Module III

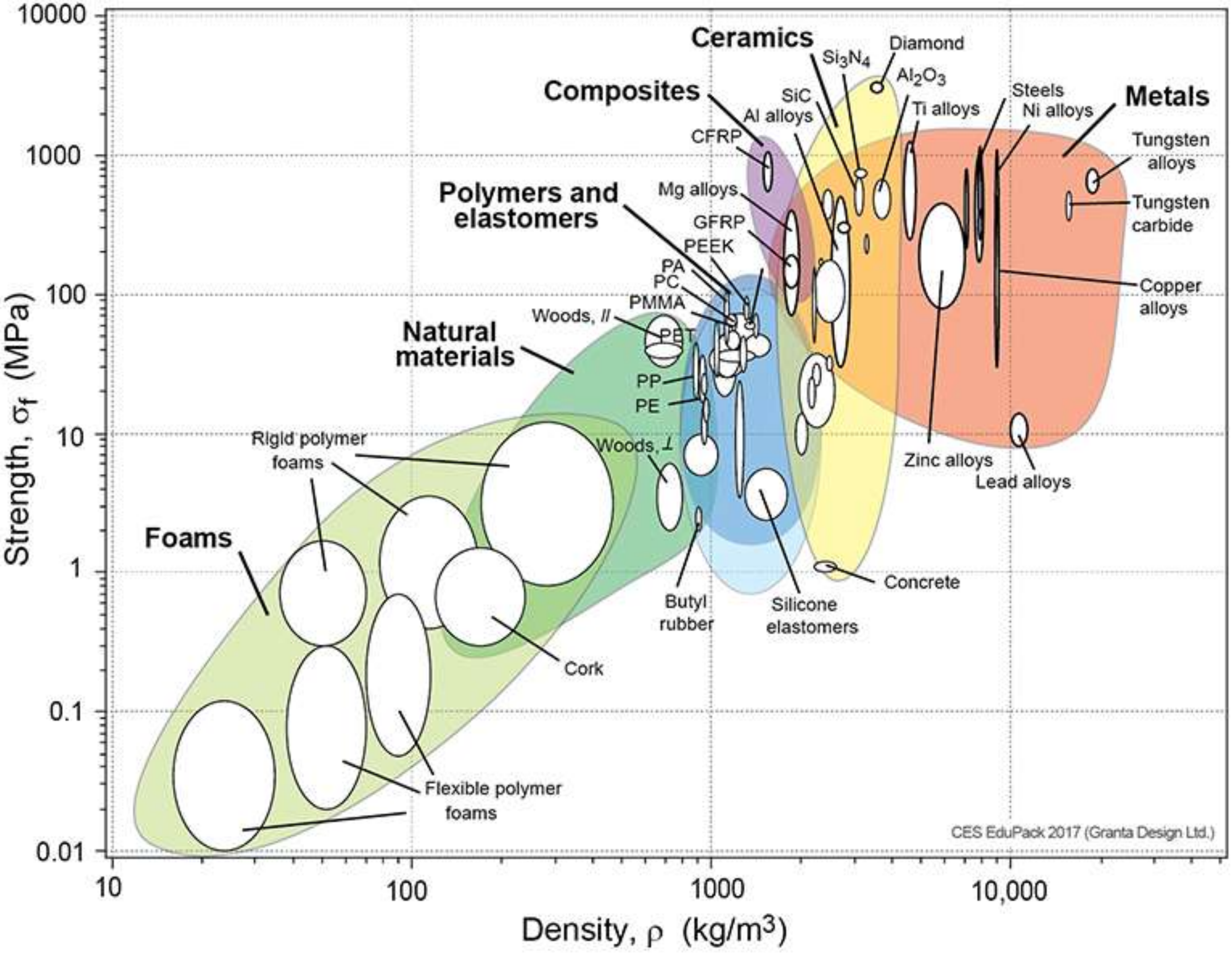
Solid solutions

Phase diagrams

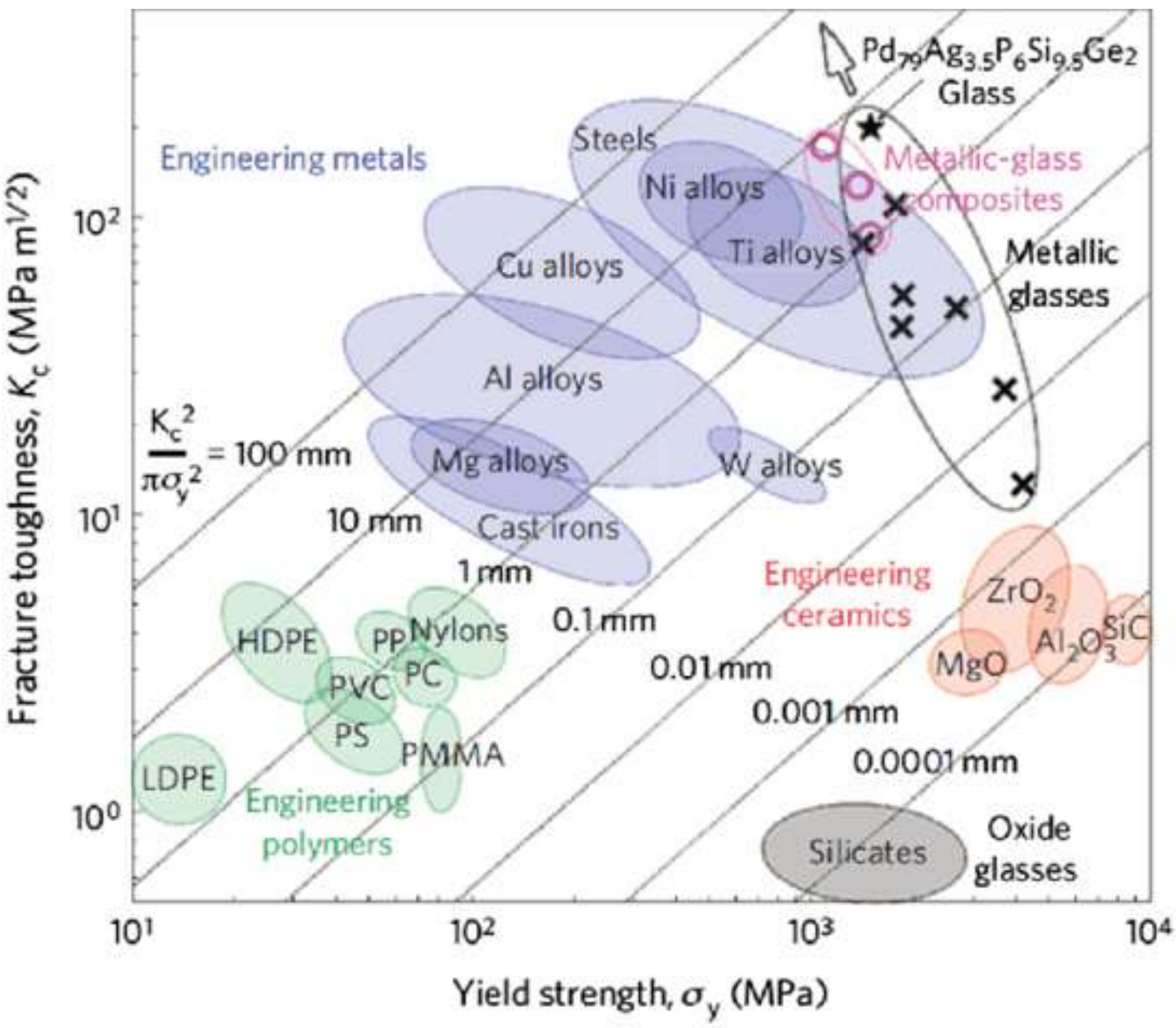
Heat Treatments

Strengthening of Materials

Michael Ashby's Diagram on material properties



CES EduPack 2017 (Granta Design Ltd.)


Pd$_{79}$Ag$_{3.5}$P$_6$Si$_{9.5}$Ge$_2$
Glass
Engineering metals
Steels
Ni alloys
Ti alloys
Cu alloys
Al alloys
Mg alloys
W alloys
Cast irons
Metallic-glass composites
Metallic glasses
$\frac{K_c^2}{\pi \sigma_y^2}$ = 100 mm
10 mm
1 mm
0.1 mm
0.01 mm
0.001 mm
0.0001 mm
Engineering ceramics
ZrO$_2$
Al$_2$O$_3$
SiC
MgO
HDPE
PP
Nylons
PC
PVC
PS
PMMA
LDPE
Engineering polymers
Silicates
Oxide glasses
Fracture toughness, K_c (MPa m$^{1/2}$)
10^2
10^1
10^0
10^1
10^2
10^3
10^4
Yield strength, σ_y (MPa)

Introduction

- Limitations of pure materials – higher cost, poor properties, lack of availability
- Examples of alloying:

  Copper added to Silver

  Zinc added to Copper
- Upon alloying it is possible to develop infinite no: of materials having varied properties
- Yield strength, Tensile strength, Hardness and Creep resistance increases
- Ductility, Electrical conductivity lowered

Solid solutions

- When two metals are melted and solidified, the resultant solid having a single crystal structure may form.
- In the unit cell both the metal atoms are present
- Such a structure in the solid state which contains two types of atoms
- Solid solutions two types:

  Substitutional solid solution

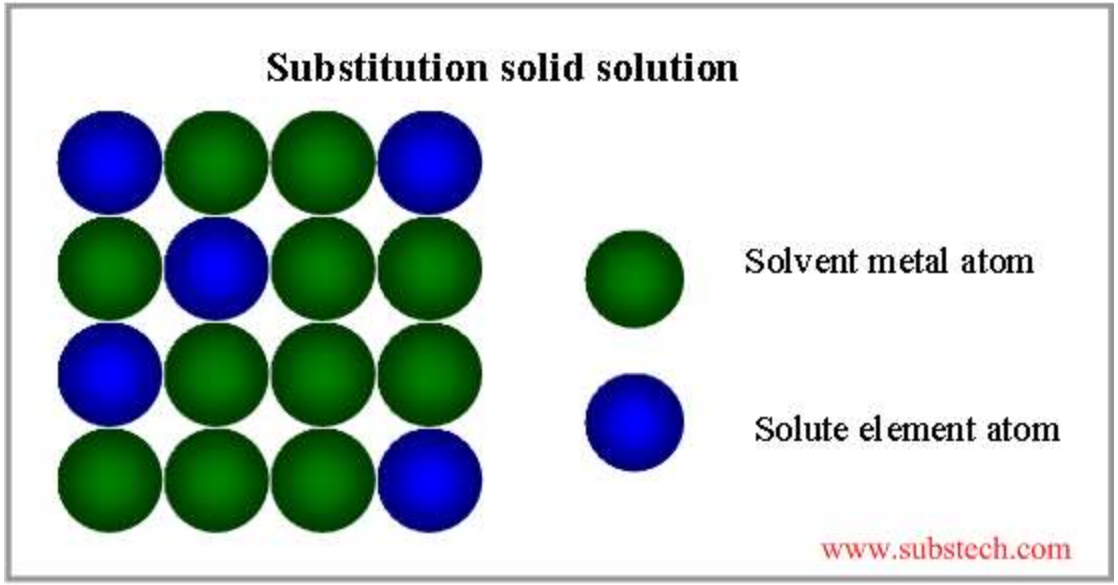
  Interstitial solid solution

Substitutional solid solutions

- Direct substitution of one type of atom for another – Substitutional solid solution
- Cu-Ni solid solution
- Disordered (random) and ordered

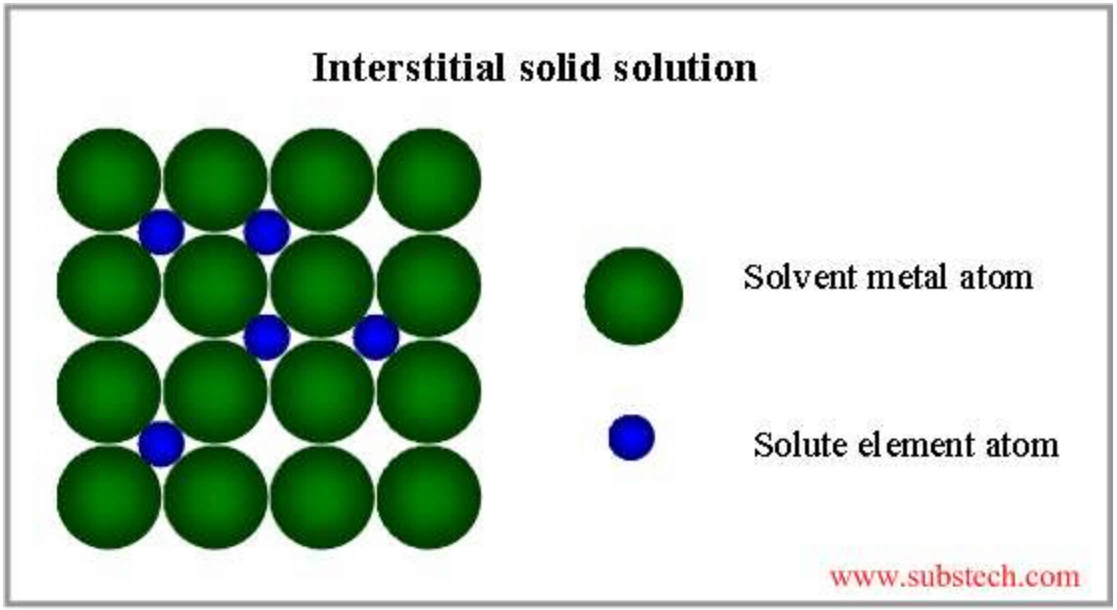
Interstitial solid solutions

- When solute atoms much smaller than solvent atoms they may occupy interstitial voids b/w solvent atoms - Interstitial solid solutions
- Carbon in iron is an example
- In some cases both are formed together – Eg: Chromium-Nickel steel



Substitution solid solution

www.substech.com



Interstitial solid solution

www.substech.com

Hume-Rothery’s Rules

- Four conditions that govern the substitutional solid solubility

1. The size difference between the solvent and solute atoms must be less than 15%
2. The crystal structure of both the metals must be the same- for complete solubility
3. The difference in electronegativity of the two metals must be small
4. The valency of the atoms must be nearly the same

Hume-Rothery’s Rules

- For an interstitial solid solution:

1. Solute atom must be smaller than the voids in the solvent lattice
2. Solute and solvent should have similar electronegativity

Alloys

- A substance that is composed of two or more elements
- The element present in largest proportion – Base metal
- All other elements – Alloying elements
- Improve physical, chemical, mechanical and electrical properties of base metal

Definitions

- System

  An alloy system is a series of possible alloys consisting of the same elements or components

- Component

  A chemical constituent (element, ion or compound) of a system which may be used to specify its composition

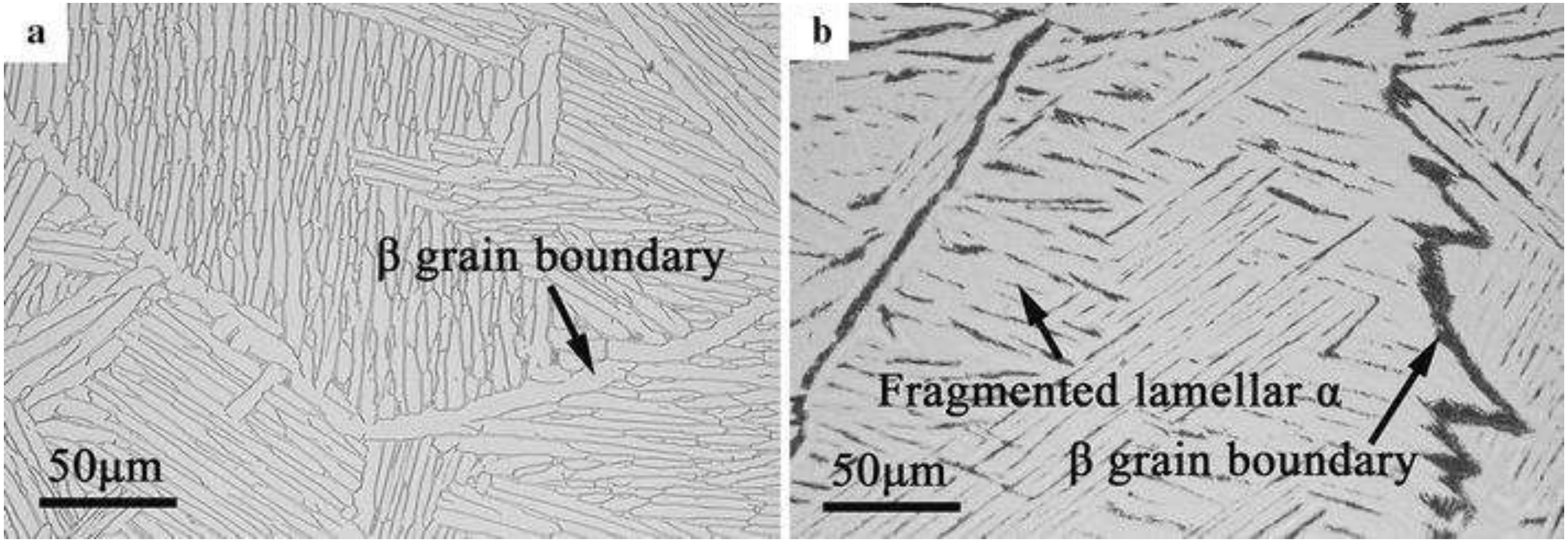
  Eg: in Brass – Copper and Zinc

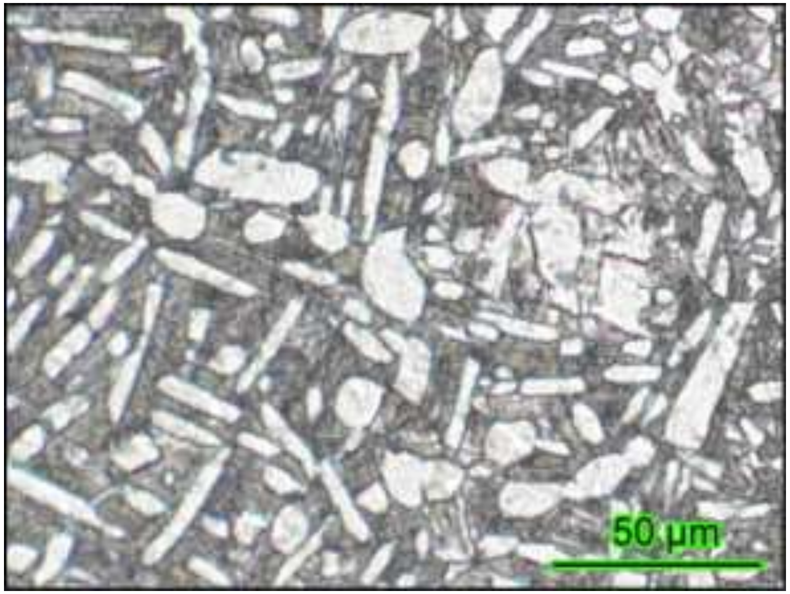
  : in ice-water-steam system - H_2O

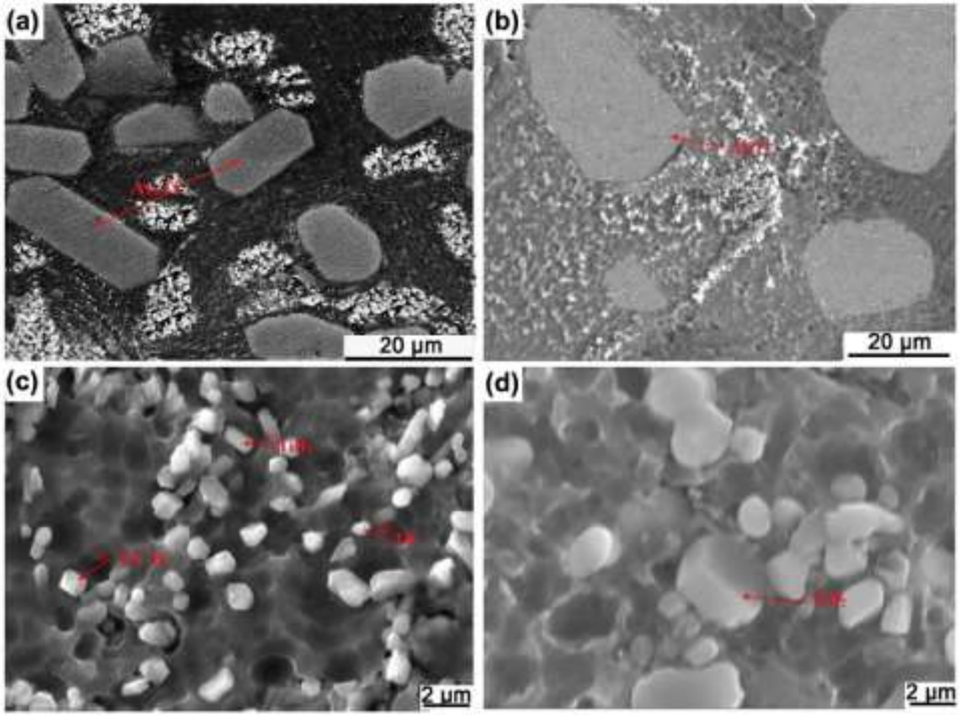
  Unary, Binary and Ternary systems

Phase

- A homogeneous portion of a system that has uniform physical and chemical characteristics
- Every pure material – a phase
- Water, ice and water vapour
- When more than one phase is present in a system each will have its own properties and a boundary separating the two will exist


a
β grain boundary
50μm
b
Fragmented lamellar α
β grain boundary
50μm


50 μm


(a)
20 μm
(b)
20 μm
(c)
2 μm
(d)
2 μm

- A mixture of different gases will be a single phase since atoms or molecules are mixed at the atomic level

