system.

It is not true that alloys solidify in the same manner at all compositions. In some alloy systems, components are completely soluble in each other in solid state. In these alloys, solid solutions are formed at all compositions. In some alloy systems, the components are partially soluble in solid state. In this case, solid solutions are formed at some compositions and phase mixtures at other compositions. If the components are completely insoluble in solid state, phase mixtures are formed at all compositions. In some alloy systems inter-metallic compounds are formed at certain compositions with solid solutions or phase mixtures.

Solid Solutions

Most of the alloys are formed as solid solutions. Like liquid solution, solid solution also contains a solute and solvent. A solidified alloy with a single crystal structure containing 2 or more types of atoms in the unit cell is called a solid solution. Solid solutions are of 2 types (a) substitutional and (b) interstitial

Substitutional solid solution

In this solid solution there is a direct substitution of one type of atom for another. In a Cu-Ni solid solution, solute atoms (Ni) takes the positions normally occupied by solvent (Cu) atoms. When solute atoms are substituted randomly, it is called random (disordered) solid solution. When solute and solvent atoms are arranged in a regular fashion, it is termed as an ordered substitutional solid solution.

Interstitial Solid solution

When solute atoms are much smaller than solvent atoms, they can occupy interstitial positions between solvent atoms. C,H, N and B atoms are very small and can form interstitial solid solutions. An example is steel containing carbon in iron. In some cases, substitutional and interstitial solid solutions can coexist. Example is Cr-Ni steel containing interstitial carbon atoms with Cr and Ni in substitutional positions.

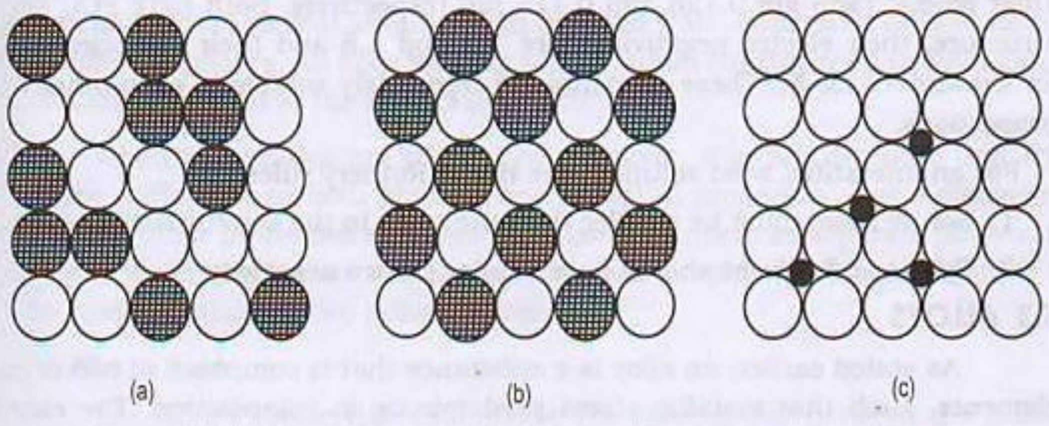


Figure 5.5 (a) *Random substitutional solid solution,* **(b)** *ordered substitutional solid solution, and* **(c)** *interstitial solid solution*

Hume Rothery’s Rules

Hume-Rothery proposed 4 conditions for forming substitutional solid solutions. These are known as Hume-Rothery’s Rules.

1. Size factor: Size difference between solvent and solute atoms must be less than 15%. For extensive solid solubility, size difference should be within 8%.
2. Crystal structure factor :The crystal structures of solvent and solute atoms must be same.
3. Electro negativity factor: Difference in electro-negativity of solvent and solute must be small.
4. Valency factor: In general a metal has a tendency to dissolve a metal of higher valency. Hence a solvent must have a lower valency than solute.

Solid solution of Cu and Ni is an example. These elements form solid solutions at all proportions. They are completely soluble in each other in solid and liquid states. If we apply Hume-Rothery’s rules:

1. Atom diameters of Cu and Ni are 0.128 and 0.125 nm respectively (apprx 2.5% difference).
2. Both have FCC crystal structure.
3. Electro-negativity values are 1.9 and 1.8 respectively.
4. Valency of Cu is 1 and valency of Ni is 2.

For interstitial solid solution, Hume-Rothery’s rules are:

1. Solute atoms must be smaller than the voids in the solvent lattice
2. Solute and solvent should have similar electro-negativity.

Equilibrium Diagrams of Common Types of Binary Systems (Five Types)

If the two components in the binary system are completely soluble in liquid and solid states, it is called isomorphous system. When the two components are completely soluble in liquid state, but completely insoluble in solid state it is known as eutectic system. Another type of binary system is one in which the 2 components are partially soluble in solid state. In this case terminal solid solutions along with eutectic reaction can be expected.

Isomorphous System

In isomorphous system, solid solution is formed at all compositions. Examples of this system are Cu-Ni, Ag-Cu, Ge-Si, FeO-MgO etc. The equilibrium diagram of the most common Cu-Ni system is given in figure.

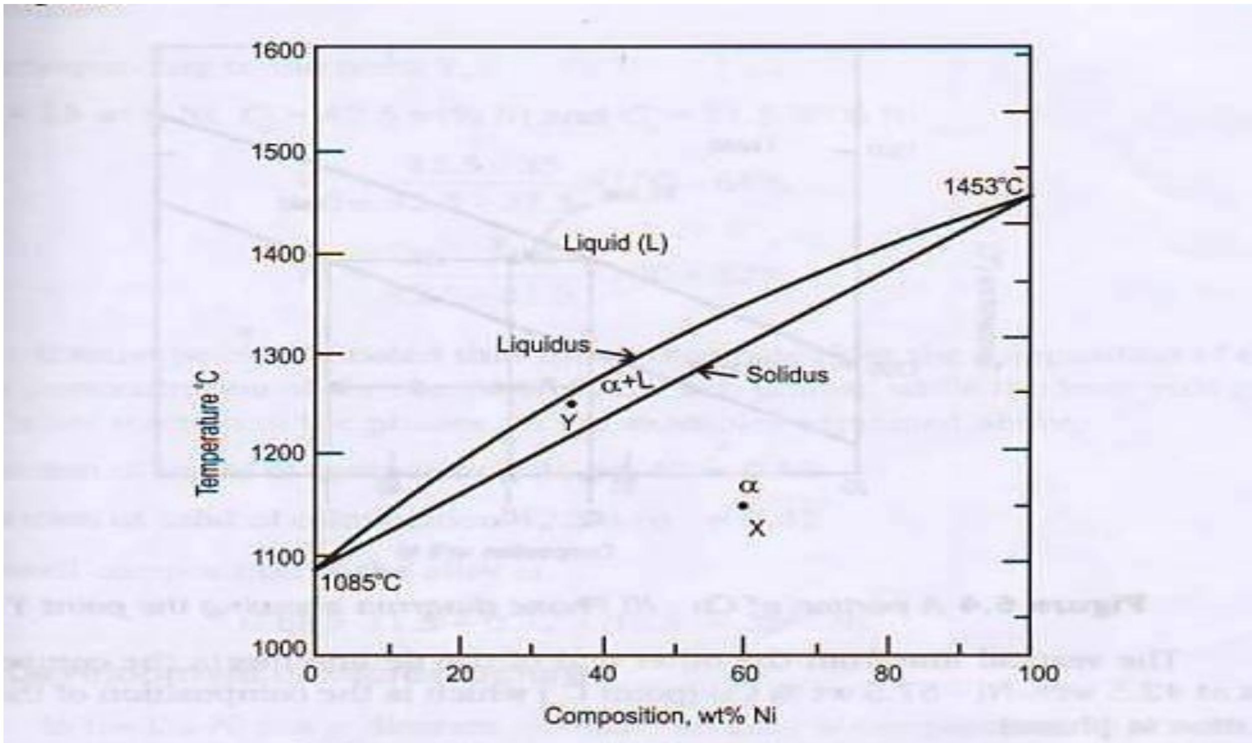


Figure 6.3 *Cu - Ni phase diagram*

Three different phase regions exist; liquid (L), solid(α) and L+α phase. Boundary between L and L+ α is called liquidus curve. The boundary between L+α and S is solidus curve. 3 kinds of information are available from phase diagram *viz.* (i) phases present (ii) composition of phases and (iii) relative percentage of the phases.

(i) Phases present

Let us select a point X. This alloy contains 60% Ni and the temperature is 1150^0 C. This point is within α (solid) region. Hence there is only α phase .Consider point Y, an alloy of 35% Ni and temperature is 1250^0 C. This point contains 2 phases; L and α, at equilibrium.

(ii) Composition of Phases

When there is only one phase, composition of the phase is same as that of the alloy. E.g. Point X has only one phase; composition is 60% Ni. When 2 phases are present, composition of each phase is determined by tie line method as given below.

Step1. A tie line is drawn horizontally touching the point and parallel to X axis.

Step2. Intersections of the line with phase boundaries at the 2 sides are noted.

Step3. Vertical lines are drawn downwards from the two intersecting points. Composition of each phase is noted from X axis.

E.g. Point Y is in 2 phase region. Horizontal line is drawn at Point Y. Verticals are drawn from the intersections. We find that α phase contains 42.5 % Ni whereas liquid phase contains 31.5 % Ni.

(iii) Amount of Phases

Phase amounts are determined using tie line and lever rule. Refer figure in section on lever rule. Distances (lever arms) R and S are noted. If W_L and W_S represents the relative amounts (in %) of the 2 phases (here liquid and α) , then

(iv) Solidification and Microstructure

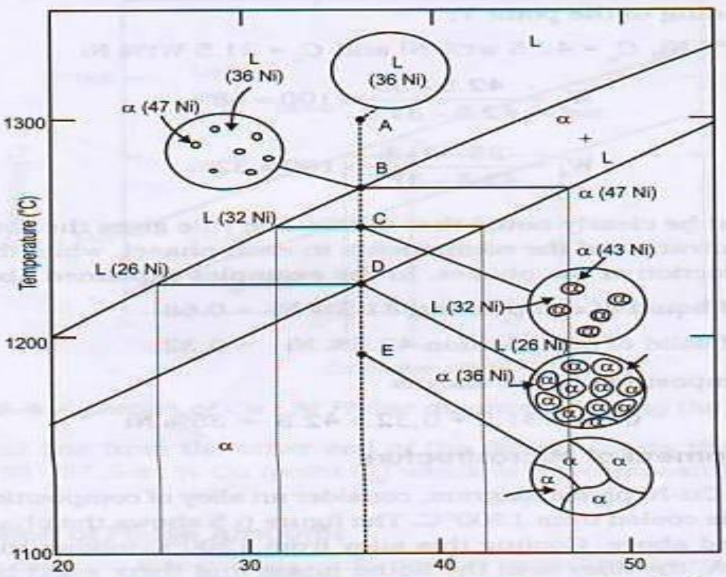


Figure 6.5 *Schematic representation of the development of microstructure*

Consider an alloy of composition 36% Ni-64% Cu as it is cooled from 1300^0 C. Cooling follows vertical dashed line. Refer Fig. At point A alloy is in liquid state (L) with36% Ni. When point B (1265^0 C) is reached solidification begins. The first solid crystals of α get formed. Microstructure shows tiny crystals of α containing 47% Ni in a liquid of 36% Ni. When melt is further cooled, more crystals are formed and existing crystals grow. Composition of liquid and solid changes following liquidus and solidus curves. At point C, liquid contains 32% Ni while solid contains 43% Ni. Above B there is 100% liquid and below D it is 100% solid. α increases from 0% to 100% while the temperature falls from point B to Point D . At point E there is only α solid solution phase with a composition of 36% Ni.

Eutectic System

An example of a simple eutectic system is shown in Figure. Here the components are completely soluble in liquid state and completely insoluble in solid state. The eutectic reaction is:L → S1 +S2 on cooling. It means that 2 separate solid phases are formed from a liquid of definite composition. It is an invariant reaction, meaning zero degree of freedom (F= C-P+1= 2-3+1=0). There is a definite composition (eutectic composition) and temperature (eutectic temperature). The point where eutectic temperature and eutectic composition meet is known as eutectic point. Eutectic means easy to melt. Eutectic alloy has the lowest melting point. It solidifies like a pure metal at constant temperature.

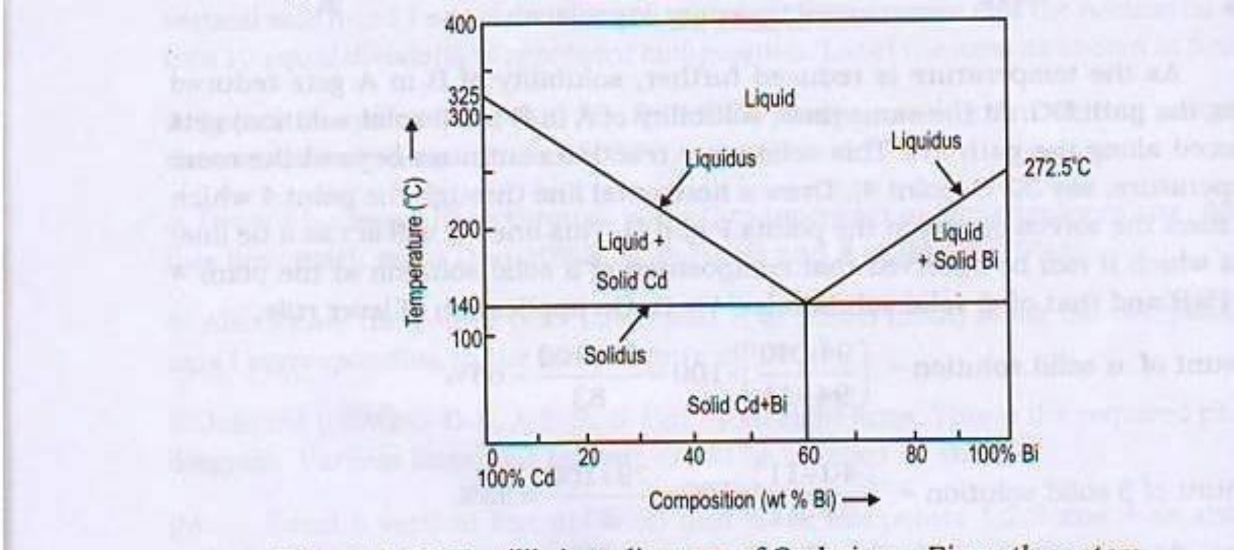


Figure 6.12 *Equilibrium diagram of Cadmium - Bismuth system*

Eutectic System with limited solid solubility

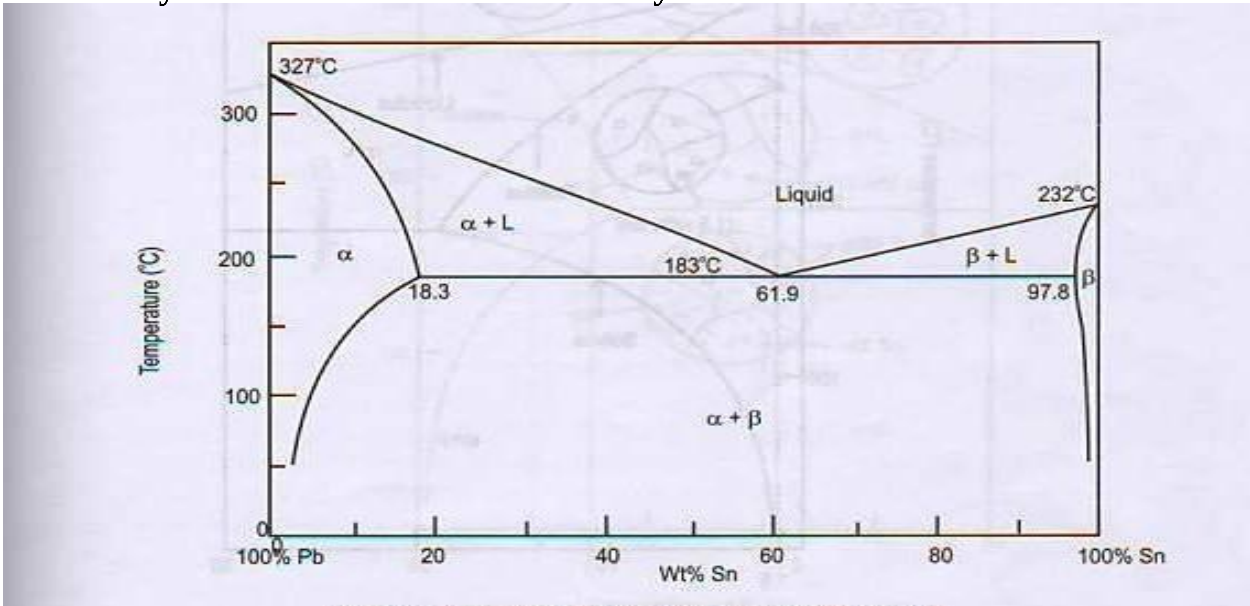


Figure 6.7 *The lead - tin phase diagram*

It has a eutectic reaction. Because of the limited solid solubility, terminal solid solution(s) are formed. If both components have limited mutual solubility, terminal solid solutions are found on both ends of phase diagram. The solid solubility limit curve is called solvus. Pb-Sn, Ag-Cu, MgO-CuO etc. exhibit this system. Pb-Sn equilibrium diagram is shown in Figure.

The terminal solid solutions are named α and β. There are 3 single phase regions viz. liquid, α and β. α is a solid solution in which Pb is solvent and Sn is solute. In β phase, Sn is solvent and Pb is solute. 18.3% is the maximum amount of Sn in Pb while 2.2 % is the maximum amount of Pb in Sn. Addition of Sn to Pb or Pb to Sn decreases melting point. The alloy having the lowest melting point is the one

where the liquidus lines meet. At this temperature, liquid phase is transformed to 2 solid phases α and β.
L (61.9% Sn) ↔ α (18.3% Sn) + β (97.8% Sn) : →on cooling, ← on heating.
L ↔ α +β The phase rule, tie line rule and lever rule can be applied to phase diagram to determine the phases, their compositions and amount of phases.

Peritectic Equililibrium Diagram

Eutectic, peritectic, eutectoid and peritectoid reactions are invariant reactions. It means that degree of freedom is zero since three phases coexist. F=C-P+1 =2-3+1=0. In a peritectic reaction L+S1 ↔ S2 on cooling→ /heating←. Ag-Pt, Fe-Ni, Fe-C and Cu-Zn alloys exhibit peritectic reaction. Fig shows Ag-Pt phase diagram. Peritectic temperature is 1186^0C and peritectic composition is 42.4% Ag.
The peritectic reaction is : L +β ↔ α

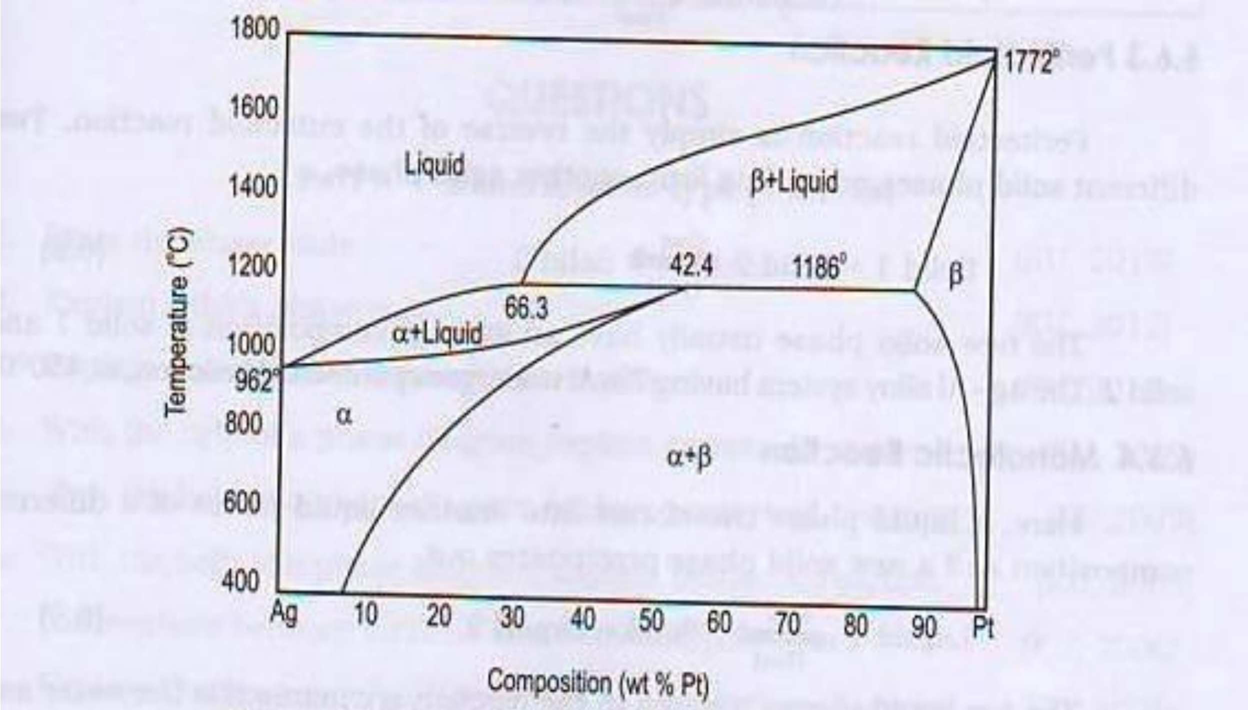
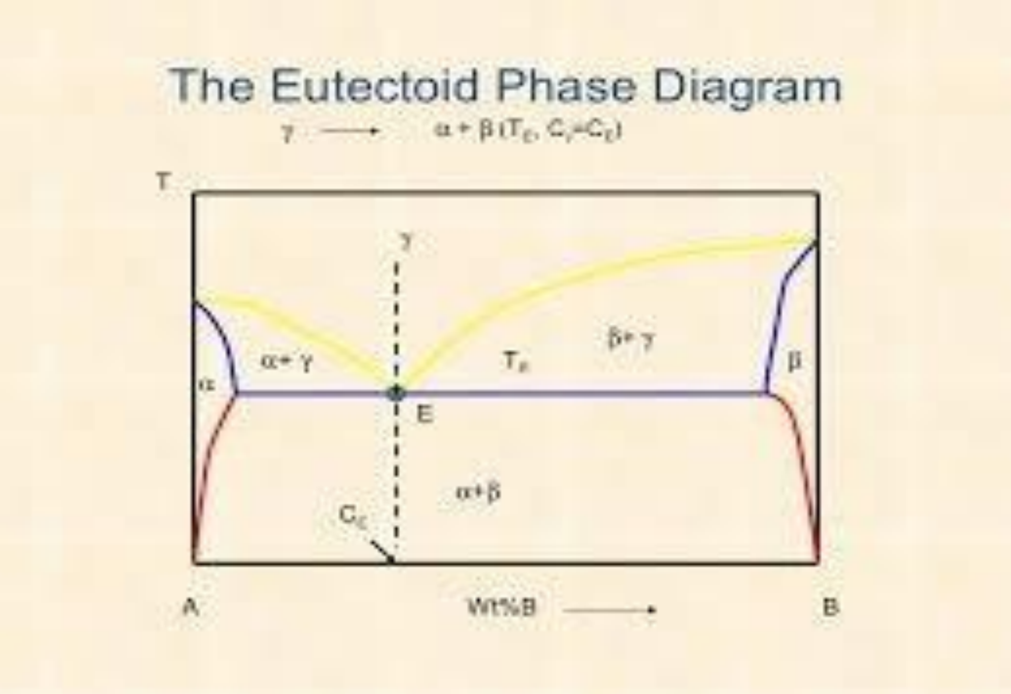


Figure 6.13 *Equilibrium diagram of Ag - Pt alloy*

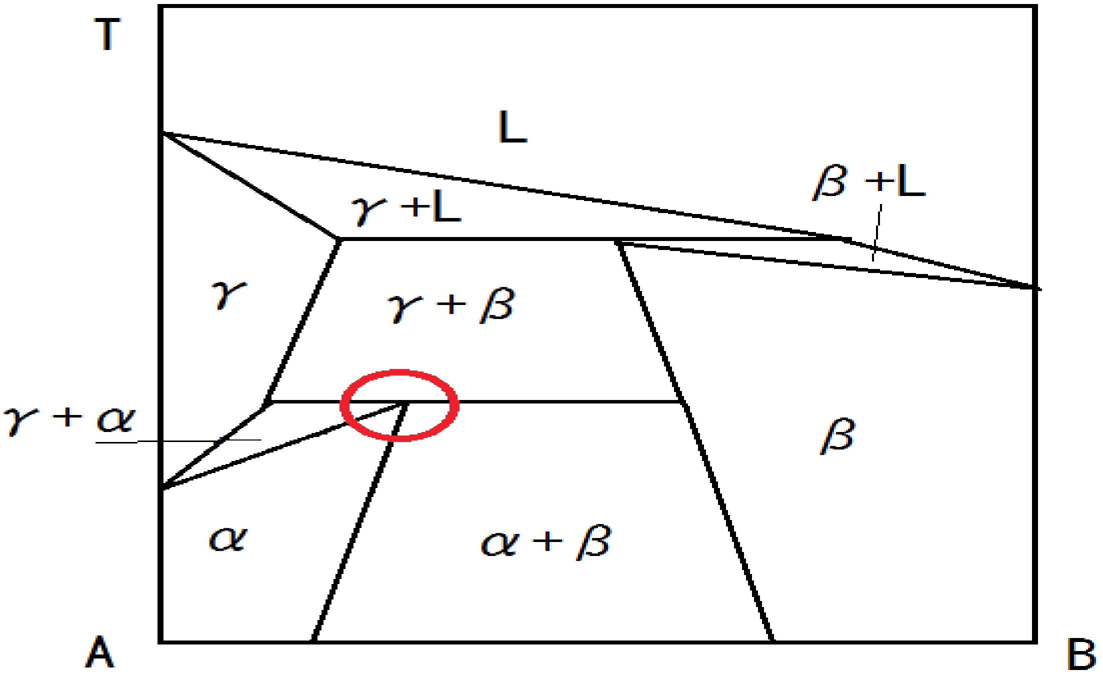
Eutectoid Reaction

_The reactions (eutectic, peritectic etc.) involve liquid as one phase as reactant during cooling.
Reactions ending with 'oid' (eutectoid, peritectoid etc.) are solid state reactions. Eutectoid reaction:

Solid 1 ↔ Solid 2+ Solid 3



Peritectoid Reaction

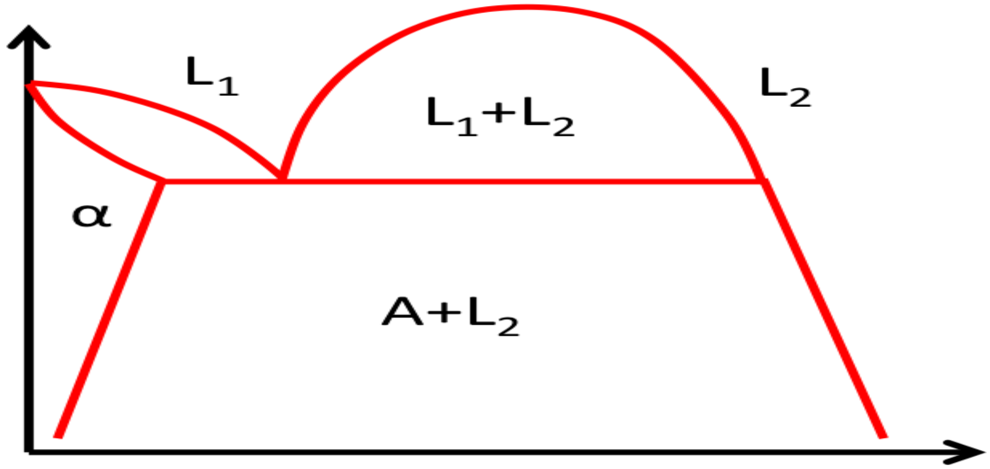


→

Solid 1+ Solid 2 ↔ Solid 3 In the figure γ □ $\beta \leftarrow \alpha$

Examples : Al-Cu, Ag- Al

Monotectic Equilibrium Diagram



The reaction is : Liquid 1 $\overset{\rightarrow}{\leftarrow}$ *Solid* □ *Liquid* 2

In the figure the monotectic reaction is : $L_1 \overset{\rightarrow}{\leftarrow} A \square L_2$

Examples: Cu-Pb

Coring

In an isomorphous (solid solution) system, the first solid is richer in high melting constituent. The concentration of the element having high melting point decreases (the component with lower melting point increases) progressively from centre of the grain to grain boundary. This variation in composition from the centre of each grain to its grain boundary is called coring (a type of segregation). Coring can be removed by homogenization (keeping at elevated temperature for sufficient time).

Lever Rule

In the case of a lever fixed on a fulcrum, we know that weight x weight arm = effort x effort arm. The lever rule can be used for determining the amount of phases (relative fraction of phases) in a 2 phase region.

A tie line is drawn horizontally across the 2 phase region corresponding to the selected temperature. The inter sections of the tie line with the phase boundaries are noted. The vertical lines are drawn from these intersections. The distance R and S are determined in terms of composition of any one phase. If W_L and W_S represents the relative amounts (in %) of the 2 phases (here liquid and α) , then

$W_L = (S/ R+S)$ x 100% $W_s = (R/ R+S)$ x100%

Since $S= C_S-C_0$ $R= C_0-C_L$ and $R+S = C_S-C_L$ then

$W_L = (C_S-C_0 / C_S-C_L)$ x100% $W_S = (C_0-C_L / C_S-C_L)$ x100%

As per the figure, at point Y C_0 =35 wt % Ni, C_S = 42.5 wt % Ni and C_L = 31.5 wt % Ni

Therefore W_L = {(42.5-35)/ (42.5-31.5)} x 100 = 68% W_S = {(35-31.5)/ (42.5-31.5)} x 100 = 32%.

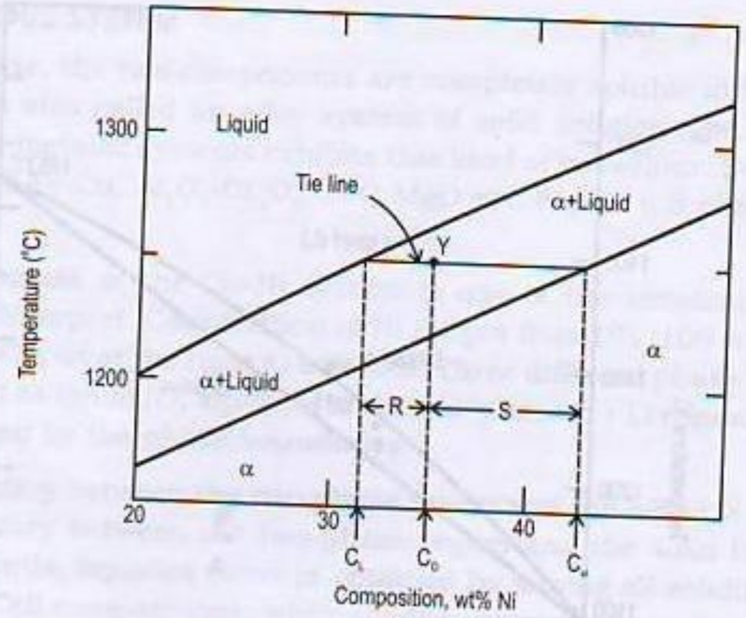


Figure 6.4 *A portion of Cu - Ni Phase diagram showing the point Y*

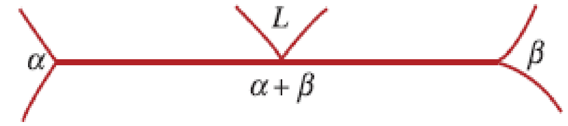
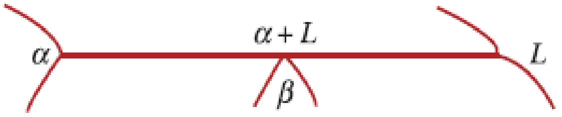
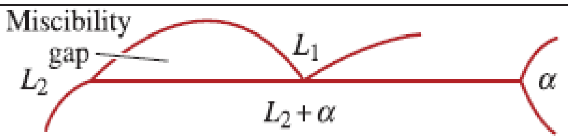
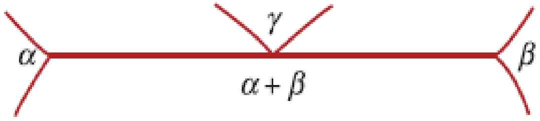
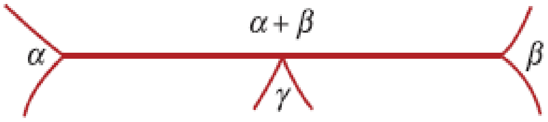
Phase Rule

Gibb’s Phase Rule establishes the relationship between number of components, number of phases and number of degrees of freedom in a system. System: A substance or substances isolated from its surroundings and subjected to changes in composition, temperature, pressure or volume. Components: A chemical constituent (element, ion or compound) of a system used for specifying composition. System with one component is unary system; with 2 components-binary system; with 3 components- ternary system. E.g. Steel (system) with Fe and C (components) Phase: A homogeneous portion of a system having uniform physical and chemical characteristics is a phase. A phase is a physically distinct, chemically homogeneous and mechanically separable region of a system. E.g. pure metal is a phase. Water (liquid), ice (solid) and water vapor (gas) are 3 phases. A solid solution is a single phase. Degree of freedom: It refers to the independent variables (temperature, pressure, composition) which can be changed without affecting other variables in the system.

Phase Rule: Phase rule is mathematically expressed as: F=C-P+2 or P+F=C+2 where F= Number of degrees of freedom, C= Number of components in the system and P=Number of phases in the system.Pressure is generally considered as 1 atmospheric pressure. In such a case, F=C-P+1 (applicable to all alloy systems).

Reactions (Monotectic, Eutectic, Eutectoid, Peritectic and Peritectoid)

Reaction	**Examples**
Eutectic	Pb-Sn, Ag-Cu, Pb-Sb
Peritectic	Ag-Pt, Fe-C, Fe-Ni, Cu-Zn
Monotectic	Cu-Pb
Eutectoid	Fe-C, Cu-Zn, Pd-Ti, Al-Cu
Peritectoid	Ag-Al, Al-Cu

Eutectic	$L \rightarrow \alpha + \beta$	
Peritectic	$\alpha + L \rightarrow \beta$	
Monotectic	$L_1 \rightarrow L_2 + \alpha$	
Eutectoid	$\gamma \rightarrow \alpha + \beta$	
Peritectoid	$\alpha + \beta \rightarrow \gamma$	

IRON CARBON DIAGRAM

The most important binary alloy system is Fe-C system. Primary engineering materials namely steels and cast irons are alloys belonging to this system. Steel is the most widely used material in the world.

Iron-Carbon Equilibrium Diagram

Fe-C equilibrium (phase) diagram can be divided into 2 parts. (a) iron rich portion containing up to 6.67 weight %C and (b) other portion containing 6.67-100% C (known as graphite. At 6.67% C, the entire structure is cementite (an intermetallic compound Fe_3C). Hence the iron rich portion of iron-carbon diagram can be called Fe- Fe_3C phase diagram.

The other portion containing 6.67-100% C does not have any technical or commercial importance. Hence Fe-Fe_3C diagram is the iron-carbon diagram of practical importance. Refer Figure

In Fe-C diagram there are 5 different phases and 3 invariant reactions under equilibrium cooling condition (very slow rate of cooling).

The family of Fe-C alloys with carbon content up to 2.14% is called steels. When carbon content is more than 2.14% up to 6.67 %, the alloys are called cast irons.

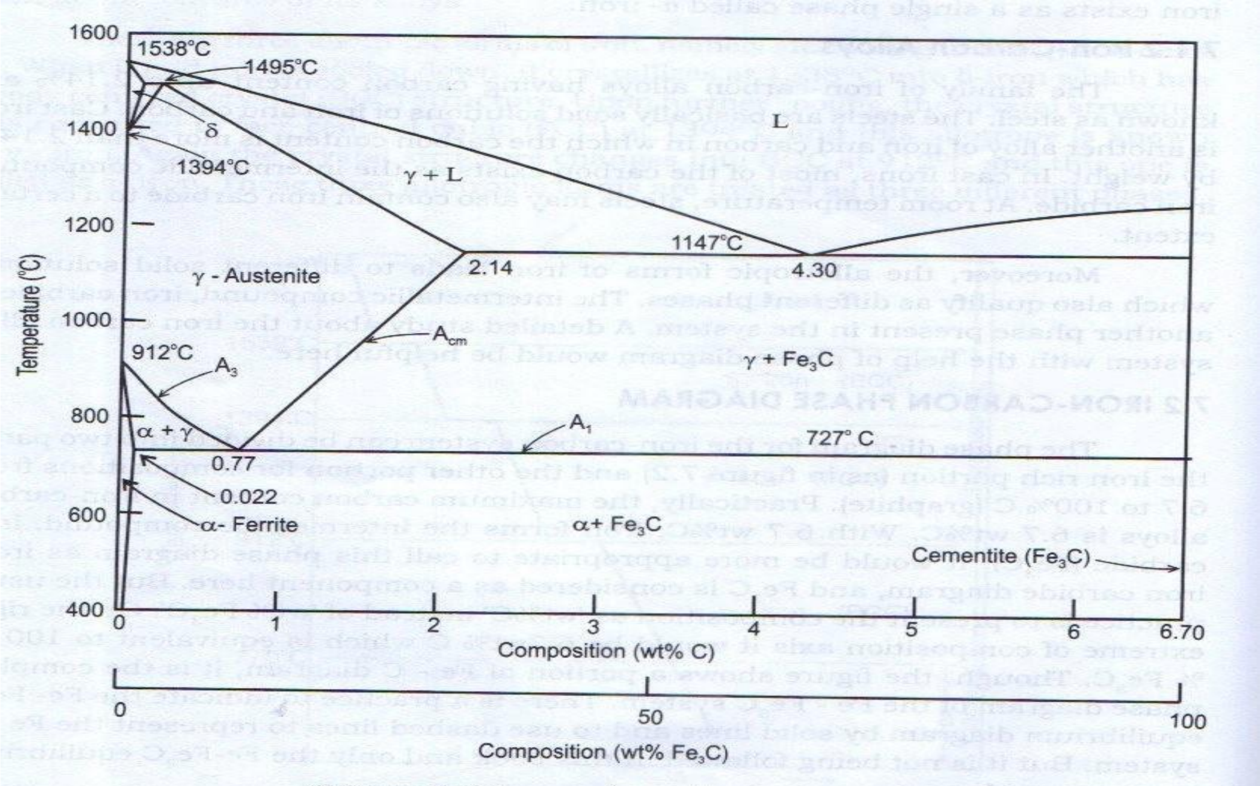


Figure 7.2 *Iron carbon phase diagram*

Phases in Fe-C diagram

1. ∂ Ferrite:

∂ ferrite is a stable phase only in the temperature range of 1394- 1538^0C. Maximum solubility of C in ∂ ferrite is only 0.09% at 1495^0C. This phase is not of much significance.

2. α Ferrite:

It is an interstitial solid solution of C in BCC iron. Maximum solubility is 0.022% C at 727^0C. At room temperature the solubility is only 0.008% C. The microstructure of α ferrite is given in Fig

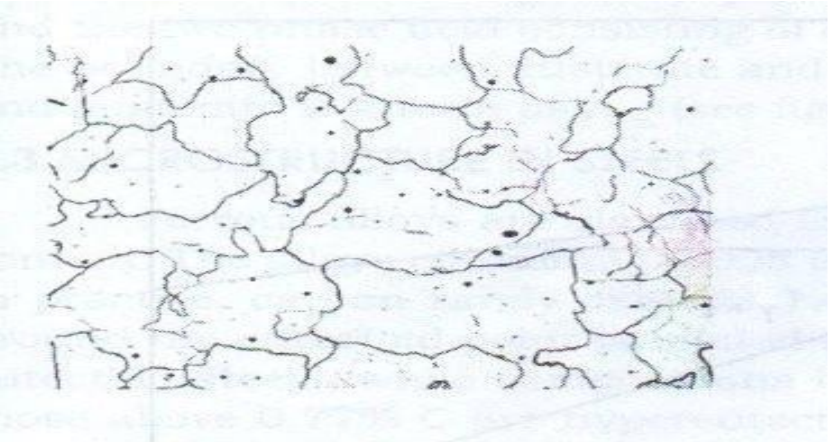


Figure 7.3 *α-Ferrite*

3. Austenite:

It is an interstitial solid solution of C in FCC iron. Solubility of C in austenite is much higher (≈100 times) than in BCC iron. Maximum solubility is 2.14 % at 1147^0C .
Austenite is known as γ phase. It is stable in the temperature range of $912\text{-}1394^0$C. Microstructure of austenite is given in Fig. The strength of austenite is higher than that of pure iron. It is due to solid solution strengthening by C.

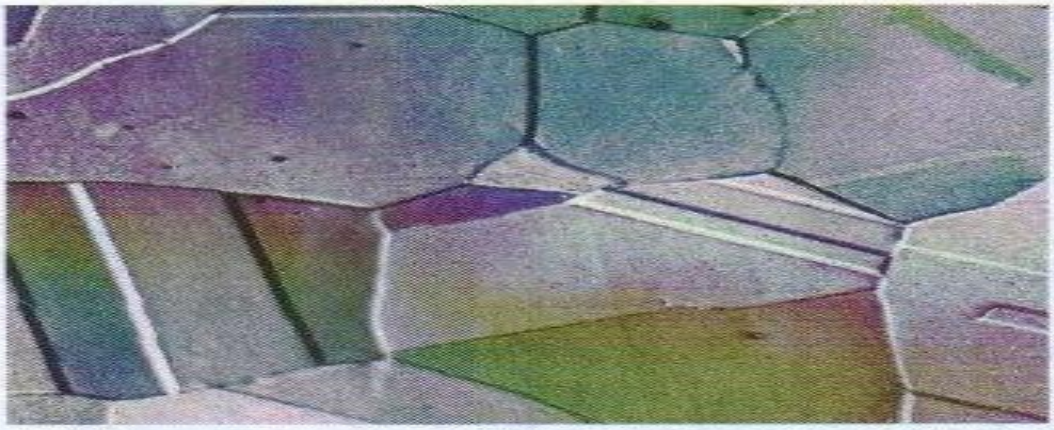


Figure 7.4 *Austenite*

4. Cementite:

Cementite is an intermetallic compound. It is iron carbide (Fe_3C).
It is formed when carbon content is more than the solubility limit in iron. It is an extremely hard and brittle phase. Properties of steel can be controlled by controlling the amount, size and shape of cementite. It is a metastable phase. That is, cementite can remain indefinitely at room temperature even though it is not a completely stable phase.

5. Liquid phase:

It is the fifth phase in iron-carbon equilibrium diagram.

Apart from these 5 phases, there are 2 phase mixtures in the Fe-C diagram.
(a) Pearlite: It is a mixture of 2 phases, ferrite and cementite. It is formed by the eutectoid reaction at 727^0C. It has the structure of alternate lamellae of ferrite and cementite.
(b) Ledeburite: It is formed by eutectic reaction. It is a mixture of austenite and cementite.

Invariant Reactions

1. Peritectic Reaction :

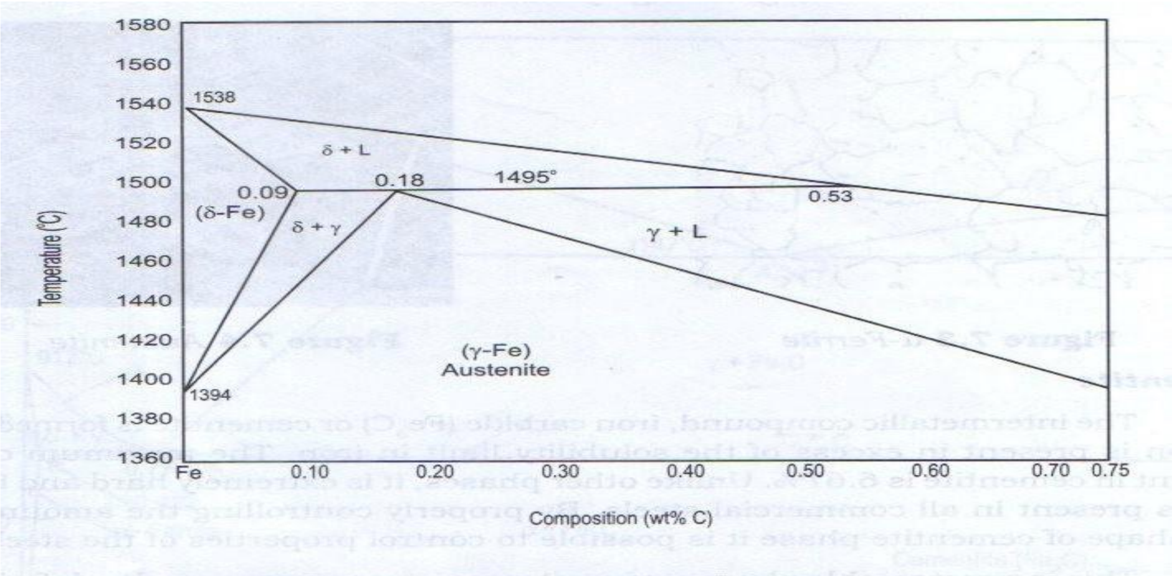


Figure 7.5 *Peritectic Reaction in Fe-C System*

2. Eutectic Reaction:

_It occurs at 1147^0C. Liquid of 4.3% C solidifies into a mixture of two solid phases, austenite (2.14% C) and cementite (6.67% C). This eutectic mixture is called ledeburite.

Liquid ↔ austenite + cementite (on cooling→/heating ←)

3. Eutectoid Reaction:

_It is the most important reaction in Fe-C diagram. This reaction can be controlled by slowing it, speeding it or completely avoiding it to obtain desired pro- perties. Eutectoid reaction occurs at 727^0 C. Austenite of 0.77%C decomposes into a mixture of ferrite(0.22% C) and cementite (6.67% C).

Austenite (solid 1) ↔ α ferrite (solid 2) + cementite (solid 3)

The eutectoid mixture of ferrite and cementite as alternate lamellae is known as pearlite.

Microstructure of Fe-C Alloys

Microstructure of Steels

Steels contain from 0.008 % to 2.14 %C. In practice C does not exceed 1.4% in steel. Steel with 0.77% C is called eutectoid steel. Steels with less than 0.77 %C are hypoeutectoid steels and those containing more than 0.77 % C are hypereutectoid steels. In Fe-C diagram, eutectoid temperature line is called A_1 line (lower critical temperatures).

The boundary line separating austenite and austenite+ferrite regions is called A_3 line (upper critical temperatures for hypo steels). Boundary separating austenite and austenite +cementite regions is called A_{cm} line (upper critical temperatures for hyper steels).

1.Microstructure Development of Eutectoid Steels:

Consider cooling of an alloy containing 0.77%C from 900^0C (along PQ).At point P the structure is fully austenite. At Q austenite transforms to a mixture of 2 phases, α ferrite and cementite at 727^0C. Slow cooling results in a microstructure consisting of alternate layers or lamellae of ferrite (thick light layer) and cementite (thin dark layer). This structure is known as pearlite. The name comes from the color of mother of pearl seen in the specimen.

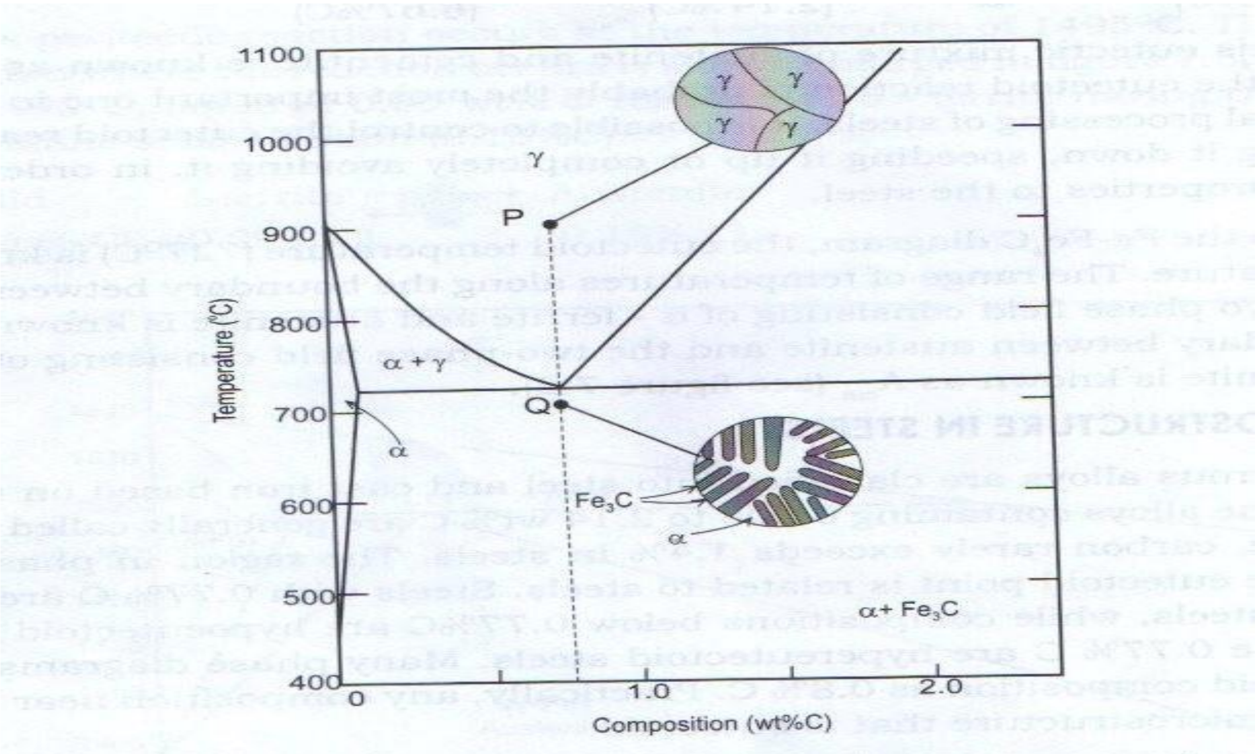


Figure 7.6 *Microstructural changes in eutectoid steel*

Mechanical properties are in between soft ductile ferrite and hard brittle cementite.

2.Microstructure of Hypoeutectoid Steel

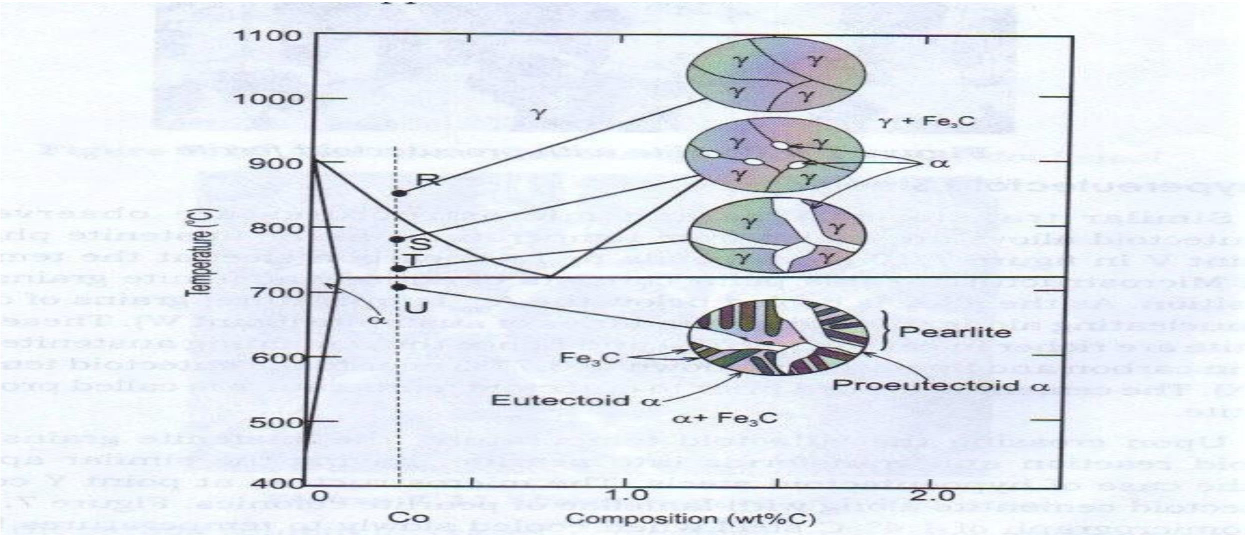


Figure 7.8 *Microstructural changes in hypoeutectoid steel*

Hypoeutectoid means “less than eutectoid” (< 0.77% C). Consider an alloy of 0.4% C (RSTU line). At R (850^{0}C): fully austenite (γ) grains.

At S: A_3 line is crossed. α ferrite nucleates on γ boundaries.

At T (730^{0}C): C content of austenite approaches 0.77% and C content of ferrite reaches 0.22%.

At U : The eutectoid temperature is crossed. Austenite transforms to pearlite. Microstructure includes proeutectoid ferrite surrounded by pearlite. Large white regions are proeutectoid ferrite. Dark patches with alternate lamellae are pearlite

3 Microstructure of Hypereutectoid Steels:

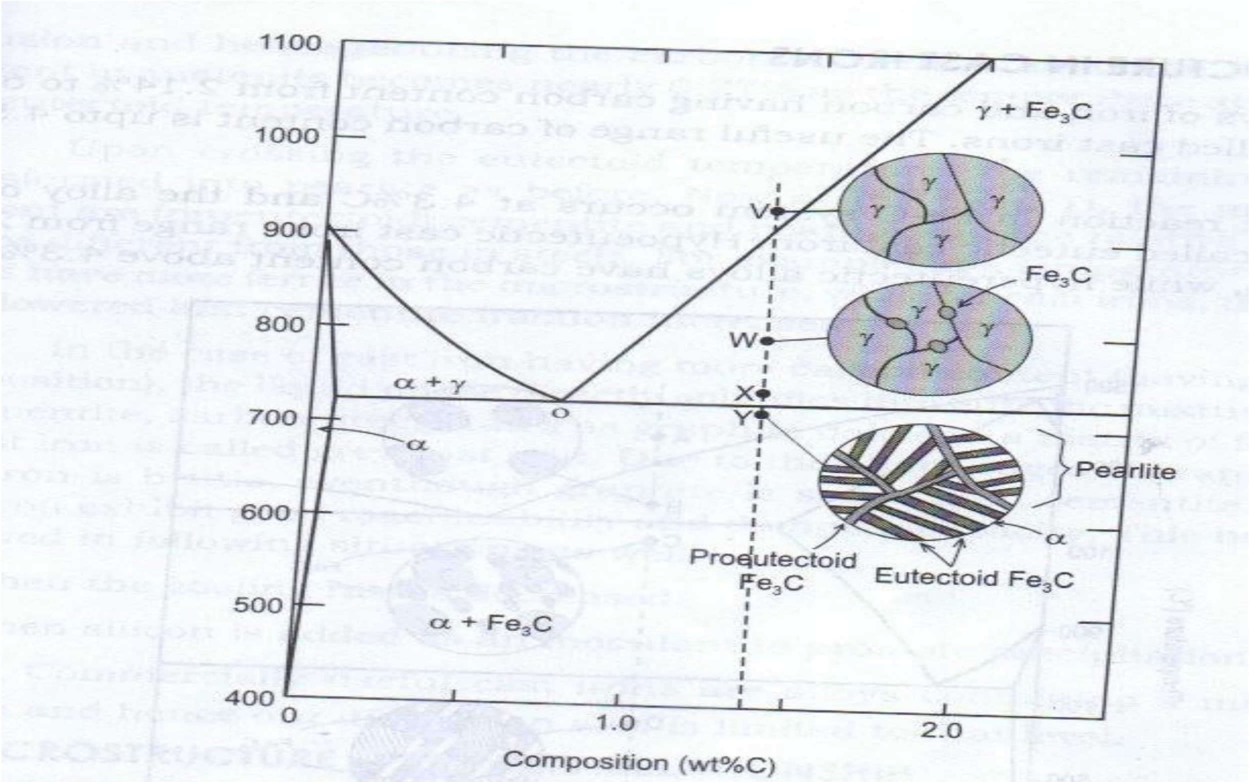


Figure 7.10 *Microstructural changes in hypereutectoid ste*

Consider cooling of a steel containing 1.4 % C at 900^{0}C.

At point V: austenite grains of 1.4% C

At W: Cementite nucleates along austenite grain boundaries. Cementite contains 6.67%C. Hence austenite becomes poorer in C (near to 0.77%C).

At X: Eutectoid temperature is crossed. Austenite transforms to pearlite with alternate lamellae of ferrite and cementite.

At Y: Microstructure consist of proeutectoid cementite and eutectic pearlite. Proeutectoid cementite appears lighter than eutectoid cementite in pearlite.

Microstructure of Cast Irons

Fe-C alloys containing 2.14-6.67 %C are called cast irons. But useful alloys contain C only up to 4.5%. Alloy containing 4.3%C is called eutectic cast iron. Alloys with <4.3 %C are hypoeutectic cast irons and those with > 4.3 %C are hyper eutectic cast irons. Consider cooling of a cast iron of 3%C from1300^{0}C.

At point A: alloy is in liquid state.

At B: liquidus line is crossed. Austenite starts to separate out from liquid. Austenite has less carbon. Hence liquid becomes richer in C.

At C: Eutectic temperature of 1147^{0}C crossed. Liquid of 4.3% C converts to ledeburite (a mixture of austenite and cementite). Microstructure contains proeutectic austenite and ledeburite.

At D: As temperature is lowered below eutectic temperature, more cementite forms. Hence C in austenite reduces. At eutectoid temperature, austenite contains 0.77%C. The austenite converts to pearlite.

At D the microstructure contains proeutectoid cementite and pearlite.

In cast irons cementite is much more than in steels. Hence cast irons are more brittle.

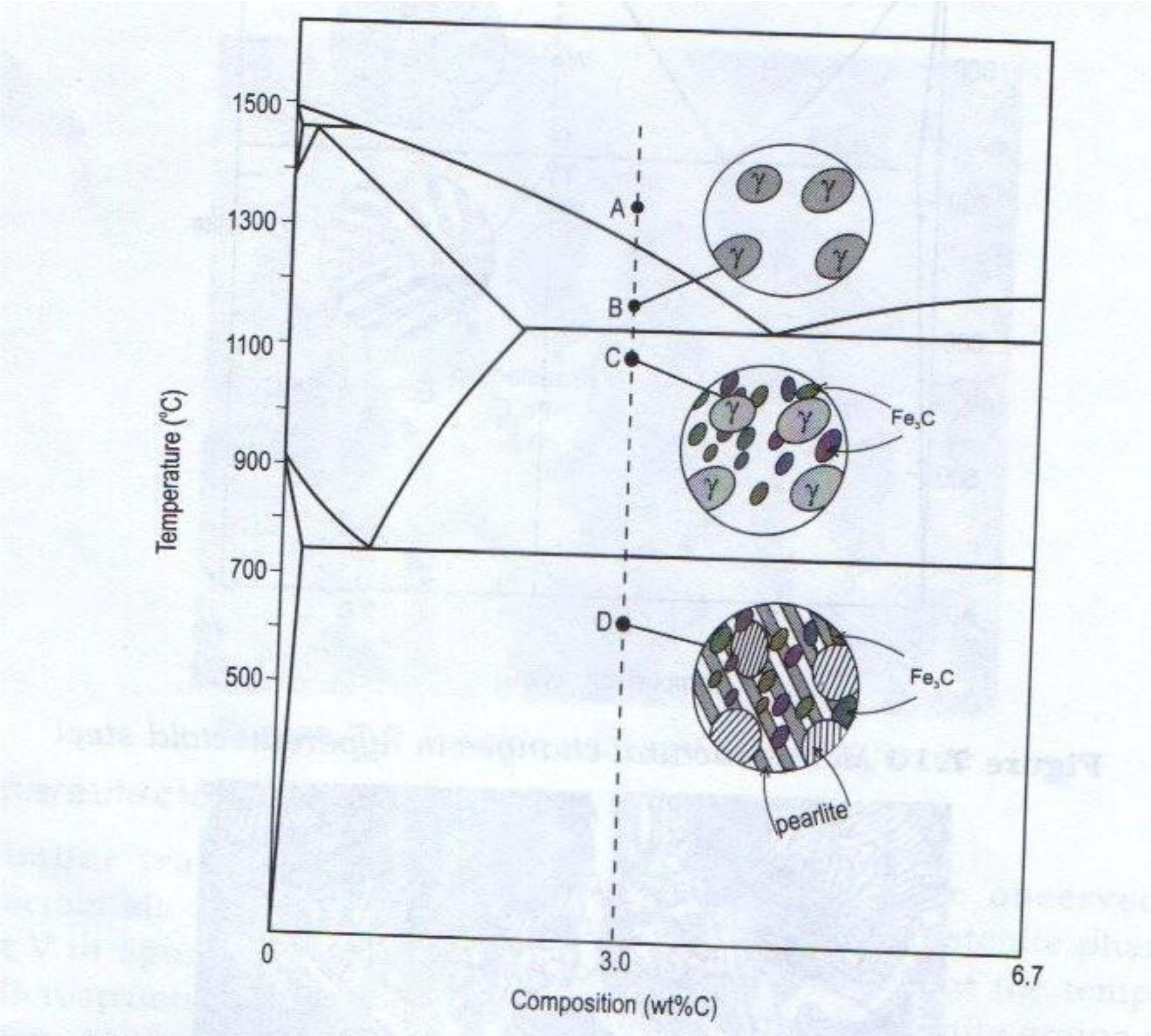


Figure 7.12 *Microstructural changes in white cast iron*

Another type of microstructure is possible in cast irons under following conditions: (a) high carbon content near to 4.3%C. (b) high cooling rates and (c) silicon added as inoculant. The structure in these cases consists of graphite flakes in a matrix of ferrite. Such cast irons are called grey cast iron. Cast irons with cementite are known as white cast iron.

Transformation of Austenite

Figure shows the transformation involving austenite.

1. Pearlite

Pearlite is formed by diffusion of carbon. Carbon in austenite is re-distributed into 2 phases (a) carbon rich cementite and (b) low carbon ferrite. When cooling rate is slow, coarse pearlite is formed. It consists of thick lamellae (layers) of ferrite and cementite.

At higher cooling rates, fine pearlite is obtained with fine layers of ferrite and cementite.

Cementite is hard and brittle. Ferrite is soft and ductile. In fine pearlite, layers are more. Fine pearlite is harder and stronger with somewhat lower ductility. Coarse pearlite has more ductility at the cost of hardness and strength.

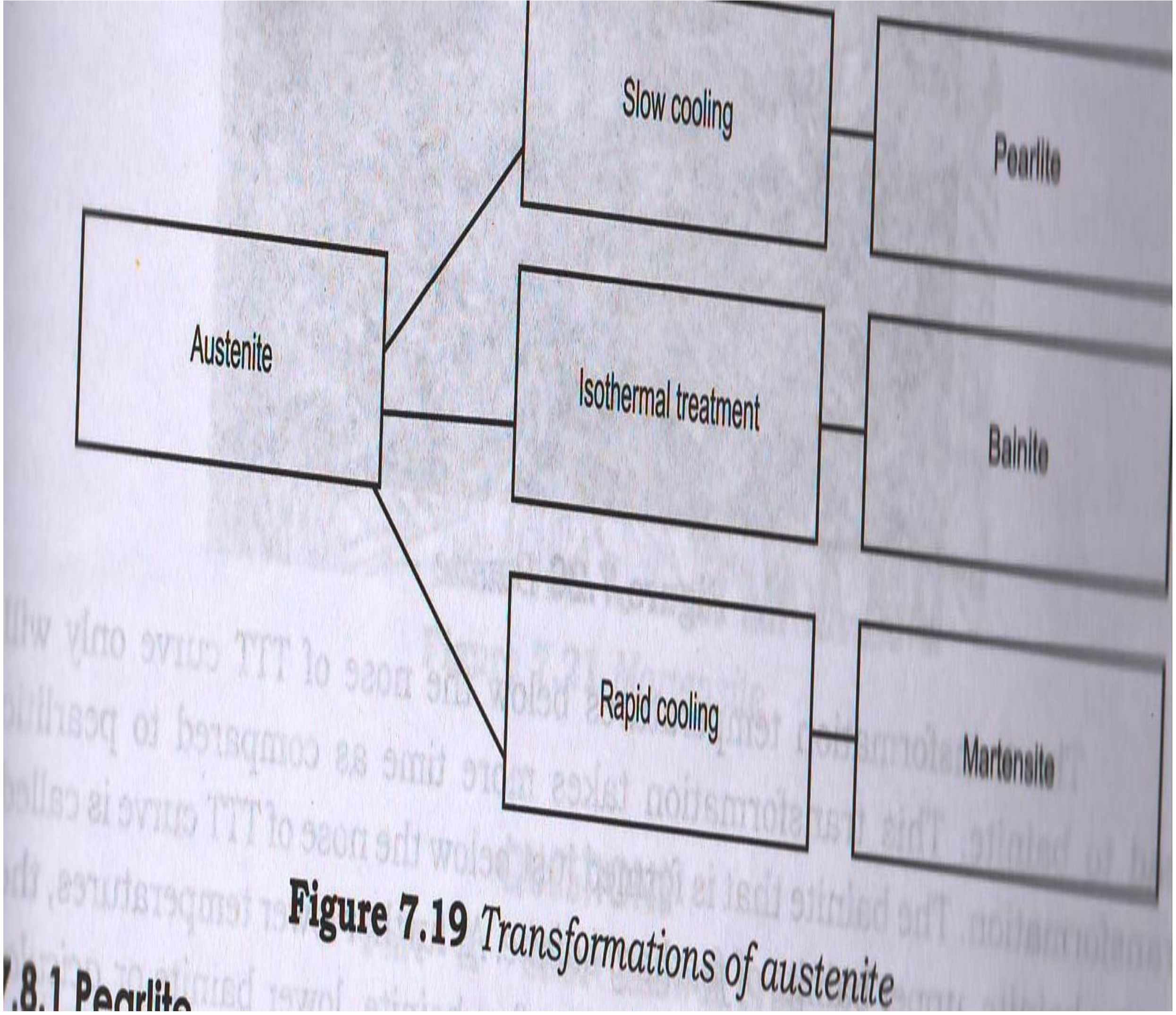


Figure 7.19 Transformations of austenite

2. Bainite

Bainite is also a mixture of 2 phases, ferrite and cementite. But the distribution is finer than in pearlite. Bainite forms as needles or plates. Transformation temperature below nose of TTT diagram can only produce bainite. Hence bainite is usually formed as an isothermal transformation. Bainite formed at just below nose of TTT is called coarse (or upper) pearlite.

At lower temperatures, lower or acicular bainite is produced. Bainite has more strength and hardness than pearlite.

3. Martensite

Martensite transformation occurs when cooling rate is very high. There is no diffusion. It is formed in a very sudden and athermal fashion. Reorientation of iron and carbon atom into a body centered tetragonal (BCT) structure occurs.

4. Spheroidite

Spheroidite structure is obtained by spheroidizing heat treatment. This structure has improved machinability and ductility especially in hyper eutectoid steel. A structure of spheroids of cementite in ferrite matrix is obtained. This is the softest state of hyper eutectoid steels.

Microstructure Property Relationship

Consider an alloy of iron and carbon containing iron and 0.77% carbon. When heated to a temperature above 727^0C, the structure becomes austenite. If this alloy is slowly cooled to room temperature, the structure changes to pearlite containing alternate lamellae of ferrite and cementite. Ductility is poor. If this same alloy is heated to a temperature below 727^0C and held for a long time the structure changes to spheroids of cementite in ferrite matrix. There is a large increase in ductility. If this alloy is rapidly cooled from austenite, a martensite structure is obtained which has very high hardness and strength but very poor ductility. This example shows that same alloy with different microstructures can result in vastly different properties.

HEAT TREATMENT

Heat treatment is defined as a combination of heating and cooling applied on a metal or alloy in solid state to produce desired properties. Main objectives of het treatment are: (i) improve strength, ductility, impact strength etc. (ii) improve surface hardness (iii) improve resistance to wear, heat and corrosion (iv) improve machinability (v) refine grain size (vi) relieve internal stresses etc.

TTT Diagram for Eutectoid Steel

Phase diagrams have following limitations

1. They give no information on form and distribution of phases (lamellae,spheroids etc)
2. They give data corresponding to equilibrium condition (very slow rate of cooling/heating). Such conditions are rarely achieved. Deviations from equilibrium condition can result in new phases (quenching produces bainite, martensite etc.)

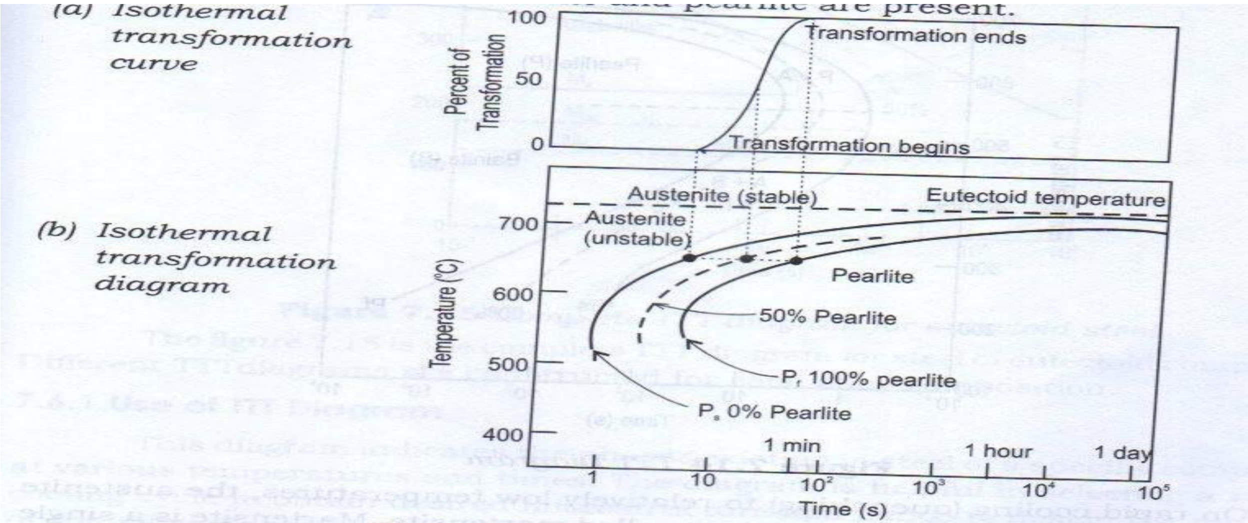


Figure 7.13 *Construction of TTT diagram*

Temperature and cooling rate (time) affect transformation of austenite critically. Let us take a eutectoid steel. Transformation of austenite to pearlite at 650^0C is given in Fig (a). Such curves are prepared for various temperatures below eutectoid temperature. The data is plotted as an isothermal transformation (time temperature transformation or TTT) diagram.