- A liquid solution is also a single phase

- Liquid mixture of water and oil – separate phases

- In solid state different crystal structures form different phases

- an alloy forming solid solution constitutes a single phase

Gibb’s Phase Rule

- Establishes relationship between no: of components, no: of phases and the no: of degrees of freedom in a system
- F=C-P+2
- The degrees of freedom refers to the independent variables (like temperature, pressure or concentration) which can be changed without affecting the other variables
- Pressure is usually ignored in case of liquids and solids
- Hence F=C-P+1
- Modified form is applicable to all alloy systems involving metals

Classification of Alloys

- When two metals are melted together and solidified any of the following 3 can happen
- The alloy is formed

  - as a solid solution

  - as a mixture of separate phases

  - as an inter metallic compound

- If X and Y are the two components, a solid solution will be formed when the strength of X-Y bond is intermediate between those of X-X and Y-Y bonds.
- Here the atoms of the metals X and Y randomly occupy the lattice positions in the crystal
- Eg: Cu-Ni Alloy

- A multiphase mixture is formed when the strength of X-Y bond is weaker than X-X and Y-Y bonds.
- The alloy solidifies by separating out into two distinct phases
- One phase will be rich in X and the other rich in Y
- Eg: Sn-Pb Alloy

- An inter metallic compound is formed when the strength of X-Y bond is stronger than X-X and Y-Y bonds
- Fe_3C is an inter metallic compound formed in the Fe-C alloy system

- All the alloys doesn’t behave in any one of the above ways in all compositions
- In some alloy systems, the components are completely soluble in each other – solid solutions are formed at all compositions
- In some other alloys, components are partially soluble in solid state – here solid solutions at some compositions and phase mixtures at other compositions
- When components are completely insoluble in solid state, phase mixtures at all compositions

- In some alloy systems intermetallic compounds are also formed corresponding to certain range of compositions
- Eg: in Fe-C alloy system

  very low Carbon contents – Solid solution increased Carbon content -phase mixtures

  higher levels of Carbon – intermetallic compound

Phase diagrams

- It is a diagram or map representing the relationships between phases in equilibrium in a system as a function of any two among temperature, pressure and composition
- Also called equilibrium diagrams or constitutional diagrams

Types of phase diagrams

- 3 externally controllable parameters – Temperature, pressure and composition
- When composition is held constant, pressure and temperature are the variables – a pure component system – UNARY PHASE DIAGRAM
- It is represented as a 2D plot of Pressure and Temperature

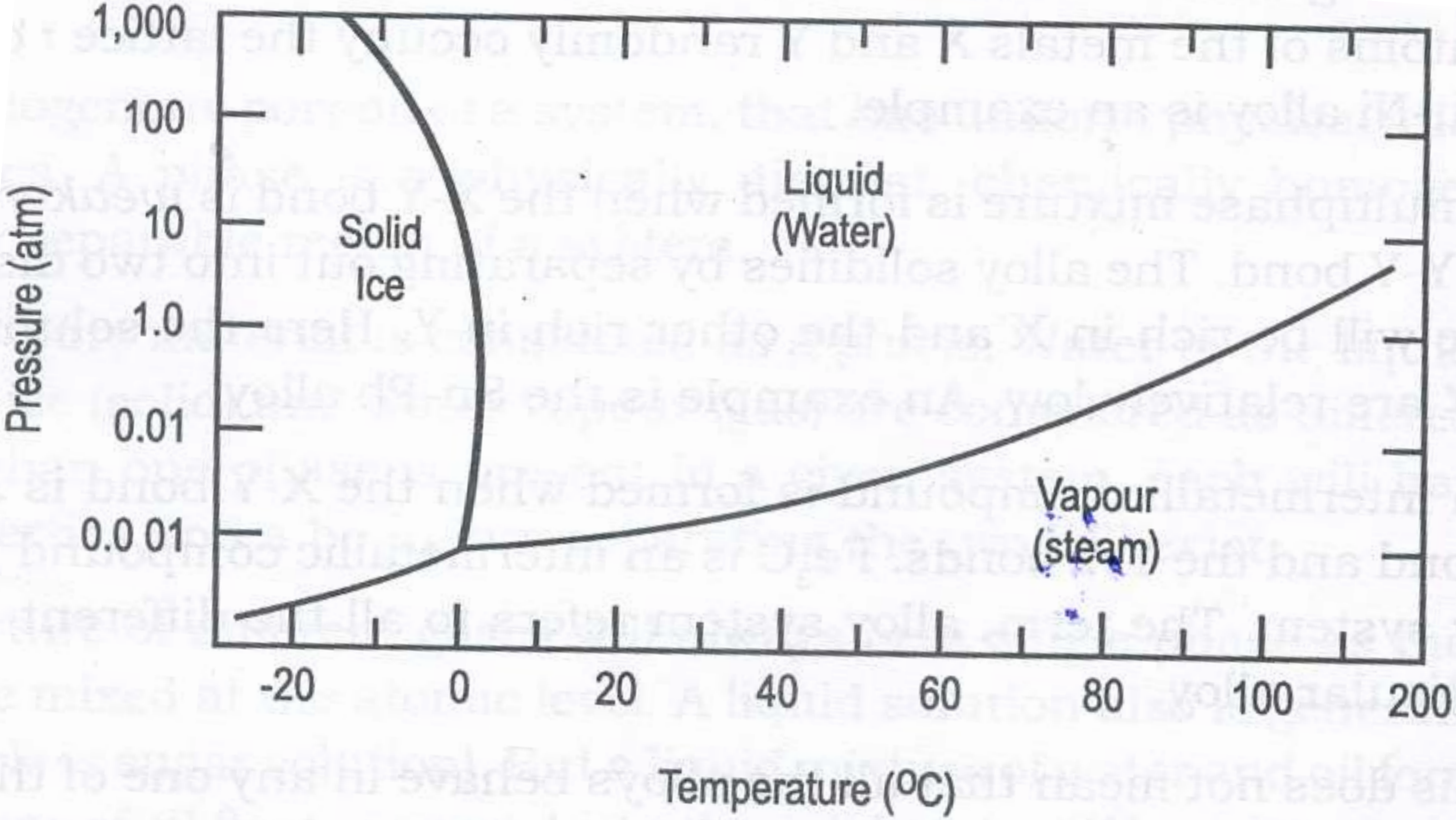


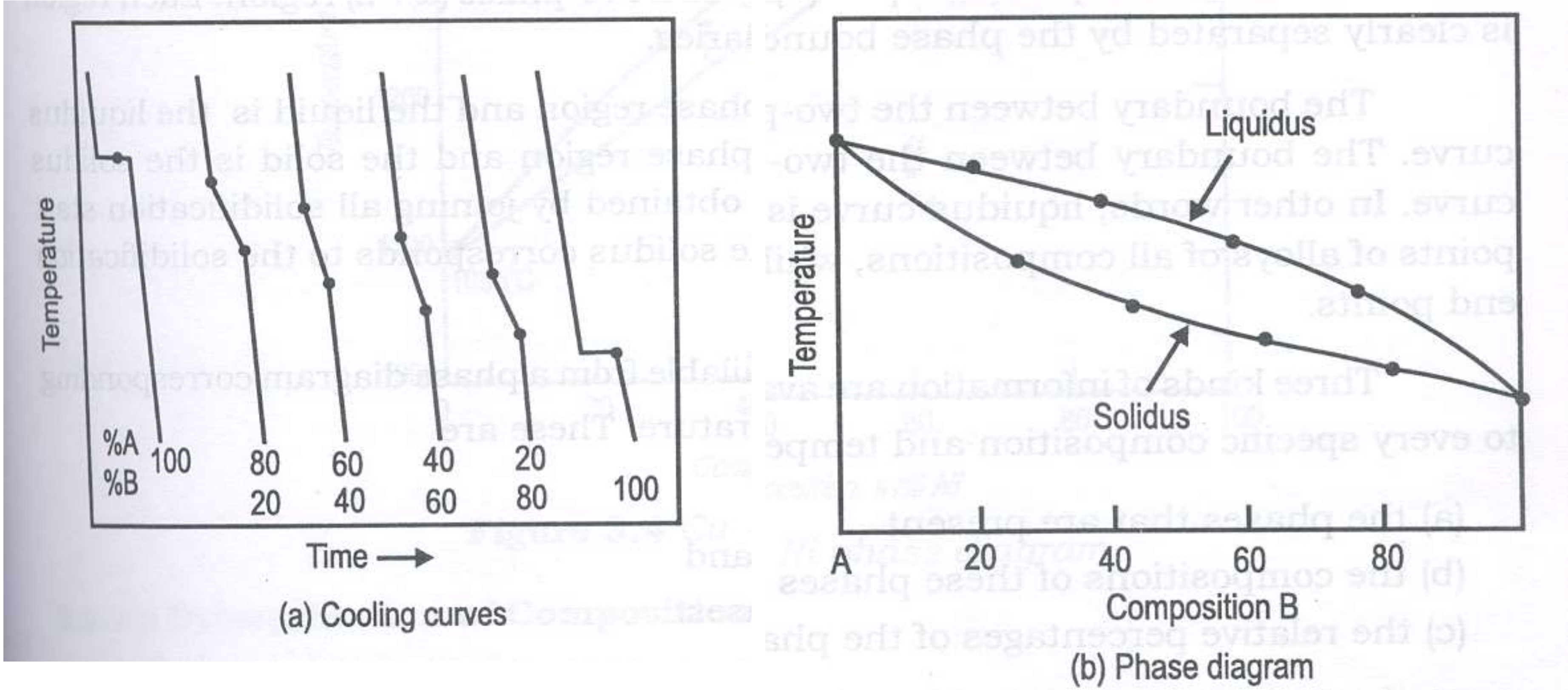
Figure. 3.2 *Unary phase diagram for water*

- If Pressure is held constant with T and Composition as variables – Binary phase diagrams with two components
- Show relationships b/w T, Composition and quantities of phases at equilibrium
- Practically most of the alloys contain more than two components
- The phase structure of a 3 component system can be represented as a ternary phase diagram

Binary Phase Diagrams

- Usually determined at atmospheric pressure – hence composition and temperature are the independent variables
- Composition along X axis, Temperature along Y axis
- The composition is represented as weight%

Construction



(a) Cooling curves

(b) Phase diagram

Classification of Binary systems

- When 2 components are mixed, they could be

1. Completely soluble in liquid and solid states

   isomorphous system

2. Completely insoluble in the solid state

   simple eutectic system

3. Partially soluble in the solid state

   eutectic system

Isomorphous system

- The components are completely soluble in the liquid and solid states
- Also known as an alloy system of solid solution type
- Examples: Cu-Ni, Ge-Si, Ag-Cu, …..
- Cu-Ni composition

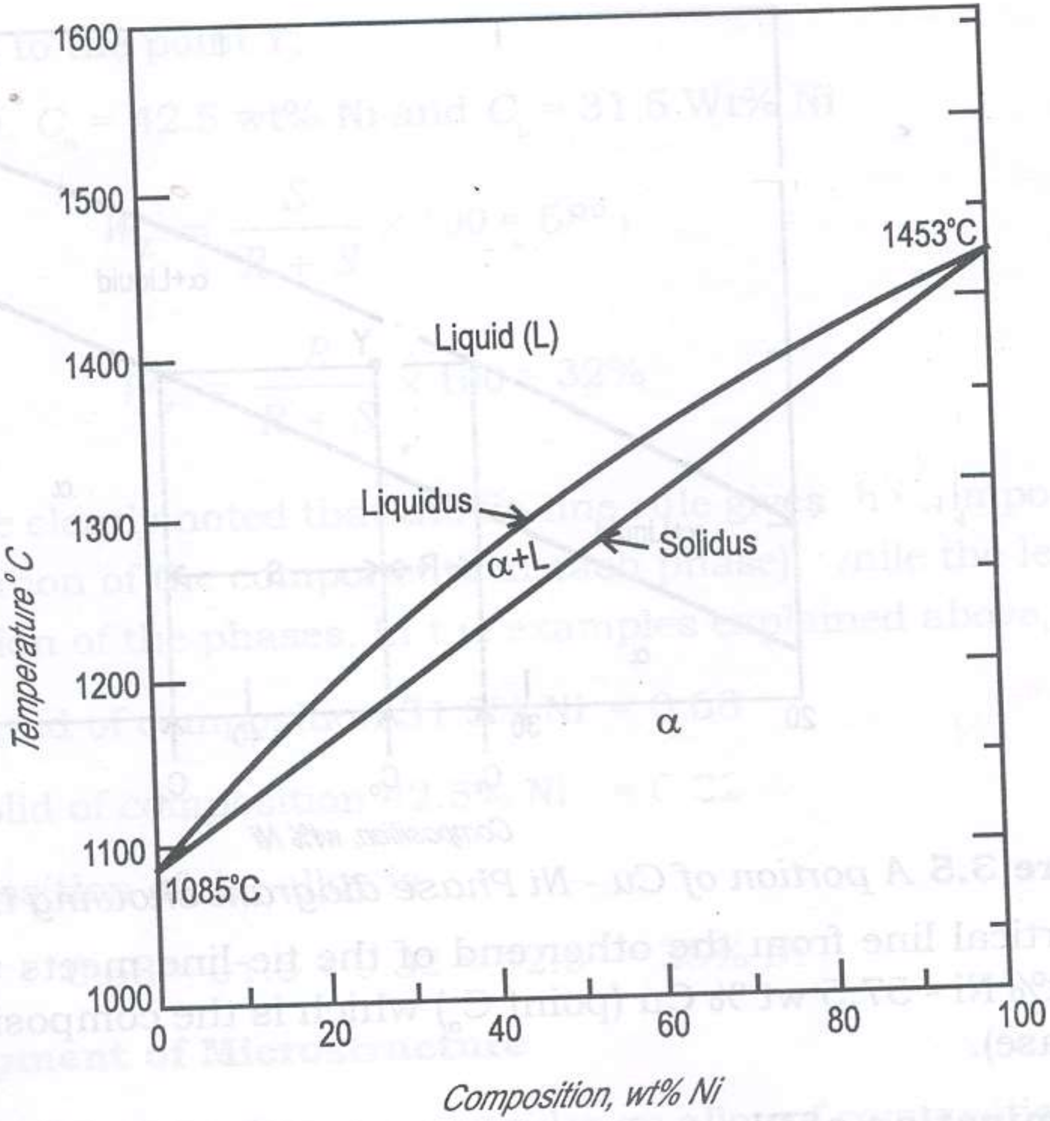


Figure 3.4 *Cu - Ni phase diagram*

- 3 different phase regions exist,

  liquid (L), alpha (α), and a two phase (α+L) region
- Liquidus curve and Solidus curve
- 3 kinds of information available from a phase diagram