X axis gives time in log scale. Y axis gives temperature. Solid curve on left (P_s) indicates time of starting the transformation to pearlite. Curve on right (P_f) gives time to complete pearlite conversion. Dashed curve provides time to complete 50% conversion at each temperature. Towards left side of P_s only unstable austenite is present. Only pearlite exists to the right of P_f .

Just below eutectoid temperature, coarse pearlite(thick layers of ferrite and cementite) is seen. At lower temperatures (apprx. 540^0C), fine pearlite (thin layers of ferrite and cementite) is observed.

Isothermal holding below 540^0C produces a new microstructure called bainite. It also contains ferrite and cementite. But cementite is present as feathers or needles.

TTT diagram after extending up to 215^0C is given in fig. All 3 curves are C shaped. There is a nose near 540^0C where transformation is fastest.

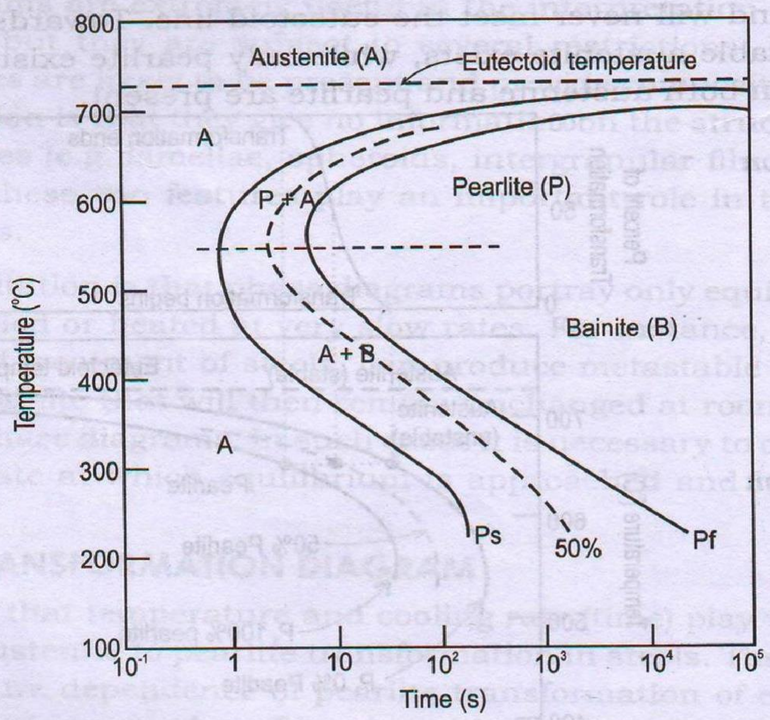


Figure 7.14 *TTT Diagram*

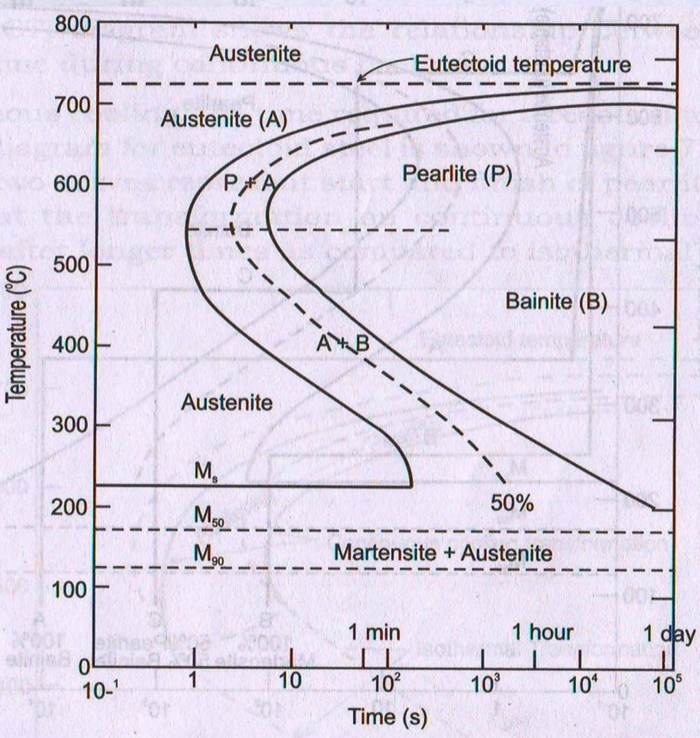


Figure 7.15 *Complete TTT diagram for eutectoid steel*

Bainite formed just below nose is called upper bainite. In this bainite, cementite is feathery. At lower temperatures, cementite becomes finer. It takes acicular or needle like shape. This is called lower bainite.

Rapid cooling (quenching) converts austenite into another structure called martensite. It is a diffusionless and very fast transformation. It does not depend on time. But it is a function of temperature to which alloy is quenched.

Martensite does not appear in Fe-C diagram because it is a non-equlibrium phase. But TTT diagram shows martensite transformation.

Complete TTT diagram for eutectoid steel is given in Fig.

Ms indicates beginning of martensite transformation. M50 and M90 indicate 50% and 90% transformation.

Separate TTT diagrams are prepared for various compositions.

Use of TTT Diagrams

Practically all transformations take place under non-equilibrium conditions. Hence Fe-C phase diagram cannot predict microstructure and properties. TTT diagram indicate phases stable at various temperatures and times (cooling rates). Therefore, they can predict and select the cooling rates to obtain desired microstructure and properties.

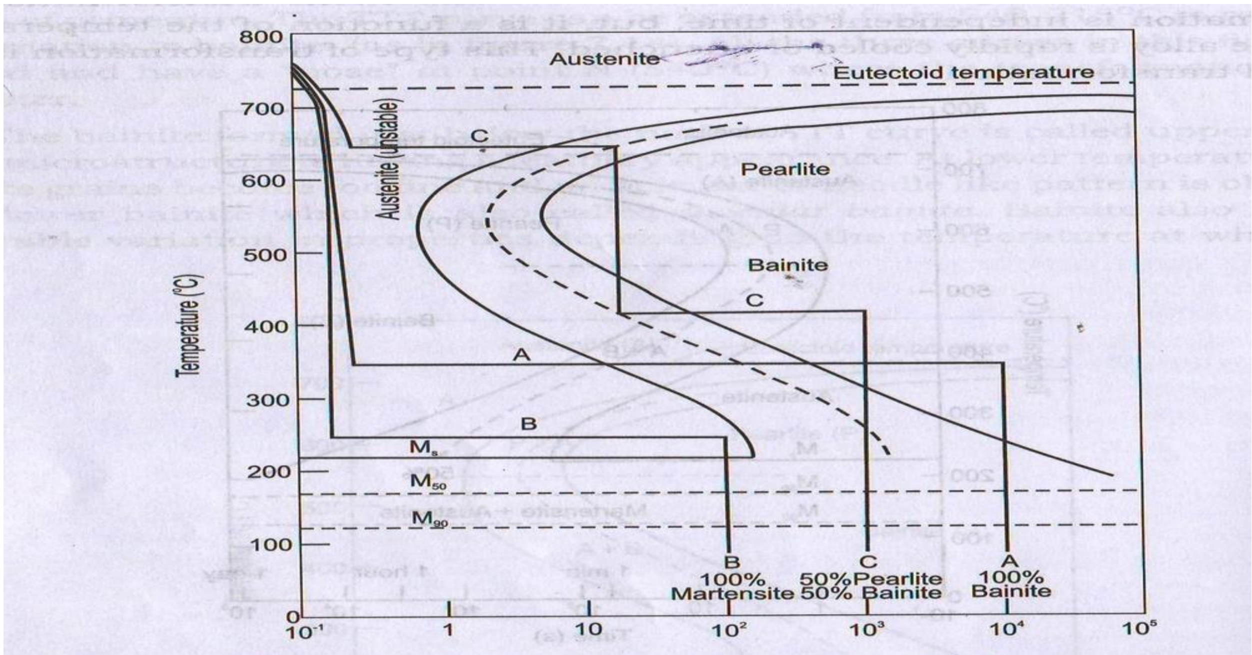


Figure 7.16 *TTT diagram for eutectoid steel*

Cooling cycle A: Complete unstable austenite transforms to pearlite.

Cooling Cycle B: Transformation to pearlite/ bainite does not start. Entire unstable austenite transforms to martensite.

Cooling Cycle C: 50 % unstable austenite transforms to pearlite and the remaining 50% transforms to bainite.

Continuous Cooling Transformation (CCT) Diagram

In actual practice steel is rarely cooled at isothermal (constant temperature) conditions. It is continuously cooled from austenitic range to room temperature. CCT diagrams are more useful to predict microstructure during continuous cooling conditions.

Fig gives CCT (full lines) and TTT (dashed lines) diagrams for eutectoid steel.

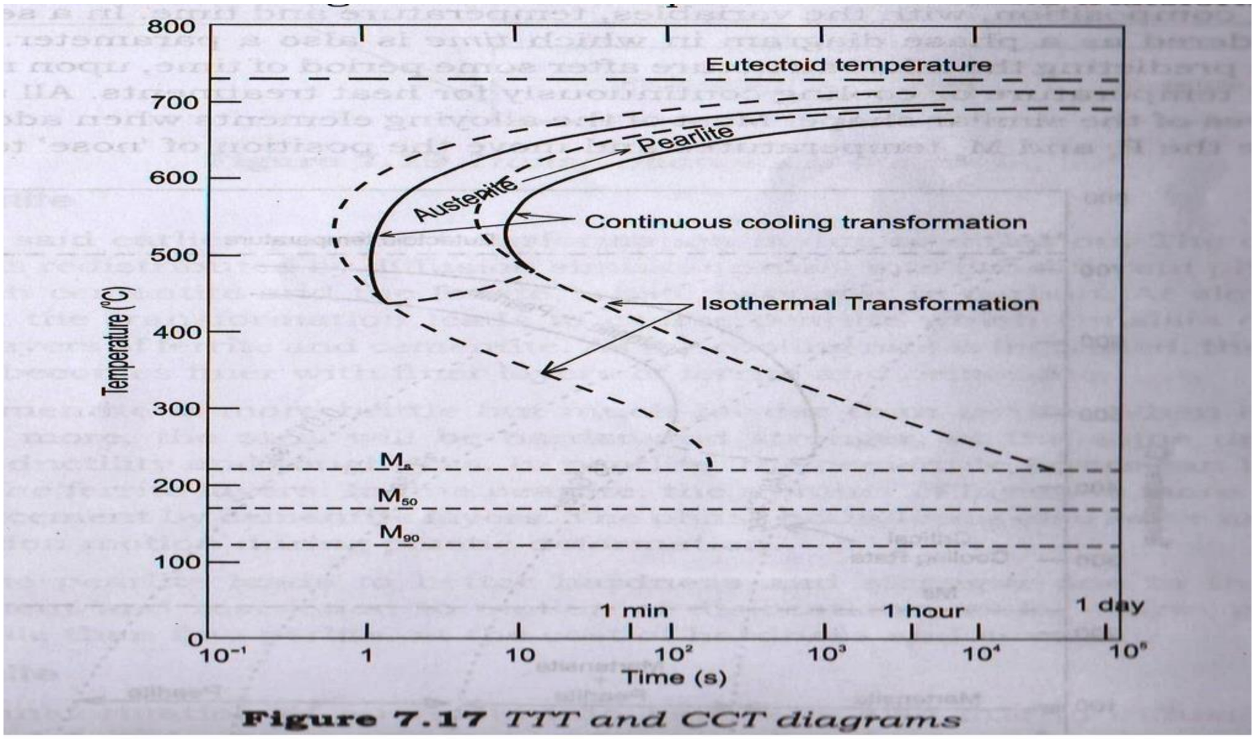


Figure 7.17 *TTT and CCT diagrams*

Use of CCT diagrams

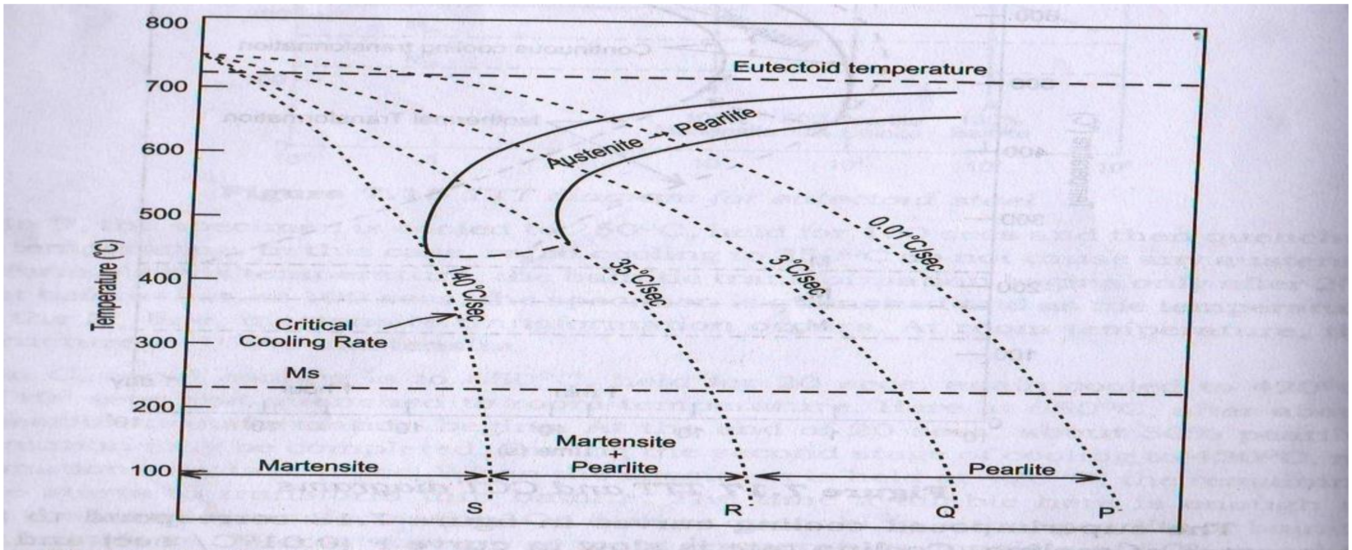


Figure 7.18 *CCT diagram for eutectoid steel with cooling curves*

At a selected temperature, transformation is slower (taking more time) in CCT compared to TTT diagram. For a selected time, transformation starts at a lower temperature in CCT.
Cooling rate curves given in Fig corresponds to both slow and fast cooling rates (from 0.01^{0}C/sec to 140 ^{0}C/sec).
Cooling rate 0.01^{0}C/sec : Coarse pearlite 3^{0}C/sec: Pearlite, 35^{0}C/sec : Fine pearlite140^{0}C/sec: Martensite. Between 35^{0}C/sec -140^{0}C/sec : Pearlite+bainite +martensite

Critical Cooling Rate:

Cooling rate which just misses the pearlitic start curve is called critical cooling rate. This cooling rate has to be exceeded to obtain full martensite.

Annealing

1. Process Annealing

It is used to increase ductility of cold worked material to facilitate further deformation. Machinability is also improved. It is used for low carbon steels. Steel is heated to 550-650^{0}C, held for sufficient time and slowly cooled in air. Refer Figure.

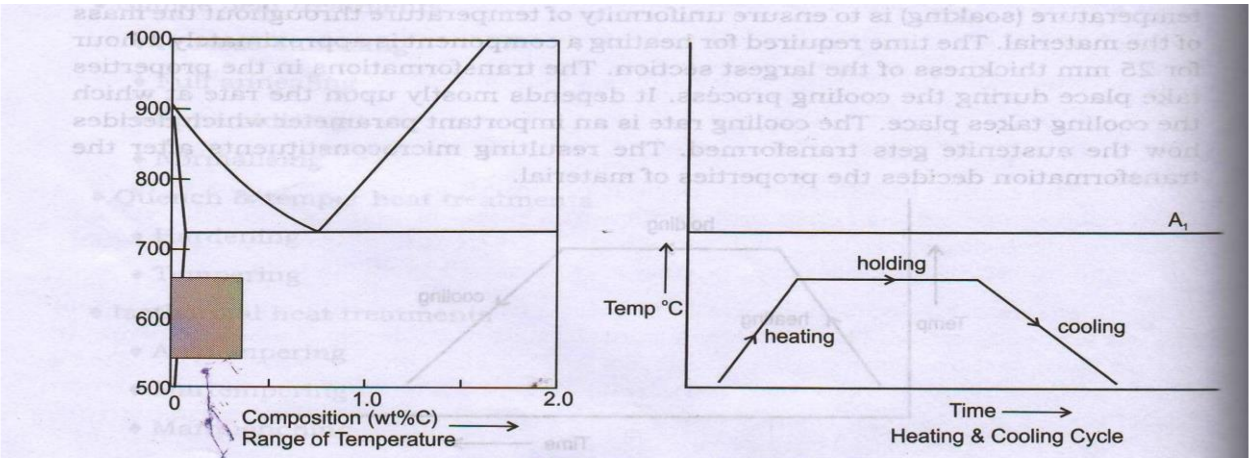


Figure 8.2 *Process Annealing*

2. Full Annealing:

This process is used to obtain complete recrystallization, relieve internal stresses and to restore ductility &machinability. Refer Fig.

Hypo eutectoid steels are heated 50-90^{0}C above A_3 line. Holding at this temperature converts the structure into austenite. Then the steels are very slowly cooled (10-20^{0}C) in the furnace.
Austenite transforms to ferrite and pearlite. Along with this, recrystallization, relief of internal stresses and restoration of ductility are also achieved.

Hyper eutectoid steels with pearlite + cementite structure are heated 50-90^{0}C above A_1 line only. They are held at the temperature to convert pearlite into austentite. There is no change to cementite..

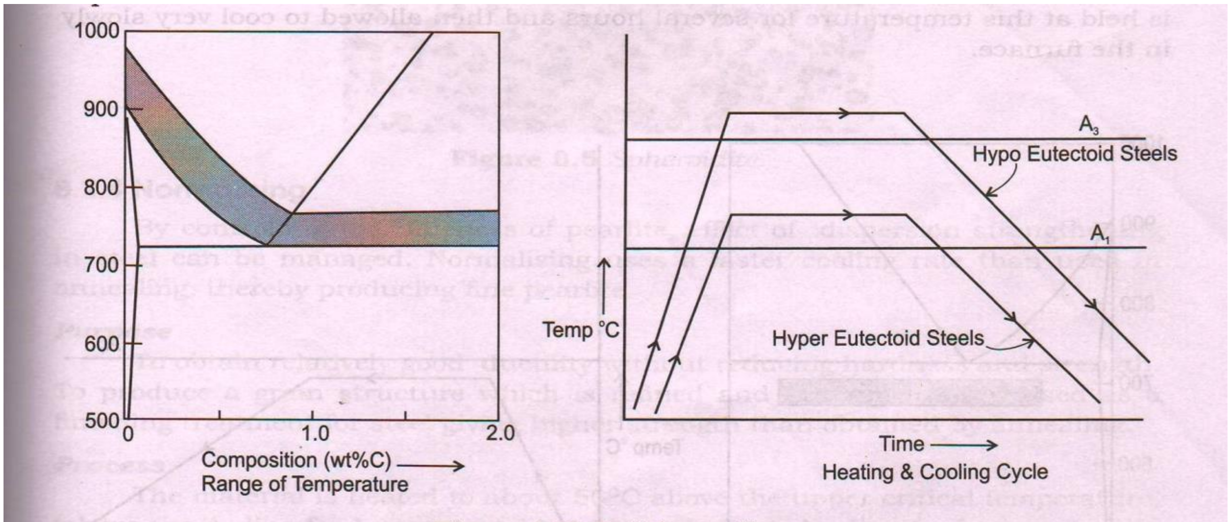


Figure 8.3 *Full Annealing*

Then the are cooled slowly in the furnace. Austenite transforms to coarse pearlite. Other required objectives of annealing are also met. These steels are not heated to full austenite range (above A_{cm} line) because machinability is drastically affected due to brittle cementite film around pearlite.

Spheroidizing

It is used to improve machinability and ductility of hyper eutectoid steel. Ref Fig.Steel is heated to about 30^{0}C below A_1 line. It is held at this temperature for sufficient time and then cooled very slowly in the furnace.

A structure of spheroids of cementite in ferrite matrix is obtained. This is the softest state of hyper eutectoid steels.

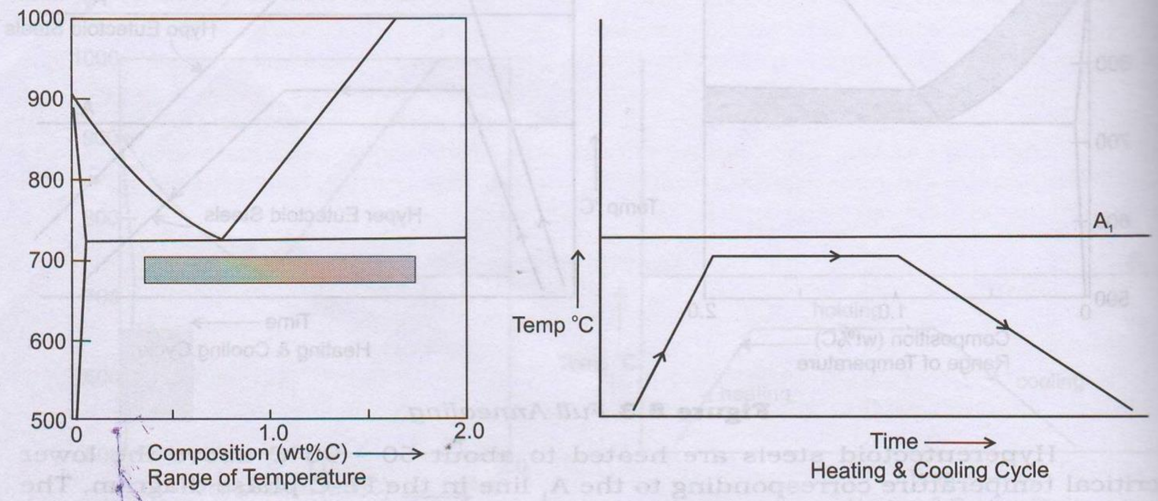


Figure 8.4 *Spheroidising*

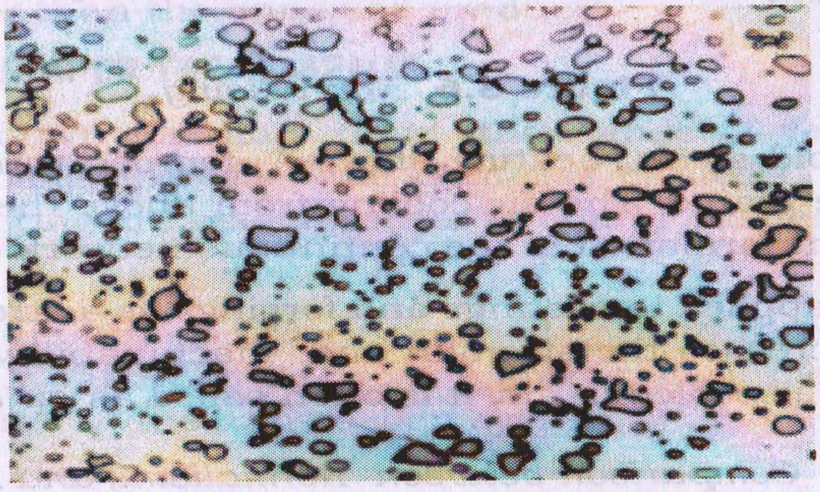


Figure 8.5 *Spheroidite.*

Normalizing

Normalizing uses a higher cooling rate (cooling in air) compared to annealing (cooling in furnace). A fine pearlite structure is obtained.

It is used to obtain a good combination of strength and ductility. Strength is much higher than annealing.

It is commonly used as a finishing operation after manufacturing. Ref fig.

Steels are heated to about 50^0C above A_3 line for hypo eutectoid steels and A_{cm} line for hyper eutectoid steels. They are held at this temperature for sufficient time and the entire structure changes to austenite. They are then cooled in air. Pearlite in the structure forms as fine lamellae.
Normalizing prevents brittle film formation of cementite as a result of fast cooling rate. Comparison of Normalizing and Full Annealing is given in table.

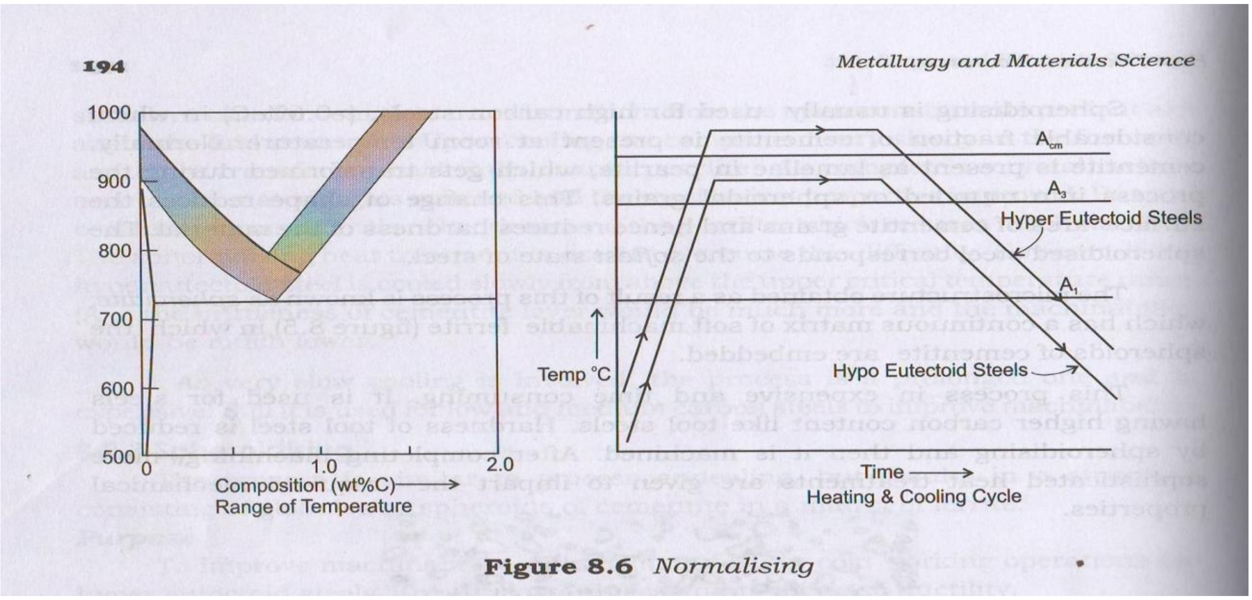


Figure 8.6 *Normalising*

Normalizing	Full Annealing
Faster cooling rate, in air	Slower cooling rate, in furnace
Heating to above upper critical temperature(A_3 and A_{cm} lines) for hypo and hyper steels	Heating to above upper critical temp. (A_3 line) for hypo steel and above lower critical temp. (A_1 line) for hyper eutectoid steel
Fine grains, fine pearlite	Coarse grains, coarse pearlite
Strength and hardness high	Ductility very high
Used as finishing operation	Used as intermediate operation to improve ductility and machinability.

Quenching (rapid cooling or very high cooling rate) increases hardness and strength of steels at the expense of ductility. The increase in hardness is due to the formation of martensite.

Hardening

_Hardening is done to increase hardness, strength and wear resistance of steel by obtaining a suitable microstructure after tempering.

First step is austenitizing. Temperature range is the same as that used for annealing (above A_3 line for hypo and above A_1 line for hyper eutectoid steels). Hyper eutectoid steels are heated to above A_1 line only because proeutectoid cementite is itself a very hard phase. Steel is held at this temperature for sufficient time. It is then quenched in water, oil or brine.

The cooling rate should be above critical cooling rate to obtain full martensite. Martensite has body centred tetragonal (BCT) structure. BCT has no close packed plane. Hence dislocations cannot move easily and results in high hardness. Martensite can absorb any amount of C in steel up to 0.77%. Highest hardness is obtained for eutectoid steel (0.77%C).

Cementite is hard, but has lower hardness than 0.77%C martensite. Hence hyper eutectoid steels with martensite +cementite structure are not as hard as eutectoid steel after hardening.

Quenching media in the order of decreasing cooling rate is as given: Brine (with 10%NaCl), water, oil, salt bath, air (lowest cooling rate)

Plain carbon steel when quenched in brine gave 60 HRc. The same steel by oil quenching gave only 28HRc. Water and oil are the most widely used quenching media. Quenching effect can be increased by agitation and circulation of the bath.

Tempering

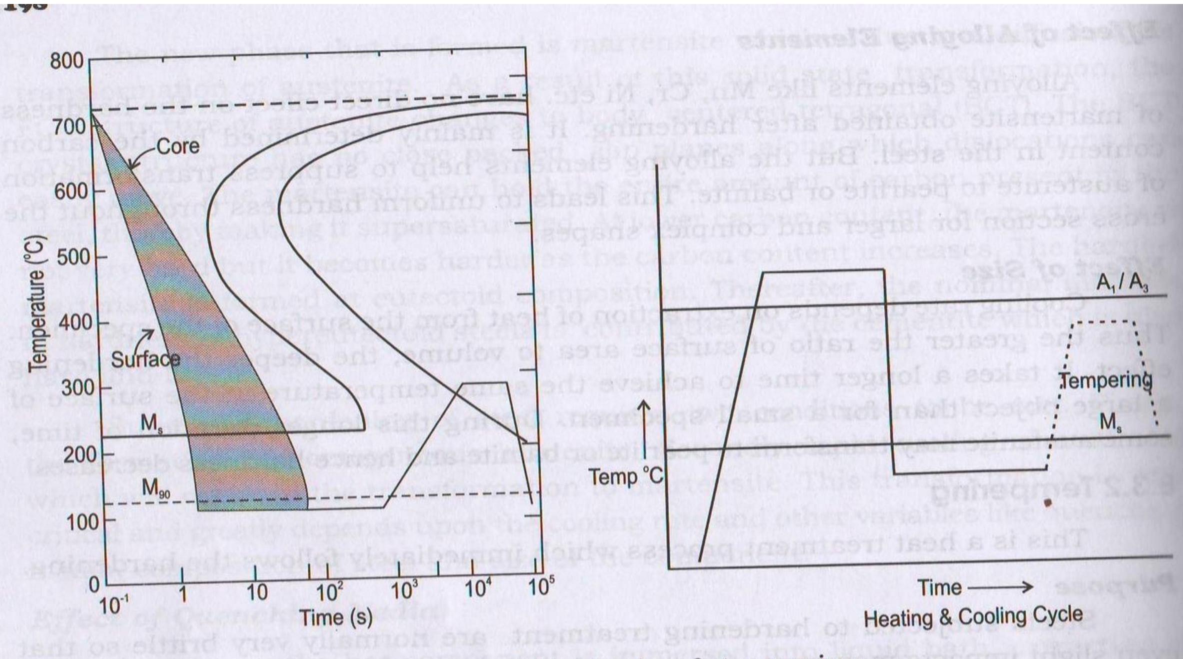


Figure 8.7 *Hardening & tempering*

After hardening, the steels are brittle, though they have high hardness and strength. Tempering reduces brittleness by relieving internal stresses and changing the microstructure.

Tempering involves reheating hardened steel to temperature below A_1 line, followed by slow cooling. Heat treatment cycle for hardening and tempering is shown in Fig. Tempering may be done at low (150-250^0C), medium(300-450^0C) or high(450-680^0C) temp.

Low temperature tempering relieves internal stresses. Medium temperature tempering produces a microstructure of martensite + troostite (very fine pearlite). This increases ductility. High temperature tempering transforms martensite to sorbite. This structure results in optimum combination of strength and ductility.

Austempering

_It is an interrupted quenching process. It is also called isothermal hardening. This process produces steels with optimum properties in a single operation instead of 2 step hardening and tempering operations. Freedom from distortion & cracking produced during hardening is another advantage. Process is shown in Fig.

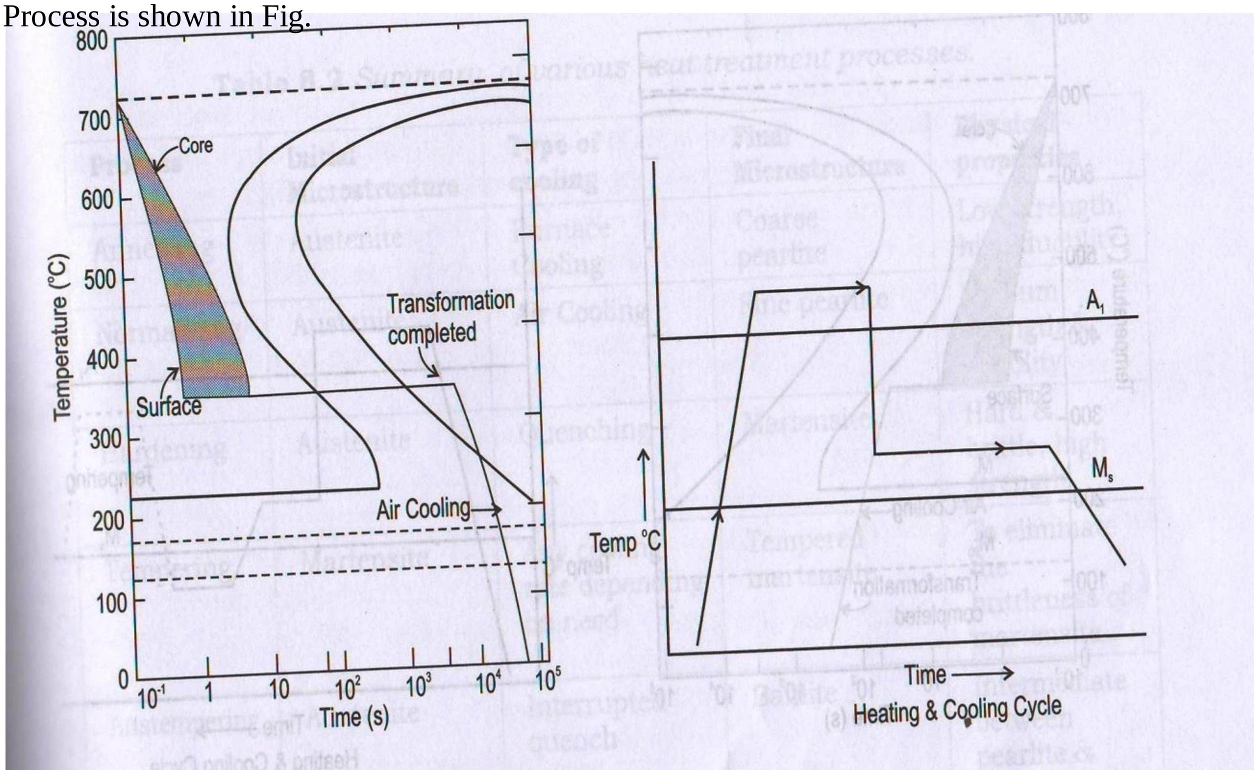


Figure 8.8 *Austempering*

At first the steel is heated to austenitic range (above A_1) and held for sufficient time. It is then quenched in a salt bath maintained at a temperature between 200-400^{0}C (lower bainite region). It is held at this temperature for sufficient time to complete transformation to bainite. It is then cooled in air to room temperature.

Structure obtained will be lower or acicular bainite. This structure has better strength-ductility combination than hardened and tempered martensite.

Martempering

It is also an interrupted quenching process, similar to austempering. Difference is that the component is slowly cooled to martensite temperature range.

Process is shown in Fig. The steel is converted to austenite at first. It is cooled rapidly to 180-200^0 C (just above Ms). This cooling is done with the help of salt bath. The cooling rate is more than the critical cooling rate. After holding for sufficient time at 180-200^0 C, component is cooled in air to room temp.

Structure after martempering is tempered martensite. Martempering may be followed by tempering if higher ductility is needed. Martempering reduces cracking, distortion and internal stresses.

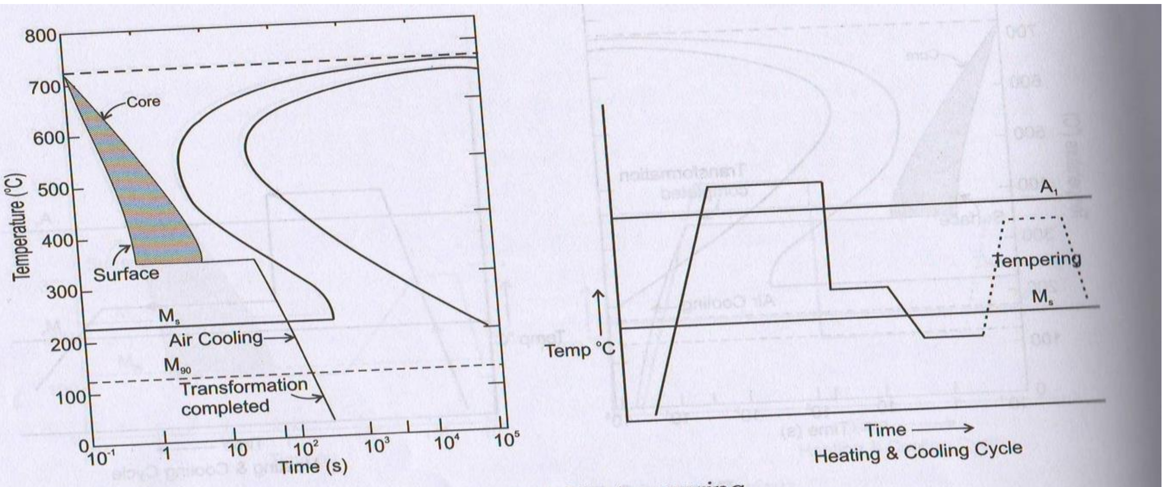


Figure 8.9 *Martempering*

Ausforming

Ausforming is a thermo mechanical process in which steel is plastically deformed in austenite condition and then quenched below Ms temperature to form martensite. High strength is obtained without affecting toughness. Plastic deformation (usually rolling) of austenite should be done without transforming to pearlite or bainite. Thus there are four process steps namely

1. Austenitize steel
2. Rapidly cool to a temperature such that the structure remains as austenite. Cooling rate should be above critical cooling rate to achieve this.
3. Deform the austenite at this temperature
4. Quench from this temperature to obtain martensite.

Comparative study on ductility and strength of various structures

Microstructure	Process	Type of cooling	Properties
Coarse pearlite	Annealing	Furnace cooling	Low strength, High ductility
Spheroidite	Spheroidizing	Furnace cooling	Low strength and high ductility in hyper eutectoid steel (intermediate between coarse and fine pearlite)
Fine pearlite	Normalizing	Air cooling	Medium strength and ductility
Bainite	Austempering	Interrupted quenching	Intermediate between fine pearlite and martensite
Martensite	Hardening	Quenching (oil/water/brine)	Very hard, high strength and very brittle

Tempered martensite	Tempering Martempering	Cooling rate optional	Hard and strong,ductile; Intermediate between bainite and martensite
Ausformed martensite	Ausforming	Quenching	Highest hardness and strength, ductility comparable to tempered martensite

Hardenability

Hardness and hardenability are two different concepts. Hardness is the resistance of the material to indentation or deformation. It is a basic material property.

Hardenability is the ability of the steel to develop a hardened layer across the cross section or thickness. After hardening operation, hardness is highest at surface and it reduces along thickness. Hardenability is specified as the distance below the surface where martensite is at least 50%. It is also expressed as the diameter of bar that will form 50% martensite at the center.

This diameter is called ideal critical diameter. Alloying elements influence hardenability to a large extent. They shift TTT curves to the right. Other factors like homogeneity of steel and austenite grain size also affect hardenability.

Jominy End Quench Test

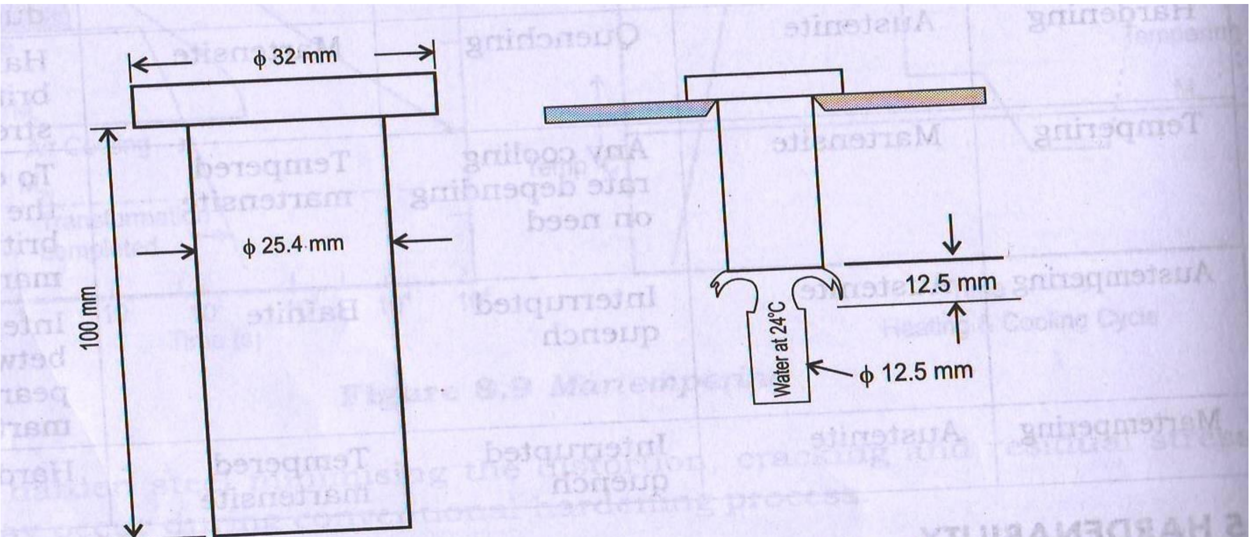


Figure 8.10 *Jominy - end quench test*

It is the most popular method to determine hardenability of steel. Standard specimens of 25.4 mm dia. and 100mm length are used. These are austenitized by heating to temperature above 727^{0}C.

The specimen is quickly transferred to a fixture. Lower end of specimen is quenched by a jet of water at specified flow rate. This results in different cooling rates along the length of the specimen ranging from maximum at the quenched end to minimum at the fixed end.

Surface hardness (in Rockwell C, HRc) is measured along the length of specimen.

A curve is made with distance from quenched end on X axis and HRc on Y axis. This plot is known as Jominy curve or hardenability curve.

Applications

Jominy curves can be used to compare hardenability of various steels. A horizontal line can be drawn at HRc 57 (corresponding to 50% martensite structure) to meet Jominy curve at a particular point. This distance known as jominy distance can also be used for comparing hardenability.

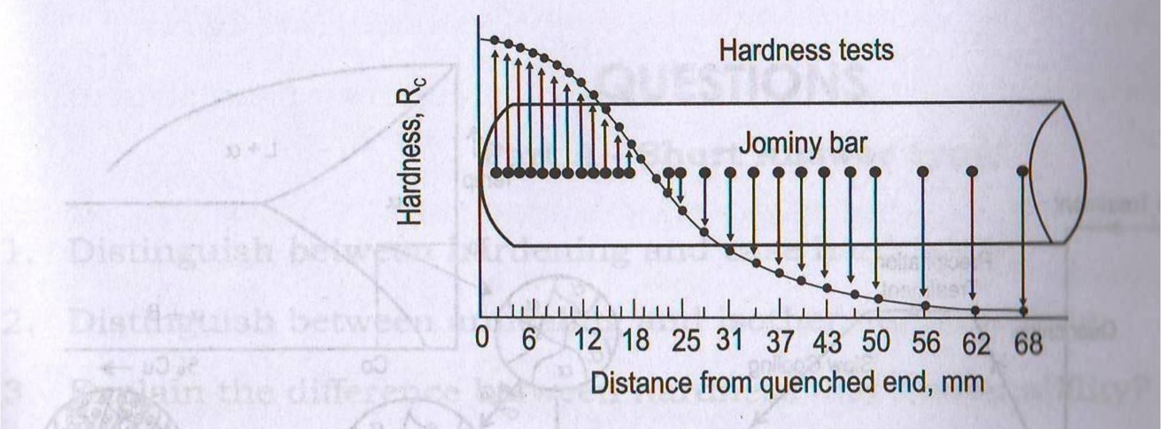


Figure 8.11 *Jominy curve*

Mass Effect: It refers to variation in hardness across a thicker component after heat treatment. Outer layers will cool faster than the core. This results in variation in hardness across the section of the component.

Surface Hardening Methods

A number of engineering applications require different properties for surface and interior of components. For example, gears, cams, rolls etc. require a very hard and wear resistant surface (case) and a ductile and tough interior (core). Chemical storage tanks require a surface of very high corrosion resistance. Such combination of properties is obtained by various surface treatments.

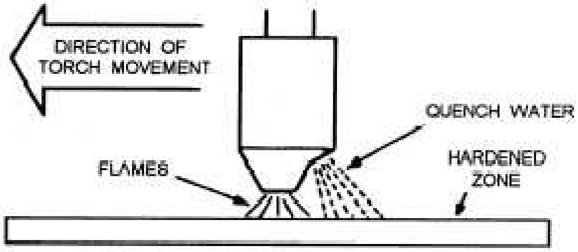
The various surface hardening treatments can be classified into two types:

1. No change in surface composition Methods (i) Flame hardening (ii) Induction hardening (iii) Laser hardening (iv) Electron beam hardening
2. Change in surface composition methods
   (i) Carburizing (ii) Nitriding

No Change in Composition Methods

1. Flame Hardening

In flame hardening an ordinary oxy acetylene torch is used to heat the part at the regions to be hardened. Flame is slightly oxidizing in nature. The flame is adjusted to achieve a temperature of about 850^{0}C. The torch is moved to heat the part uniformly. It is then quenched by the jet of water from nozzle. Carbon content should be between 0.3-0.6 percent. Tempering is done after flame hardening.



Advantages

1. Rapid and efficient method. Deep cases up to 6mm.
2. Small regions (zones) can be hardened. Hence low distortions.
3. Also suitable for large components that cannot be fitted in furnace and for heavy components which cannot be transported.

Disadvantages

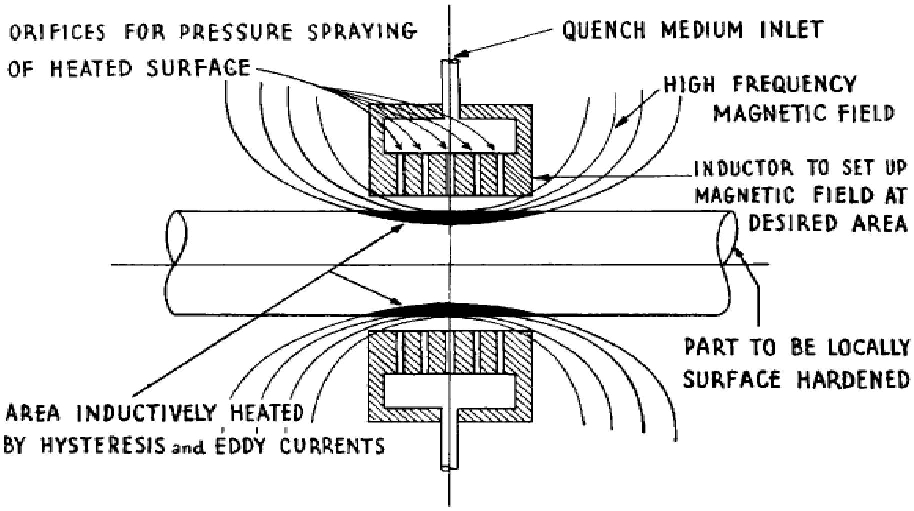
1. Case depth is difficult to control. Hence thin cases are difficult.
2. Low carbon steel cannot be hardened.

Applications

Gear teeth, cylindrical pins, lathe beds, cam surface, engine push rods, pulleys and sprocket teeth.

2.Induction Hardening

Induction hardening can produce a hard and wear resistant surface with a soft core. Job to be hardened is placed within an induction coil of several turns of copper wire. A high frequency current is passed. This sets up an induced alternating current which heats the job surface to a temperature of $750-800^0$C. Heated surface is quickly quenched by water.



• Schematic diagram of piece being inductively heated. Note limited effective magnetic field.

Advantages

1. Very fast process. Hardening to a depth of 0.8 mm can be achieved within 1 to 5 seconds.
2. Irregular shapes can be hardened easily. Current dips into crevices and holes.
3. Case depth can be controlled effectively by varying frequency, current and time.
4. Outstanding resistance to warpage, distortion, oxidation and scaling. This is due to small heating time and small portion being heated at a time.
5. Unskilled operators can be employed

6. Environment is clean.

Disadvantages

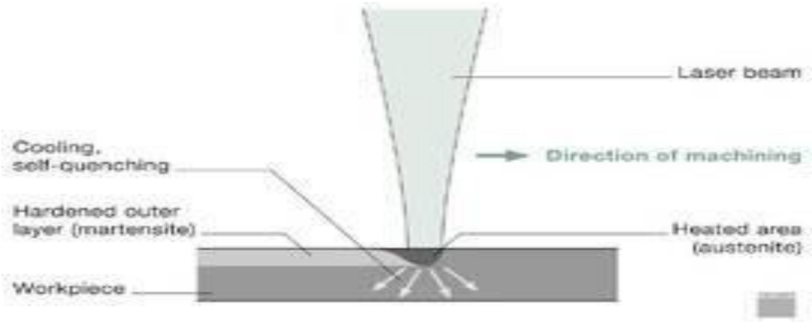
1. Medium carbon steel containing 0.35 to0.60% can be hardened. Low carbon and low nitrogen steels cannot be used.
2. Hardness depends on carbon content. If carbon content is low, high hardness is possible only in expensive high alloy steels.

Applications

Cams, gear teeth, shaft splines, bearing surfaces, pump shafts, piston rods, chain links etc.

Laser Hardening

It is a variant of flame hardening. A phosphate coating is applied over the steel surface to facilitate laser absorption. Selected areas are exposed to laser energy. The surface gets heated to 900-1400^{0}C. Heat can be controlled by varying power of laser. Parts are then self -quenched (transferring heat to cooler surface) and tempered. Case depth is usually 0.1 to 1.5 mm.



Advantages

1. Process is precise. Selective areas can be hardened accurately.
2. Useful for ferrous materials containing more than 0.2% carbon. Steels and cast irons can be hardened.
3. Minimum distortion.
4. Core remains soft.
5. Process is environmentally clean. Work piece need not be cleaned.

Applications

Process is primarily used in automobile industry for axle shaft housings, power steering gear housings etc..

3. Electron Beam Hardening

It is similar to laser beam hardening. Heat source is a high energy electron beam. Beam is focused by electromagnetic coils. Quenching is through self quench process (heat transfer to external cooler surroundings). Case depth is in the range of 0.1 to 1.5 mm.

Advantages

1. Surface can be hardened precisely in terms of depth and location.
2. Extremely low energy consumption.
3. Very low distortion

Change in Composition Methods

1. Carburizing

It involves adding excess carbon to surface of steel. Surface carbon may be about 1.2% while interior may be mild steel (less than 0.25% C). The process involves heating the parts with a carbon rich substance above critical temperature for a long time. There are 3 carburizing methods.

(a).Solid carburizing (pack carburizing)

Solid substances such as coke, coal, charcoal, calcium carbonate etc are used. The steel parts are placed in a closed chamber filled with carbon rich solid powder. Chamber is heated to 870-980^{0}C and held at the temperature for 5-10 hours. At this temp steel is austenitized. Carbon enters the surface up to a level of 1.2%. It is a slow, dirty, effective and cheap process

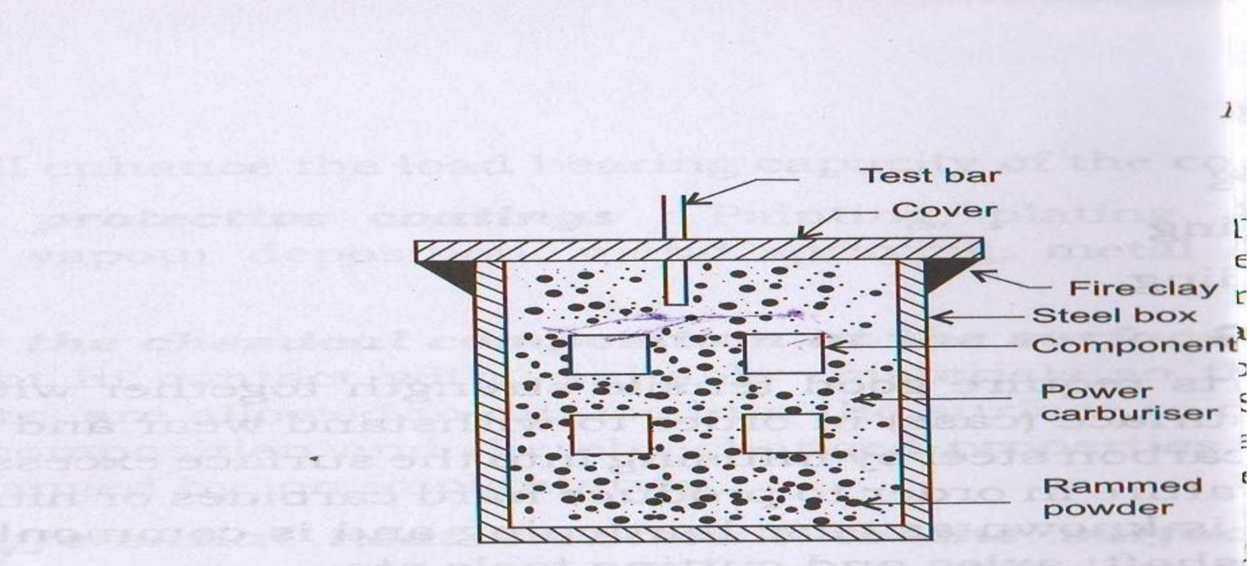


Figure 9.1 *Pack carburising pro*

(b).Gas Carburizing

Parts are heated in a furnace filled with carbon rich gases such as methane, propane, butane etc. Temperature is 820-980^{0}C and sufficient holding time is given. Hydrocarbons decompose and carbon gets deposited on the surface. This process is faster than pack carburizing. Case depth can be controlled more accurately. But it is more expensive.

(c) Liquid carburizing

In this process liquid hydrocarbons are used. Immersing in the liquid bath or spraying methods are employed. Components are heated to 820-980^{0}C. Bath is prepared with NaCN, Na_2CO_3 and NaCl. The process is faster and more efficient

2. Nitriding

Nitriding is very effective for alloy steels containing strong nitride forming elements like Al, Cr, Mo, V and W. Process involves heating to 650^0C and holding at 650^0C in an atmosphere ofNH_3 gas for 20-100 hrs. NH_3 decomposes into N & H. N penetrates into the surface of steel and forms hard nitrides. Parts are cooled in furnace. Nitriding improves corrosion resistance, but the process is costly and time consuming.

3. Cyaniding

In this process C &N are simultaneously introduced into the steel surface. Parts are immersed in a salt bath of NaCN at $800\text{-}960^0$ C. NaCN decomposes. C & N diffuse into steel surface and forms a carbo nitride phase. The process takes about 30-90 minutes. After cyaniding, components are quenched in water or oil. Cyaniding is a cheap and fast process. The case is thin and hard.

Carbo- nitriding is a variation of this process. Here a carburizing gas and ammonia gas are used together. E.g. 15% NH_3, 5% CH_4 and 80% neutral carrier gas. Temperature is $800\text{-}870^0$ C (somewhat less than carburizing temp). Here again quenching in oil is practiced and then tempered at $150\text{-}180^0$C. Lower temp and cooling rates are adequate. Internal stresses cracks and distortion are less.

4.Applications

Case hardening (carburizing, nitriding etc) methods are used when parts require a tough core and a hard, wear resistant case. Case hardening is commonly used for machine parts like gears, shaft, axles, cutting tools etc. Nitriding provides the hardest case of all surface hardening processes. This method is used for case hardening of dies, mandrels, gauges, parts of pumps and internal combustion engines

MODULE - 4

TYPES OF STRENGTHENING MECHANISMS

Work Hardening

Plastic deformation by cold working results in strengthening (work hardening or strain hardening). Cold working increases number of dislocations. These dislocations interact and form obstacles for the movement of dislocations. This results in increase in strength. Strain hardening is more in cubic than in HCP metals. Annealing removes strain hardening effects. Lower temperature favours work hardening. It is the reason why cold working increases work hardening.

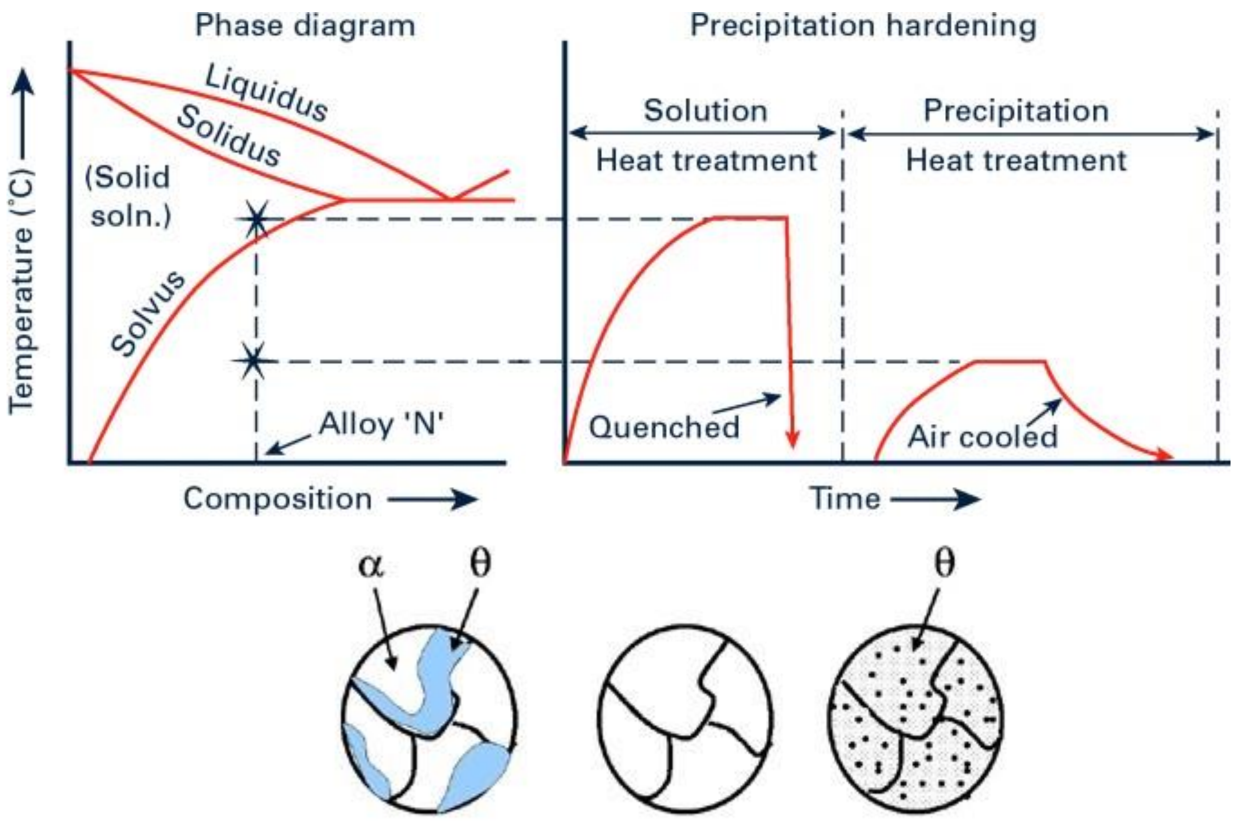
Precipitation Hardening and Overaging

Strength is improved by fine uniformly distributed very fine particles (precipitates) in the matrix phase. Precipitates are formed by a heat treatment called precipitation hardening. This process is also called age hardening since strength develops with passage of time (aging). Two conditions are essential for age hardening (a) appreciable solid solubility of the alloying element in matrix and (b) solid solubility decreasing with temperature (sloping solvus line). Al-Cu, Cu-Be and Mg-Al alloys are age hardenable. Age hardening is carried out in two different steps.

Step1: Solution Treatment

All the solute atoms are made to dissolve in the solvent metal. A single phase solid solution is formed. Consider an alloy of composition C_0. The alloy is heated to temperature T_0 within the α phase field. The alloy is held at that temperature for sufficient time so that entire phase becomes α. Now the alloy is quenched in water to room temperature. Normal structure at room temperature is α □ θ

Quenching prevents diffusion and thereby the formation of θ. Thus, at room temperature, the α phase is supersaturated with respect to copper atoms. At room temperature the diffusion rate is very small. Therefore the supersaturated α is retained at room temperature.



Start:
α + coarse θ
(equilibrium at
room temperature)

After quench:
supersaturated α

Fine
precipitate θ
appears in α
to strengthen

Step2 Precipitation Treatment

The supersaturated α solid solution is reheated to an intermediate temperature within the $\alpha + \theta$ region. At this temperature, diffusion rate is higher than at room temperature. θ phase precipitates out as fine particles throughout the α matrix. The strength and hardness of alloy depends on the precipitation temperature and holding time at this temperature. There is an optimum time for any particular temperature at which maximum strength and hardness are obtained. Holding the alloy beyond this time results in coarsening (increasing size) of precipitates. This leads to reduction in strength and hardness. This phenomenon is known as over- aging.

In some alloys, significant precipitation hardening can occur even at room temperature after quenching operation. This is known as natural aging. If the aging is carried out at a temperature above room temperature, the process is called artificial aging which is more common.

.

Dispersion Hardening

Fine particles of one phase dispersed in to the weak parent (matrix) phase increase strength. Soft phase is the continuous phase and hard phase is the dispersed phase. These particles hinder dislocation movement. Dispersed phase in very small amounts is sufficient to enhance strength. The particle sizes are to be small enough to impose obstacles to dislocation movement. Particles in precipitation hardening have coherency with the matrix. Dispersion hardening particles have no such coherency. In eutectic and eutectoid reactions where two solid phases are present, the second phase acts as dispersion phase which provides the strength.

COLD WORKING

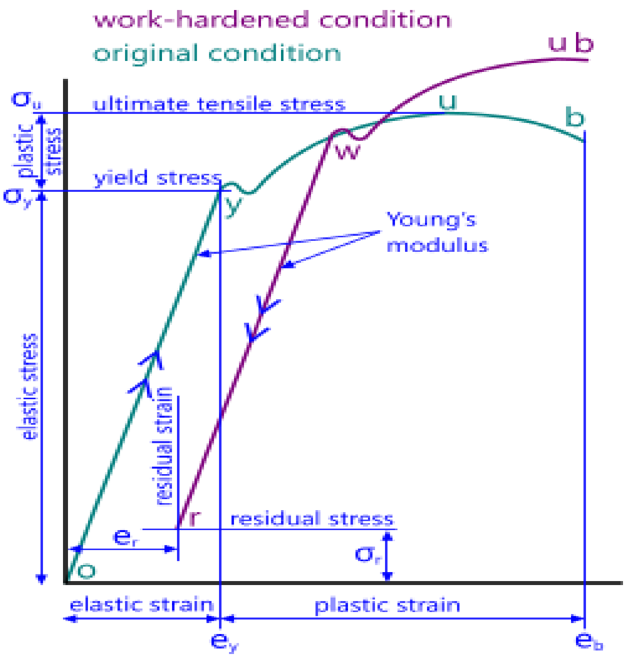
Mechanical working is defined as a process for making change in shape of material by the application of external force (stress). The process changes the properties also apart from shape changes. Commercial materials are generally poly crystalline. Deformation at first starts in those grains in which slip system is favorably oriented. As deformation proceeds, the grains tend to elongate in the direction of deformation.

There are two types of mechanical working processes namely cold working and hot working. Cold working refers to working below recrystallisation temperature. It is commonly done at room temperature. Strain hardening occurs by cold working. The grains get distorted by cold working. Structure sensitive properties like tensile strength, yield strength, ductility and electrical conductivity are all affected by cold working.

Detailed Discussion on Strain Hardening

A part of the energy (about 10%) used for deformation is stored as internal energy. Major part of this stored energy is present at the grain boundaries. Thus grain boundaries which are high energy areas resist movement of dislocations and therefore work hardening occurs. In order to strain the metal further, a much higher stress is required.

Metal with original yield stress (point Y) is plastically deformed up to point W. The stress is completely released and then the stress is reapplied. It can be seen that the yield stress has increased very much. This increase is due to strain hardening.



Before deformation, the materials usually have dislocation densities of 10^4 to 10^6 mm^{-2}. Cold work increases dislocation density to 10^8 to 10^{10} mm^{-2}. One may think that the increased dislocation density makes more dislocations to move. But it is not true. Dislocation interactions occur and resulting jogs, kinks etc. create obstacles to motion of dislocations. Also dislocations become closer when numbers are more and the stress fields associated with these dislocations create obstacles. Net result is that higher dislocation density makes dislocation movement more difficult thereby increasing the strain hardening.

Recovery, Recrystallization and Grain Growth

Cold working results in high strain energy. Annealing is a process for changing the distorted, cold worked structure into a strain free structure. Annealing involves heating to the required temperature and cooling slowly. There are 3 stages during annealing *viz.* Recovery, Recrystallization and Grain growth.

1. Recovery:

Recovery treatment is at relatively low temperatures. There are no changes in microstructure and mechanical properties. Internal stresses (residual stresses) get relieved. Electrical conductivity increases. Small atomic movements occur. Atoms move to positions near equilibrium positions.

2. Recrystallization:

At temperatures above recovery temperature, vibrational energy of individual atoms increases significantly. Atoms break loose from lattice and forms into strain free nuclei. This is called nucleation. Nucleation generally occurs in most severely deformed areas and grain boundaries. Nuclei grow until the whole structure has strain-free equiaxed grains. The entire process is called recrystallization.

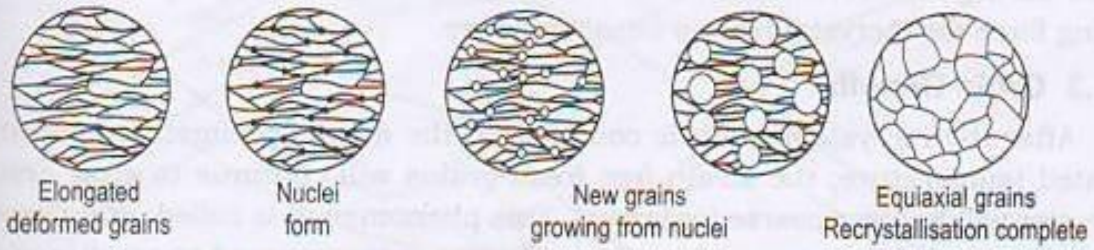


Figure 3.21 *Progress of recrystallisation process*

Recrystallization results in complete release of strain energy, reduction in strength and hardness and increase in ductility and malleability. In pure metals, recrystallization temperature is in the range of 0.3 to 0.5 of melting point in K. Common definition for recrystallization temperature : It is the temperature at which severely cold worked (80% minimum) metal recrystallizes in one hour. Recrystallization temperature is affected by amount of cold work (lowering), time of annealing (lowering), composition (raising by alloying), initial grain size(finer the grain size lower the temperature) etc.

3. Grain Growth

If the metal is kept at elevated temperature after recrystallization, the new strain-free grains will continue to grow, resulting in coarse grains. This process is called grain growth. Driving force for growth is lowering of energy by increasing grain size. Factors favouring rapid nucleation and slow growth lead to fine grain size and vice versa. Factors affecting grain growth are (i)degree of prior deformation (higher deformation, lower grain growth), time (more time, more grain growth) and temperature (lower the temperature, lesser grain growth).

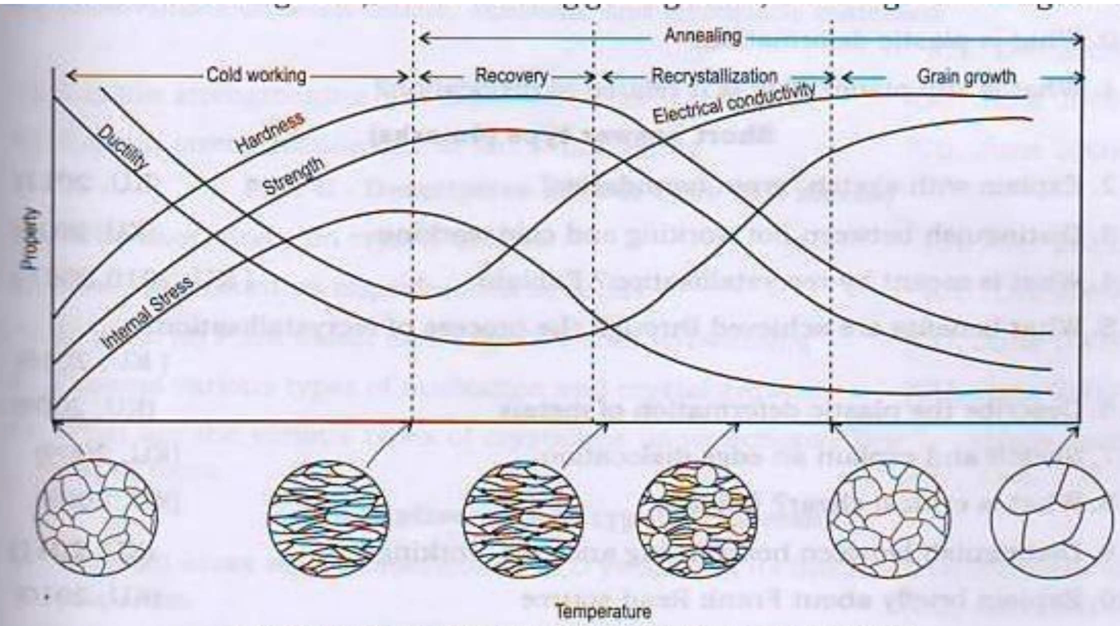


Figure 3.22 *Microstructural and property changes during cold working and subsequent annealing.*

Effect of Stored Energy

A part of energy expended during plastic deformation (about 10%) is stored as internal energy in the material. This energy is stored at dislocations, point defects and grain boundaries. This stored energy plays a pivotal role in annealing (recovery, recrystallization and grain growth). The driving force for these processes is given below:

Recovery: Stored energy at point defects and dislocations

Recrystallization: Energy stored at dislocations

Grain growth: Energy stored at grain boundaries.