  a) the phases that are present

  b) the compositions of these phases

  c) the relative percentages of these phases

Phases present

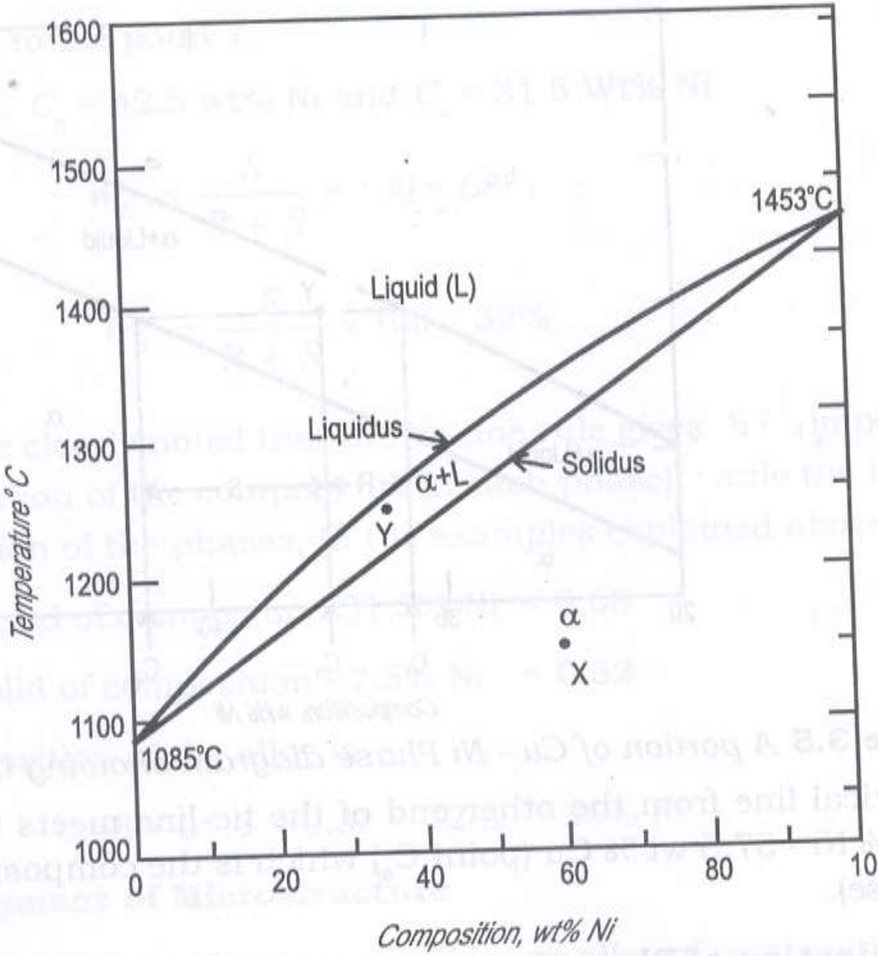
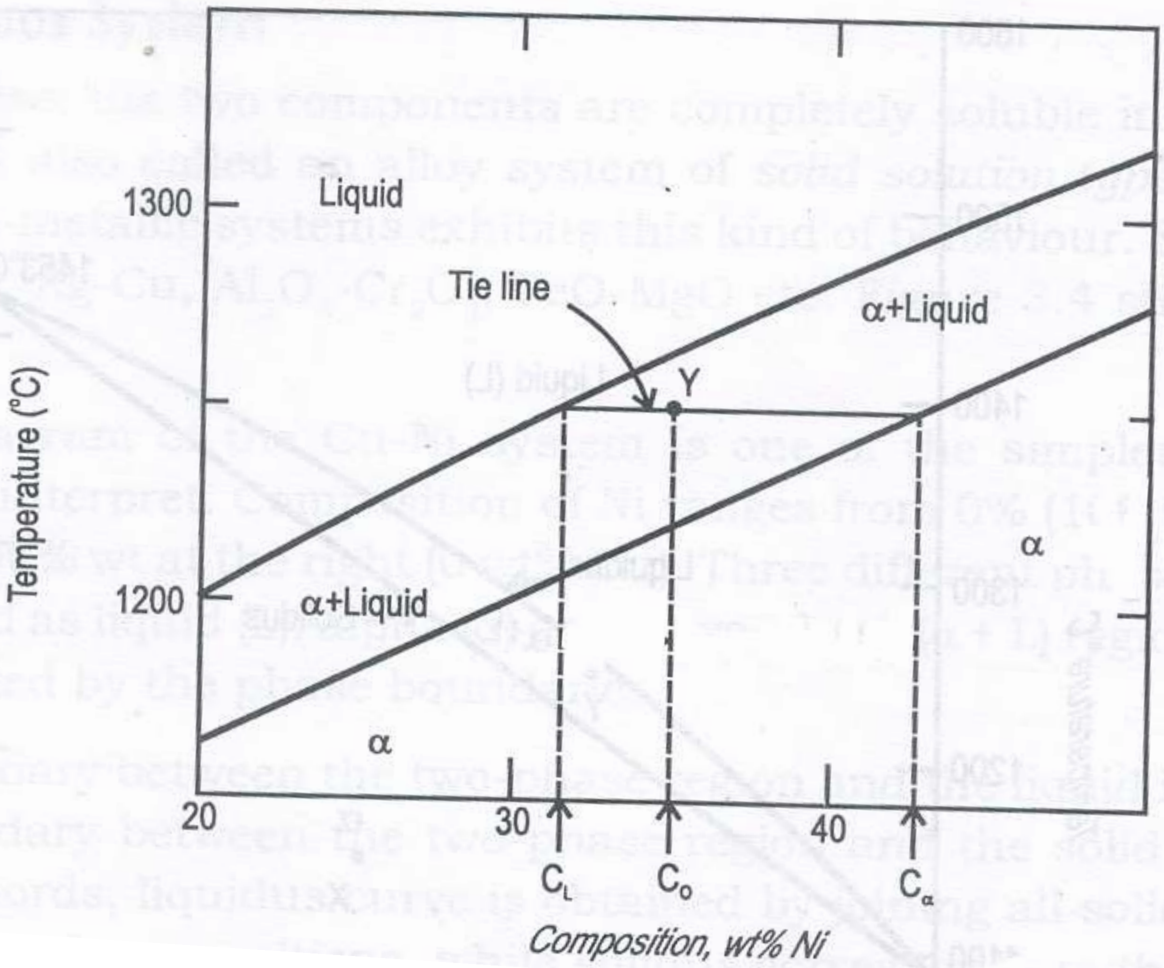
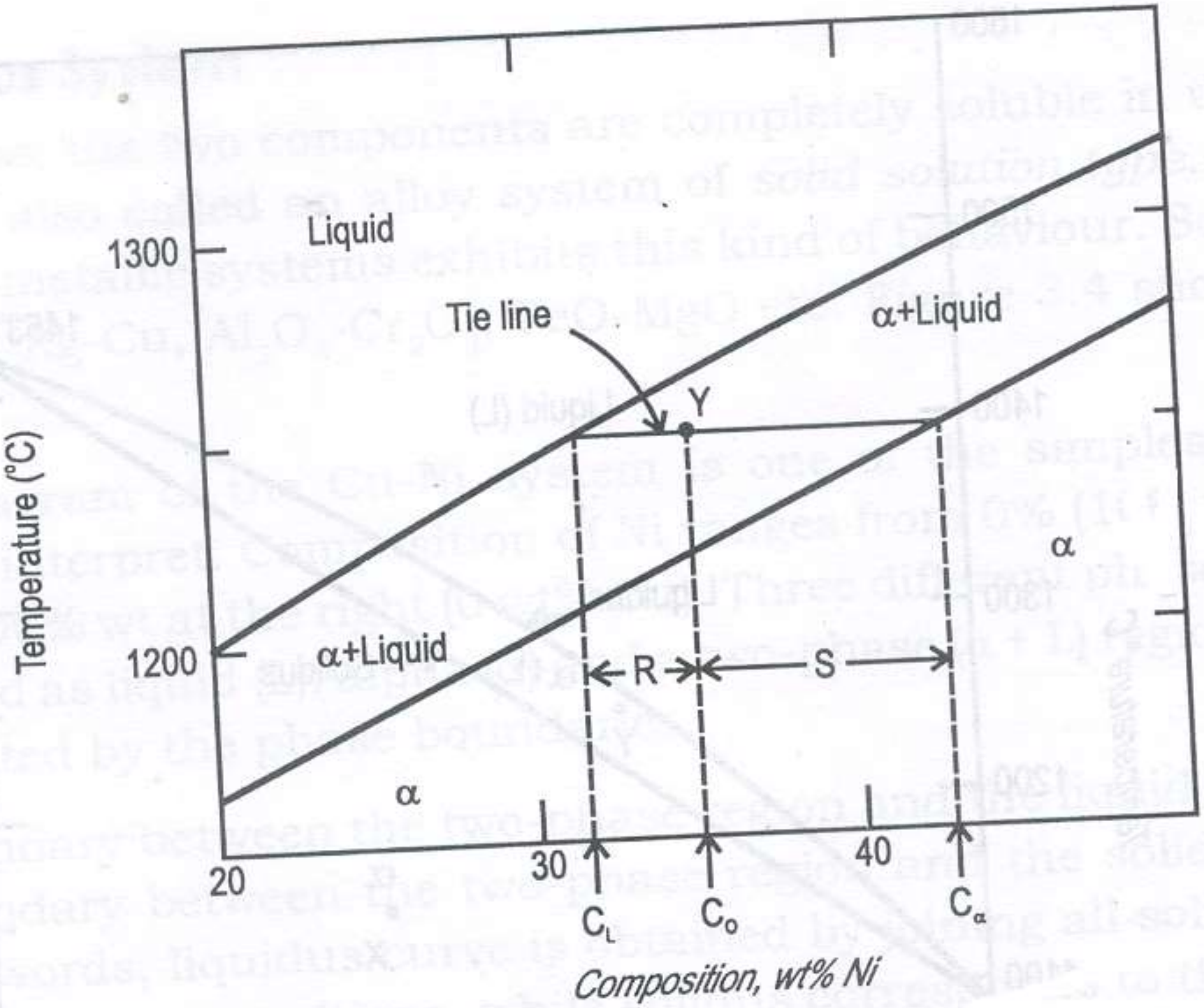


Figure 3.4 *Cu - Ni phase diagram*

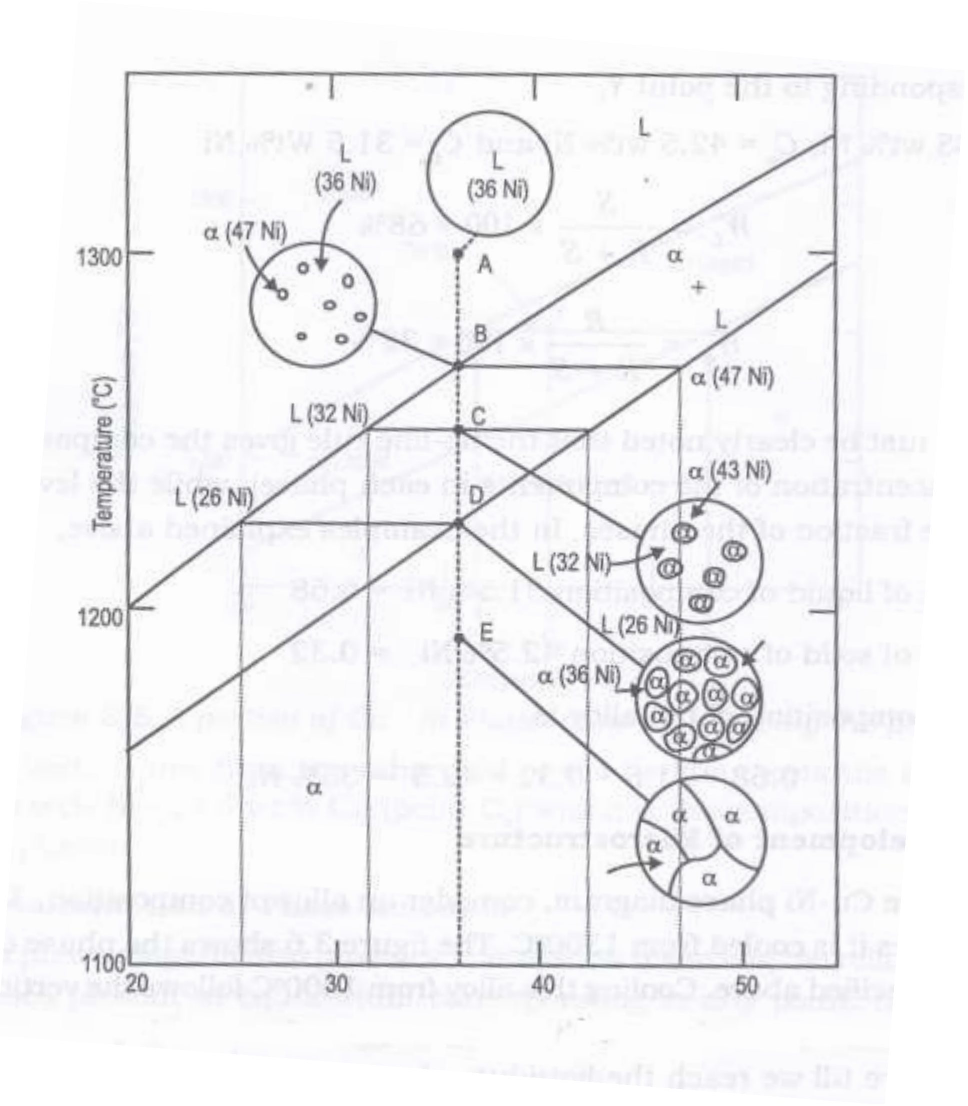
Determination of composition



Determination of phase amounts



Development of Microstructure



Coring

- As an alloy of isomorphous type solidifies, the centre of a grain will be rich in the component having higher melting point.
- The concentration of the element having high melting point increases with position from centre to the grain boundary. This is called coring
- Can be eliminated by heat treatment (homogenisation) below solidus temperature

Binary systems

i) Simple eutectic system

ii) Eutectic system

Alloy system with limited solubility at solid state

- Eutectic Phase Diagram
- Copper-Silver system
- As the two components are mutually soluble to some extent in the solid state solid solutions are formed near both ends of the phase diagram – **Terminal solid solutions**

Alloy system with limited solubility at solid state

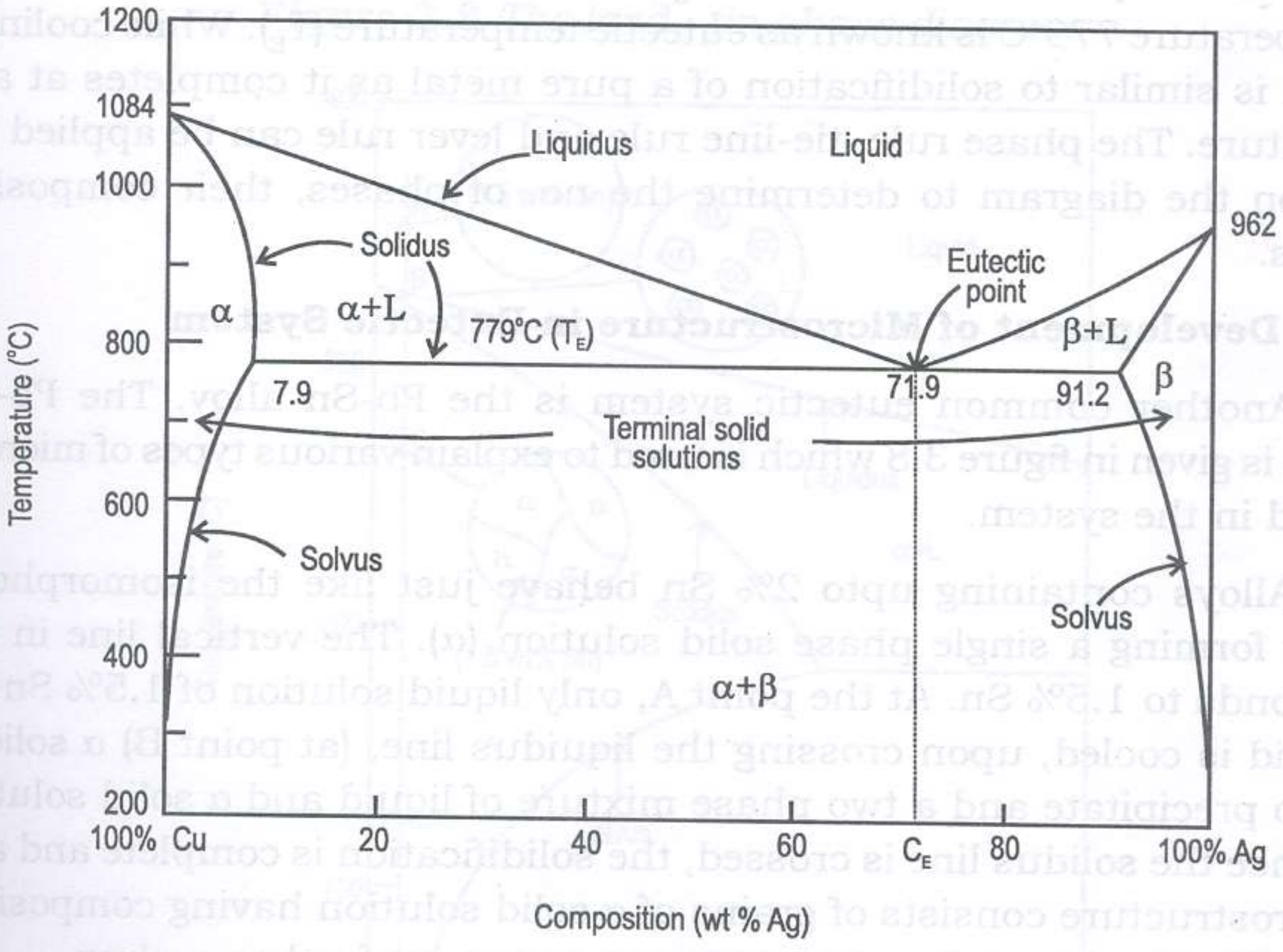


Figure 3.7 *The Copper Silver phase diagram.*

Development of microstructure in Eutectic system

- Lead-Tin phase diagram

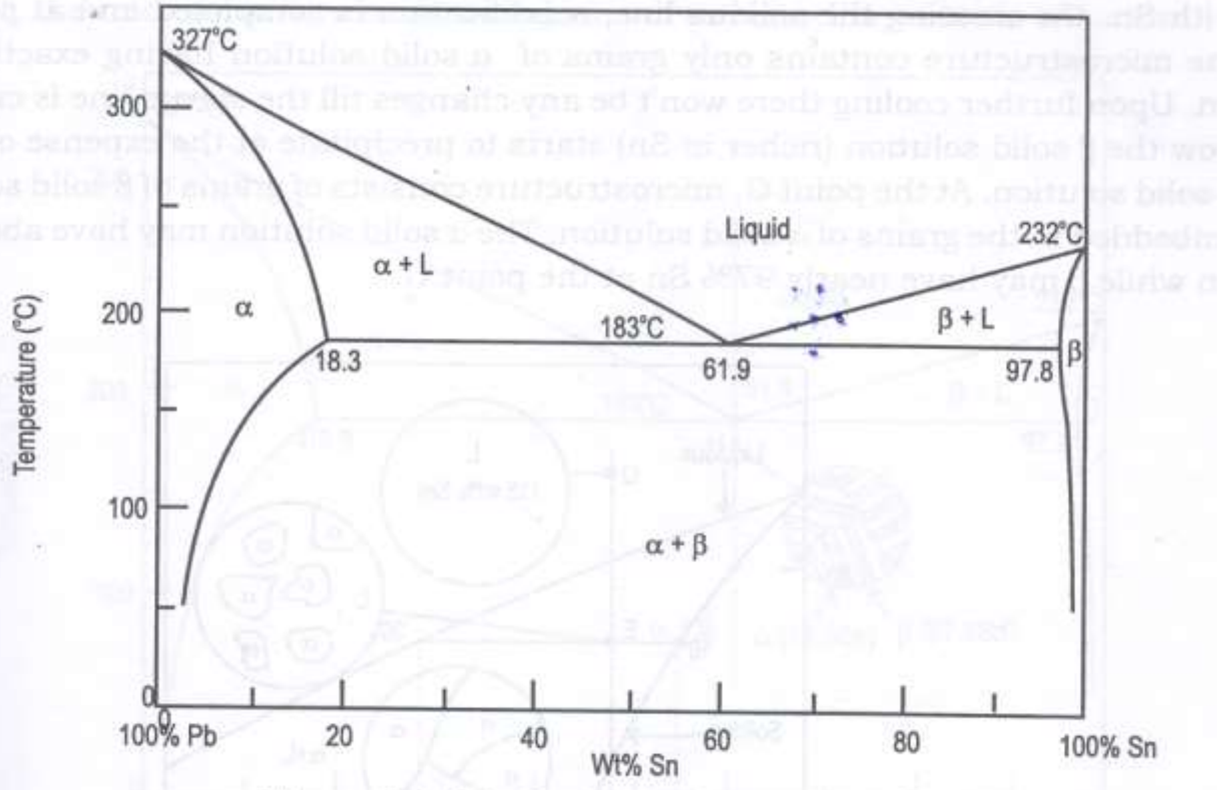
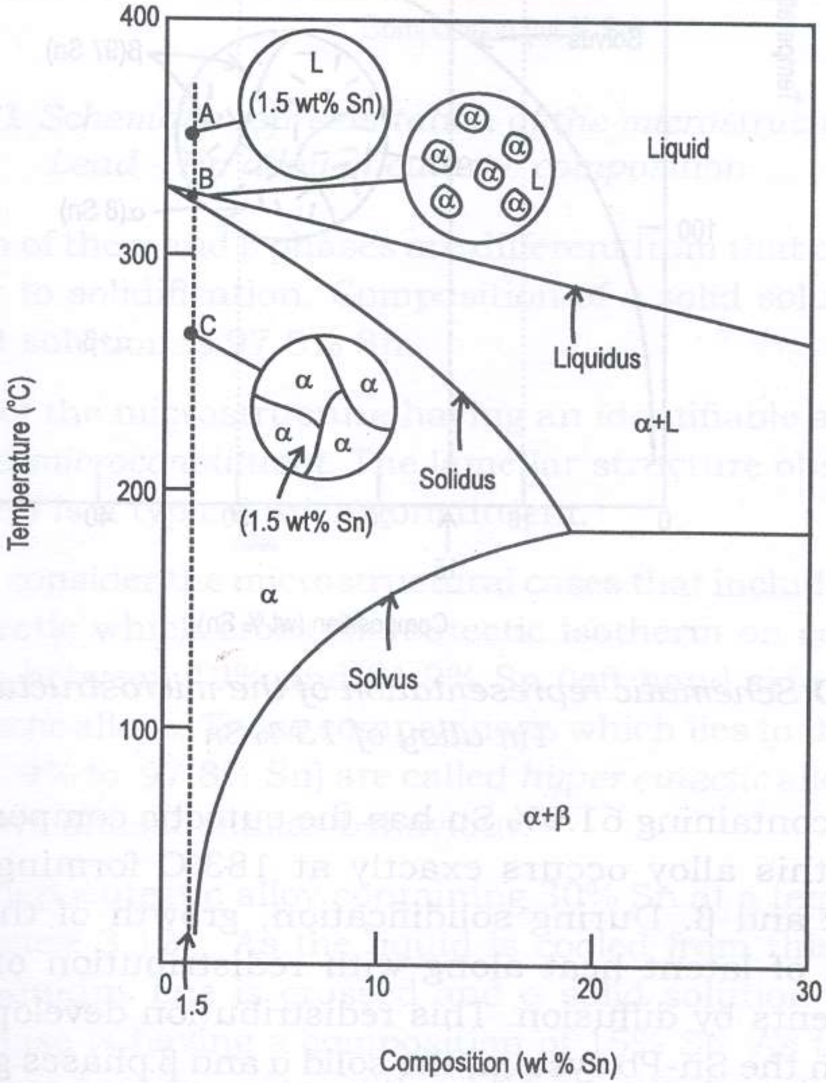


Figure 3.8 *The lead - tin phase diagram.*



Schematic representation of the microstructures for a Lead Tin alloy of 1.5 % Sn

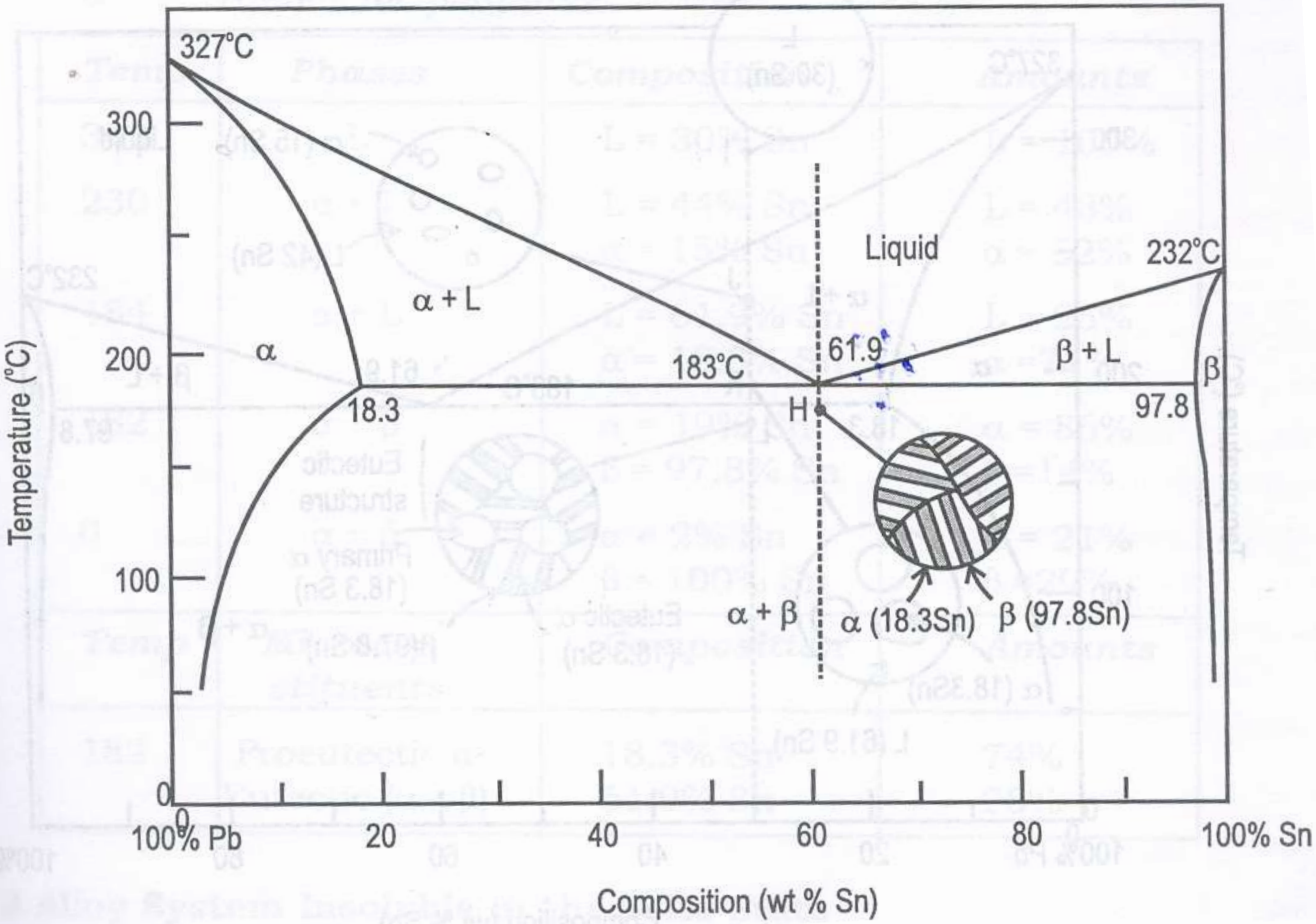
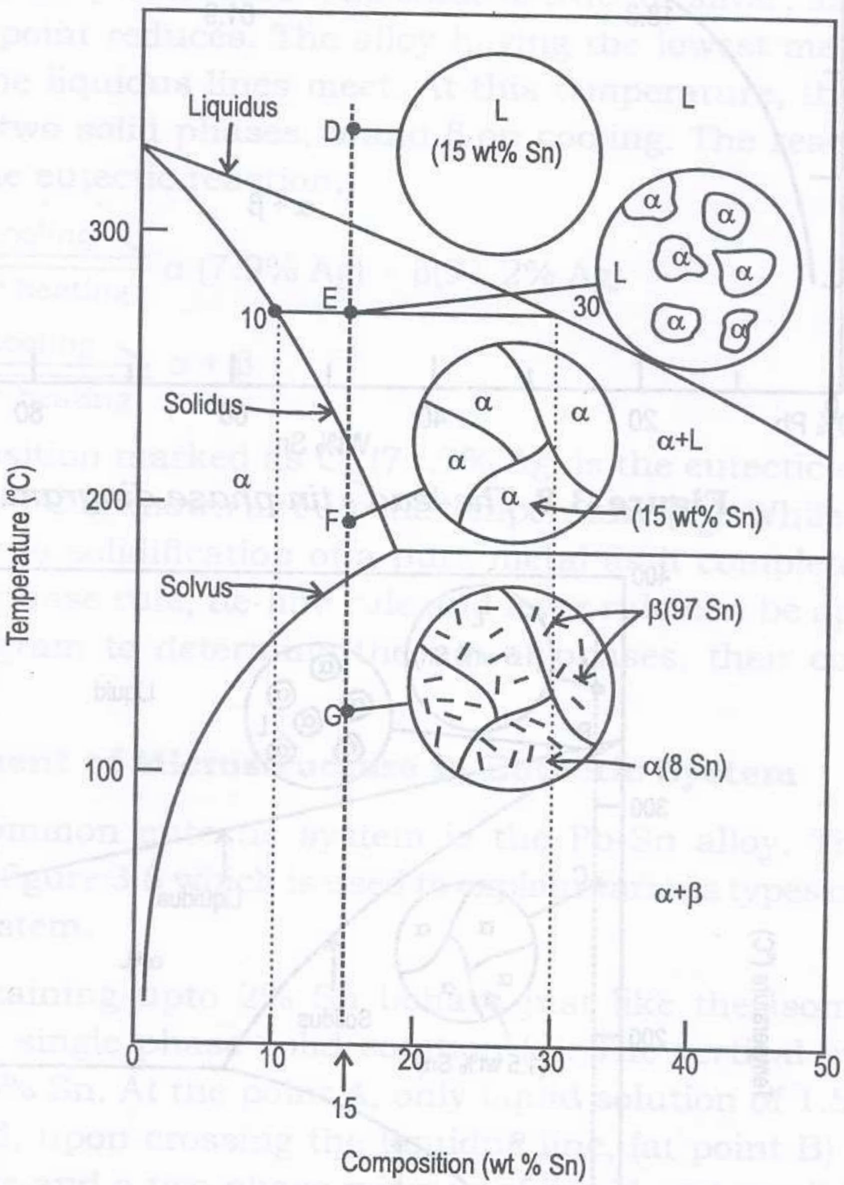
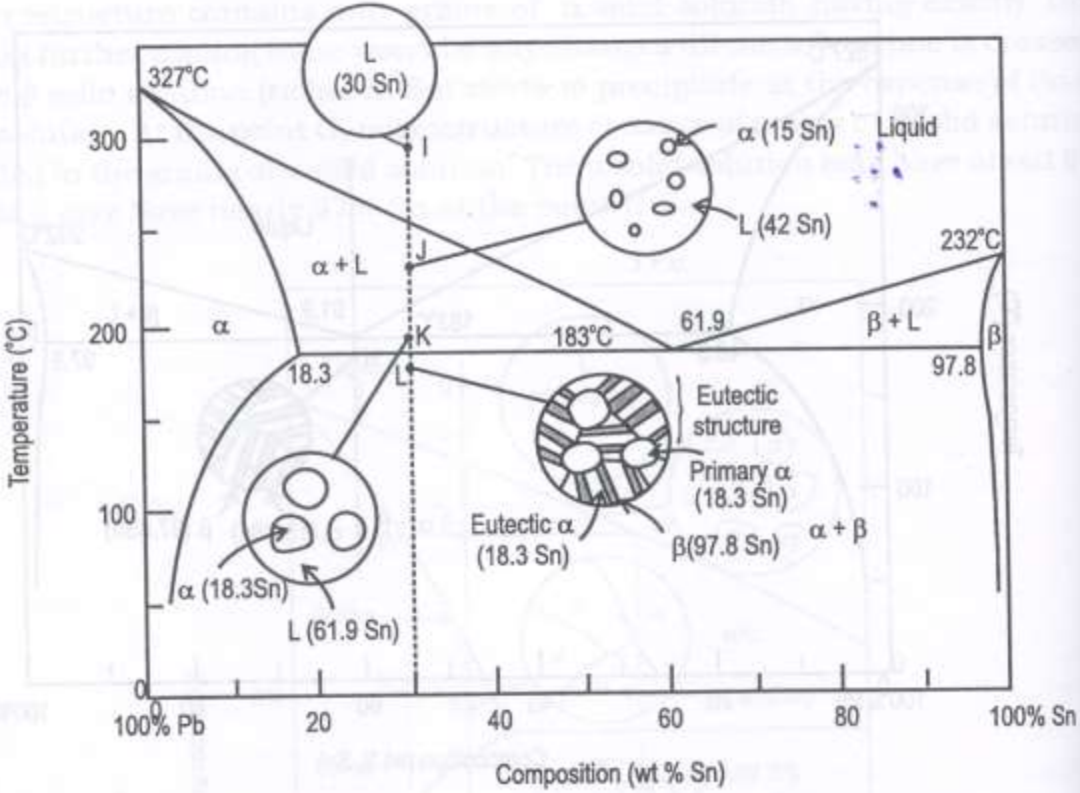


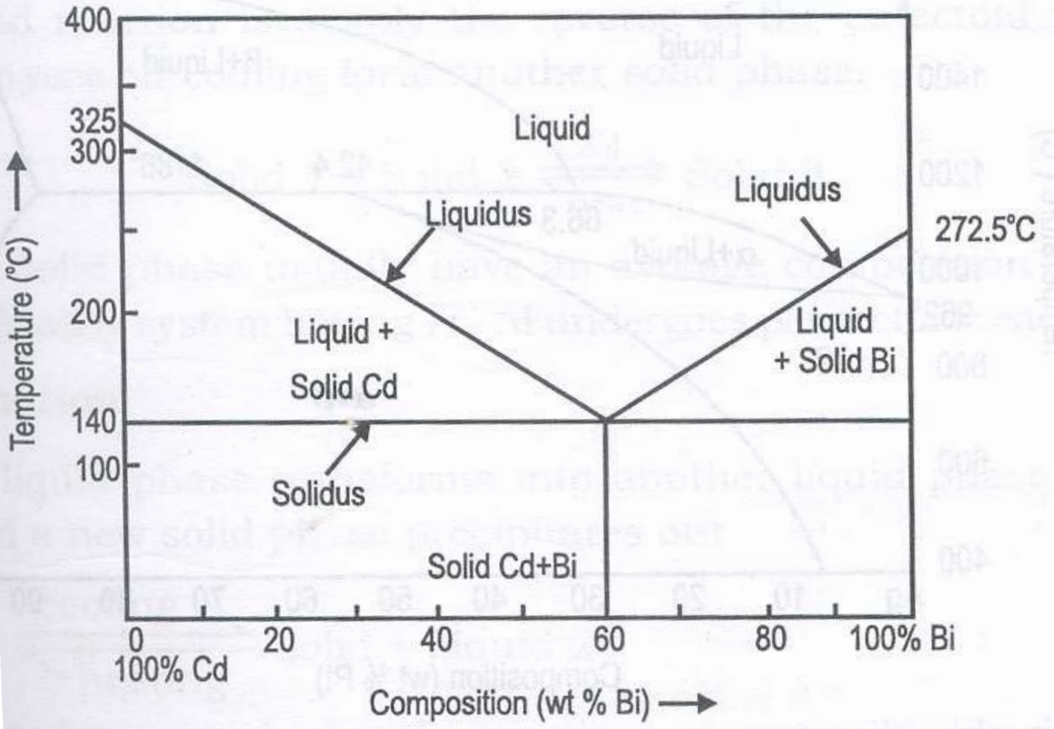
Figure 3.11 *Schematic representation of the microstructures for a Lead - Tin alloy of eutectic composition*



re 3.10 *Schematic representation of the microstructures for a Le*
Tin alloy of 15 % Sn


L
(30 Sn)
327°C
300
I
α (15 Sn)
Liquid
L (42 Sn)
232°C
J
α + L
200
α
K
183°C
61.9
β + L
β
18.3
L
97.8
Eutectic
structure
Primary α
(18.3 Sn)
100
Eutectic α
(18.3 Sn)
β(97.8 Sn)
α + β
α (18.3Sn)
L (61.9 Sn)
0
100% Pb
20
40
60
80
100% Sn
Temperature (°C)
Composition (wt % Sn)

Alloy system insoluble in the solid state (simple eutectic type)



3.13 *Equilibrium diagram of Cadmium - Bismuth system*

Invariant reactions

- Three phase reactions
- Observed along horizontal lines (fixed temp)
- Degrees of freedom – Zero (invariant)
- Eutectic, Eutectoid, Peritectic, Peritectoid, Monotectic

Peritectic reaction

- Occurs when a liquid and a solid react and form a new solid
- Liquid+solid 1 $\xrightleftharpoons[\text{Heat}]{\text{cool}}$ solid 2

- Ag-Pt, Fe-Ni, Fe-C
- Melting points of the components are vastly different

Ag-Pt phase diagram

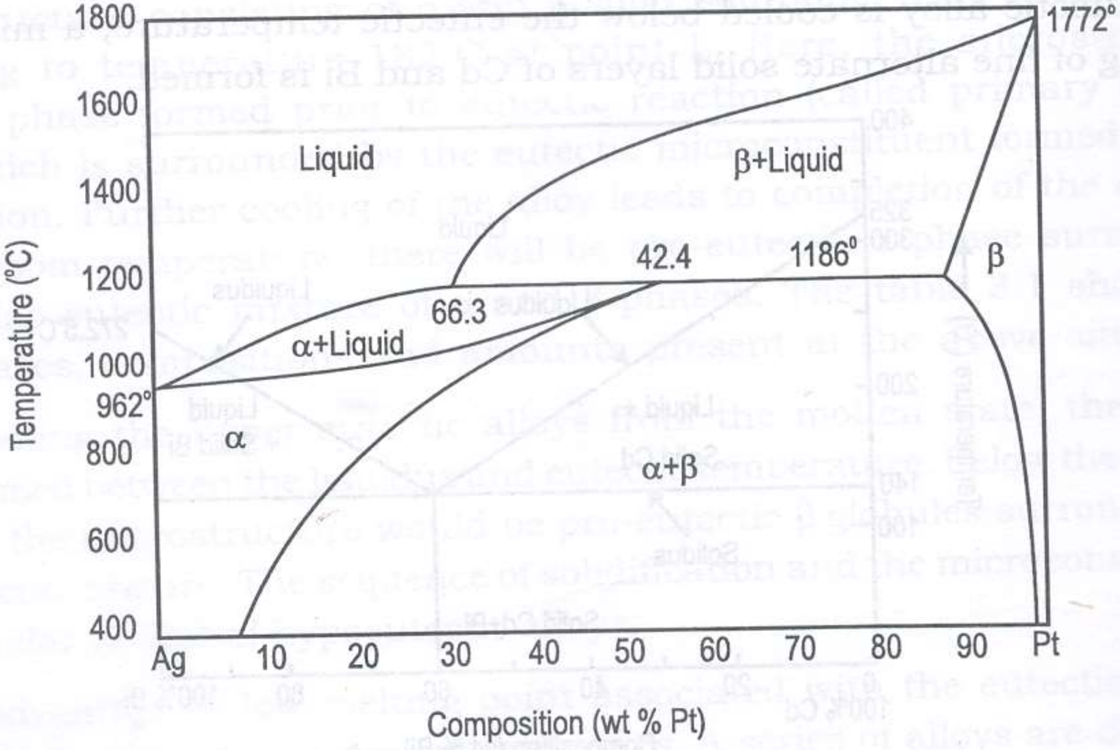


Figure 3.14 *Equilibrium diagram of Ag - Pt alloy*

Eutectoid reaction

- Transformation of a solid phase on cooling to two other solid phases of different compositions
- solid 1 $\xrightleftharpoons[\text{Heat}]{\text{cool}}$ solid 2+solid 3
- Fe-c, Cu-Zn, Al-Cu
- In Fe-C system at 723˚C and 0.77% C