Higher the amount of stored energy, lower is the recrystallization temperature and finer the recrystallized grains. After completion of annealing, amount of stored internal energy due to plastic deformation is fully released.

Recrystallization Temperature

The approximate minimum temperature at which complete recrystallization of a cold worked metal occurs within a specified time (usually one hour). It is the lowest temperature at which the distorted grain structure of a cold-worked metal is replaced by a new, strain-free grain structure, during prolonged annealing. Common definition for recrystallization temperature : It is the temperature at which severely cold worked (80% minimum) metal recrystallizes in one hour.Recrystallization temperature is typically one-third to one-half the melting point (in degrees Kelvin), and raises the atomic mobility, which results in recrystallization.

Recrystallization temperature is affected by the following factors:

1. Amount of cold work: More the cold work, lower the the recrystallization temperature
2. Time of annealing: More the time, lower the recrystallization temperature
3. Composition: Alloying raises the recrystallization tempature
4. Initial grain size: Finer the grain size, lower the recrystallization temperature.

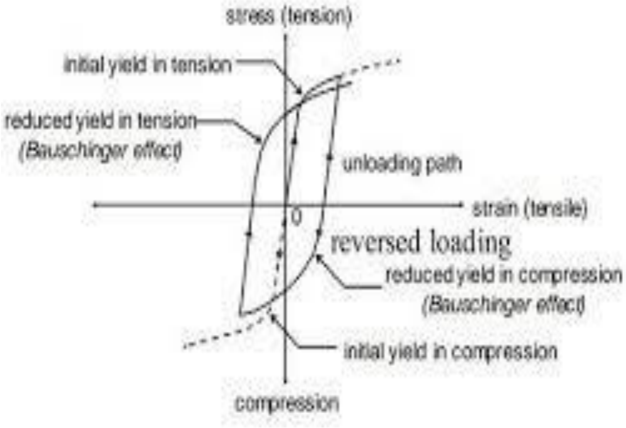
Hot Working

Mechanical working done above recrystallization temperature is known as hot working. During or immediately after hot working the material will anneal itself and become soft and ductile.

Differences between Hot working and Cold working

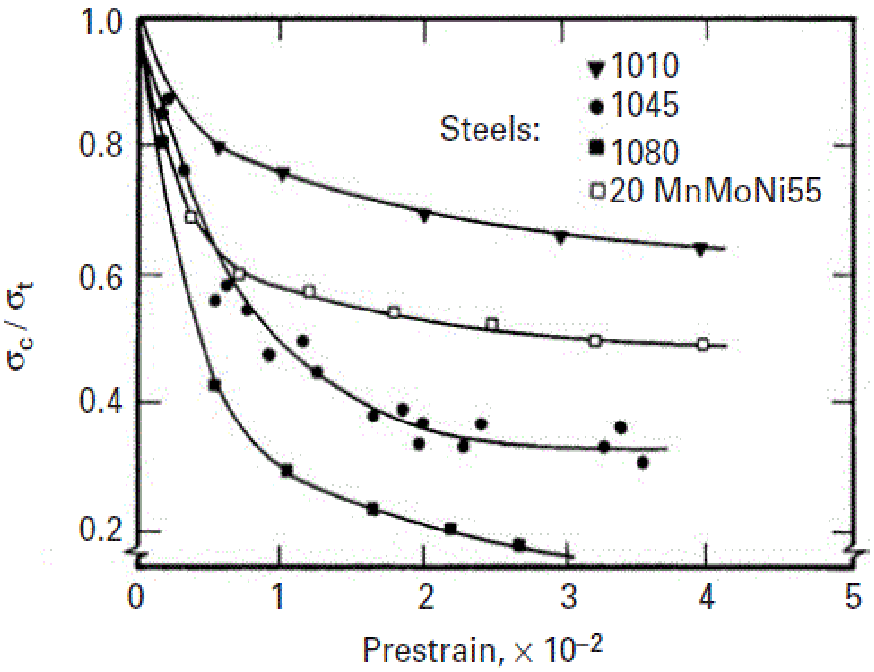
Sl No	Hot working	Cold working
1	No strain hardening	Significant strain hardening
2	Low stresses sufficient for deformation	High stresses needed
3	Large amount of deformation possible	Limited deformation. Strain hardening makes deformation difficult.
4	Refines grain structure by annealing	Grain structure become distorted
5	Ductility increased. Strength properties and hardness decreases marginally	Increases strength and hardness. Ductility decreases significantly
6	Used for shaping metals into useful Products and to produce raw materials for cold working	Used for making finished products To obtain good surface finish To obtain high mechanical properties

Bauschinger Effect and Attributes in Metal Forming



Plastic deformation in one direction affects subsequent deformation in another direction. For example, a material pulled in tension shows a reduction in compressive strength on reversal of loading and vice versa. This effect is known as Bauschinger effect. Material softens when loading direction is reversed.

An actual example is shown in the Figure. The 0.2 % proof stress (the stress at which 0.2% plastic strain occurs) in compression is divided by the 0.2 % proof stress in tension that precedes it. The curves are given for three plain carbon steels and one alloy steel. It can be seen that the change in flow stress is quite significant and increases with the plastic strain in tension.



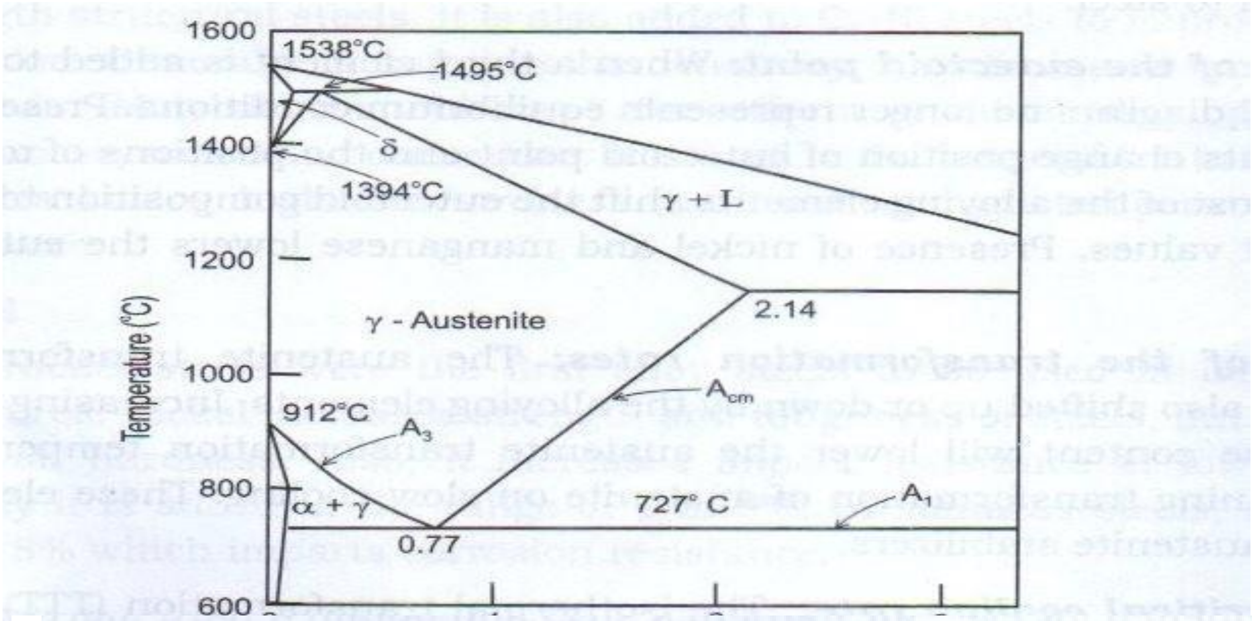
Thus, this factor cannot be ignored in design considerations when a component is to be subjected to compressive stresses in service after being plastically deformed in tension. A combination of tension and compression during metal forming can significantly reduce the load requirement and can make forming easier.

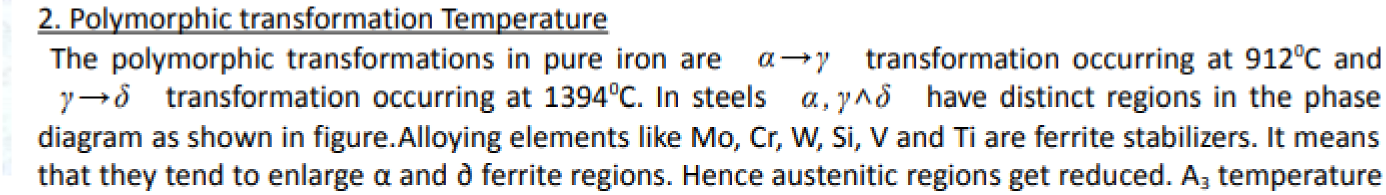
ALLOY STEELS

Effect of Alloying Elements

1. Dislocation movement

Atoms of alloying elements create obstacles for dislocation motion, mainly due to stress field around these atoms. Addition of an alloying element creates a pinning point for dislocations. Since an atom of alloying element is like a point defect, it will have a stress field around it. The size of an alloying atom may be different from the parent atom. Hence lattice stresses will be formed which will also act as barriers. Alloying atom may have a different elastic modulus than the parent atom. This also introduces barriers to dislocation movement. Thus alloying elements added to steel retards dislocation movement and thereby increase strength and hardness.





2. Polymorphic transformation Temperature

The polymorphic transformations in pure iron are $\alpha \rightarrow \gamma$ transformation occurring at 912^0C and $\gamma \rightarrow \delta$ transformation occurring at 1394^0C. In steels $\alpha, \gamma \wedge \delta$ have distinct regions in the phase diagram as shown in figure.Alloying elements like Mo, Cr, W, Si, V and Ti are ferrite stabilizers. It means that they tend to enlarge α and ∂ ferrite regions. Hence austenitic regions get reduced. A_3 temperature is raised and A_4 temperature is lowered. Ni, Mn, Cu and Co are austenite stabilizers. Austenite region gets enlarged. A_3 is lowered and A_4 is raised.

2. Strengthening of ferrite

Most of the alloying elements form solid solutions with ferrite. They increase strength and hardness marginally. Elements like Ni, Al, Si and Co have better solubility in ferrite and they increase the strength of steel.

3. Formation of Carbides

Alloying elements can combine with carbon in steel and form carbides. These carbides are hard and brittle. They provide better hardness, wear resistance and strength to steels. The carbides of chromium and vanadium are especially useful in this regard. Undissolved carbides help to reduce grain growth also. Ni, Al and Si do not form carbides. They promote the formation of graphite. Elements like Cr, Mo, Ti, W and Nb form carbides. Complex carbides are formed when more than one such element are present.

4. Displacement of eutectoid point

When alloying elements are added to steel, binary iron-carbon equilibrium diagram undergoes changes. Positions of eutectoid point, α field and δ field are changed. Most of the alloying elements tend to shift eutectoid point to lower carbon levels. Ni and Mn lower the eutectoid temperature.

5. Retardation of transformation rates

The austenite transformation temperature is shifted up or down by alloying elements. Ni and Mn lower the austenite transformation temperature. Therefore, transformation of austenite is slowed down.

6. Lowering of critical cooling rates

Most alloying elements tend to shift TTT curve to the right. Maximum effect is for Cr,Mo, Mn & Ni. Therefore a lower cooling rate is sufficient for conversion to full martensite (like oil quench instead of water quench). In short, the hardenability is increased.

7. Improvement in corrosion resistance:

Al, Si and Cr impart corrosion resistance by forming a thin, tenacious oxide film. Cr is effective only when it is above 13%.

8. Influence on grain growth

Presence of some elements accelerates grain growth. Chromium is one such element. Grain growth is retarded by presence of elements like nickel and vanadium which are grain refiners.

9. Mechanical Properties

The most commonly added alloying elements to steel are manganese, nickel, chromium, molybdenum, tungsten, vanadium, copper, boron, aluminum and silicon. All these elements improve the properties of carbon steels. Alloy steels have higher hardness, strength, toughness, wear resistance and corrosion resistance. Alloying elements also provide finer grain size and improved machinability.

Nickel Steels

Nickel is the most important alloying element in steel. Its solubility is unlimited in austenite. It is also highly soluble in ferrite. It lowers the A_3 line and raises A_4 line. It retards the transformation of austenite and does not form carbides. Nickel has the effect of lowering the carbon content of the alloy. In nickel steels, pearlite is formed at lower temperatures. Hence pearlite is finer and tougher. Nickel steels have better toughness and fatigue resistance. Typical composition of nickel steel is: 0.35%carbon, 3.5% nickel and balance iron. Nickel steels are used for storage cylinders of LPG, components intended for low temperature use etc.

Chromium Steels

Chromium is a less expensive alloying element than nickel. It forms carbides with the carbon in steel. . Chromium steels have high hardness and wear resistance. Chromium has unlimited solubility in α ferrite and can dissolve up to 13% in γ iron. With more than 5% chromium, high temperature properties and corrosion resistance are improved. Plain chromium steels contain 0.7-1.5% chromium and 0.15- 0.65% carbon.

Nickel –Chromium Steels

They contain both nickel and chromium as alloying elements. Ratio of nickel to chromium is 5:2. The combination of nickel and chromium results in improved toughness, ductility, strength, wears resistance and hardenability. A typical composition contains 0.35% carbon, 0.6%chromium and 1.25% nickel. These steels are used for axles, crankshafts, connecting rods, aircraft components etc.

Molybdenum Steels

Molybdenum is a costly alloying element. It has limited solubility in γ and α irons. It is a strong carbide former. Molybdenum improves hardenability. It increases high temperature strength and hardness of steel. A typical alloy contains 0.35% carbon and 0.75% molybdenum. The steel is used for aircraft landing gear, fuselage, coil spring, leaf spring etc. Sometimes nickel and chromium are also used as additional alloying elements to realize the attractive properties of Ni-Cr steel and Mo steel.

Enhancement of Steel Properties by adding Alloying Elements

Alloying element	Composition range %	Important functions
Molybdenum	0.1-0.4	Expensive element. Improves hardness, wear resistance, corrosion resistance and hardenability. Eliminates temper embrittlement. Forms carbides with high red hardness
Nickel	1.0-5.0	First alloy steels. Increases strength, toughness and impact strength. In stainless steels, nickel is above 8% for corrosion resistance.
Chromium	0.5-4.0	Less expensive than Ni. Most common alloying element. Forms carbides of high hardness and wear resistance. Improves oxidation and corrosion resistance, hardenenability and high temperature strength. Added to tool steels(>5%). More than 12% in stainless steels.
Vanadium	0.1-0.30	A powerful deoxidizer, strong carbide former and prevents grain growth. Expensive element. Increases hardenability, elastic limit, wear and fatigue resistance
Tungsten	2.0-3.0	Strong carbide former. Performs functions similar to Mo. Increases hardenability, red

		hardness and wear resistance. Used in high speed steel (6-18%) to increase hardness and high temperature strength.
Cobalt	5.0-10.0	Increases heat and wear resistance. High Co tool steels have excellent heat and corrosion resistance. Increases cutting efficiency and red hardness of tool steels
Silicon	1.5-2.5	Upto 0.3% added to removes oxygen from molten metal (Deoxidizer). Improves strength, toughness and hardenability when added as alloying element. Added up to 5% for increasing magnetic permeability of transformer steels.
Copper	0.15-0.25	Improves corrosion resistance.Promotes precipitation hardening and thereby higher strength and hardness.
Lead	0.35 max	Improves machinability without affecting other properties.

HIGH SPEED STEELS

Steels which retain high hardness up to 550^{0}C are called High Speed Steels (HSS). These are used as cutting tools operating at high speeds where high temperatures are developed. They readily form alloy carbides (tungsten carbide, molybdenum carbide etc.). Presence of hard and wear resistant carbides in a hard matrix makes the high speed steels suitable for cutting tool applications. These steels possess high wear resistance, hardness and shock resistance.

Molybdenum and tungsten Types of HSS

These are the two types of HSS. Tungsten based HSS contains tungsten as the principal alloying element along with other alloying elements like chromium, vanadium and cobalt. A typical HSS based on tungsten is called 18:4:1 (containing 18% tungsten, 4% chromium, 1% vanadium, 0.7% carbon and balance iron). In molybdenum based HSS, molybdenum is present as an alloying element. A typical HSS based on molybdenum is 6W6Mo4Cr1V (containing 6% tungsten, 6% molybdenum, 4% chromium, 1% vanadium, 0.6-0.7% carbon and balance iron).

Effect of different Alloying Elements in HSS

Tungsten and molybdenum provide resistance to softening at elevated temperature. Chromium content varies from 0.5-12% and its function is to increase strength and hardness. Cobalt is added to increase red hardness (hardness at elevated temperature). Vanadium in small amounts, improves hardness and abrasion resistance. Manganese content (0.6-2.0%) improves hardenability. Silicon when added in small amounts increase toughness.

CAST IRONS

Iron-carbon alloys containing more than 2% C are called cast irons. However most of the cast irons contain 3-4.5 % C. The cast irons melt at 1150-1300^{0}C, which is much lower than that of steels. Thus they are easily melted and cast. Cast irons are brittle. Hence casting is the only manufacturing method. It is a low cost material.

Cast irons have higher compressive strength, damping capacity (ability to absorb vibrations), wear resistance and machinability than steels. Cast irons are classified based on the following:

Carbon content: Carbon may be present as combined carbon (Fe_3C) or as free carbon (graphite). Graphite may be in the form of flakes, irregular nodules or round globules. Carbides of alloying elements may also be present.

Presence of other elements: Alloying elements or impurities may be present in cast iron. Some elements stabilize carbide and may keep carbon as Fe_3C. Few other elements like silicon may promote presence of graphite. Some elements may form their own carbides.

Cooling rate: Higher cooling rates favor carbide formation while slower cooling rates help to form graphite.

Heat treatment: Heat treatments can aid formation of either carbide or graphite. Heat treatment can also alter the shape, size and distribution of graphite particles.

The main types of cast irons are grey cast iron, white cast iron, spheroidal graphite cast iron (ductile iron) and malleable cast iron.

Gray Cast Iron

Gray cast iron contains2.5-3.5 % C together with 1-3% Si and 0.4-1.0 % Mn. Carbon exists in free form as graphite flakes in a matrix of α ferrite or pearlite. Moderate cooling results in pearlite matrix, while slow cooling forms ferrite matrix. Fractured surface appears gray due to graphite flakes. Gray cast iron has low strength and ductility in tension, but the values are much higher in compression. It has all the attractive properties of cast irons such as damping capacity, machinability, wear resistance etc. It is the lowest cost cast iron. Gray cast iron is used for automobile parts(cylinder block, cylinder head, brake drum, gear box), underground pipes, centrifugal pump parts, machine tool frames like lathe beds, electric motor frames etc.

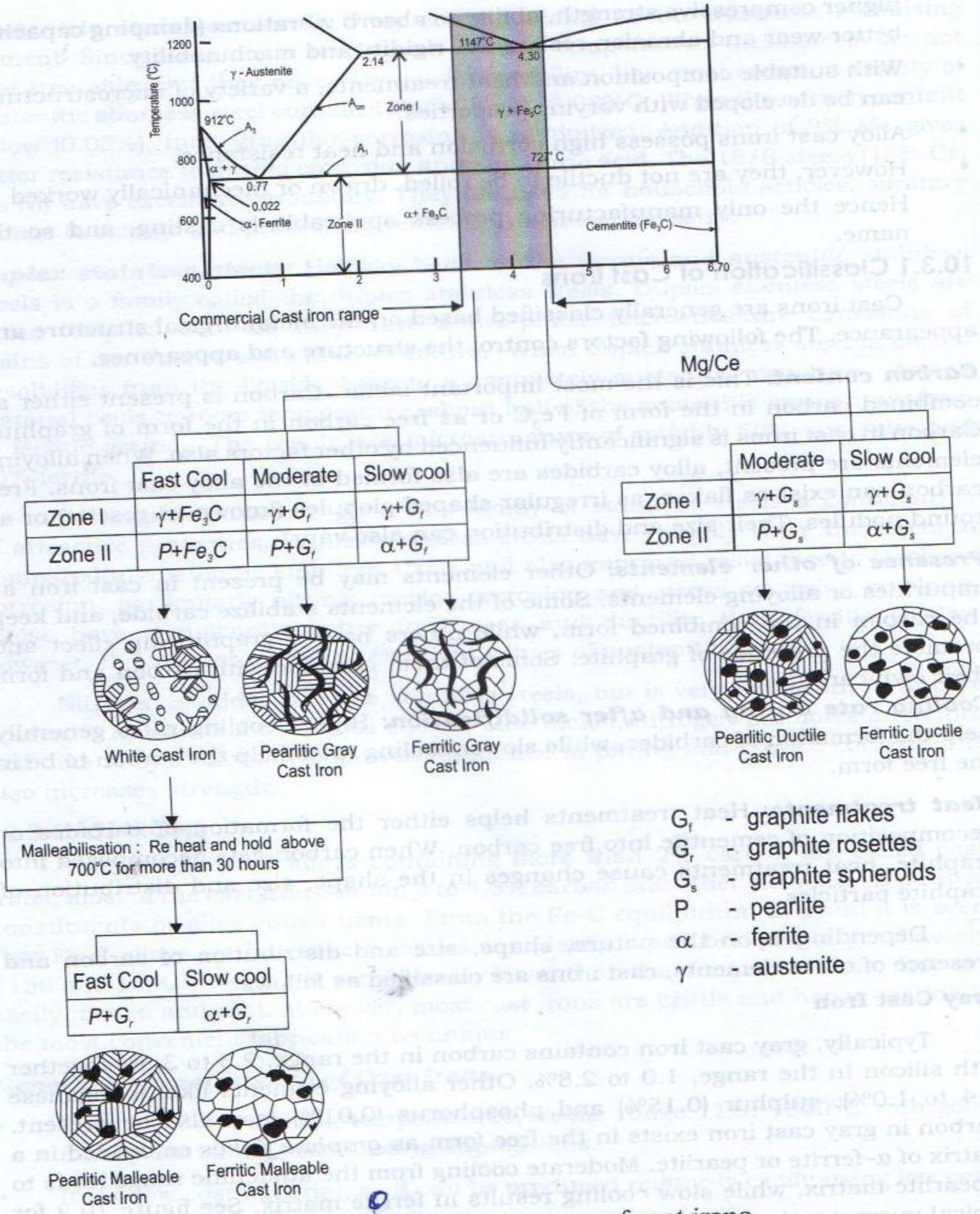


Figure 12.2 *Different types of cast irons*

Ductile Cast Iron

If Mg or cerium is added to gray cast iron in molten condition, a different microstructure is obtained after solidification. Carbon exists as graphite. But graphite is in the form of nodules or spheroids. Hence this type of cast iron is called spheroidal graphite iron (SG iron) or nodular cast iron. This type of structure has much higher ductility than graphite flakes. Hence the name ductile cast iron is given. A typical composition is: 3-4.3% C, 1-3.5 % Si, 0.3-0.8% Mn and 0.08% P. Ductile cast iron is stronger and more ductile than gray cast iron. Mechanical properties are comparable to steel.

Typical applications include manufacturing parts in automobile, farm machinery, earth moving machinery, rolling mill parts etc. Ferritic ductile iron is used for valves and pump bodies. Pearlitic ductile iron is used for crank shafts, gears and rolls. After a hardening and tempering operation, martensitic ductile iron is obtained. It has use in manufacture of gears and rolls.

White Cast Iron

In cast irons having lower silicon content when cooled rapidly, carbon forms as cementite (Fe_3C) instead of graphite. Fracture surface appears white. Hence it is called white cast iron. A typical composition is: 2-3.5% C, 0.5-1.3% Si, 0.2-0.8% Mn, 0.2% S and 0.1% P.

White cast iron contains large amount of cementite. Therefore it is very hard, brittle and difficult to machine. It has high compressive strength. But, it has only limited uses due to its brittleness like pump liners, rolls and also for making malleable cast iron.

Malleable Cast Iron

Malleable cast iron is produced from white cast iron by a heat treatment called malleabilization. The white iron is heated to a temperature above 700^0C and held at that temperature for a long period of time (>30 hours) and then cooled. Cementite (Fe_3C) changes to graphite in the shape of irregular globules or rosettes. Matrix is ferrite or pearlite depending on cooling rate. Matrix phase can be converted to martensite after a quench and temper treatment. The microstructure is similar to ductile cast iron. It has good combination of properties like ductile cast iron. These cast irons are used in automobile, electrical and railway industries. They can be used for connecting rods, brackets, hubs, brake drum, cam shafts, crank shafts, housings etc.

Alloy Cast Irons

Alloying elements are added to cast iron to improve properties. ‘Nihard’ is an alloy cast iron with 4 % nickel and 1.5% chromium. It has an excellent wear resistance due to the presence of carbides. ’Niresist’ is another alloy cast iron containing 20% nickel and 2% chromium. It has excellent heat resistance and corrosion resistance due to a microstructure containing graphite and alloy carbide particles in an austenite matrix.

PRINCIPAL NON-FERROUS ALLOYS

Copper and its Alloys

Copper has two important properties namely high electrical conductivity (second only to Ag) and corrosion resistance. In addition it has good thermal conductivity, machinability, weldability etc. Pure copper is widely used for electrical conductors, heat conductors and water pipes. Over 50% copper is used for electrical purposes (wires, switches etc.). Automotive radiators, refrigerators, water heaters, heat exchangers, condensers etc also use copper. Strength of Cu is increased by (a) solid solution strengthening by alloying with Zn, Sn, Al etc (b) strain hardening and (c) precipitation hardening.

Brass

Brass is an alloy of Cu and Zn. Zn varies from 5-50%. Small amounts of Pb, Sn or Al may be added to provide specific properties. Important properties of brass are: (i) good strength, ductility, formability and machinability (ii) good electrical and thermal conductivity (iii) good wear and corrosion resistance (iv) non-magnetic and (v) good appearance. A variety of brasses are in use. Cu rich portion of Cu-Zn phase diagram is given in Fig. Commercial brasses are of 2 types; α brasses and duplex brasses.

1. α Brasses

These are brasses with Zn up to 38%. The structure is α solid solution. These are highly ductile and can be cold worked easily. Few important α brasses are given below:

(a). Red α brass: Zn content is 5-20%. Red color is due to higher Cu. It has good corrosion resistance and workability. It is used for condenser and heat exchanger tubes, pipes and radiators.

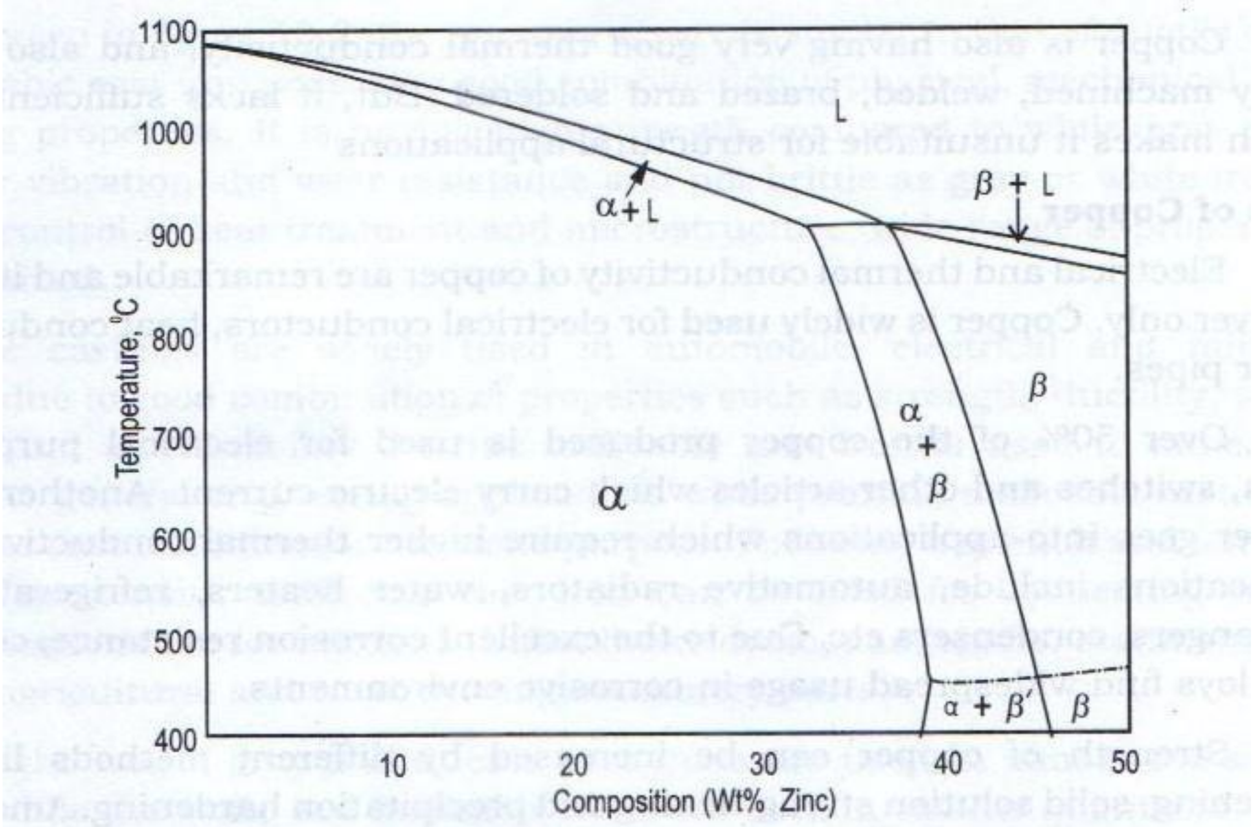


Figure 10.3 *Copper rich portion of the Cu-Zn phase diagram*

b)Gilding metal: It contains only 5 % Zn. It has a golden color. It has high ductility and corrosion resistance. It is used for coins, medals, jewelry etc.

(c). Yellow brass: It contains 20-35% Zn. It has good corrosion resistance.

(d). Cartridge brass: Zn content is 30%. It is used for cartridges and shell cases of rifles.

(e). Admirality brass: Small amount (about 1%) of Sn is added. Zn content is about 30%. It is used for marine applications.
(f). Aluminum brass: It contains 20% Zn and 2% Al. It is also used for marine applications. 2. Duplex (α +β) brasses:
Zn content is above 38%. It has a structure containing α solid solution and β solid solution phases. Common alloys are:
(a).Muntz metal: It contains 40% Zn. It has high strength and good hot working properties. It is used for springs, chains and as a brazing alloy for steel.
(b).Naval brass: It has 39% Zn and 1% Sn. It has a higher corrosion resistance than Muntz metal.It is widely used for marine applications. It is also used for propeller shafts, valve stems, impellers for pumps etc.

Bronze

Bronze represents Cu alloys containing elements other than Zn. Tin is the most common alloying element. Other elements like Al, Si or Be are also added. Sometimes small amount of Zn may also be present. Bronzes are weaker and softer than steel. But conductivity and corrosion resistance are better. They have good antifriction or bearing properties.
1. Tin bronze: It contains 1-10% tin. Tin bronze containing 0.1-0.5% P is called phosphor bronze. Bronzes are used to produce springs, bellows, taps, electrical contacts, bushes etc.
2. Gunmetal: A popular gun metal composition is 88% Cu, 10% Sn and 2% Zn. Another type of Gunmetal is called 85/5/5/5(85% Cu- 5% Sn- 5% Zn-5% Pb). These are used for marine applications.
3. Aluminum bronze : It contains 4-10% Al and balance Cu. It is often called imitation gold.
4. Silicon bronze: It contains 1-4% Si and balance Cu. It has excellent corrosion resistance and weldability. It is used for making rivets, bolts, nuts, other fasteners etc.
5. Beryllium bronze: Be is in the range of 0.6-3% and balance Cu. It has high strength and high conductivity. It is a costly alloy. It is an excellent material for springs due to its high elasticity.

Aluminium and its Alloys

Important characteristic of aluminum is its low density (2.8g/cc). Hence an aluminum component is much lighter in weight compared to identical component in steel (density-7.8g/cc) or copper (density-8.9g/cc). Aluminum also has low melting point (660^0C) compared to Fe(1538^0C) and Cu(1083^0C). Aluminum has high electrical conductivity and thermal conductivity, but lower to copper. Pure Aluminum has low strength and hardness but high ductility. Pure aluminum is mostly used for electrical cables and wires.

Aluminum Alloys

Poor tensile strength of aluminum can be improved by strain hardening (cold working), solid solution hardening (alloying) and age hardening (precipitation hardening). Strain hardening can increase strength by 2times where as alloying can increase it by 4 times.
The most important alloying element for Al is Cu. Al-Cu phase diagram at the Al rich end is given in Fig. It can be seen that solubility of Cu in Al is 5.65% at 547^0C which reduces to 0.45% at 300^0C. Alloys containing 2.5-5% Cu are widely used. At room temperature microstructure of the alloy contains α solid solution + β (intermetallic compound $CuAl_2$). These alloys can be age hardened. The first step in age hardening is to heat the alloy to a temperature above 500^0C to convert the entire structure to single phase α. This step is called solution treatment.
Second step is quenching the single phase alloy to room temperature in water. Rapid quenching retains the single phase structure. Third step is aging; that is keeping the alloy at room temperature (natural

aging) or at temperature within 250^{0}C (artificial aging) for sufficient time. This step results in precipitation of fine β. This step increases strength very much.

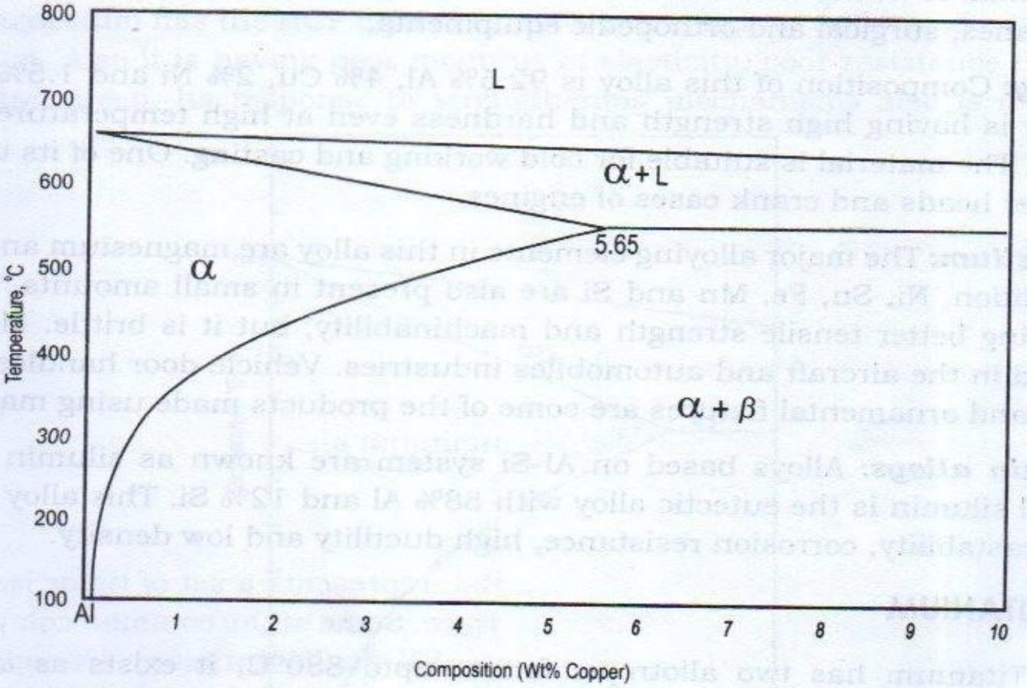


Figure 10.4 *Aluminium rich end of the Al-Cu phase diagram*

The figure 10.4 shows the aluminium rich end of the Al-Cu phase diagram

There are 2 types of commercial Al alloys.