  γ-Austenite $\xrightleftharpoons[\text{Heat}]{\text{cool}}$ α-Ferrite+ Cementite

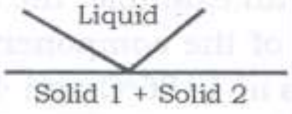
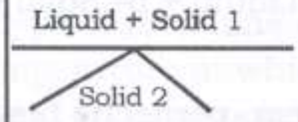
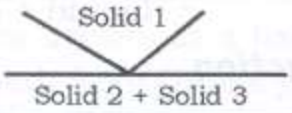
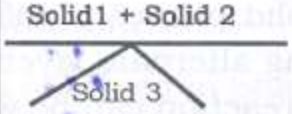
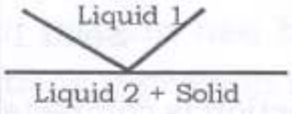
Peritectoid reaction

- The reverse of Eutectoid reaction
- Two different solid phases on cooling forms another solid phase
- Solid 1+ solid2 $\xrightleftharpoons[\text{Heat}]{\text{cool}}$ solid 3
- Ag-Al system having 7% Al at 450° C

Monotectic reaction

- A liquid phase transforms in to another liquid phase of a different composition and a new solid phase precipitates out
- Liquid1 $\underset{\text{Heat}}{\overset{\text{cool}}{\rightleftharpoons}}$ solid + Liquid2
- Two liquid phases are immiscible

Table 3.2 *Invariant Reactions*

Reaction	Characteristics	Schematic Representation	Examples
Eutectic	$\text{Liquid} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \text{Solid 1} + \text{Solid 2}$		Pb-Sn, Ag-Cu Pb-Sb
Peritectic	$\text{Liquid} + \text{Solid 1} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \text{Solid 2}$		Ag-Pt, Fe-C, Fe-Ni, Cu-Zn
Eutectoid	$\text{Solid 1} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \text{Solid 2} + \text{Solid 3}$		Fe-C, Cu-Zn Pd-Ti, Al-Cu
Peritectoid	$\text{Solid 1} + \text{Solid 2} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \text{Solid 3}$		Ag-Al, Al-Cu
Monotectic	$\text{Liquid1} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \text{Solid} + \text{Liquid 2}$		Cu-Pb

Allotropic forms of Iron

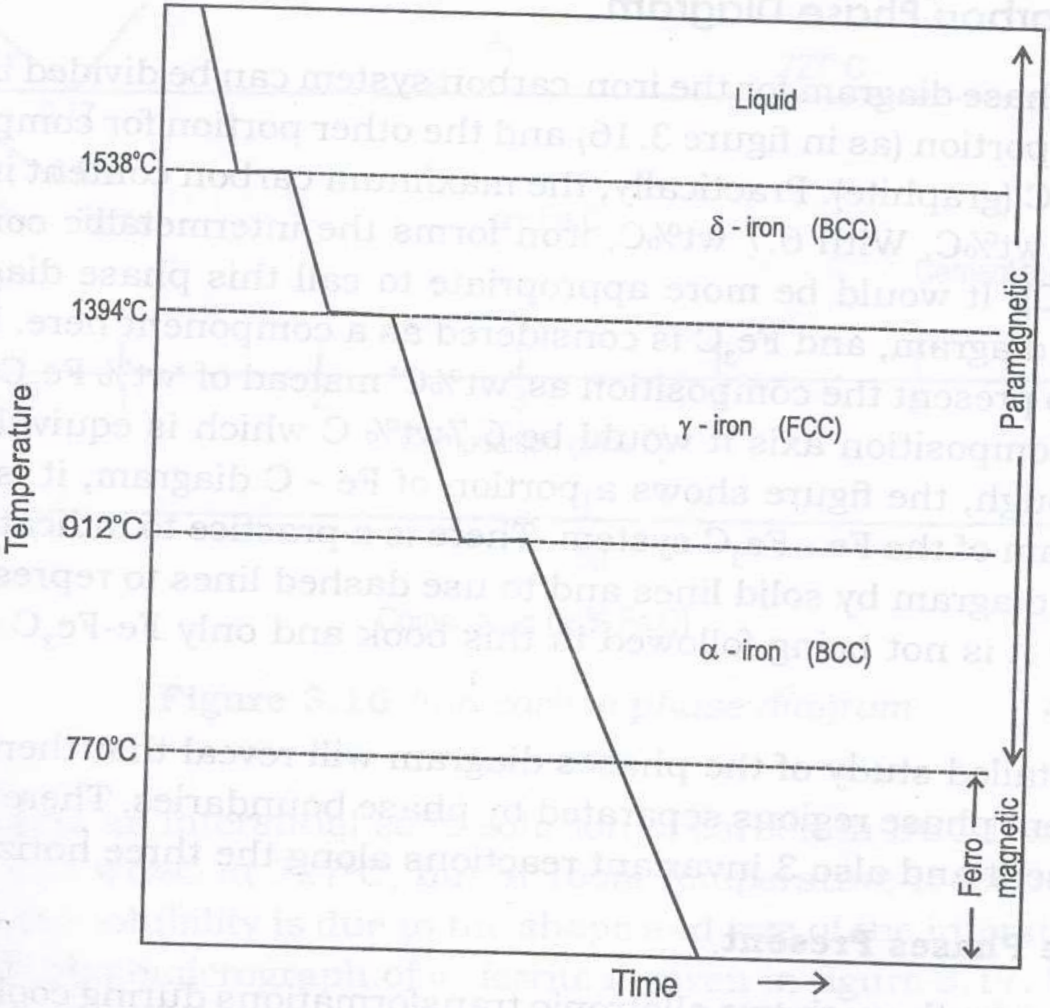


Figure 3.15 *Allotropes of iron*

Iron-Carbon alloy system

- Most important binary alloy system
- Steel and cast iron are alloys of Fe and C
- Alloys having Carbon content up to 2.14% are known as steel
- Steels are mostly solid solutions of Fe & C
- Carbon content more than 2.14% - **Cast Iron**
- In CI most of the C exists as the intermetallic compound (Fe_3C)

Iron-Carbon phase diagram

- Two parts
  - → iron rich portion - upto 6.7wt%C
  - → 6.7 to 100% C
- The max C content in Fe-C alloy is 6.7%

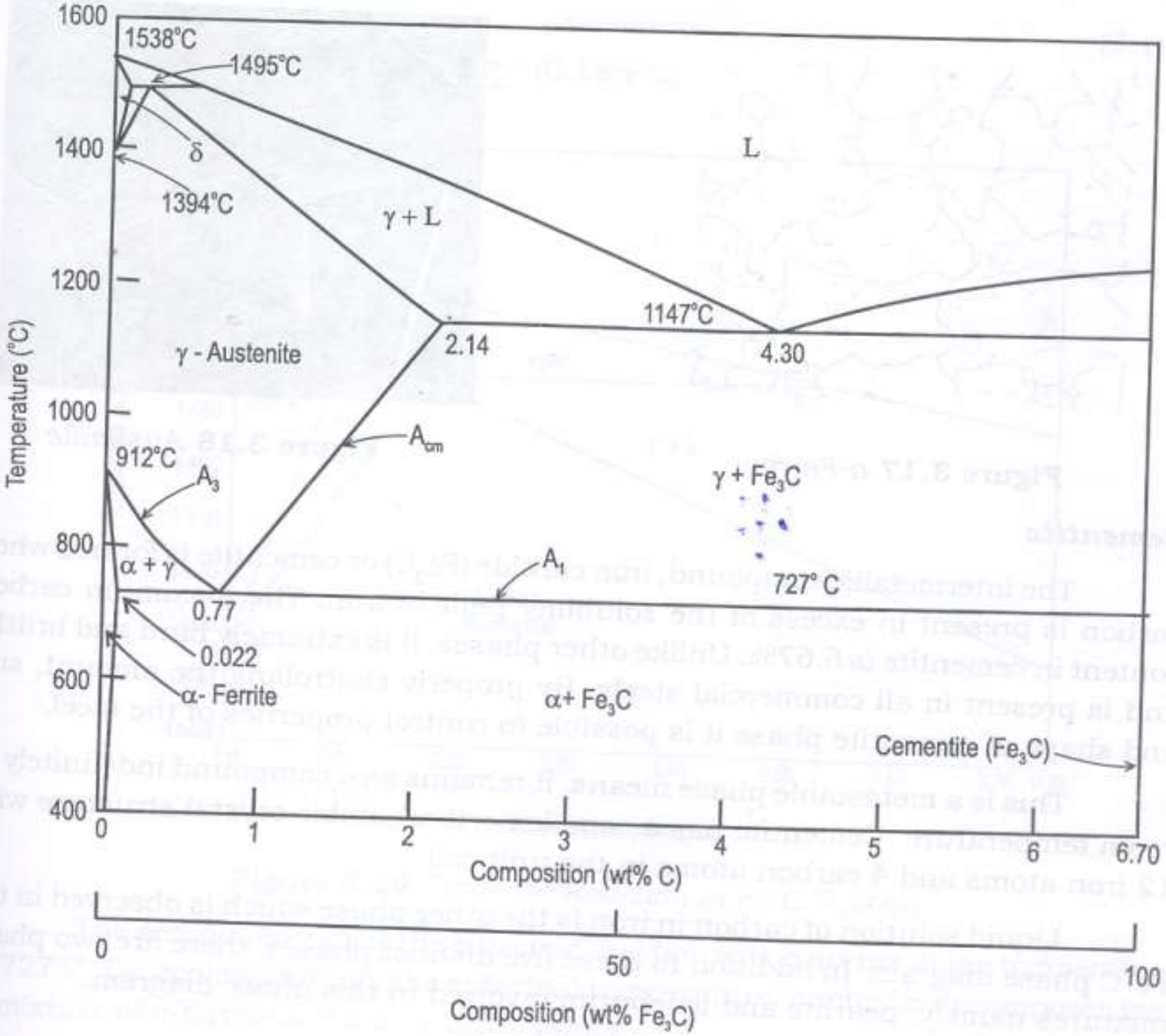
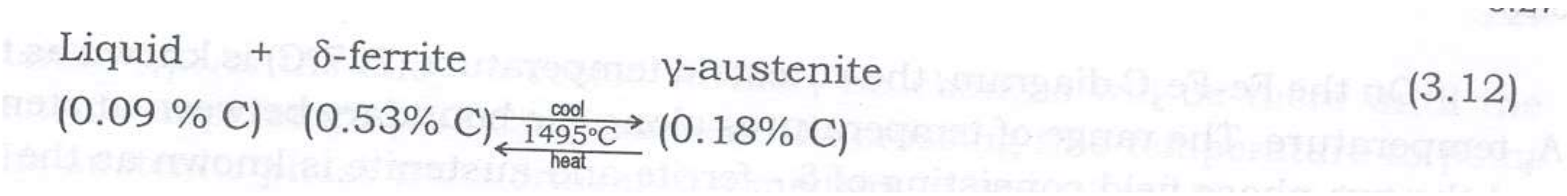


Figure 3.16 *Iron carbon phase diagram*

α-Ferrite

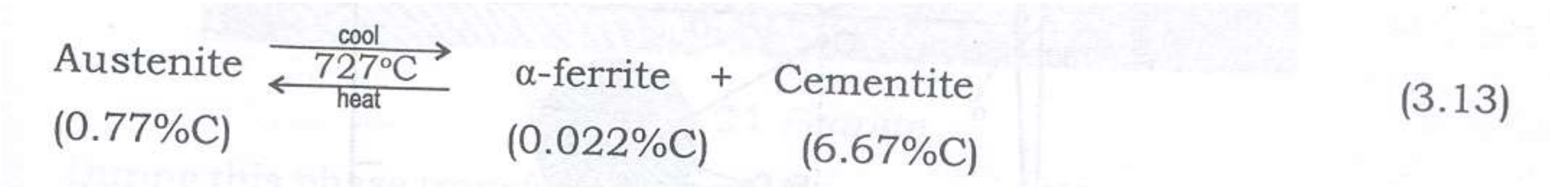
Invariant reactions

- Peritectic



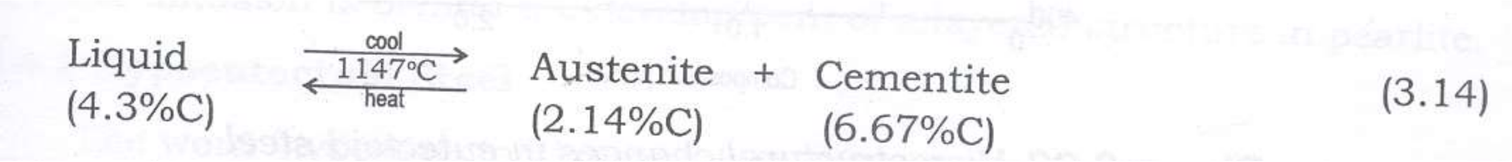
$$\underset{(0.09\ \%\ \text{C})}{\text{Liquid}} + \underset{(0.53\%\ \text{C})}{\delta\text{-ferrite}} \underset{\text{heat}}{\overset{\text{cool}}{\underset{1495^{\circ}\text{C}}{\rightleftarrows}}} \underset{(0.18\%\ \text{C})}{\gamma\text{-austenite}} \tag{3.12}$$

- Eutectoid



$$\underset{(0.77\%\text{C})}{\text{Austenite}} \underset{\text{heat}}{\overset{\text{cool}}{\underset{727^{\circ}\text{C}}{\rightleftarrows}}} \underset{(0.022\%\text{C})}{\alpha\text{-ferrite}} + \underset{(6.67\%\text{C})}{\text{Cementite}} \tag{3.13}$$

- Eutectic



$$\underset{(4.3\%\text{C})}{\text{Liquid}} \underset{\text{heat}}{\overset{\text{cool}}{\underset{1147^{\circ}\text{C}}{\rightleftarrows}}} \underset{(2.14\%\text{C})}{\text{Austenite}} + \underset{(6.67\%\text{C})}{\text{Cementite}} \tag{3.14}$$