1.Wrought Alloys: In wrought alloys the parts (components) are made by hot/cold working. Strength is mainly increased by cold working. Al-Cu, Al-Mn, Al-Mg, Al-Cu-Mg, and Al-Mg-Si are the main wrought alloys. Wrought alloys have much higher strength and ductility than cast alloys.

2.Cast Alloys: In cast alloys, the final shape of the component is obtained by a single operation, namely casting. In general amount of alloying elements is considerably more in cast alloys. Hence cast alloys are not ductile and cannot be worked. Strength is increased by age hardening. Al-Si, Al-Cu and AL-Cu-Si are the main cast alloy systems.

Few commercial alloys are given below:

1. Duralumin: It is a wrought alloy. Composition (typical) is: 4% Cu, 0.5% each of Mg, Mn, Si & Fe and balance Al. It is widely used as plates, sheets, forgings, tubes etc in aero space, surgical and general engineering applications.

2. Y Alloy: It can be a wrought or cast alloy. It typically contains 4% Cu, 2% Ni, 1% Mg and balance Al. It has high strength and hardness up to 200^{0}C. It is used for cylinder heads and crank case of automobiles. 3. Magnalium: It is an aluminum cast alloy with Mg as the main alloying element (5-10% Mg). Cu is another alloying addition. Small amounts of Ni, Sn, Fe, Mn and Si may also be present. The alloy has

high tensile strength and machinability. But it is brittle. Magnalium is used in aircraft and automobile industries. Vehicle door handles, luggage racks are other few products.

4. Silumin Alloy: It contains about 12% Si (eutectic composition) and balance Al. It is a cast alloy with excellent castability. It is non-heat treatable. It is widely used for die cast products for automobile and transportation industries.

Magnesium and its Alloys

Magnesium (density 1.8g/cc) is the lightest metal which can be used for structural applications. It has HCP structure. Its strength, modulus of elasticity and ductility are less than that of aluminum. It is difficult to work and form.

Magnesium alloys containing Al as the principal alloying element are most widely used. The phase diagram is shown in Fig. Alloys containing up to 12% Al are age hardenable because of the sloping solvus line. Second phase γ is an intermetallic compound $Mg_{17}Al_{12}$. Zn is added to Mg-Al alloys to increase strength further. Addition of Mn improves corrosion resistance. Important wrought alloy belonging to this system is AZ31 (Mg-3% Al-1% Zn) and cast alloy is AZ91 (Mg-9%Al-1%Zn).

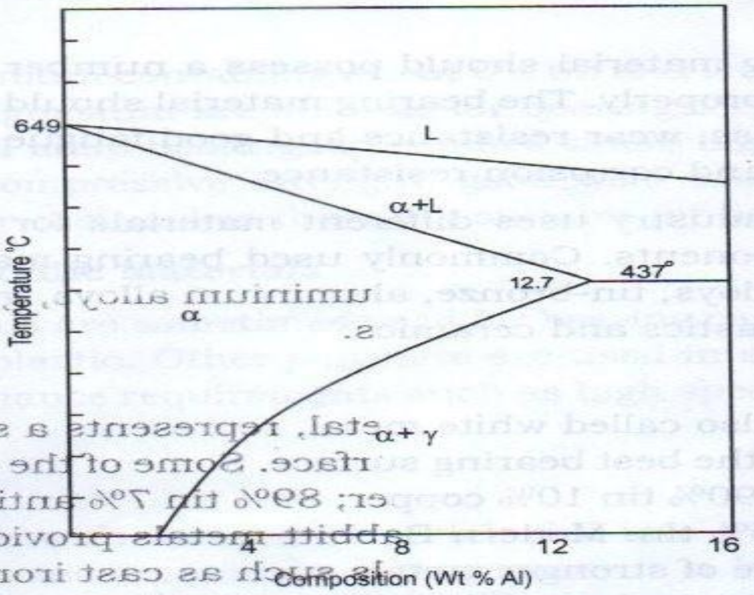


Figure 10.5 *Magnesium rich end of Al-Mg phase diagram*

Another major alloy system is Mg alloys containing Zr. Zr is a powerful grain refiner for Mg. Other alloying elements compatible with Zr are Zn, rare earths, Ag, Th etc. These elements are added to increase strength further by solid solution hardening and age hardening. Important uses of Mg alloys are in aerospace, transportation and material handling fields.

Nickel and its Alloys

Nickel is a metal having good corrosion and heat resistance. It has a high melting point. Common alloying elements to nickel are iron, copper, chromium, molybdenum, manganese and aluminum. They can be strengthened by strain hardening, dispersion hardening and age hardening.

Nickel base super alloys have a combination of high strength at elevated temperatures, creep resistance up to 1000^{0}C and corrosion resistance. The most important alloys are:

Hastelloy(1-30% Cr, 5-28% Mo, 2-18% Fe, 1-3% Co, Balance
Ni) Inconel (14-30% Cr, 3-10% Fe, 1-10% Mo, Balance Ni)
Waspaloy / Rene alloy (18-20% Cr, 10-15% Co, 5-10% Mo, Balance Ni)

Nickel based super alloys constitute 40-50% of the total weight of an aircraft engine. They are extensively used in the combustor and turbine sections of the engine where high temperatures are developed.

Nickel –Copper alloys

Copper is completely soluble in Ni. When Ni and Cu ar alloyed in the ratio of 2:1, important alloy 'monel' is obtained. These alloys have better corrosion resistance and mechanical properties than bronzes and brasses. Copper-nickel alloys suitable for elevated temperature service are known as cupro nickels. Cupro nickel with 30% nickel is widely used for condenser tubes in naval application

MODULE 5

FATIGUE

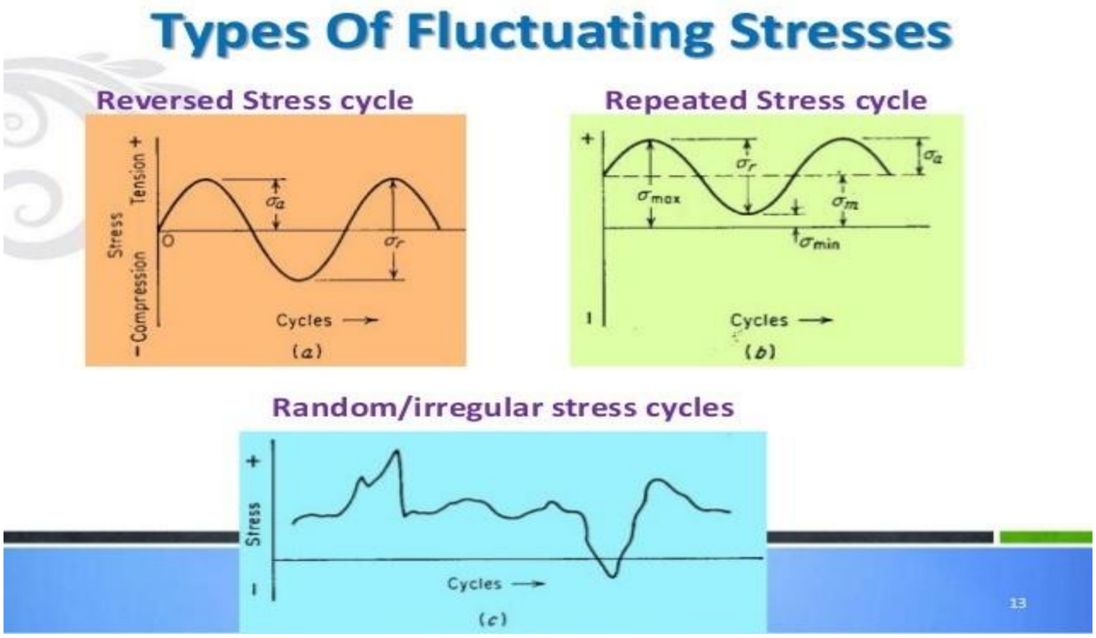
ASTM definition of fatigue: *Fatigue is the process of progressive, localized, permanent structural changes occurring in a material subjected to fluctuating stresses and strains at some point or points which may culminate in cracks or complete fracture after sufficient number of fluctuations*

Materials subjected to alternating (also called repetitive, cyclic or fluctuating stresses) will fail at a much lower stress compared to those loaded with steady stresses. Behavior of materials under such fluctuating or cyclic stresses is called fatigue. Rotating shafts, bridges, machine components, automobile parts etc. are some of the components subjected to fatigue. Fatigue is observed in all types of materials. More than 80% failure in metallic materials is due to fatigue. It is very dangerous because failure occurs without any warning in a brittle fashion.

Stress Cycles

In general there are three types of cyclic loading.

1. Sinusoidal stress cycle: The stress alternates from maximum tensile stress to maximum compressive stress of equal magnitude. Mean stress is zero.
2. Repeated stress cycle: Maximum and minimum stresses are not equal. Mean stress is non-zero. This type of cycle is commonly observed in engineering applications.
3. Irregular or random stress cycle: Stresses vary randomly. Stress experienced by automobile shock absorber is an example.



Types Of Fluctuating Stresses

Reversed Stress cycle

Repeated Stress cycle

Random/irregular stress cycles

Primary and Secondary Stress Raisers

A stress raiser is defined as a flaw which has the ability to amplify the applied stress in its vicinity. The stress raisers are divided into two types namely primary stress raisers and secondary stress raisers.

Primary stress raisers:

Non-uniformities like steps at change in cross section, collars, holes, abrupt corners, key ways, grooves, threads, spline, press fitted/shrink fitted attachments etc. are primary stress raisers. Primary stress raisers initiate the failure.

Secondary stress raisers

Surface discontinuities arising from fabrication such as surface roughness, seams, nicks, notches, machining marks, identification marks, forging laps, pitting and corrosion etc. are secondary stress raisers. Internal discontinuities like porosity, inclusions, cracks and voids also come under the category of secondary stress raisers.

For example, a change in diameter of a shaft (primary stress raiser) can result in stress intensification at the transition zone. If there is a surface discontinuity (secondary stress raiser) in this zone, stress is sharply increased around the discontinuity resulting in failure of shaft.

Characteristics of Fatigue Failure

1. Fatigue involves nucleation (initiation) and growth of cracks resulting in final fracture. Fatigue life consists of two periods namely crack initiation period and crack growth period. Crack initiation includes crack nucleation at the material surface and growth into microstructurally small cracks. Small microscopic cracks can be nucleated at stress amplitudes below fatigue limit. Crack growth period covers propagation of macroscopic cracks away from the material surface leading to fatigue failure and fracture of the material. Micro crack growth occurs along maximum shear stress planes and final macroscopic crack growth is along maximum tensile stress plane. It has been observed that crack initiation period covers relatively larger percentage of total fatigue life.
2. Fatigue in the crack initiation period is a surface phenomenon. It is sensitive to various surface conditions. Surface discontinuities like surface roughness, seams, nicks, notches, machining marks, identification marks, forging laps, pitting and corrosion etc play a very important role in crack initiation phase. During crack growth period, fatigue depends on crack growth resistance of material and not on material surface conditions. Certain material characteristics may favor good crack nucleation resistance, microcrack growth resistance or macrocrack growth resistance, but not necessarily all three.
3. There are two distinct regions in the fracture surface of materials failed by fatigue. (i) a smooth region where there is constant rubbing of surfaces during cyclic stressing. In this region, only micro-plastic deformations which are reversed in each cycle occur. Concentric lines known as beach marks, ripples or striations are present. Spacing of ripples will be larger if variation in stress amplitude is more. Width between ripples is indicative of the distance by which the crack has grown during one cycle.(ii) a granular region due to sudden fracture of the material. This happens when the reduced area remaining after formation of crack is not able to withstand the applied stress.
4. Fatigue fractures are normally transgranular, meaning that the crack moves through the grain interior.

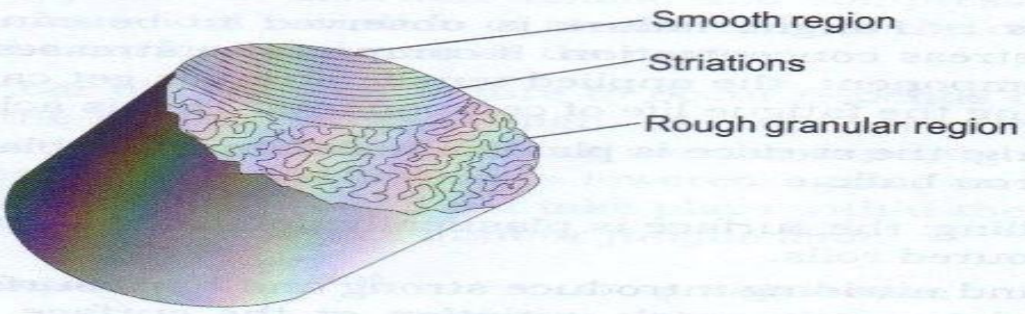
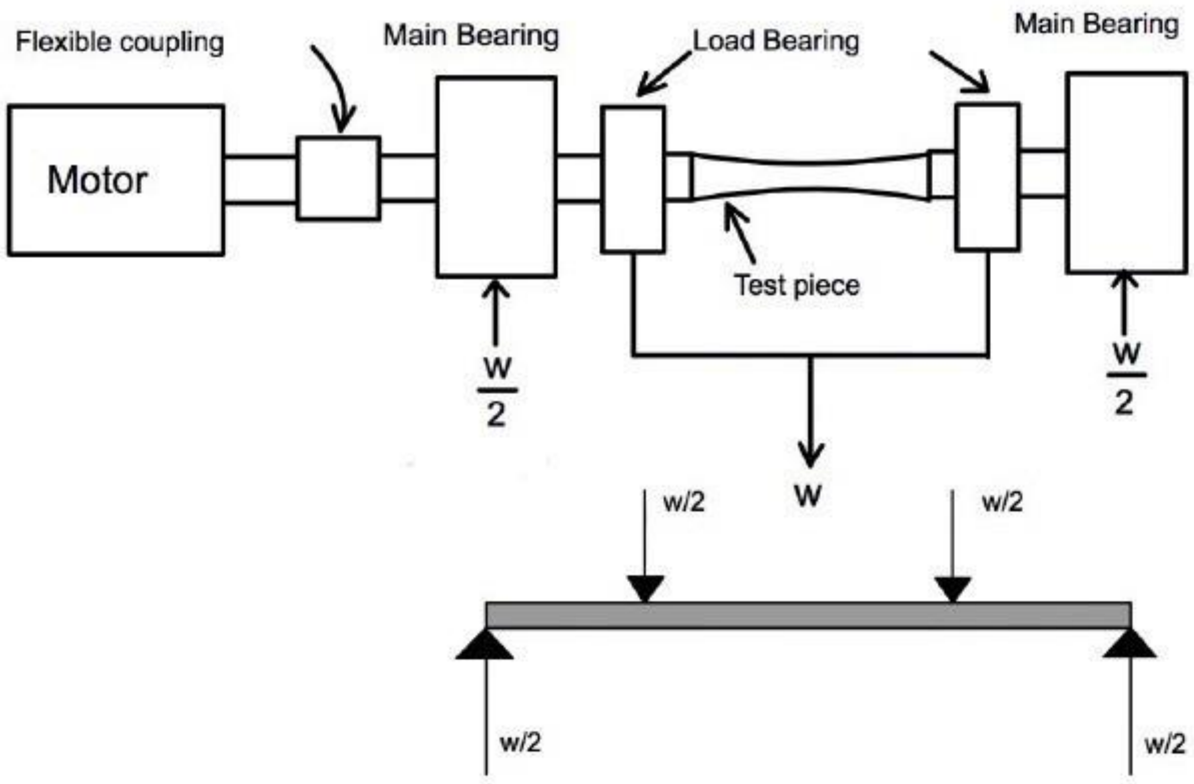


Figure 4.9 *Fatigue fracture surface*

Fatigue Tests

Fatigue tests are conducted to generate S-N curves and to assess the capability of the material to withstand cyclic loading. Many different types of machines are used which are classified based on type of load and method of application of load. The most commonly used machine is the rotating beam fatigue testing machine shown in figure.

The machine is a constant load type. It contains an electric motor for rotating the machine, bearings and collets to support the specimen and a revolution counter to determine number of cycles. Test specimen is placed in the machine. A dead weight is attached at the center portion of the specimen. When the specimen is rotated, the centre of the specimen is under tension on the lower surface and compressive on the upper surface due to the dead weight. Hence during rotation, the specimen is subjected to alternate tensile and compressive stresses in a sinusoidal fashion. The stress is maximum at the surface.



Number of cycles to failure (N) depends on applied stress (S). When the stress is high, N is small. When S is lowered, N increases. As S is lowered continuously, an ultimate value will be reached at or below which failure does not occur. A number of specimens are tested at various S values and the corresponding N values are obtained. A semi-logarithmic plot with N along X axis and S along Y axis is plotted. This is the S-N curve for the material.

S-N Curve

Fatigue is represented by a curve called S-N curve. Typical S-N curves for alloy steel and aluminum alloys are shown in figure. Fatigue test is conducted on a specimen by stress cycling at a maximum stress amplitude of σ_{max} (less than tensile strength). No of cycles to failure is counted. Test is repeated at progressively lower stress levels. A plot of stress (S) versus log number of cycles to failure (log N) is prepared. This is the S-N curve for the material.

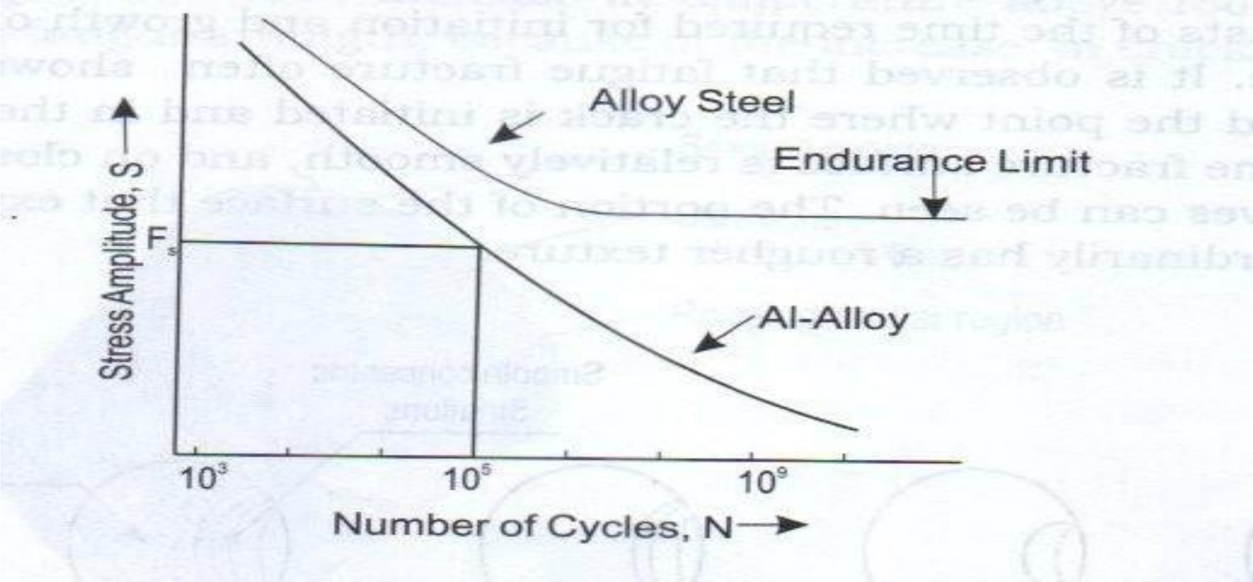


Figure 4.7 *S-N curve*

In general, higher the stress lower is the cycles to failure. For materials like steel, S-N curve become horizontal at higher N values. Corresponding stress level at horizontal portion is called Endurance Limit. It is the largest fluctuating stress which will not cause failure after infinite number of cycles. Generally it is 40-50% of tensile strength. For materials like aluminum alloys there is no specific endurance limit. In such materials, fatigue strength is taken as the stress level at which failure occurs after a given number of cycles (usually 10^7 cycles).

FACTORS AFFECTING FATIGUE STRENGTH

Stress Concentration

Non-uniformities like steps at change in cross section, collars, holes, abrupt corners, key ways, grooves, threads, spline, press fitted/shrink fitted attachments etc. are primary stress concentrations. Surface discontinuities arising from fabrication such as surface roughness, seams, nicks, notches, machining marks, identification marks, forging laps, pitting and corrosion and internal discontinuities like porosity, inclusions, cracks and voids come under the category of secondary stress concentration. All these can reduce fatigue strength drastically. Stress concentration factor is the ratio of stress in a notched specimen to the stress in an unnotched specimen of same material.

Size Effect

Generally, larger component has more number of imperfections (defects) and hence lower fatigue strength. In carbon steel, it has been found that fatigue factor is 1 for diameter less than10mm,0.9for diameter between 10 and 50 mm

Surface Roughness

Generally maximum stress occurs at the surface. The surface is also exposed to harsh environments like corrosion and unexpected loads like impact. Therefore surface roughness has a significant effect on fatigue strength. Rough surface gives much lower fatigue life than fine surface as given below:

Finish	Surface roughness (microns)	Average fatigue life (kilocycles)
Lathe finish	2.67	24
Hand polished	0.13	137
Ground & hand polished	0.05	234

Change in Surface Properties

Decarburization at the surface of steel significantly reduces fatigue strength. The strength can be regained by recarburizing the surface. Surface alloying methods like carburizing, nitriding and carbo-nitriding can appreciably increase fatigue strength. Surface hardening processes using flame, induction, laser and electron beam also improves fatigue strength. Mechanical working of the surface of steel part by shot peening and skin rolling enhances the fatigue strength.

Surface Residual Stress

Residual stresses are produced by fabrication and finishing operations. Residual stresses on the surface can seriously affect fatigue properties. Compressive residual stresses at the surface of a part increase fatigue appreciably. Tensile residual stresses at the surface reduce the fatigue strength. Compressive residual stresses may be produced by surface alloying, surface hardening and mechanical working of the surface.

Ways to improve Fatigue Life

1. Surface Treatments: Fatigue occurs due to tensile stresses at stress concentration. Introducing compressive stresses at the surface cancels the applied tensile stresses and thereby increase fatigue life. This is done by plastically deforming the surface using the following methods.

(i) shot peening : blasting of surface with hard steel or cast iron balls.

(ii) surface rolling: pressing between contoured rolls.

Carburizing or nitriding can provide hard and strong surfaces which increase resistance to crack initiation. Polishing is another method for improving surface finish which removes surface irregularities acting as stress concentrations. Care is also taken to prevent decarburization of the surface.

2. Grain refinement: Fine grains improve fatigue resistance. Hence grain refinement improves fatigue life.

3. Proper Design: Avoiding stress concentrations like notches, sharp corners, sudden changes in cross section etc. improves fatigue resistance. Manufacturing methods which reduce surface and internal defects (discontinuities) should be adopted. Prevention from corrosive, chemical or abrasive conditions can also increase fatigue life.

Effect of Temperature on Fatigue

It is well understood that temperature affects fatigue life of a structure. Under the same cyclic or repeated stress or strain loading conditions, fatigue life of a structure could vary significantly in different temperature environments. An increase in temperature decreases fatigue strength. At higher temperatures, the initiation and propagation of slip bands/micro-cracks within grain is increased, grain boundary cavitations occur, phase transformations, oxidation, corrosion and creep damage happen in the material. Net effect of all these is reduction in fatigue life.

Thermal Fatigue

Thermal stresses can develop when change in dimensions of a member due to high temperature is prevented by some constraints. If a bar with fixed supports is heated, thermal stresses will develop by the temperature change. The value of this thermal stress is σ □ $\alpha E\,\Delta T$ where σ □ □ thermal stress, α= coefficient of linear expansion, E=Elastic modulus and ΔT □ □ change in temperature. If the failure occurs by a single application of thermal stresses, it is called thermal shock. If the failure occurs after repeated application of thermal stress, it is called thermal fatigue. It is obvious that stress levels for thermal fatigue is appreciably lower than the stresses for thermal shock.

Application of Thermal Fatigue on Metal Cutting

Principle of thermal fatigue is made use of in thermo-mechanical machining. The method is used for removing burrs and fins. The components are exposed to hot corrosive gases for a short time. These gases are produced by detonating an explosive mixture of oxygen, hydrogen and natural gas in a chamber with components. A thermal shock wave vaporizes the burrs and fins on gears, valves, die castings etc. Thermo-mechanical machining is particularly effective with materials of low thermal conductivity.

Another area, where thermal fatigue is significant, is in metal cutting tool life. In machining operations with interrupted cutting, heating and cooling cycles are generated. If thermal conductivity of tool material is low, the failure of tool can take place after limited number of thermal cycles. Similar phenomenon can happen for forging dies also. Hence proper selection of tool material is required to avoid early tool failure.

FRACTURE

The ultimate rupture or failure of material by breaking into 2 or more pieces under the action of external load is called ‘fracture’. Fracture is generally by tensile loading. Cohesive strength (maximum strength between atoms) is to be exceeded for fracture to occur. Theoretical cohesive strength is very high. Hence it is clear that fracture has to be initiated at defects like microscopic cracks (micro cracks). On stressing, the crack acts like a notch (stress raiser). The stress at crack tip increases many fold and reaches cohesive strength value. The crack propagates and fracture occurs.

Brittle and Ductile Fracture

There are 2 types of fracture. (a) Ductile fracture: Fracture occurs after considerable plastic deformation (b) Brittle fracture: Fracture occurs with little or no plastic deformation (usually within elastic range). Refer Figure.

Crack in ductile fracture is said to be stable. Stable cracks resist propagation. Hence fracture occurs slowly. In brittle fracture, crack is unstable and propagates very rapidly. Fracture occurs without warning. Ductile fracture is always preferred. Preventive steps are possible since warning is obtained from plastic deformation. It is therefore safer. Metals and alloys exhibit ductile fracture. Ceramics generally show brittle fracture. Polymers may have ductile or brittle fracture.

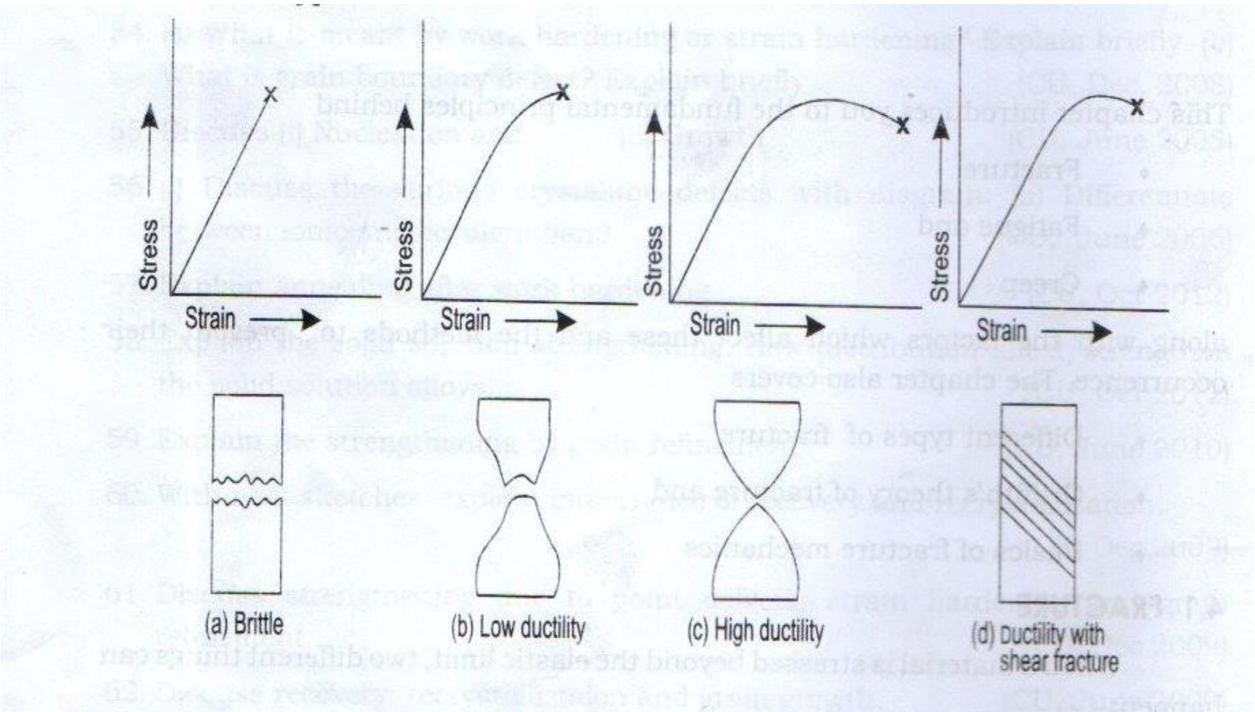


Figure 4.1 *Different types of fracture*

Table: Differences between Brittle and Ductile Fractures

Brittle	**Ductile**
1. Minimum or no plastic deformation	Large plastic deformation
2. Occurs suddenly without warning. Minimum energy absorption.	Occurs slowly with large plastic deformation
3.Fracture in a direction normal to load axis. Flat & planar fracture surface.	Fracture direction 45^0 to load axis. Cup & cone type fracture. Fracture surface dirty and rough.
4. Initiates at micro cracks	Initiates at regions of large plastic deformation
5. Commonly observed in BCC &HCP	Commonly observed in FCC
6. Fracture along cleavage planes	Fracture along slip planes

Characteristics of Ductile Fracture

Necking indicates plastic deformation. Highly ductile materials necks down to a point (Eg. Ag, Au, Pb etc.). The various stages in a normal ductile fracture are shown in Fig. The two fractured surfaces a cup and a cone. Hence it is called a cup and cone fracture. Ductile fracture is a shear type fracture due to shear component of the applied stress causing extensive slip. It has a dull and fibrous appearance.

Characteristics of Brittle Fracture

Crack propagates perpendicular to tensile loading axis. Fracture surface is flat. In most brittle materials atomic bonds break along specific crystallographic planes. Such planes are called cleavage planes and the fracture is called cleavage fracture. The fracture appearance is shiny and granular.

Griffith's Theory of Brittle Fracture

Fracture occurs at stresses much lower than the cohesive strength of material (calculated from atomic bonding energy considerations). Explanation for this phenomenon is provided by Griffith.He proposed that brittle materials contain a large number of fine micro-cracks. These cracks produce stress concentrations. Hence such cracks are called stress raisers. As a result, even a normal stress much lower than cohesive strength can create a stress exceeding cohesive strength near the crack tip. Under this local stress concentration, crack propagates resulting in fracture.

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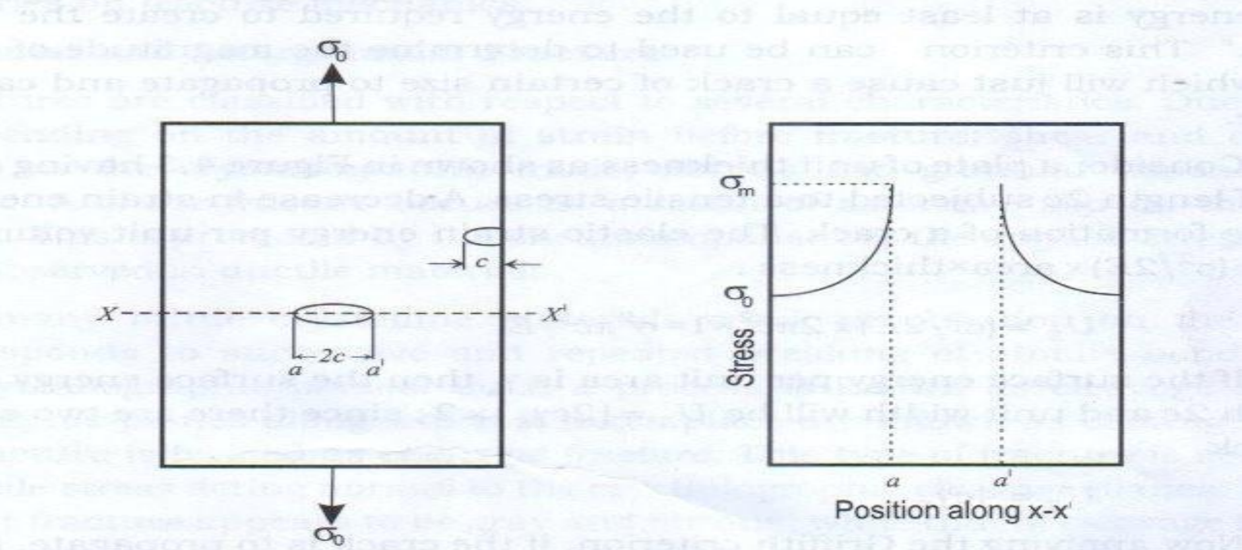


Figure 4.3 *Stresses around a crack*

Crack is assumed to be elliptical with major axis perpendicular to applied stress. Refer Fig. Maximum stress at crack tip $\sigma_m = 2\sigma_0 \sqrt{c/\rho}$ where σ_0 =applied stress c= length of external crack or half length of internal crack and ρ= radius of curvature at the crack tip.For a long micro crack with a very small radius of curvature, $\sqrt{c/\rho}$ is very large. Therefore σ_m will be many times σ_0. σ_m / σ_0 is known as stress concentration factor K. $K = 2\sqrt{c/\rho}$. Elastic strain energy is stored during elastic deformation. This energy increases with increasing stress. At sufficiently high stresses, the crack becomes larger and finally material fractures.

Effect of Plastic Deformation on Crack Propagation

Ductile fracture occurs after considerable plastic deformation. It happens with slow tearing of metal. Plastic deformation introduces strain hardening which necessitates higher stresses for further deformation. Plastic deformation reduces the stress intensity in the vicinity of stress raisers thereby avoiding brittle failure. Ductile fracture is preceded by localized reduction in area called necking. It exhibits three stages after necking, namely (i) cavities formation (ii) cavities coalescence and crack formation. Crack grows outward in direction perpendicular to stress direction.(iii) final fracture involving rapid propagation at about 45 ° to tensile axis. Stages in ductile fracture are shown in Figure.

Brittle fracture occurs with little or no prior plastic deformation. Crack propagates very rapidly. The three stages in brittle fracture are: (i) dislocation pile ups at obstacles during the small plastic deformation (ii) micro crack nucleation and (iii) fast crack propagation and failure.

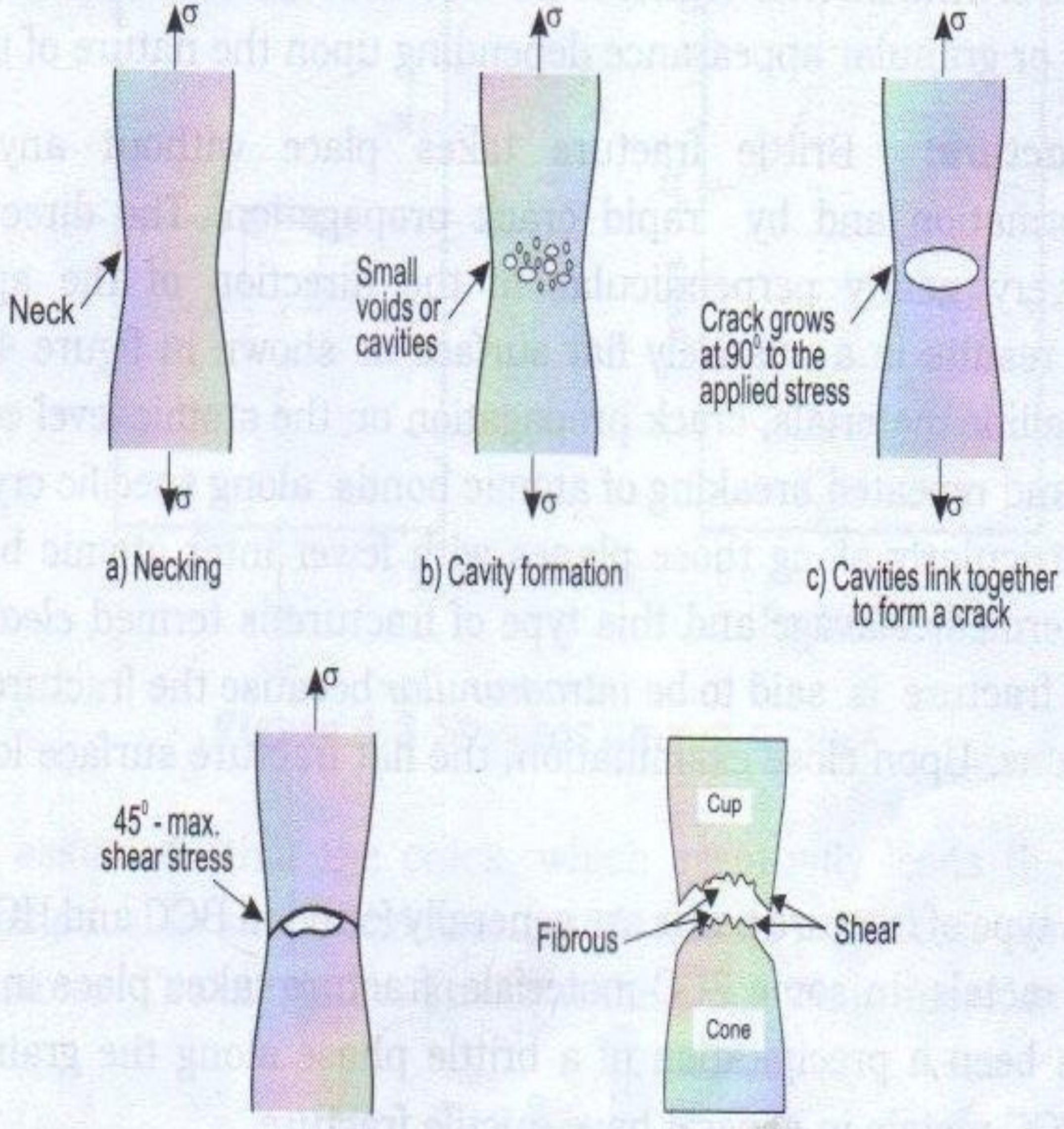
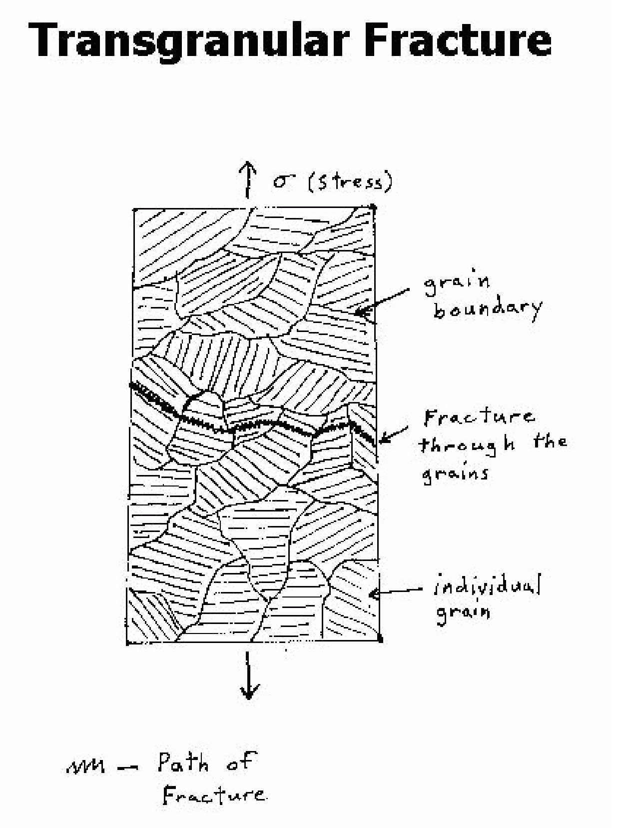
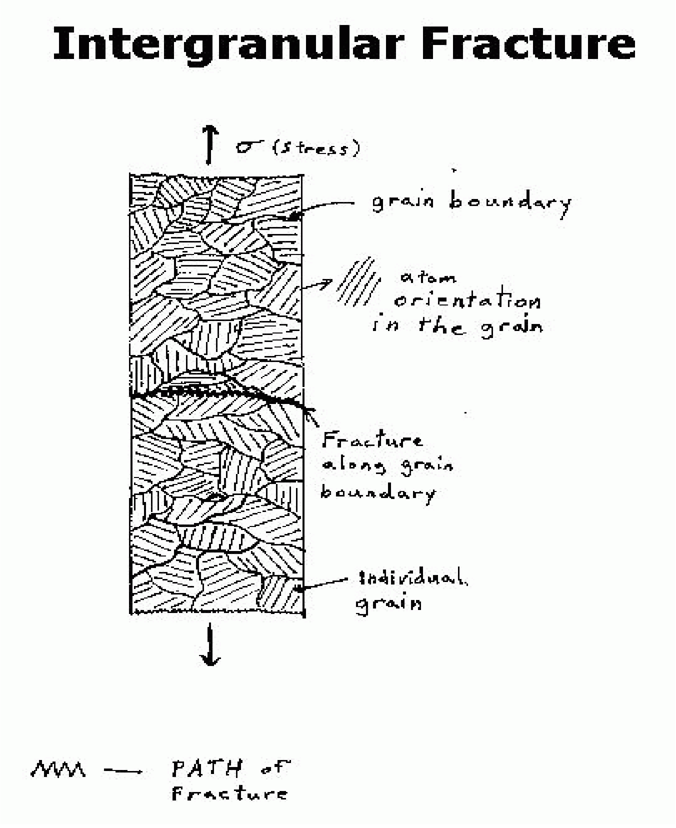


Figure 4.2 *Stages of ductile fracture*

Triangranular and Intergranular Fracture



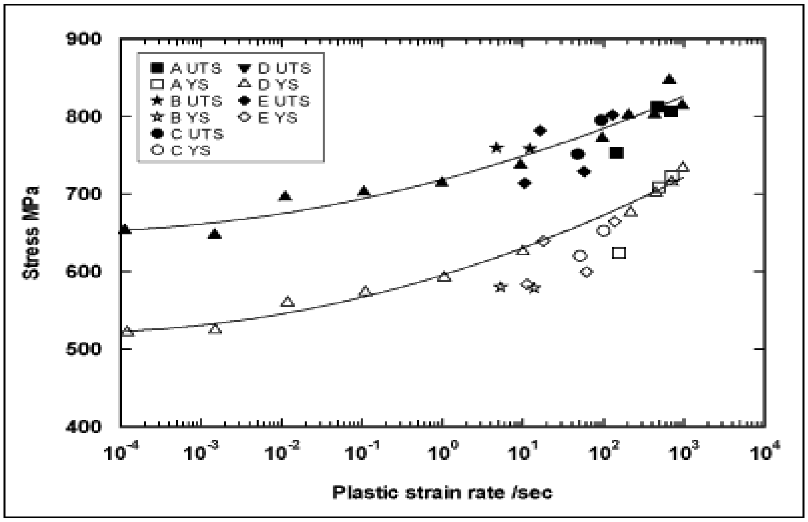


Transgranular fracture: Fracture passing through the grains is called transgranular or intragranular fracture. Cracks change direction from grain to grain in transgranulat frature. Brittle materials usually fail in a transgranular fashion.

Intergranular fracture: Fracture along the grain boundaries is termed as intergranular fracture. It occurs when the grain boundaries are weak and brittle due to deposition of brittle phases.

Effect of Impact Loading on Ductile Material and its Application in Forgings

The behavior of materials at high strain rates (like in impact loading) cannot be predicted based on slow strain rate tension tests or compression tests. General effect of increasing the loading rate (deformation rate) (strain rate) is to increase the strength (positive strain rate influence). At the same time it reduces fracture toughness.



A material can be shaped in manufacturing processes at different speeds. A hydraulic press forging is done at very low speeds (strain rate of 0.05- 0.3/s) whereas a hammer forging is done at high speeds (strain rate of 100-1000/s). It is possible to strain a specimen at the strain rate corresponding to that of the selected manufacturing process. Low strain rate testing, high strain rate testing and impact testing are available.

Mechanism of Fatigue Failure

A microscopic crack is initiated at some internal or surface flaw. Stress concentration occurs near the crack. Crack grows larger under the action of cyclic stress. At some stage, the remaining intact portion is not able to withstand the applied load. Then the crack propagates rapidly and material fails without warning.

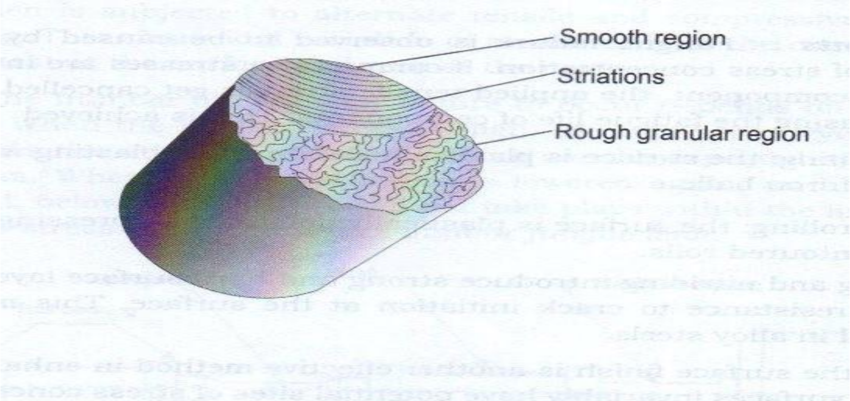


Figure 4.9 *Fatigue fracture surface*

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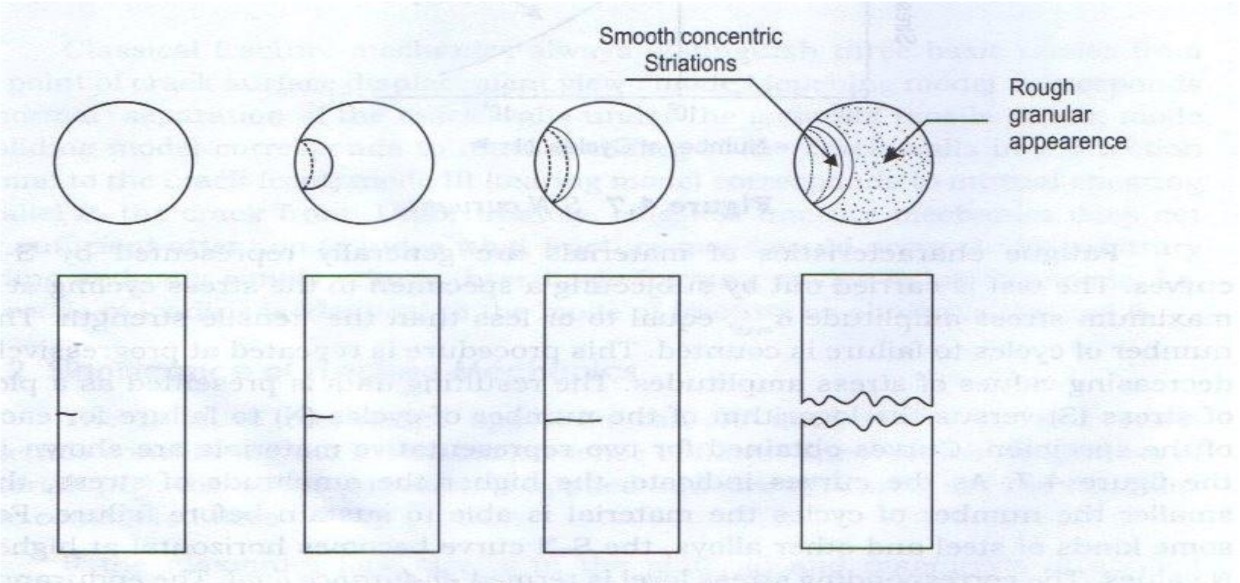


Figure 4.8 *Stages of fatigue failure*

In the region of slow propagation of crack, the fracture surface is smooth due to constant rubbing. On close examination concentric rings can be seen. Region where rapid crack growth happens has a rough granular appearance due to sudden fracture.

Structural Features of Fatigue: Crack Initiation, Growth and Propagation

Fatigue failure is characterized by three distinct stages.

1. **Crack initiation:** A small crack forms at some points of high stress concentration.
2. **Crack Propagation:** Crack advances incrementally with each stress cycle.
3. **Final failure:** This occurs very rapidly once the advancing crack reaches a critical size.

Cracks associated with fatigue failure almost always initiate (nucleate) on the surface of the component at some points of stress concentration like surface scratches, sharp fillets, keyways, threads etc. Cyclic loading can produce microscopic surface discontinuities resulting from slip steps which may also act as stress raisers.

Region of fracture surface during crack propagation stage is characterized by two types of markings called beach marks and striations. They appear as concentric ridges in a circular or semicircular pattern. Beach marks are of macroscopic dimensions and can be observed with naked eye. But striations are microscopic in size and can only be observed using TEM or SEM. There could be thousands of striations within a single beach mark.

Beach marks or striations will not be present in the region of final rapid failure. This region has ductile or brittle appearance. In ductile mode, evidence of plastic deformation will be present and in brittle mode, there will not be evidence of plastic deformation.

Fracture Toughness (Definition only)

Fracture toughness measures the ability of the material containing a flaw (a micro crack) to withstand applied load. Fracture toughness is measured by tensile loading of a specimen containing a flaw of known size and shape. The flaw acts as a stress raiser and intensifies the stress near it. Stress intensity factor $K = f \sigma \sqrt{\pi c}$ where f-geometry factor for specimen; σ- tensile stress; c-flaw size. K_C is the critical value of K above which the flaw propagates and leads to fracture of material. It is called fracture toughness. K_C depends on specimen thickness. When the specimen thickness is much greater than flaw size, K_C is constant. It is then called K_{1C} (plane strain fracture toughness). K_{1C} is a material property. It has a unit of MPa√m.

Ductile to Brittle Transition Temperature (DBTT) in Steels

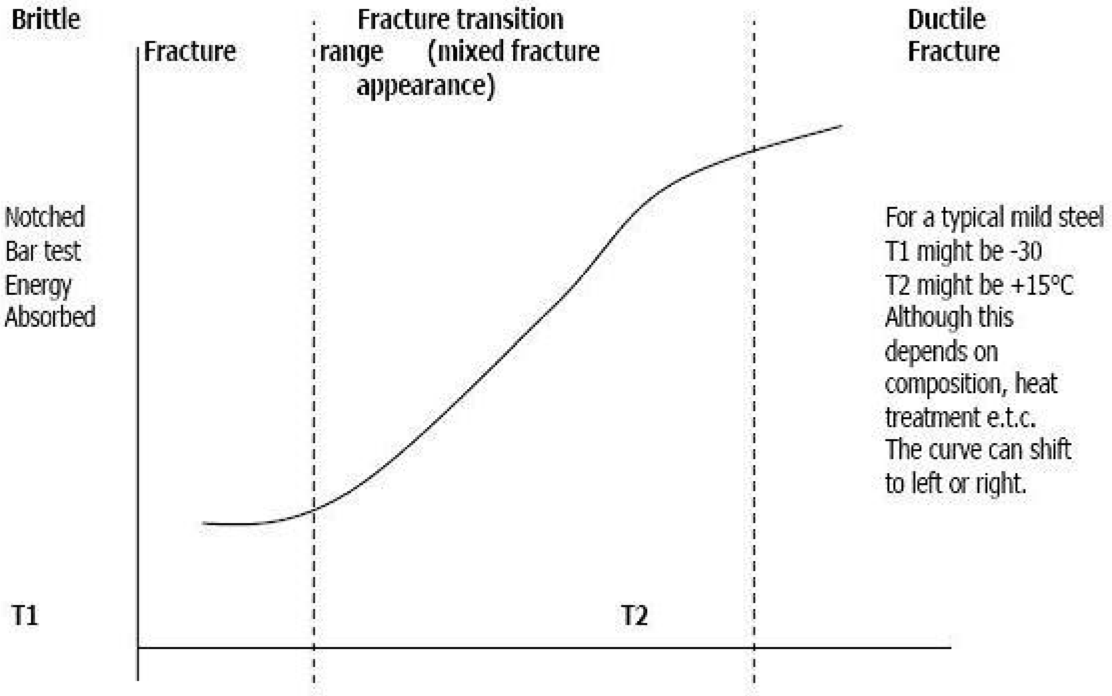
Under some conditions, normally ductile materials can fracture in a brittle fashion. Thus there can be a transition from ductile to brittle fracture. The conditions favoring this transition are (a) lower temperature (b) higher strain rate and (c) presence of notches or stress raisers. In steels, DBT occurs with decreasing temperature. It is an important engineering phenomenon.

Ductile to brittle transition temperature: DBTT is the temperature or range of temperature at which a normal ductile fracture in a material turns into brittle fracture. At this temperature, stress needed to propagate a crack (fracture) σ_f equals stress to move dislocation (σ_y). When actual temperature is more than transition temperature, $\sigma y < \sigma f$. Material deforms plastically and then only fails. When actual temperature is less than transition temperature $\sigma y > \sigma_f$. Material fails in brittle fashion.

Ductile to brittle transition is seen in BCC (steels) and HCP, but not in FCC. It is because slip is easy in FCC since number of slip systems are more. DBT temperature is generally below room temperature.

Structural Changes During 'DBTT'

Appearance of failure surface is indicative of the nature of fracture. In ductile fracture, the surface appears dull or fibrous (shear character). Totally brittle surfaces have a granular (shiny) texture and cleavage character. During DBTT, features of both types will be present. DBTT can have different definitions. But the most conservative definition is that DBTT is the temperature at which 100% fracture is a ductile fracture.



For a typical mild steel
T1 might be -30
T2 might be +15°C
Although this depends on composition, heat treatment e.t.c.
The curve can shift to left or right.

MODULE - 6

Creep is defined as the time dependent strain when load is applied continuously over a long period of time. Creep can become very large and result in final fracture without any increase in load. Some components in which creep occurs are turbine rotors in steam engines and jet engines, beams in roof of buildings, high pressure pipe lines etc. Creep occurs in all materials at all temperatures. However it is more pronounced at high temperature, generally above 0.4 T_m (T_m = melting temperature in K) for metallic materials. Amorphous polymers like plastics exhibit creep even at room temperature. Creep stress is generally much below the yield stress.

Creep Curves

Creep curve shows the relationship between creep strain and time at any particular temperature. A specimen is subjected to a constant stress at a constant temperature. The strain is measured with respect to time. Creep strain at any instant has 3 components (a) elastic and plastic strain (b) steady state or viscous creep and (c) transient creep. Transient creep is rapid at first but becomes slower progressively as time elapses. It is important even at very low temperatures. Steady state creep continues at a constant rate. But it is insignificant at temperatures < 0.4-0.5 T_m .

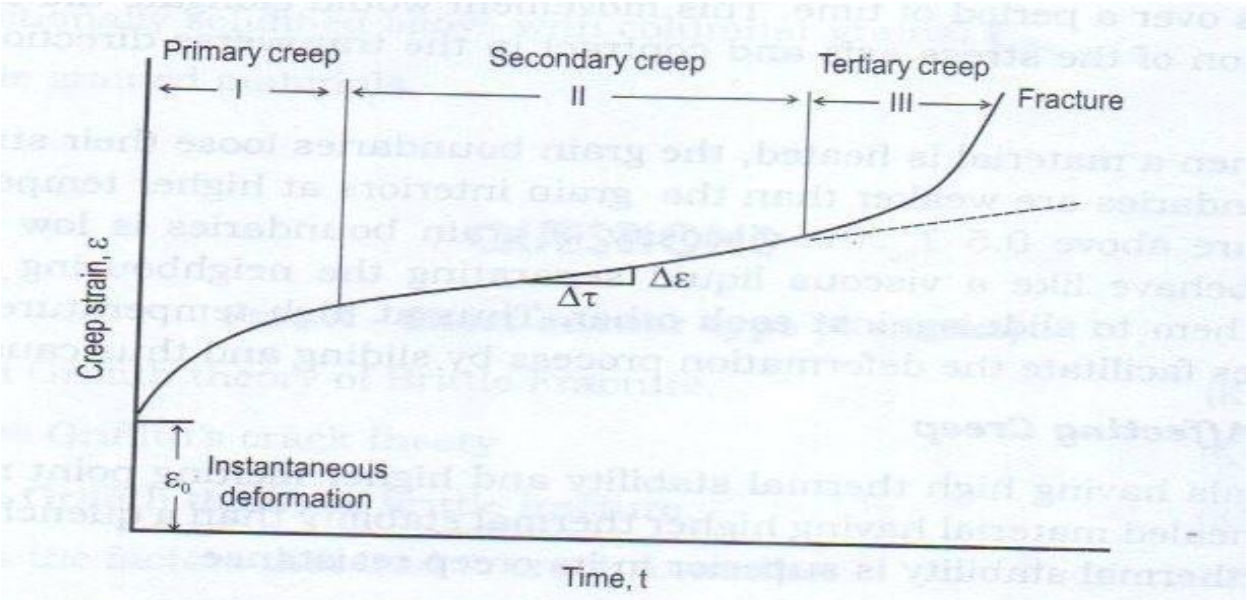


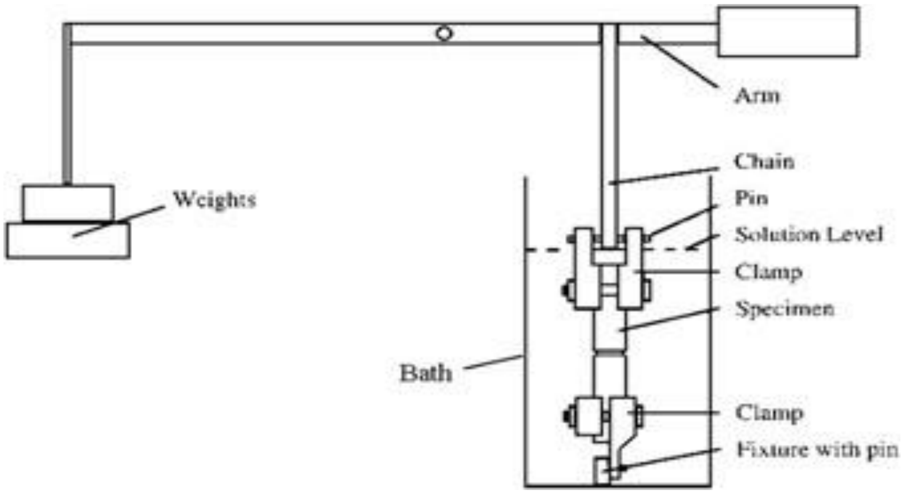
Figure 4.12 *Complete Creep curve for metals*

Figure shows that there are three distinct regions in a creep curve. The first stage is called *primary creep*. It is the time during which most of the transient creep takes place. Initial strain rate is high, but it rapidly decreases to a constant value. The second stage is referred to as secondary creep. The strain continues to increase at a constant rate during this region. Steady state creep prevails over this region.

Δt remains constant and the shape of the curve in this region is a straight line. In the third stage called tertiary creep, there is an increasing creep rate and finally necking and fracture (rupture) occur.

In general metals with high melting points have higher creep resistance. Stainless steels, super alloys and refractory alloys possess high creep resistance.

Creep Test



Four variables are measured, namely stress, temperature, strain and time. The individual tests are conducted at constant stress and at constant temperature. The strains are determined at regular intervals of time. Creep curve for the particular stress and temperature can then be plotted. Such curves for varying stress and temperature are determined which give the complete set of creep curves for the material.

Dead weights and system of levers help to maintain constant load (stress). For maintaining high temperatures, the specimens are to be kept in a furnace or salt bath. Strains are measured using strain gauges or extensometers. Generally four or five specimens are tested under different loads at each temperature. Then the temperature is varied and tests are repeated.

Structural Changes during Creep

Various structural changes occurring in a material during creep deformation are given below:

1. Deformation by Slip

New slip systems become operative at high temperatures. At these temperatures, slip occurs simultaneously on many slip systems. Many dislocations which are held at obstacles also get freed due to climb. Net effect is that the dislocations move freely causing creep strain.

2. Sub Grain Formation

Subgrains are regions separated by low angle grain boundaries (sub boundaries). These sub boundaries are formed after annealing of cold worked (bending) material by rearrangement of dislocations of the same sign. In creep deformation lattice bending can occur near grain boundaries and consequently sub grains can get formed. Sub grain boundaries serve as less effective barriers to dislocation motion.

Therefore dislocation motion can be continued thereby increasing creep strain.

3. Grain Boundary Sliding

As temperature increases, grain boundaries lose strength faster than grains. At a temperature called 'equi-cohesive temperature", the strength of grain boundaries is equal to that of grain interior. Above this temperature, grain boundaries are weaker. At temperatures above 0.5 T_m (T_m is melting point in Kelvin) the grain boundaries behave like a low viscosity fluid. Hence they can slide (move) relative to each other. This process is called grain boundary sliding. The strain resulting from grain boundary sliding can be as high as 50% of total strain. It contributes to creep strain

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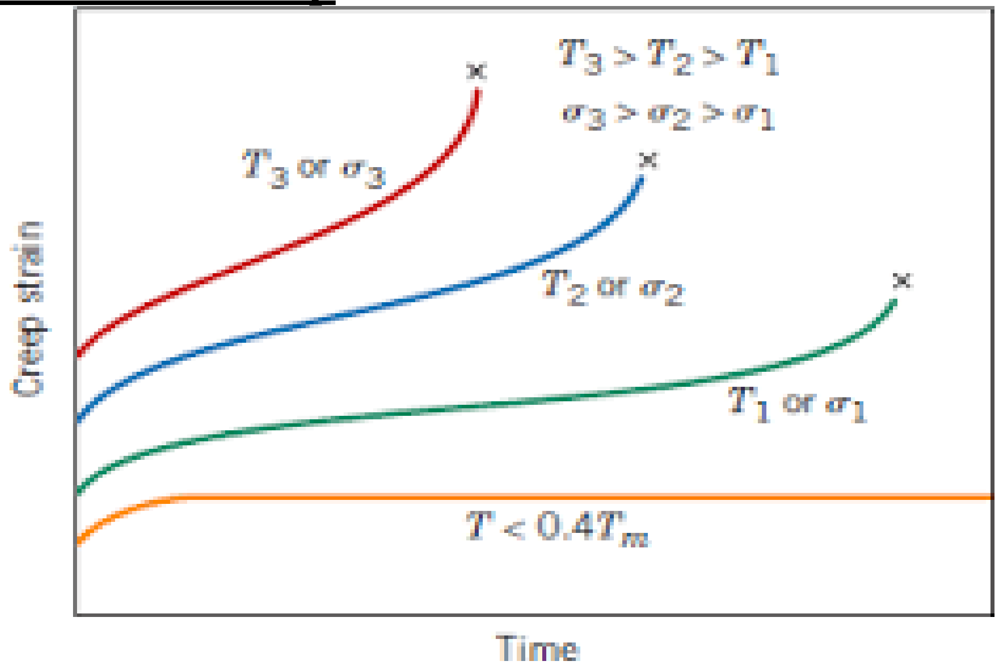
Mechanism of Creep Deformation

Creep strain is due to atomic processes *viz,* (i) dislocation cross slip (ii) dislocation climb (iii) vacancy diffusion and (iv) grain boundary sliding. Cross slip happens when a screw dislocation encounters an obstacle. The dislocation shifts to a new intersecting slip plane and continue moving. Thus plastic strain continues with time. Dislocation climb is seen in edge dislocations. If an edge dislocation is faced with a barrier, it moves in to a parallel slip plane. Again plastic strain occurs with time. Vacancies move in response to applied stress. The movement is from a perpendicular direction to a parallel direction with respect to stress axis. This will elongate the specimen resulting in creep. At higher temperatures, grain boundaries lose their strength. They become weaker than the grain interior. At temperatures above 0.5 T_m grain boundaries behave like a viscous liquid. They allow the neighboring grains to slide against each other. This is called grain boundary sliding. This sliding creates creep strain.

Threshold for Creep



Both temperature and applied stress influence creep behavior. Figure shows that below 0.4 Tm the creep strain is independent of time. With increasing stress or temperature, the following will happen:

1. Instantaneous strain increases
2. Strain rate $\Delta\epsilon$ □ Δt increases
3. Time to rupture decreases

The combination of stress level and temperature at which the strain remains constant at the instantaneous strain level (horizontal creep curve) is known as threshold for creep.

Prevention against Creep

1. Materials with high thermal stability and high melting point: They have better creep resistance. For example, an annealed material having high thermal stability is more creep resistance than a quenched material with low thermal stability. Alloys of high melting point materials like refractory alloys, super alloys and ceramics have excellent creep resistance.

2. Coarse grained materials: Fine grained materials have higher mechanical properties at low temperatures. However coarse grains have better creep resistance because at high temperature the grain boundaries are weaker than grain interior. Similarly, dendritic grains are preferred over equiaxed grains for applications involving creep. Single crystal alloys have excellent creep resistance. Directionally solidified alloys with columnar grains show high creep resistance.

3. Precipitation hardened alloys: Fine insoluble precipitates prevent dislocation motion and grain boundary sliding. Hence such alloys are more creep resistant.

4. Dispersion hardened alloys: Fine, hard, insoluble particles, uniformly distributes in the matrix material enhance creep resistance by resisting movement of grain boundaries.

5. Substitutional solid solution alloys: These alloys exhibit improved creep resistance since solute atoms introduce lattice strains which hinder dislocation movement.

SUPER PLASTICITY

Super plasticity refers to the ability of some materials to deform extensively (as much as 2000%) at elevated temperature and slow strain rates. The following conditions are to be satisfied for obtaining super plasticity.

1. Very fine grain size (5-10 μm)
2. High strain rate sensitivity
3. High temperature (0.5 T_m)
4. Low strain rate (0.01-0.001/s)

In addition, presence of second phase which inhibit grain growth, is preferred. Most super plastic alloys are of eutectic or eutectoid compositions. Deformation mechanisms like grain boundary sliding and grain boundary diffusion, which are operative at elevated temperature, are reported to be responsible for super plasticity.

Applications of Superplasticity

Super plastic phenomenon is widely employed in metal forming processes like thermo forming, blow forming, vacuum forming, deep drawing etc. Large, deep and complex shapes can be made in one piece in a single operation. The force requirements are also significantly lower due to reduced flow stress. In thermoforming, sheets are made to conform to a heated die by the application of vacuum or pneumatic force. Production of aerofoils in gas turbines is an important application of super plasticity.

COMPOSITES

A composite is defined as a multiphase (two or more) materials with chemically dissimilar constituents, separated by a distinct interface. The composites have better combination of properties than the individual materials. Most composites have 2 phases. The phase in larger amount is called matrix. It is the continuous phase. Other phase which is surrounded by the matrix phase is called reinforcing phase.

Need of Development of Composites

Modern technological applications necessitate materials with unusual and often conflicting combination of properties which existing materials like metals, alloys, ceramics and polymers do not have. For example, aerospace engineers were looking for materials which are light, strong, stiff and abrasion resistant, corrosion resistant and high temperature resistant. This combination of properties cannot be obtained with any existing material. Most of metals and alloys are generally dense and therefore heavy. They lose their strength at high temperatures. Ceramics on the other hand are brittle and dense materials with low impact strength. Polymers are light, but lack strength and high temperature resistance. It was found that certain combination of materials (composites) yielded the desired combination of properties. Demand for materials with specific properties for applications in automobile, marine, manufacturing etc. also accelerated development of composites. There is also a need for developing totally new materials with precise combination of properties to meet specific design requirements for the future.

Geometrical and Spatial Characteristics of Particles

The properties of composites are dependent on the properties of the constituents, particularly by the geometrical and spatial characteristics of the dispersed phase. These characteristics are:

1. Concentration: volume fraction or percentage of dispersed phase

2. Shape : Particles- plate/flake/needle/spherical or polygon shaped
   Fiber- continuous or discontinuous
3. Size: Large (particle strengthening), Small/fine (dispersion strengthening)
4. Distribution: Uniform distribution is preferred.

Classification of Composites based on Fiber Phase

In most of the composites, load is mainly borne by reinforcing phase which is embedded in the matrix. The reinforcing phase is in the form of particles or fibers.

Classification of composites based on the reinforcing phase is given below:

1. Particle reinforced composites (i) large particle (ii) dispersion strengthened
2. Fiber reinforced composites (i) continuous (ii) discontinuous

1. Large particle reinforced composites

Particle size is 1-50μm and concentration is 15-40% by volume. Particles are stiffer and harder than the matrix. Generally properties of these composites increase with increasing volume fraction of the particles. But there is an optimum amount above which the properties deteriorate. For best properties, the particles should be small and uniformly distributed. Particles may be preferably equiaxed (same dimensions in all directions). Examples: cemented carbides (tungsten carbide or titanium carbide in a matrix of cobalt or nickel) and concrete. In concrete, cement is the matrix and sand & gravel is reinforcement.

2. Dispersion strengthened composites

The particles are fine (less than 0.1μm) and hard. The volume fraction of particles is between 5-15%. The particles can be metallic, inter metallic or non-metallic. Generally carbides, oxides and borides are used as particles. Particle shape may be round, disc or needle shaped. In these composites, matrix is the load bearing phase. Dispersoids strengthen the matrix by impeding dislocation motion. The strengthening depends on particle size and inter-particle spacing. Smaller particles and spacing provides high strength. Composites belonging to this category include (a) SAP (sintered aluminum product) obtained by dispersing alumina (Al_2O_3) in aluminum matrix (b) TD Nickel (thoria dispersed nickel) (c) thoriated cobalt/tungsten etc..