- A1
- A3
- Acm

Microstructure in steels

- Eutectoid steels

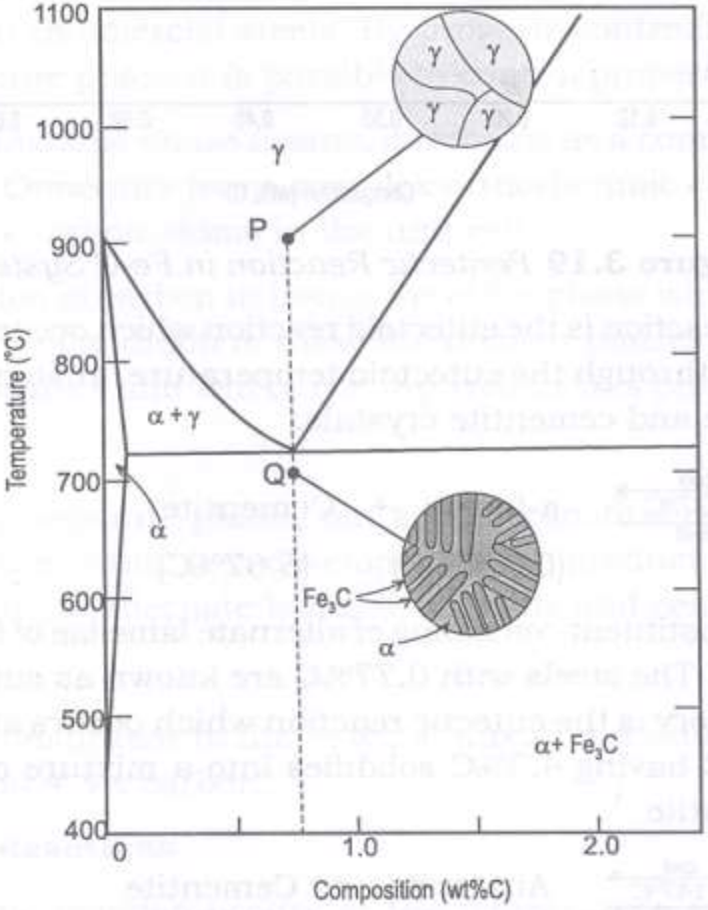


Figure 3.20 *Microstructural changes in eutectoid steel*

iate between the soft, ductile ferrite and the hard brittle cementi

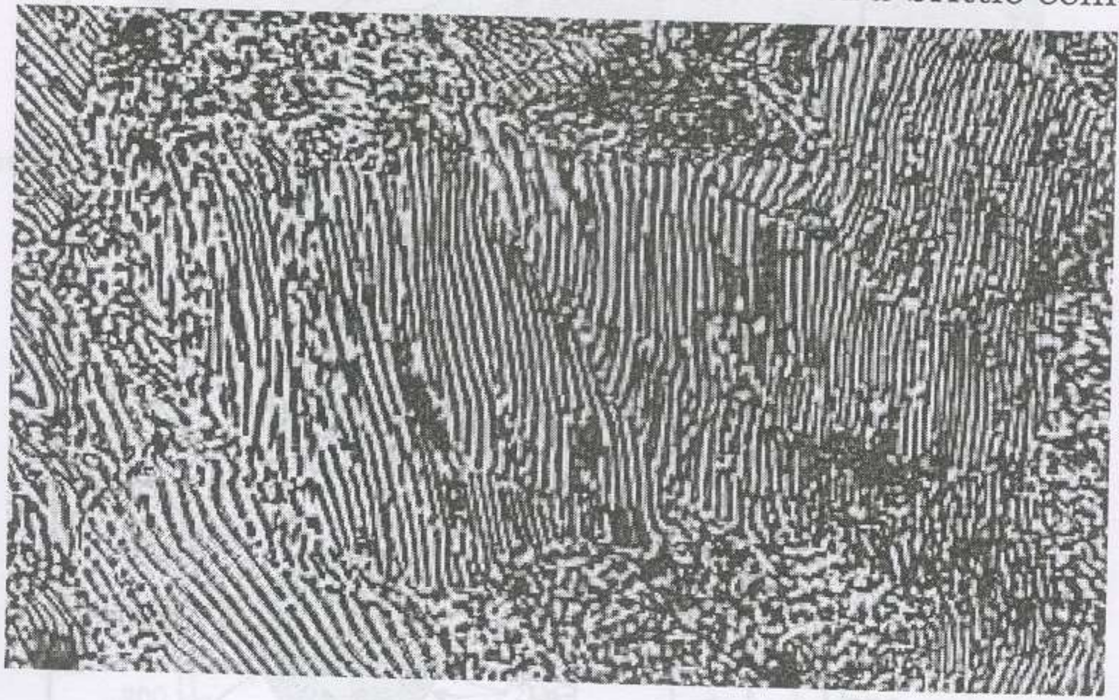


Figure 3.21 *Pearlite*

Hypoeutectoid steel

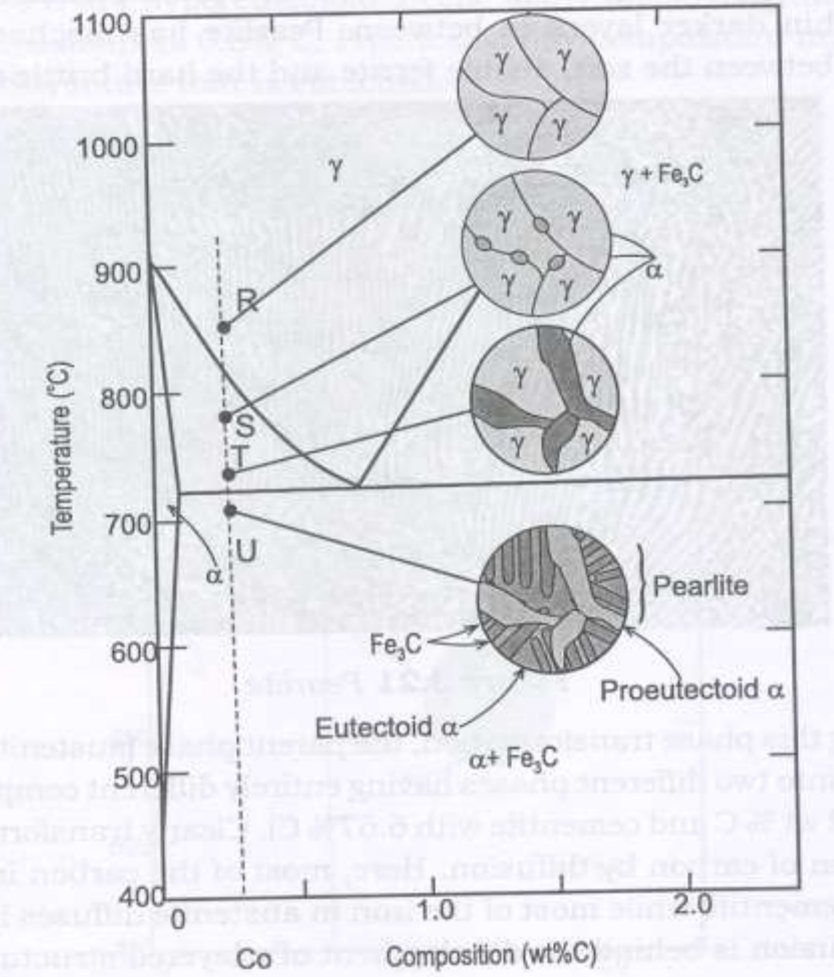


Figure 3.22 *Microstructural changes in hypoeutectoid steel*

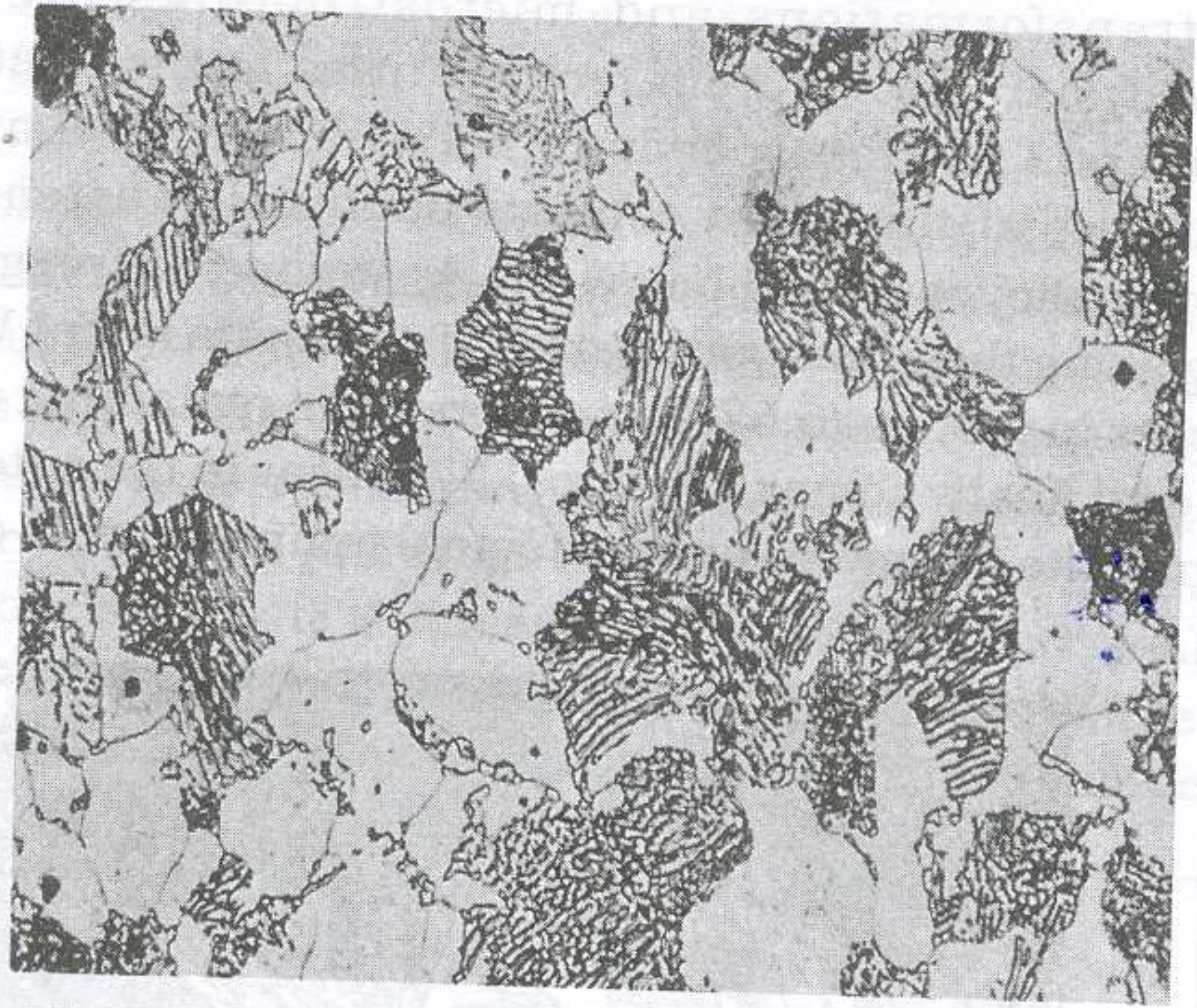


Figure 3.23 *Pearlite with proeutectoid ferrite*

Hypereutectoid steel

ypereutectoid Steel

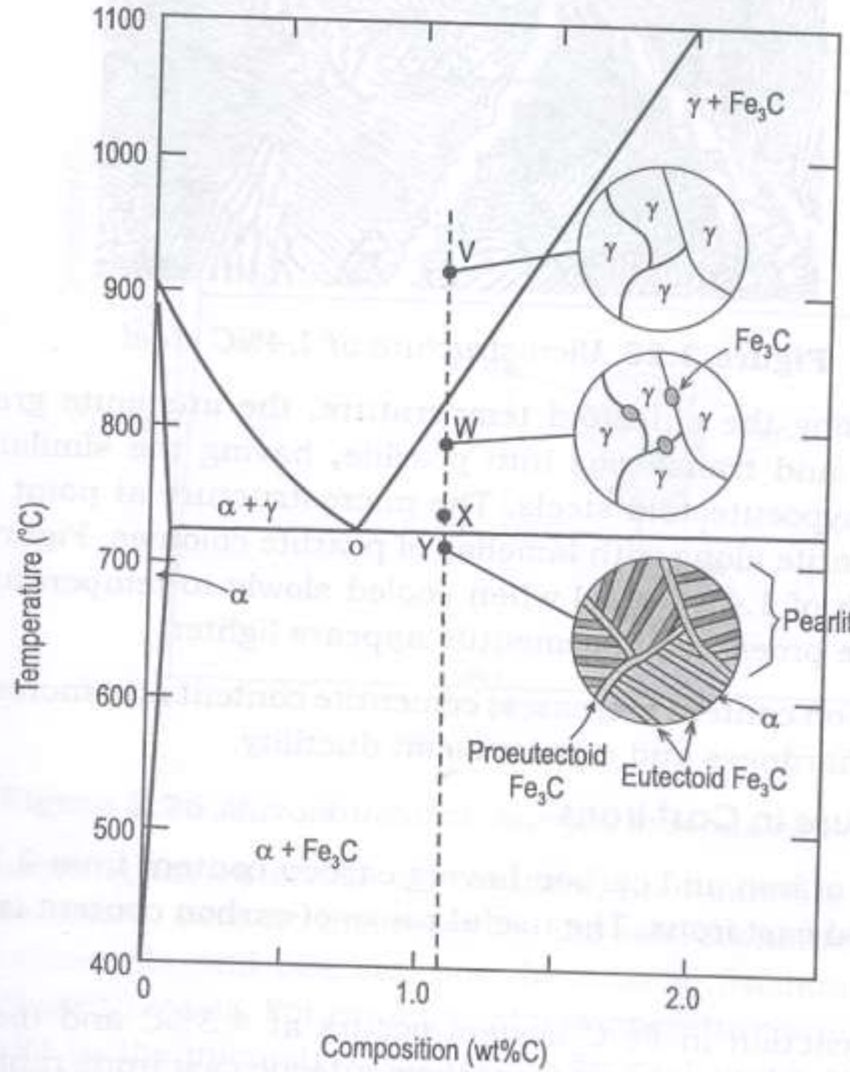


Figure 3.24 *Microstructural changes in hypereutectoid steel*

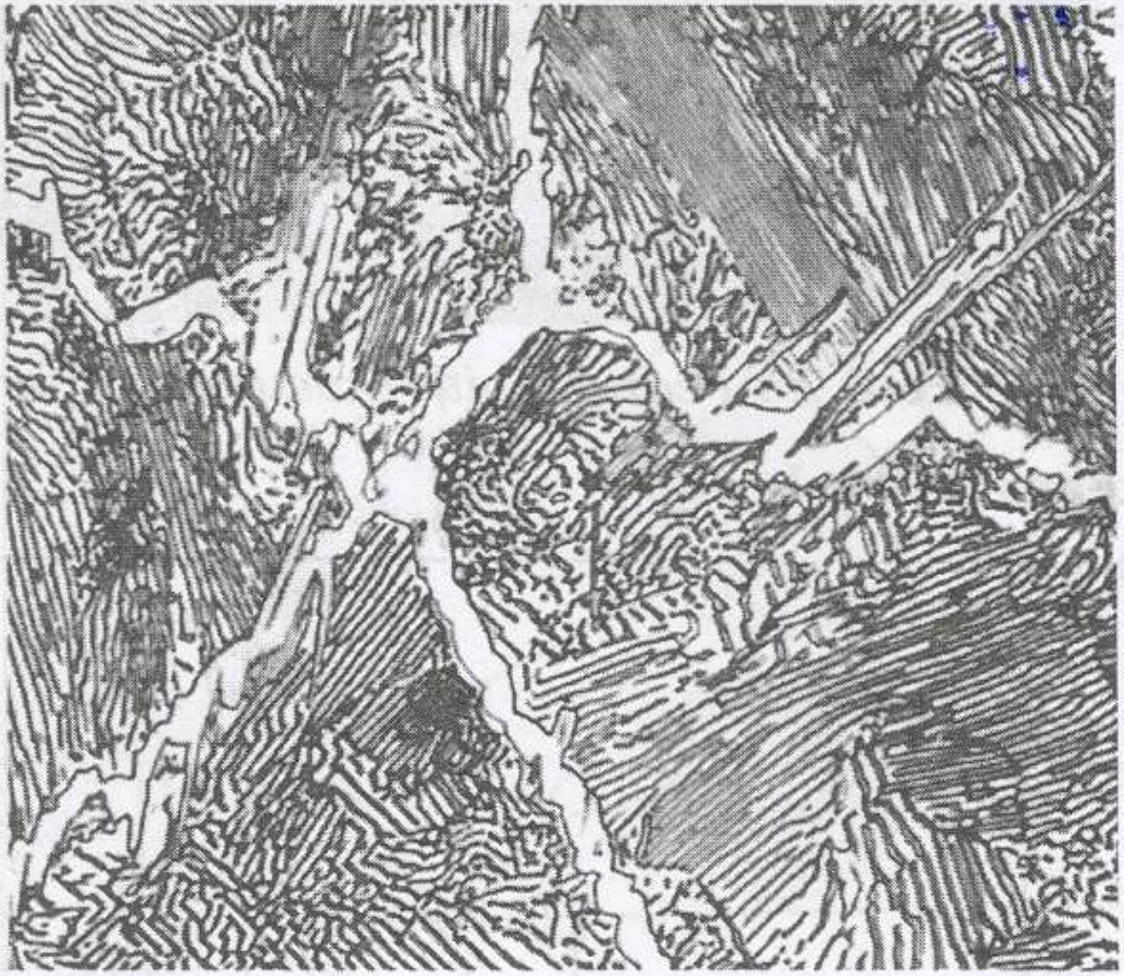


Figure 3.25 *Microstructure of 1.4%C steel*

Microstructure in Cast irons

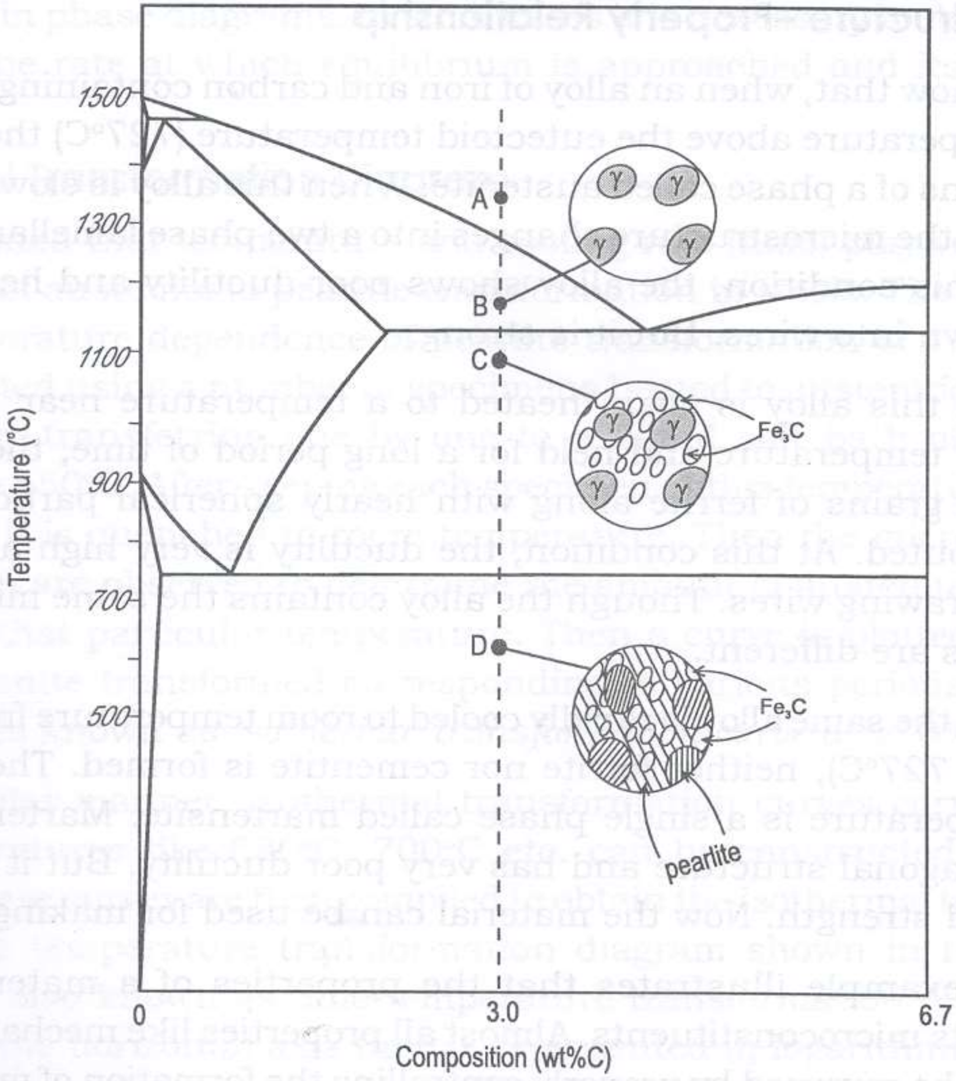


Figure 3.26 *Microstructural changes in white cast iron*

Microstructure-property relationship

3.25

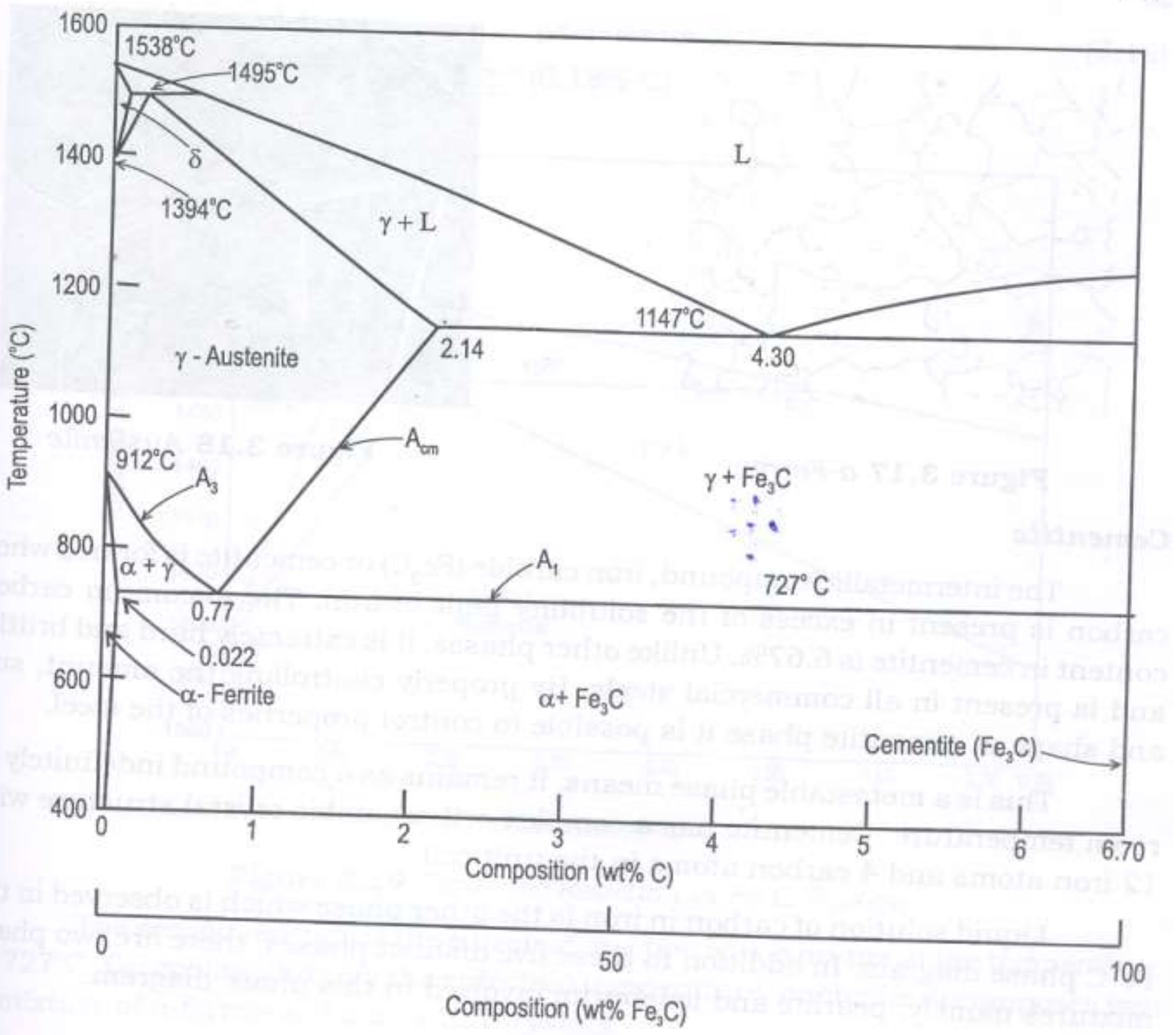


Figure 3.16 *Iron carbon phase diagram*

Microstructure-property relationship

- Properties of a material are strongly governed by its microconstituents
- By properly controlling their formation, the properties can be controlled
- Modification in mic: leads to desired properties being imparted
- Phase transformations and its dependence on time and other parameters
- cooling or heating at extremely slow rates – phase transformations at equilibrium
- Supercooling and Superheating

Limitations of Phase diagrams

- They give no information on the structural form and distribution of phases (lamellae, spheroids, intergranular films)
- They show only equilibrium states

Isothermal transformation diagram (TTT Diagram)

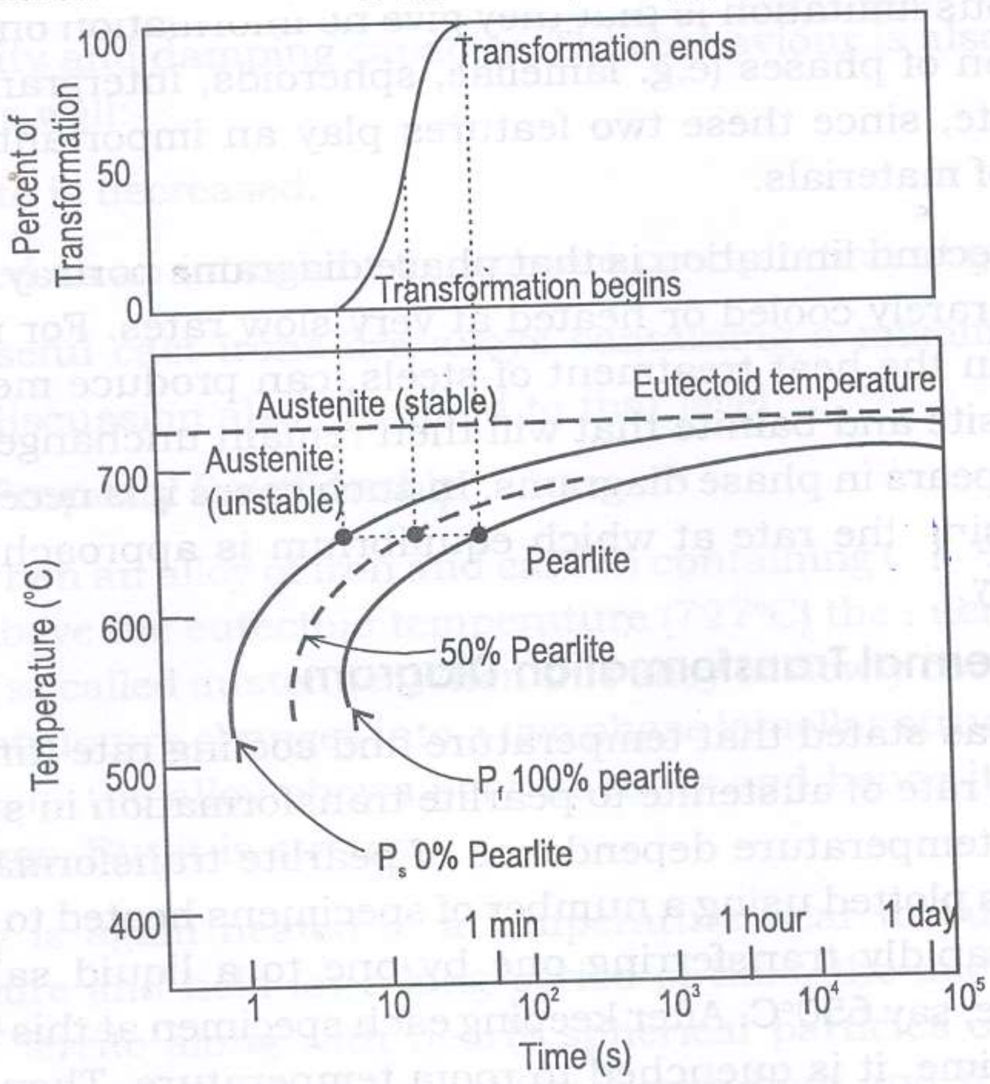


Figure 3.27 *Construction of TTT diagram*

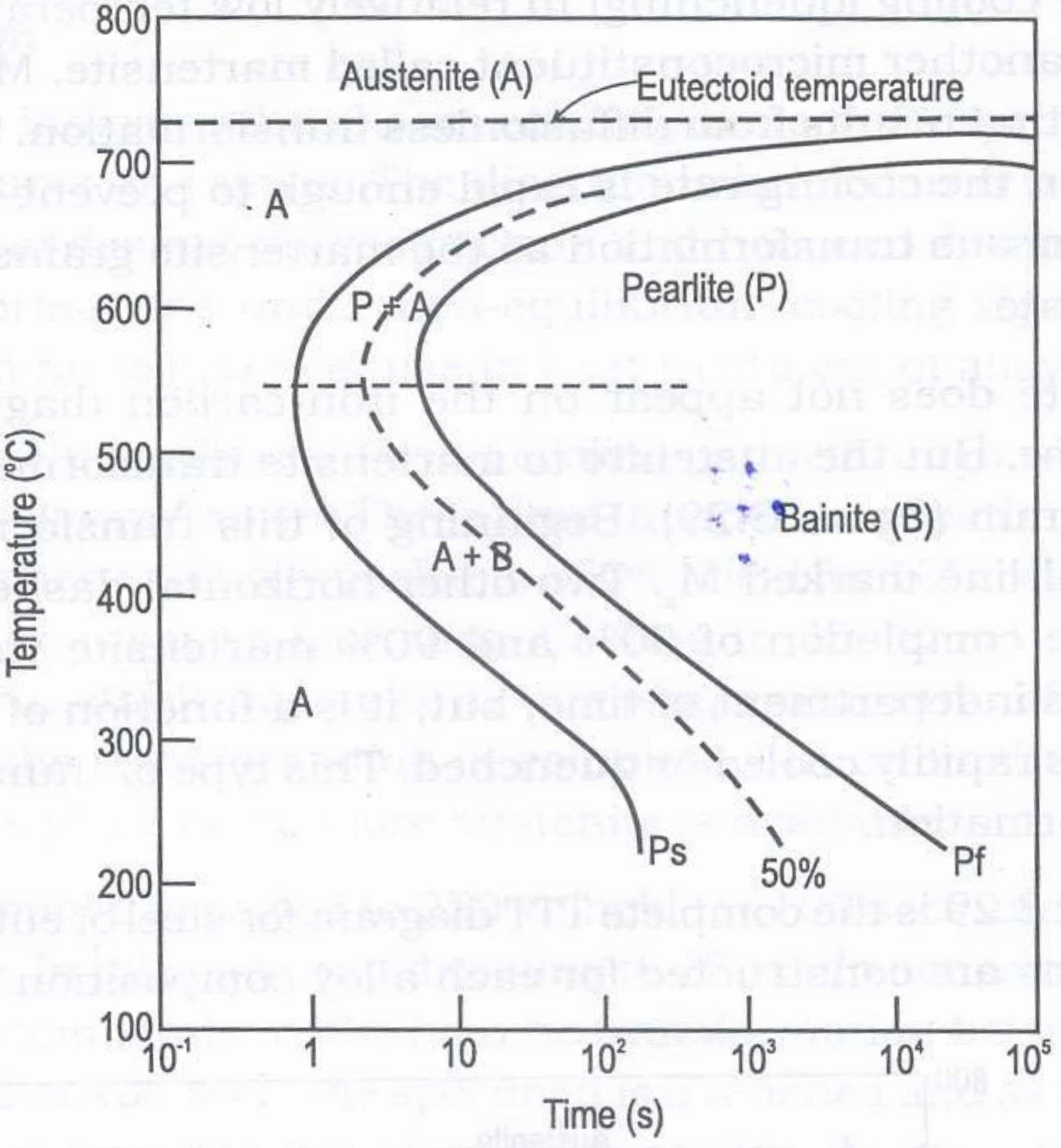


Figure 3.28 *TTT Diagram*

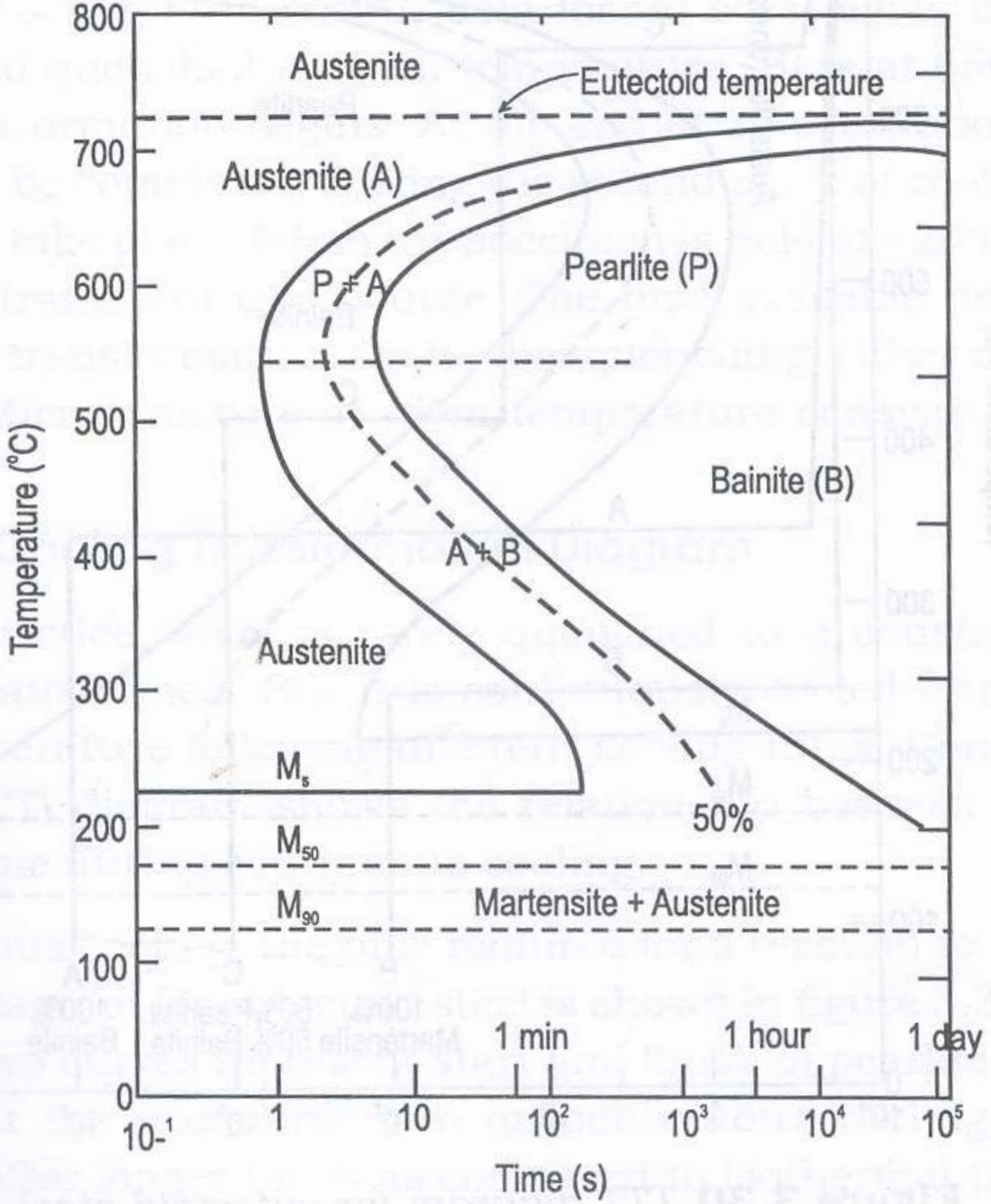


Figure 3.29 *Complete TTT diagram for eutectoid steel*

Use of TTT Diagram

- Indicates the phases existing in steel of a specific composition at various temperatures and times
- It is helpful in selecting a suitable cooling cycle to obtain desired mic: and hence to design the properties of the alloy
- Non equilibrium transformations in the diagram useful in Heat Treatment of alloys

Use of TTT Diagram

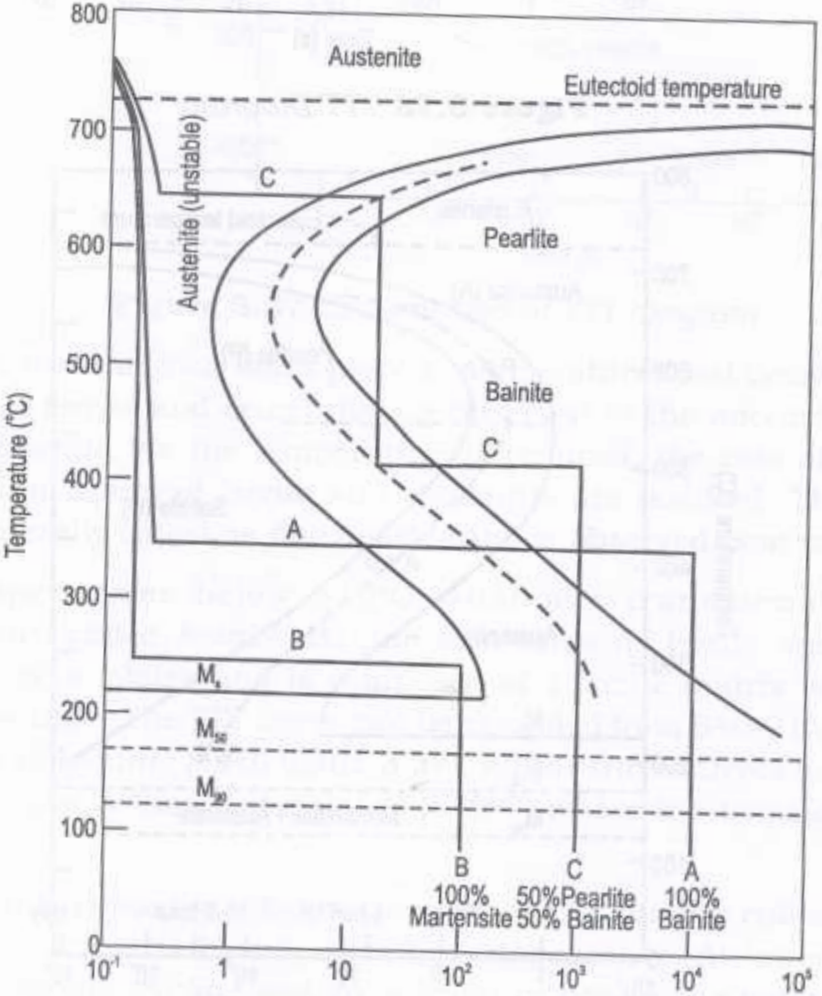


Figure 3.30 *TTT diagram for eutectoid steel*

Continuous cooling transformation diagram (CCT Diagram)

- In actual practice steel is rarely quenched to a constant temperature and isothermally transformed
- But it is continuously cooled from the austenitic range to room temperature
- CCT diagram shows relationship b/w transformation, temperature and time <u>during continuous cooling</u>
- Here the time required for reaction to begin and end is delayed

Continuous cooling transformation diagram (CCT Diagram)