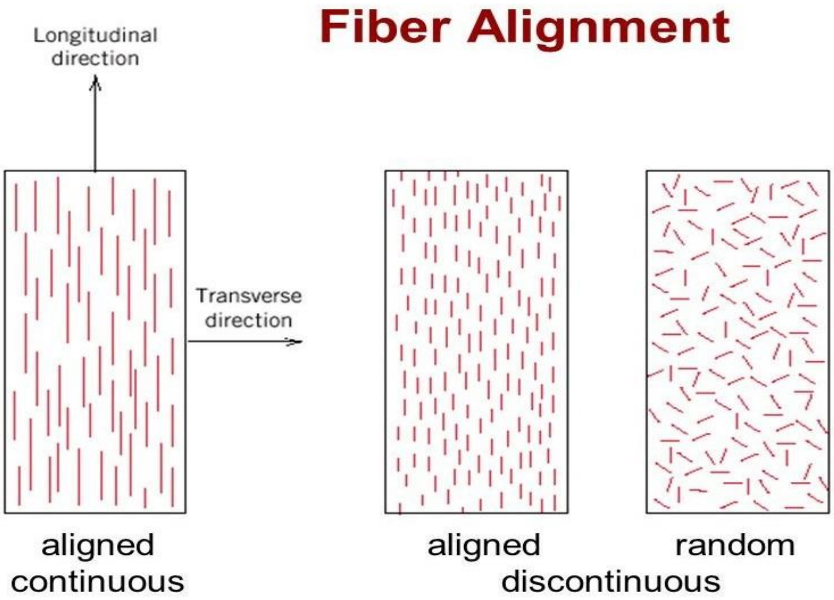
3. Fibre Reinforced Composites (FRC)

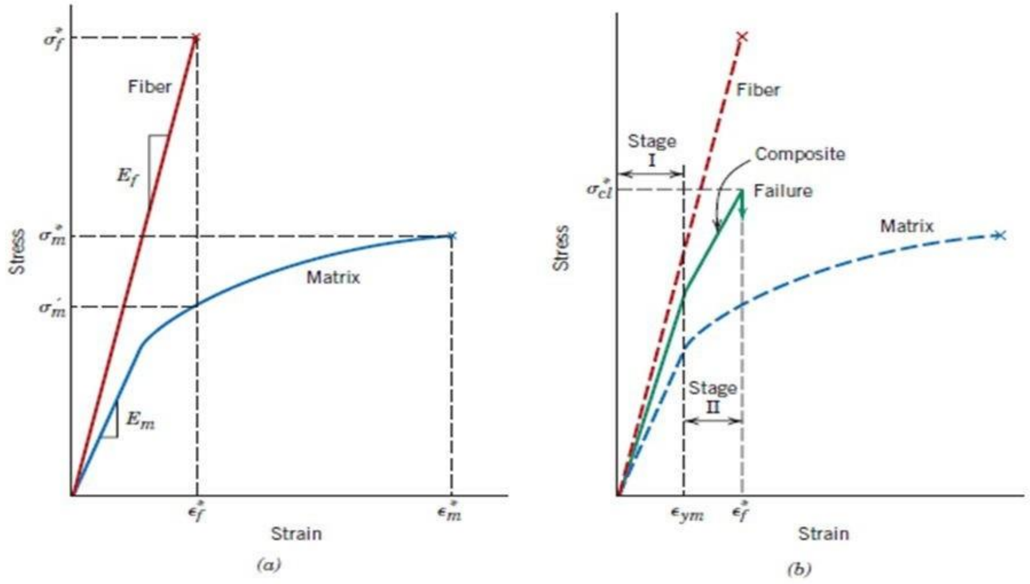
It is the most important composite. Matrix is metal, ceramic or polymer (plastic). Fibers may be amorphous or polycrystalline with length at least 100 times the diameter. An important characteristic of small diameter fiber is that it is much stronger than large diameter wires or the bulk material. The reason for this trend is due to reduction of flaws (defects) in fine or nano fibers. There are three types of fiber materials. (a) whiskers which are very thin, long single crystals having very high strength (b) fibers with small diameters (5-10μm) and moderate strength and (c) wires having relatively large diameters with minimum strength. Most of the composites of this type use only fibers. Properties of FRC are dependent on the kind of fiber, its volume fraction and fiber orientation. Composites with high specific strength (tensile strength divided by density) and high specific modulus (Elastic modulus divided by density) can be made. Oriented fibers provide directional properties while randomly oriented fibers yield non-directional properties.

Influence of fiber length: Ability to transfer applied stress depends on fiber length (l). There is a critical length of fiber (lc) required to obtain effective strengthening. For a number of fiber materials critical length is about 1mm. If l > 15 lc, fibers are called continuous and if l<15 lc, such fibers are called short or discontinuous. Continuous fibers provide higher strength to composites.

Influence of fiber concentration and orientation: Two extreme orientations are possible, namely (i) arranged parallel to longitudinal direction (aligned or oriented) (ii) arranged in different directions (random). Continuous fibers are aligned and discontinuous fibers may be aligned random or partially aligned. When continuous or discontinuous fibers are aligned, reinforcing efficiency is maximum in direction parallel to alignment and negligible in perpendicular direction. When discontinuous fibers are oriented randomly and uniformly distributed in three dimensions, the composite has isotropic properties with a reinforcing efficiency of 20%. Schematic sketches depicting the various fiber orientations and stress strain curves for aligned composite during uniaxial loading are shown in figures. Fiber Reinforcing Materials

Whiskers have very high strength, but they are highly expensive. Hence they are not widely used. Graphite, silicon carbide, silicon nitride and aluminum oxide whiskers are available. Fibers are used most as reinforcements. The advantages of fibers over particles include more efficient load transfer and more interface area resulting in better properties. Common fiber materials are glass, graphite/carbon, silicon carbide, boron, aluminum oxide, aramids (Kevlar) etc. Steel, molybdenum and tungsten fibers are also used to a limited extent.





(a) Schematic stress–strain curves for brittle fiber and ductile matrix materials. Fracture stresses and strains for both materials are noted. (b) Schematic stress–strain curve for an aligned fiber-reinforced composite that is exposed to a uniaxial stress applied in the direction of alignment; curves for the fiber and matrix materials shown in part (a) are also superimposed.

Classification of composites based on matrix phases

The primary function of the matrix phase in a composite is to hold and bind the reinforcing phase. Polymers and metals are used as matrix materials. Inorganic materials and ceramics are not as popular as polymers and metals. Other functions of matrix phase are:

(a) It acts as a medium through which the applied stress is transmitted to reinforcing phase. Sometimes the matrix also serves to bear the load.
(b) Matrix separates fibers from each other. As a result, propagation of brittle cracks is avoided.
(c) Matrix protects the fibers fro surface damage.
(d) Matrix being ductile improves fracture toughness of composites.

1. Polymer matrix composites (PMC)

In these composites a polymer (high molecular weight plastic) is used as matrix and high strength or high stiffness continuous fibers are used as reinforcements. These are used in the largest quantity. PMCs possess low density, high specific strength, high specific stiffness, ease of fabrication, good mechanical and electrical properties. Thermosetting plastics like epoxies and phenolics are the common matrices. Epoxies are better in terms of properties, but costlier. Thermo plastics are also used as matrix in a limited way. Glass, graphite, carbon and aramid (Kevlar) are commonly used as reinforcing fibers.

(a) Fiber glass

Glass fiber reinforced polymer (GFRP) is known as fiber glass. Glass fibers are embedded in polymer matrix. Fibers may be continuous or discontinuous. Fibers have diameter between 3-20μm. This composite has high strength, stiffness and rigidity. It cannot be used at high temperatures. It is used for automobile bodies, storage containers, industrial flooring, rocket motor cases etc.

(b) CFRP:

Carbon fiber reinforced polymer (CFRP) composites are advanced composites. Carbon fibers have the highest specific strength and specific modulus and they retain their properties at high temperatures. These are used for air craft and space applications as structural materials. C fibers of 4-10μm are used as reinforcement. Polymers may be polyesters, vinyl esters and epoxy resins. These composites are also used for sports equipments, pressure vessels and structural components.

(c) Kevlar (Aramid) fiber reinforced composites

Aramids, chemically known as polyamides, have specific strength and specific modulus greater than metals. They have high toughness, impact resistance, creep resistance and fatigue limit. Fibers are stable between -200 to +200^{0}C. Typical applications of these composites include bullet proof vests, armor, sporting goods, tires, ropes, pressure vessels, brake lining, gaskets etc.

2. **Metal Matrix Composites**.

Some of the advantages of MMC over PMC are their high operating temperatures, non flammability and greater resistance to degradation by organic fluids. However MMCs are much more expensive. Ductile metals such as Al, Cu, Ti, Mg and their alloys are used as matrix. Particulates and fibers (continuous/discontinuous) are commonly used as reinforcements. Concentration range is between 10-60% by volume. Reinforcing phase could be carbon, silicon carbide, boron, aluminum oxide and refractory metals. Al alloy matrix reinforced with aluminum oxide and carbon fibers are popular. They have light weight and good wear resistance. They are more expensive than polymer matrix composites. They are used in aero space and automobile sectors. MMCs with super/ refractory alloy matrices are used for high temperature applications like gas turbines.

3. Ceramic Matrix Composites

Ceramics have high melting points, good resistance to oxidation and excellent high temperature properties. But they are brittle. They also have poor tensile strength, impact strength and thermal shock resistance. Particles, fibers and whiskers (thin long single crystals) of one ceramic material is embedded into a matrix of another ceramic material. Such materials are called ceramic matrix composites. Fracture toughness is improved due to restriction of crack propagation by the dispersed phase. Strength and thermal shock resistance are also improved. Silicon carbide/silicon nitride/stabilized zirconia particle reinforced alumina composite is used as cutting tool inserts for machining hard alloys.. CMCs are also used for components in automobile and aircraft gas turbine engines. Carbon fiber reinforced carbon matrix composites is an advanced engineering material. It has high strength even at 2000^0C. It also has high creep resistance and fracture toughness. Carbon –carbon composite is highly expensive. It is used in aircraft, aerospace and high performance automobiles.

Applications of Composites

1. Aircraft and Aerospace applications

A wide range of load bearing and non-load bearing components are made using composites. PMCs are used for windows, ceiling panels, overhead storage bins, consoles, landing gear, doors etc of aerospace vehicles. They are also used for structural components like body, wings, rudder, helicopter rotor blades and propellers. MMCs with aluminum or super alloy as matrix are used for compressors and fan blades. Carbon-carbon composites are used for elevated temperature applications like rocket motors and gas engine components.

2. Industrial applications

Automotive applications: Light weight PMCs are used as body components for automotive applications. Al-SiC composites are used for engine block, piston, piston rods, connecting rods, push rods, chassis, motor cycle frames etc. MMCs are employed for transmission shafts. Epoxy/polyester matrix- aramid fiber composites are used for brake and clutch lining, gaskets etc. Rubber-carbon or epoxy-are used for manufacture of tires.

Other industrial applications: Injection molded reinforced thermoplastics and polyester composites are extensively used for many consumer items like Kitchen equipment, electrical equipments, television and computer casings furniture, helmets etc. Storage vessels, pressure vessels, pipings, valves, centrifuges etc for chemical industries are also made of GFRP or CFRP.

Electrical and civil Engineering Industries: Electrical industries use components such as electrical contacts, printed circuit boards, casings for electrical equipments and high strength insulators made out of composites. GFRP and CFRP composites are fast replacing wood in civil engineering.

3. Marine Applications

A vast range of components like hull, body, ladder, walkways, storage tanks, piping, flooring etc. are made of GFRP composites. Applications include surface vessels, under water systems and offshore structures.

4. Sporting Industry

High strength, rigidity and light weight make composites ideal for sports goods. Examples of components are tennis rackets, hockey sticks, cricket bats, golf clubs, vaulting poles, skiing poles, archery equipment, surf boards, canoes, skate boards etc. PMCs are mostly used for such applications.

5.Biomaterials

CFRP and carbon composites are used for prosthetic applications like orthopedic fixation plates, femoral stems, hip replacements, jaw remodeling etc Certain ceramic composites are used in dental applications.

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MODERN ENGINEERING MATERIALS

Intermetallics

Fundamentals and need: It is a solid phase containing two or more metallic elements. Sometimes one or more nonmetallic elements may also be present. Intermetallics have ordered arrangement of different atoms. Type of bonding is covalent or metallic. Generally it has a different crystal structure than those of pure components. The constituent elements have opposite electrochemical behavior. Intermetallics are chemical compounds. They are formed when a strongly metallic element (Mg) combines with some weakly metallic elements (Sb, Sn, Bi). Examples of intermetallics are Mg_2Sn, Mg_2Pb, Mg_3Sb2, Fe_3C, Zr_3Al, Al_6Mn, Ti_3Al and Mg_3Bi_2.

Properties: Generally intermetallics are brittle. These hard and strong compounds can be used for strengthening multiphase materials. However, intermetallics like Ti_3Al and Ni_3Al can exist as stand-alone materials having high strength and useful ductility at high temperature.

Applications: Intermetallic platinum silicide is used in micro-electronics.Nb_3Sn is used as superconductor. Titanium aluminides Ti_3Al and TiAl are considered for a variety of applications including gas turbines.

Maraging Steel

Fundamentals and need: Maraging steels are carbon free iron-nickel alloys with additions of cobalt, molybdenum, titanium and aluminum. The term maraging is derived from 'martensite aging', that is age hardening of iron-nickel martensite. Air cooling the alloy to room temperature from 820^0C produces a iron-nickel martensite (much softer than iron-carbon martensite). Unlike in iron-carbon martensite, quenching is not needed in maraging steel to obtain martensite. A further heat treatment at 480- 500^0C results in strong hardening, due to fine precipitation of a number of intermetallic compounds based on molybdenum, titanium and aluminum.

Properties: Freedom from decarburization, minimum distortion during heat treatment, good formability, machinability and weldability and low coefficient of thermal expansion are some of the attributes of maraging steel. With yield strength between 1400-2400 MPa, maraging steels belong to the class of ultra high strength steels. The high strength is complemented with high fracture toughness and weldability.

Applications: Typical applications of maraging steels include: rocket motor casings, light aircraft landing gear, power shafts, low temperature tooling etc.

Super Alloys

Fundamentals and Need: Super alloys are high performance alloys for elevated temperature applications. They are classified into three categories namely nickel based, iron based and cobalt based. Properties and applications: Super alloys exhibit high strength and creep resistance at high temperatures. These properties are achieved by mechanisms of solid solution strengthening, precipitation hardening and dispersion hardening. Other important properties of super alloys are fatigue life, oxidation resistance and corrosion resistance. Typical applications are in the aerospace and industrial gas turbine blades, hot sections of aircraft engines and bimetallic engine valves for use in diesel and automotive applications. Hastelloy, nichrome, kanthal, udimet and inconel are nickel based super alloys. They possess excellent thermal shock resistance and high electrical resistivity. Cobalt based super alloys contain chromium, nickel, molybdenum and tungsten as alloying elements. Stellite, haynes alloyand vitallium are typical cobalt base alloys. Incoloy is an example of iron-nickel base super alloy. It is widely used for heat exchangers.

Titanium

Fundamentals and need : Titanium is an allotropic metal. It exists as α (hcp) up to 880^{0}C. Above 880^{0}C it has a β structure (bcc). It can be hot worked and cold worked. Important alloying elements to titanium are Al, V, Cr, Mn, Fe, Mo and Sn. They increase the mechanical strength. Among these, Fe, Cr and Al provide highest strength. Ti alloys respond to age hardening.

Properties and applications: Pure Ti is strong, ductile and light weight (density 4.5g/cc). It has very good corrosion resistance and high strength at elevated temperature. Hence Ti is widely used as a structural metal. Ti-6Al-4V is the most widely used titanium alloy. Another popular alloy is Ti-5Al-2.5.Sn. Ti alloys exhibit high creep resistance, fatigue strength, specific strength and high temperature strength. Ti alloys are used for aircraft structures, aircraft turbines, rocket motor cases, gas bottles etc. Ti is used in the construction of leaching and purification plants. It is also widely used for chemical processing equipments, valves and tanks.

Introduction to Nuclear Materials

Nuclear fission means splitting of a heavy nucleus (uranium 235 or plutonium 239) into two or more lighter nuclei. It happens when the heavy nucleus is bombarded with a neutron. The fission reaction releases high amount of kinetic energy and gamma radiation. The reaction is controlled by moderators. Primary materials in a nuclear reactor are nuclear fuel, moderator and coolant. Secondary materials are structural and shielding materials.

Nuclear fuels are the densest sources of energy. They contain heavy fissile elements. They are used in the form of rods, plates or wires. The popular moderator materials are graphite, ordinary water and heavy water. Heavy water is expensive, but it can make the reactor compact. Generally the moderators can also serve as coolant.

The structural materials include materials used for:

1. constructing the reactor
2. cladding the fuel for containing the fission products
3. forming conduits for the coolant
4. strengthening the control rods

Aluminum alloys, stainless steel, zirconium and its alloys like zircalloy are used as cladding materials. Engineering materials used for structural applications are concrete, carbon steel, stainless steel, nickel alloys like inconel and ceramic materials like silicon carbide.

Introduction to Smart Materials

Smart materials are also called intelligent materials. They have one or more properties which can be changed by external stimuli such as stress, temperature, moisture, pH, electric field, magnetic field etc. They sense and react with a predictable action. Hence they have a sensor and an activator. Advantages of smart materials are (a) no moving parts (b) high reliability (c) low power consumption etc. Some applications of smart materials are (a) removing toxic pollutants from water (b) liquid crystal displays (c) artificial muscles and (d) embedded sensors.

Some smart materials are given below:

1. Piezoelectric materials

These materials can convert one form of energy into another. They produce voltage when stress is applied or vice versa. They can be made to bend, expand or contract when a voltage is applied. They can act both as sensor and actuator. Typical applications are in inkjet printers, medical diagnostics, computer key boards and microphones.

2. Shape Memory Alloys (SMA)

Large deformation can be induced and recovered through temperature or stress changes. Large deformation occurs through a martensitic phase change. SMA remembers its original shape. In one way shape memory, material remembers the shape in heated state. In 2 way shape memory, material remembers shape in both hot and cold conditions. Nitinol (50% Ni+50% Ti) is the most popular SMA. SMAs are used in medical science, aerospace and mechanical engineering.

3. Magnetostrictive materials

They exhibit shape change under magnetic field and change in magnetization under mechanical stress. In effect they can convert magnetic energy into kinetic energy. Terfenol-D (terbium+iron-fe + naval ordnance lab+ dysprosium) is the most popular magnetostrictive material. These materials are used in sonar transducers, motors and hydraulic actuators.

4. Magnetic shape memory alloys

These are ferro- magnetic metals (Fe, Ni and Co) which exhibit change in size and shape in response to change in Magnetic field.

Introduction to Biomaterials

These are materials are used to make devices to replace a part or function of the human body. These are materials for medical application. A biomaterial ia any material, natural or man-made that comprises whole or part of a living structure or biomedical device which performs, augments or replaces a natural function. Use of biomaterials in different human organs is given in table.

Sl No	Organ	Examples
1	Heart	Pace maker, heart valve, artificial heart, blood vessels
2	Lung	Oxygenerator machine
3	Eye	Contact and intraocular lens
4	Ear	Cochlear implant
5	Bone	Bone plate, Screws

6	Kidney	Catheter, Stent, Dialysis machne
7	Bladder	Catheter, Stent

Polymers, metals , ceramics and composites are used as biomaterials.

1. Polymeric Biomaterials

Acrylics, polyamides, polyester, polyethylene and polyurethanes are used as biomaterials. Some applications include: artificial heart, kidney, liver, pancreas, bladder, catheters, contact lens, cornea and eye lens replacement, heart valves, pumps, pace maker etc.

2. Metallic Biomaterials

Total hip, knee joints, bone plates and screws, dental implants, vascular stents, catheter wires etc are some of the uses of metallic biomaterials. Corrosion of the implant is the major concern. Stainless steels, Co-Cr alloys & Ti alloys are used.

3. Ceramic biomaterials

Alumina, zirconia and silicon nitride are inert bioceramics.

4. Composite biomaterials

Composites are used for dental filling, bone cement and orthopaedic implants. Polymer matrix with inorganic fillers such as quartz, barium glass and colloidal silica ceramics are used. Rubber is usually reinforced with $SiO_{2.}$.

CERAMICS

Ceramics are compounds formed by the combination of metallic and non-metallic elements. All metal oxides, carbides, nitrides and silicates are considered as ceramics. Refractories, glasses, abrasives, clays, cement etc are ceramic materials. Ceramics have high hardness, melting point and creep resistance; but they are brittle. They are chemically inert and electrically insulating. They are atomically bonded by ionic and covalent bonds.

Coordination Number and Radius Ratio

In ionic compounds (NaCl, CsCl, ZnS etc) or ceramic materials (MgO, WC etc) there are two types of ions. Metallic ions (Na, Mg etc.) are positively charged and are called catiEons. Non metallic ions (Cl, O etc) are negatively charged and are called anions. The ratio of radii of cation and anion is called radius ratio.

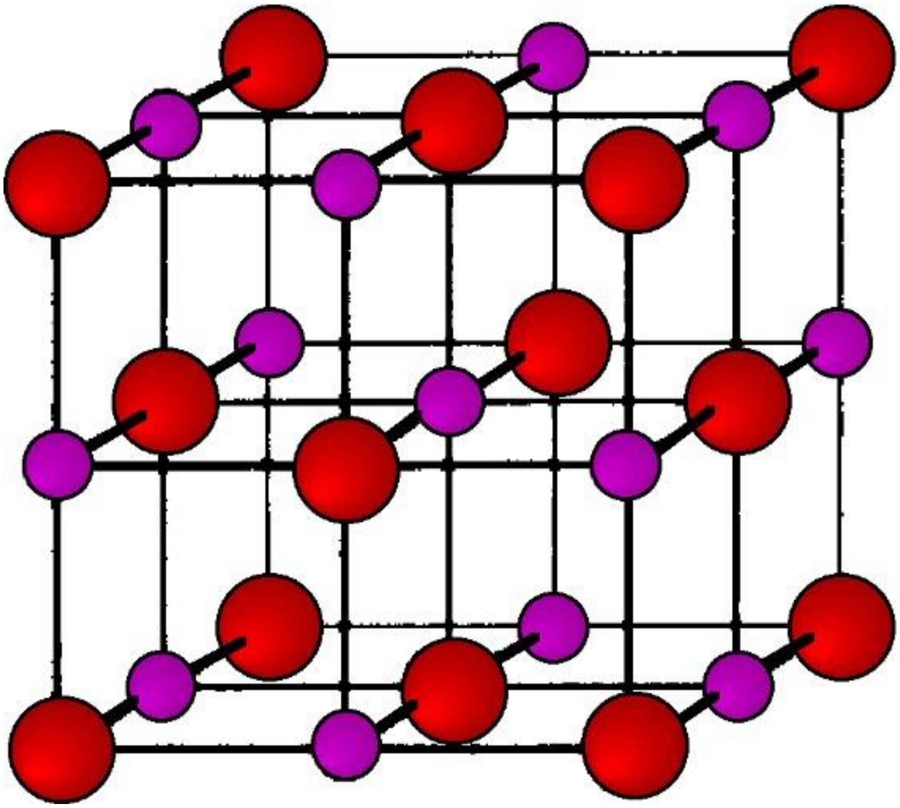
In general, non-metallic ions (anions) are larger in size. Hence radius ratio is less than one. Each cation likes to have as many anion neighbors as possible. Likewise, anion is surrounded by many cations. Coordination number refers to nearest neighboring atoms. Hence there is a close relation between radius ratio and coordination number. In fact coordination number can be predicted from the calculated radius ratio for various ionic compounds as given below:

Radius Ratio	Coordination number	Example
< 0.155	2	----
0.155 - 0.225	3	B_2CO_3
0.225 - 0.414	4	ZnS, CuCl
0.414 - 0.732	6	NaCl, MgO
0.732 - 1.000	8	CsCl, NH_4Br

Crystal Structures of Ceramic Materials

1. AX Type Structure

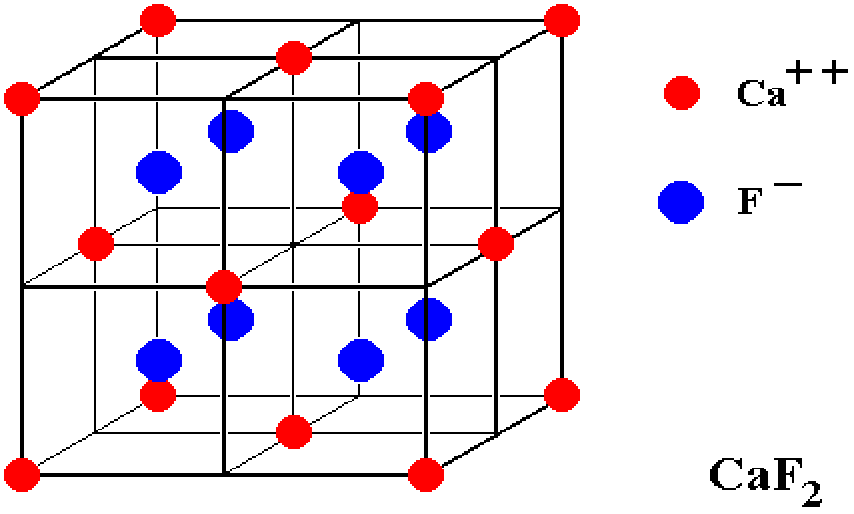
Ceramic materials having equal numbers of cations and anions are called AX compounds. ‘A’ represents cation and ‘X’ represents anion. Well known AX type structure is that of NaCl. The coordination number is 6 and radius ratio is 0.414-0.732. Some other ceramic materials having AX type crystal structure are MgO, MnS, LiF and FeO. In CsCl (cesium chloride) coordination number is 8 while in Zns and SiC, it is 4.



In the figure Na atoms are smaller and Cl atoms are larger.

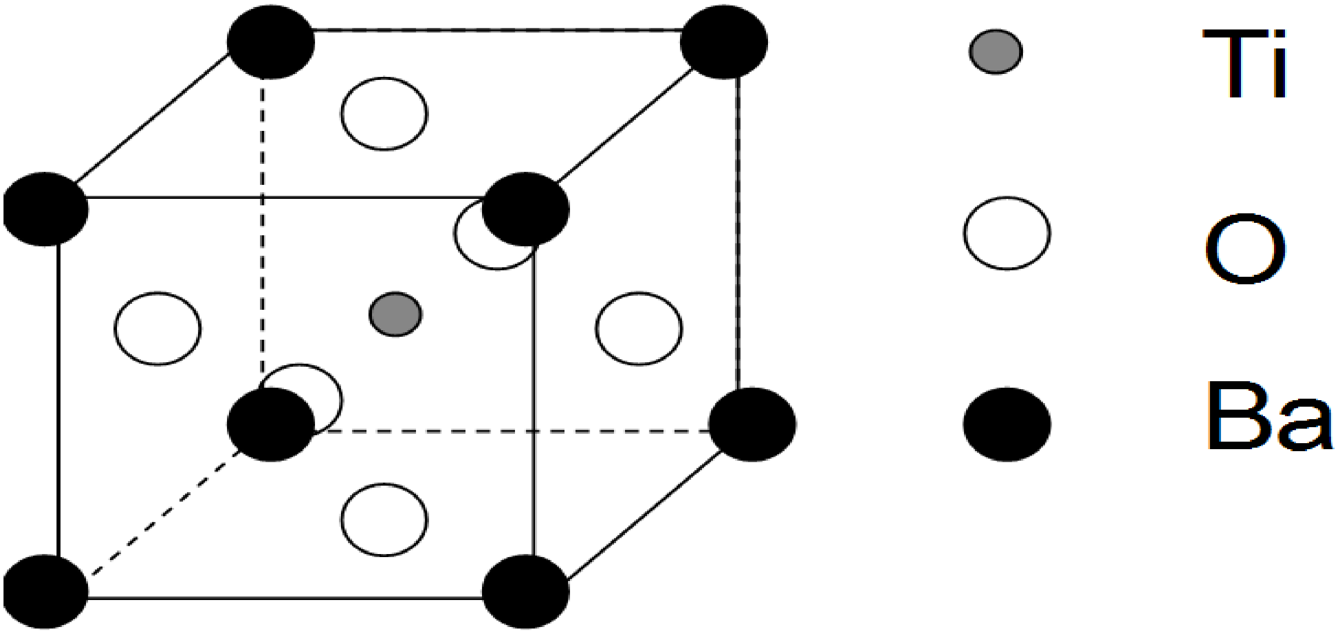
2. $A_m X_p$ Type Structure

Ceramic materials in which cations and anions are not equal form $A_m X_p$ type structure where m and p are not equal. A common example is CaF_2 which has a radius ratio of 0.8 and coordination number of 8. Some other compounds of this type are ZrO_2 and ThO_2.



3. $A_m B_n X_p$ Type Structure

There is another category of ceramics having more than one type of cations. Their structure is denoted by $A_m B_n X_p$. Some examples are $BaTiO_3$, $SrZnO_3$, $MgAl_2O_4$ and $FeAl_2O_4$.



Applications of Ceramics

1. Glass

Glass is a super cooled viscous liquid. Main ingredient of glass is silica (SiO_2). The prime properties of glass are optical transparency and ease of fabrication by glass blowing. Glass is widely used in construction and engineering applications. Glass fibers are used for insulation purpose and as reinforcement in composites. Safety glasses are used in automobiles.

2. Glass - Ceramics

Non-crystalline glass is heat treated at high temperature and it is converted into fine grained, polycrystalline material. This material is called glass-ceramics. They have a relatively higher strength, lower coefficient of expansion and superior high temperature resistance. They are used for table ware, oven ware, electrical insulators, heat exchangers etc.

3. Clay –Ceramics

Clay ceramic is a widely used raw material to produce bricks, tiles and pipes. Another type of clay ceramic becomes white after high temperature firing. This whiteware is used for porcelain, pottery, sanitary ware and tableware.

4. Refractory Ceramics

These ceramics can withstand very high temperatures without decomposing. Fire clay, alumina, silica, magnesia (MgO), zirconia (ZrO2) are examples. An important application is as linings for furnaces used for glass manufacturing, metal refining and heat treatments. Fire clay bricks are used for thermal insulation of structural members in furnaces. Silica refractories are used for high temperature load bearing applications. Basic refractories like MgO are used for providing basic lining to steel making furnaces. Some special applications of refractory ceramics are electrical heating elements, crucible materials etc.

5. Abrasives

Abrasive ceramics are used to grind or cut away softer materials. Silicon carbide, tungsten carbide, aluminum oxide and silica are the commonly used abrasive ceramic materials.

6Cements

Portland cement, plaster of Paris (gypsum) and lime belong to this group of ceramics. These are used for construction applications and for metal casting molds. Lime stone is used for metal refining operations.

6. Advanced Ceramics

Lead zirconate titanate (PZT) shows good piezo electric effect. It is used for making ultra sound transducers, ceramic capacitors and for sensors and actuators. It can be used as sensors for detecting heat. When PZT is doped with lanthanum, it is called PLZT (lead lanthanum zirconium titanate). It is a better material and used for applications where PZT is used.

CONTENT BEYOND SYLLABUS

Practical Aspects of Metallurgical Thermodynamics

Thermodynamic principles and data are very useful in the solution of industrial problems, particularly in assessing the feasibility and economics of a projected process. This article reviews the application of thermodynamics to the oxidation of platinum and to the life expectancy of platinum coatings on base metal substrates when operating at high temperatures, and describes the derivation of equilibrium diagrams of platinum alloys from the thermochemical properties of the constituent phases.

As yet metallurgists have hardly appreciated the immense potentialities of chemical thermodynamics for the application to industrial and other practical problems. This is partly due to the belief that the application of chemical thermodynamics requires complicated mathematics. Students of science at university are fed, it is true, with involved derivations of thermodynamic equations and are then left “hanging in the air” with no indication how thermodynamic principles and data are to be put to practical use. No wonder that the puzzled student asks: “So what?”

In fact, all that is required is a working knowledge of arithmetic, the ability to think in terms of molar quantities and a good portion of metallurgical “commonsense”. Once a problem has been broken down into one or more chemical equations, the evaluation of the equilibrium conditions becomes mere routine.

An important equation is the reaction isochore which connects the equilibrium constant of a chemical reaction (Kp) with the standard Gibbs energy change (ΔG°) in calories per mole

$$\Delta G^\circ = -RT \ln Kp = -4.574T \log Kp$$

Since the Gibbs energy is a function of temperature, it is convenient to list the thermodynamic properties of chemical substances in terms of entropies (S) and heat contents (H). The three functions are connected by the equation

$$G = H - TS$$

For a chemical reaction involving several substances, the heat of reaction is obtained by a simple summation,

$$\Delta H = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

This equation is known as Hess’ Law and is the form in which the chemist uses the First Law of Thermodynamics. Likewise, the entropy of reaction is obtained by the following summation:

$$\Delta S = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$$

In the first approximation and for the present purpose, ΔH and ΔS may be taken to be independent of temperature.

Of course, for the appraisal of a chemical reaction, not only a knowledge of the equilibrium is important but also the rate with which it is attained. Unfortunately in reaction chemistry, the prediction of the kinetic conditions is far more difficult than that of the thermodynamic ones. However, the higher the temperature the more rapidly equilibrium is approached and the less the influence of the kinetic delays. This is why chemical thermodynamics finds important applications in the field of metallurgy.

The main restriction on the application of thermodynamics is imposed by the relative scarcity of accurate values for the heats and entropies. These are usually tabulated as standard heats of formation from the component elements and standard entropies, both quantities at a temperature of 25°C. Several tabulations of critical values are available of which only one by the present author and his colleagues (1) will be mentioned here.

These tabulations show that relatively little thermodynamic information is available for systems involving the platinum metals, perhaps because their relatively high cost has discouraged measurements. On the other hand, experiments with platinum metals present few difficulties in general because of their *relative* inertness towards oxidation.

Such experimental thermodynamic data as are available have been obtained in a rather haphazard manner. The investigators either wanted to understand the fundamental nature of chemical bonding on the basis of systematic studies or had no reason other than that the particular metallic system suited an available apparatus. Neither of these approaches is very helpful to the applied thermochemist.

Before turning to some practical examples, there is one more fact that should be explained. The applied thermochemist is more often than not confronted with chemical reactions involving solutions of metals or non-metals in metals. In most of these cases it is more appropriate to work with partial rather than integral thermodynamic functions, i.e., heat, entropy, and Gibbs energy. The integral thermodynamic functions pertain to the formation of a compound or a solution of given composition from the component elements, e.g., $xA+yB=A_xB_y$, whereas the partial thermodynamic functions pertain to the solution of one mole of A or B in the substance A_xB_y, the latter being assumed to be so much in excess that no change in concentration takes place on assimilation of the extra mole of A or B. It is usual to denote partial thermodynamic values by bars over the respective symbols, where i denotes the solute.

Equations of the form of equation [2] apply equally to partial and integral values, i.e.,

$$\Delta G = \Delta H - T\Delta S$$

[5]

and

$$\Delta \bar{G}_i = \Delta \bar{H}_i - T\Delta \bar{S}_i$$

[6]

where equation [6] refers to the ith component.