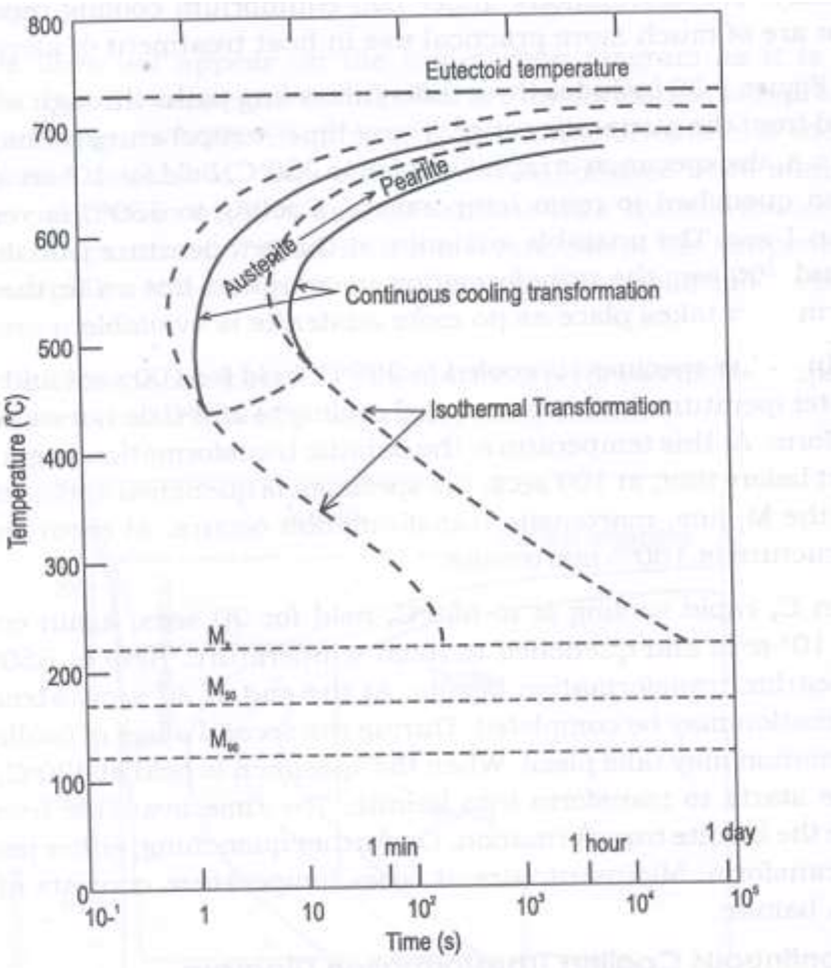


Figure 3.31 *TTT and CCT diagrams*

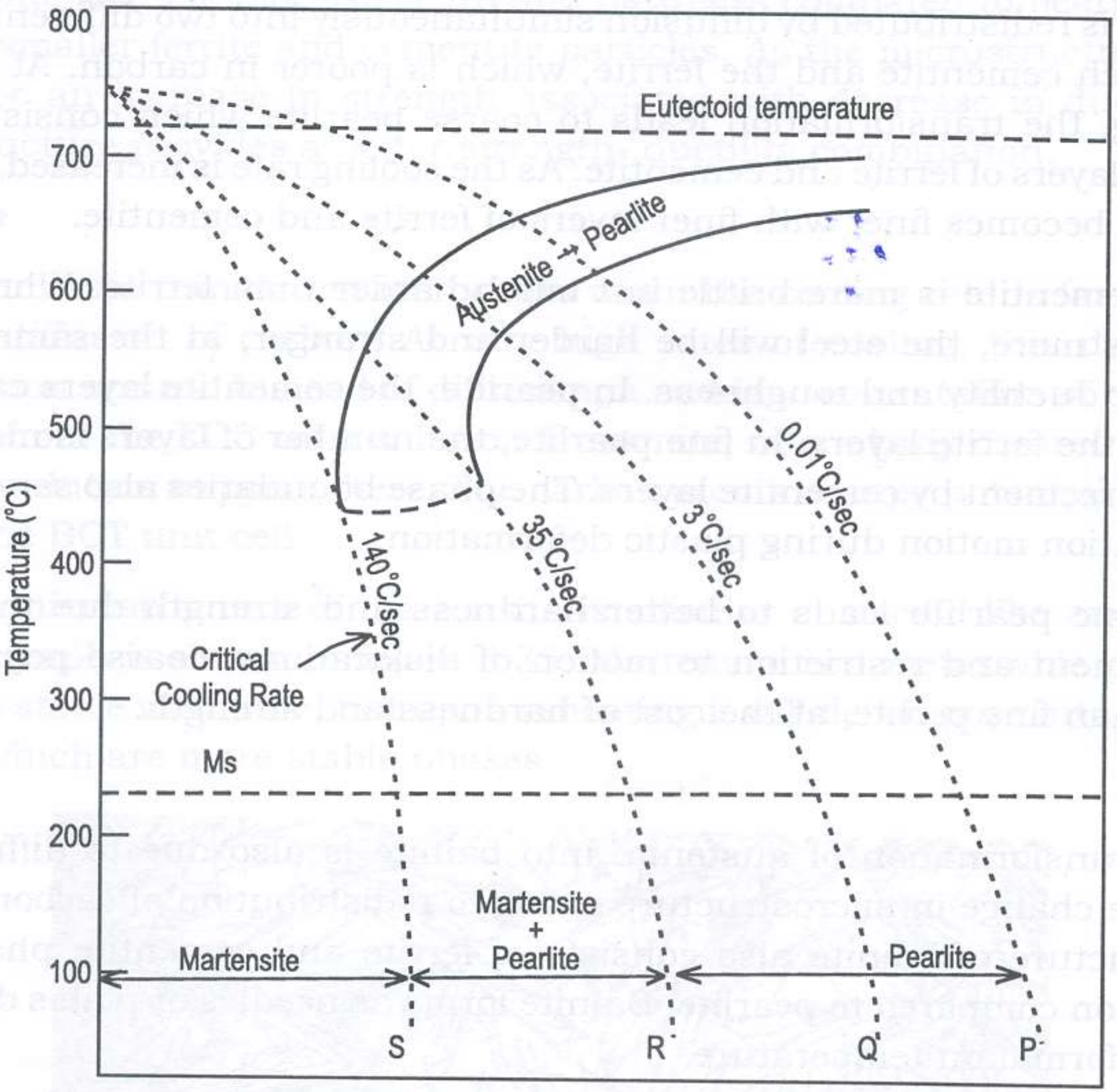


Figure 3.32 *CCT diagram for eutectoid steel with cooling curves*

Phase Transformations

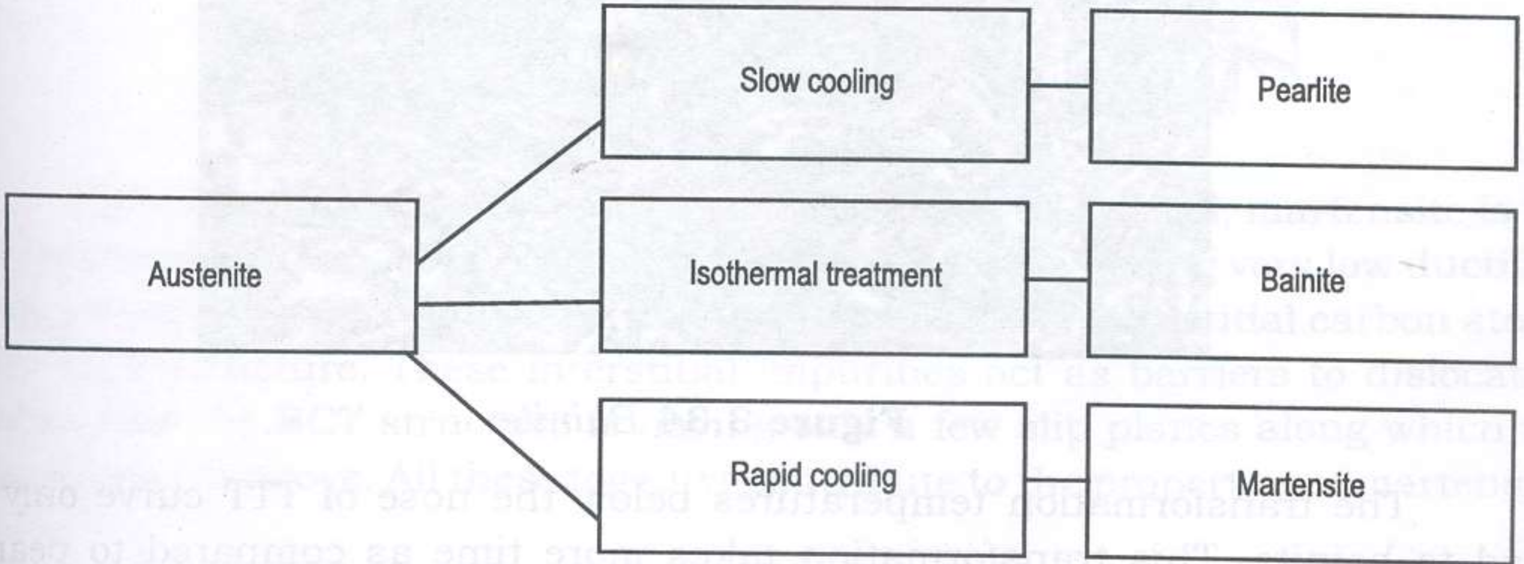
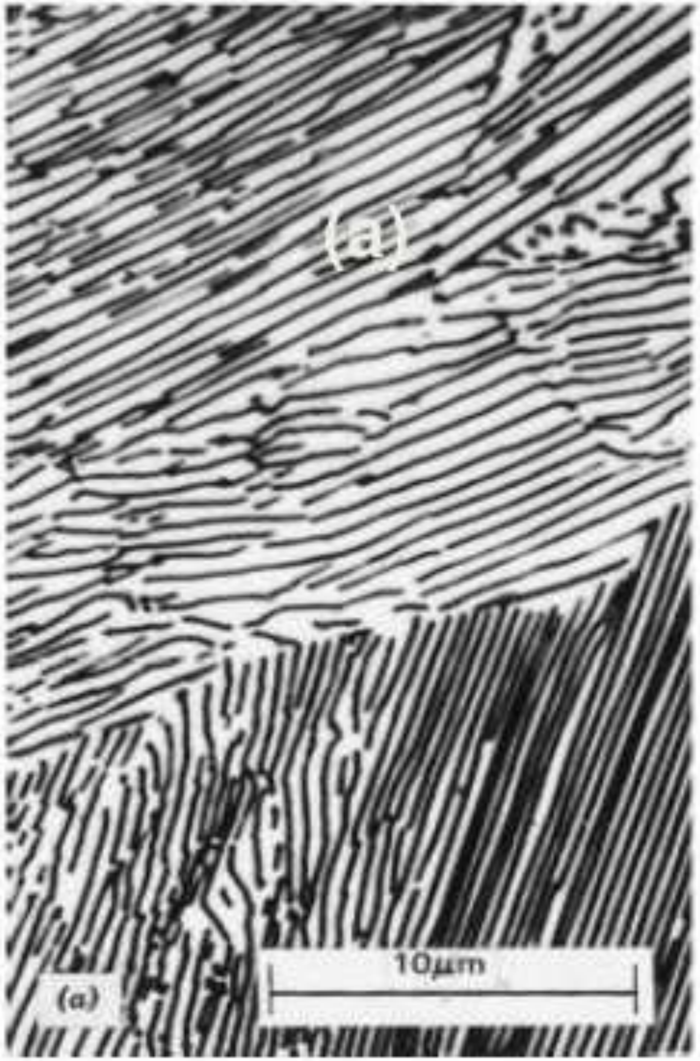


Figure 3.33 *Transformations of austenite*

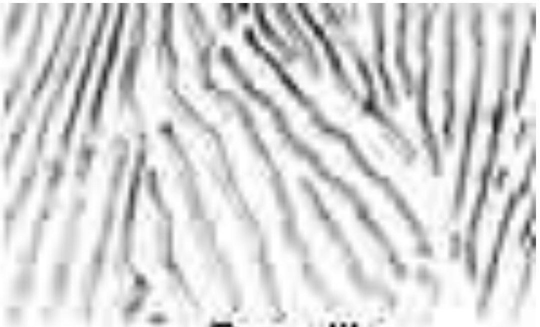
Morphology of Pearlite



(a) coarse pearlite

(b) fine pearlite 3000X

Austenite



Pearlite

Martensite

Bainite

Ferrite

Cementite

Pearlite

- Transformation due to diffusion
- C in Austenite redistributed by diffusion in to Cementite and Ferrite
- Coarse pearlite and Fine pearlite
- The Cementite layers reinforce the Ferrite layers
- Fine pearlite-Hard, Coarse pearlite-Ductile

Bainite

- Also due to diffusion
- Mic: consists of Cementite and Ferrite, but a finer distribution than in Pearlite
- Forms as needles or plates depending on transformation temperature
- Below the nose of TTT
- Transformation time more
- Coarse Bainite/Upper Bainite/Feathery Bainite
- Fine Bainite/Lower Bainite/Acicular Bainite
- More strength and Hardness

Martensite

- Cooling rate faster enough to prevent diffusion
- FCC (Austenite) to BCT (Martensite)
- C atoms occupy interstitial spaces in BCT unit cell
- Acicular or needle like Mic:
- Strongest and hardest; most brittle with very low ductility
- Interstitial C atoms act as barriers
- Also BCT has only a few slip planes

Heat treatment pocesses

- Heat treatment – “A combination of heating and cooling operations timed and applied to a metal or alloy in the solid state to produce desired properties”.
- Heat treatment of steels
- Plain Carbon steels and Alloy steels
- Low carbon steels (0.04-0.15% C)
- Medium carbon or MS (0.15-0.6 % C)
- High Carbon steel (above 0.6 % C)

- HT processes are designed based on information available from phase diagram, TTT and CCT diagrams
- First step – Heating to Austenitic temp:
- Austenite decomposes in to different forms on cooling
- Objectives of HT

HEAT TREATMENT PROCESSES

1. Simple Heat Treatments

a. Process Annealing
b. Full Annealing
c. Spheroidising
d. Normalising

2. Quench & Temper

a. Hardening
b. Tempering

3. Isothermal Heat treatments

a. Austempering
b. Martempering
c. marquenching

4. Surface heat treatments

<u>Diffusion Methods</u>

- Carburising
- Cyaniding
- Nitriding
- Carbonitriding

<u>Selective Hardening</u>

- Flame hardening
- Induction hardening
- Laser hardening
- Selective carburising

Steps in Heat Treatment

1. Heating the material to a specified temperature
2. Holding the material at this high temperature for a specified period of time
3. Cooling the material according to specified rate of cooling

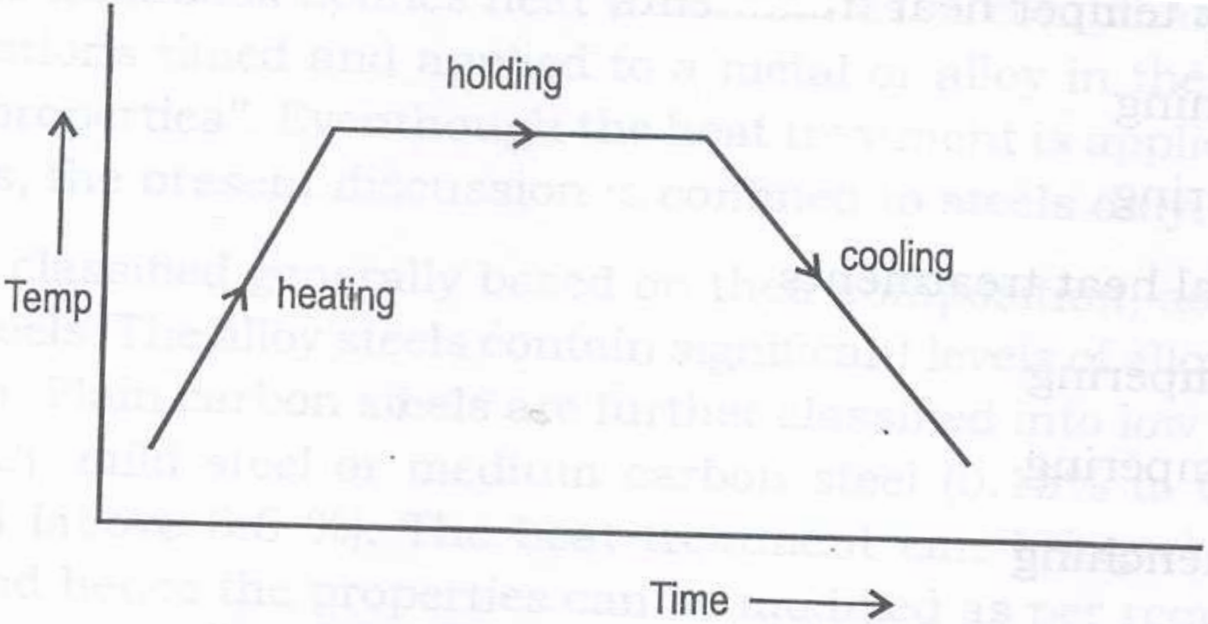


Figure 3.36 *Heat treatment cycle*

Simple Heat Treatments

Process Annealing:

- HT used to soften and increase the ductility of a cold worked material to facilitate further deformation
- Done in b/w different stages of cold working
- Purpose: to eliminate the effect of cold working in steels

Process Annealing

- Used for steels having less than 0.25% C
- Heating the material to 550-650˚C (ie, just below A_1)
- Holding for a certain duration and then slowly cooled in air
- Relieves effects of cold working, reduces hardness and increase ductility
- Also called sub-critical annealing

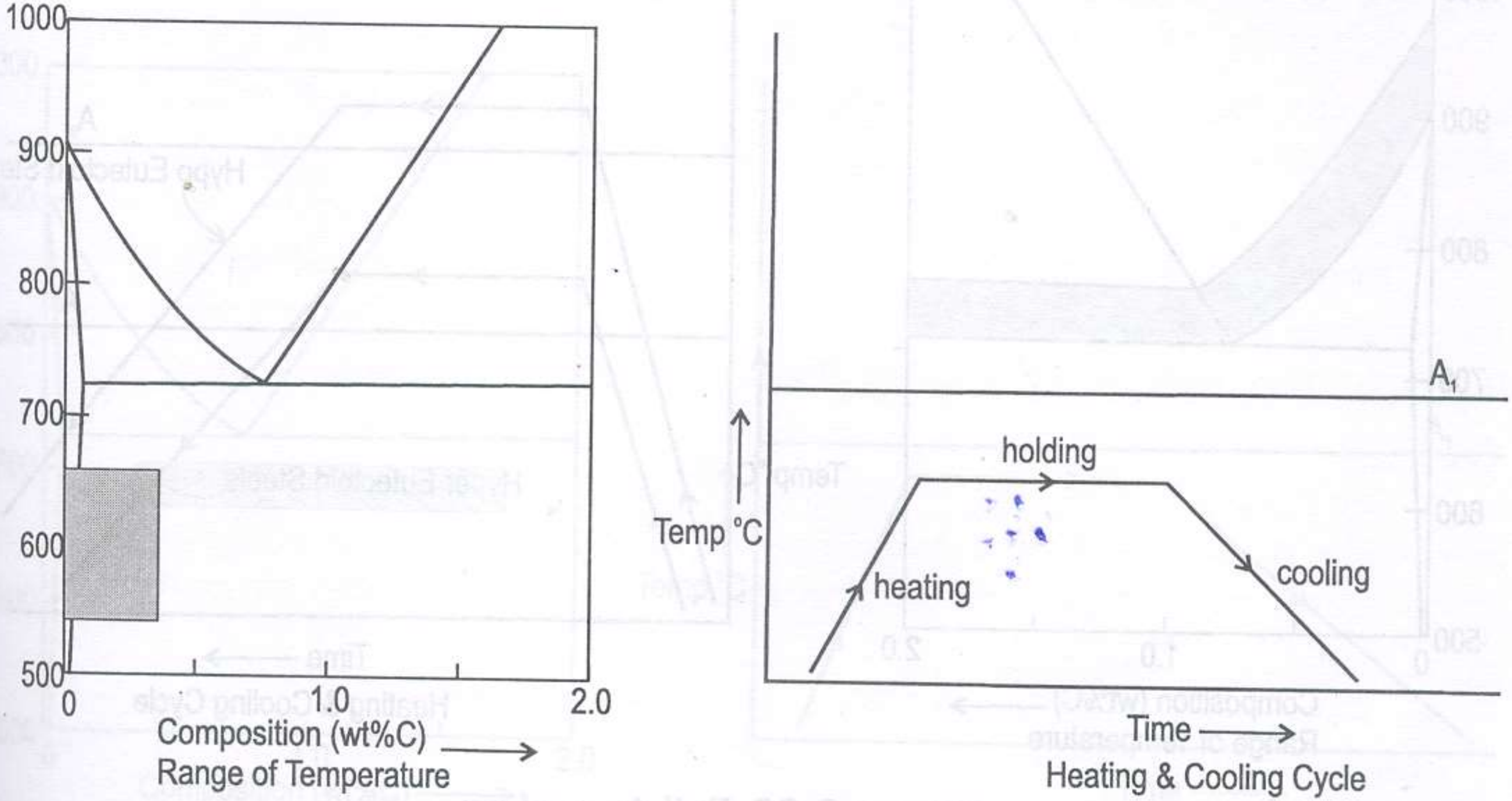


Figure 3.37 *Process Annealing*

Full Annealing

- The heat treatment process which involves heating steel to the austenite state followed by very slow cooling
- **Purpose** :
- to remove all structural imperfections by complete recrystallization
- To relieve internal stresses and hence to improve ductility

Full Annealing

<u>Hypoeutectoid steels</u>

- heated about 50-90˚C above A_3 line
- Holding, converts the mic: in to Austenite (Austenising)
- Very slow cooling in the furnace (10-20˚C/Hr)
- Austenite → Ferrite+Cementite
- Complete recrystallization and structure gets refined
- Material gets softened and mechanical properties improved

Full Annealing

Hypereutectoid steels

- Heated to about 50-90˚C above the A_1 (Eutectoid temperature) line
- Pearlite transforms into Austenite
- Holding time facilitates complete transformation
- Very slow cooling in the furnace – Austenite transforms back in to coarse Pearlite

- Complete recrystallization – material softened and mechanical properties improved
- But the Cementite forms a brittle network around the Pearlite – reduces machinability
- Spheroidising overcomes this
- Long process, hence expensive

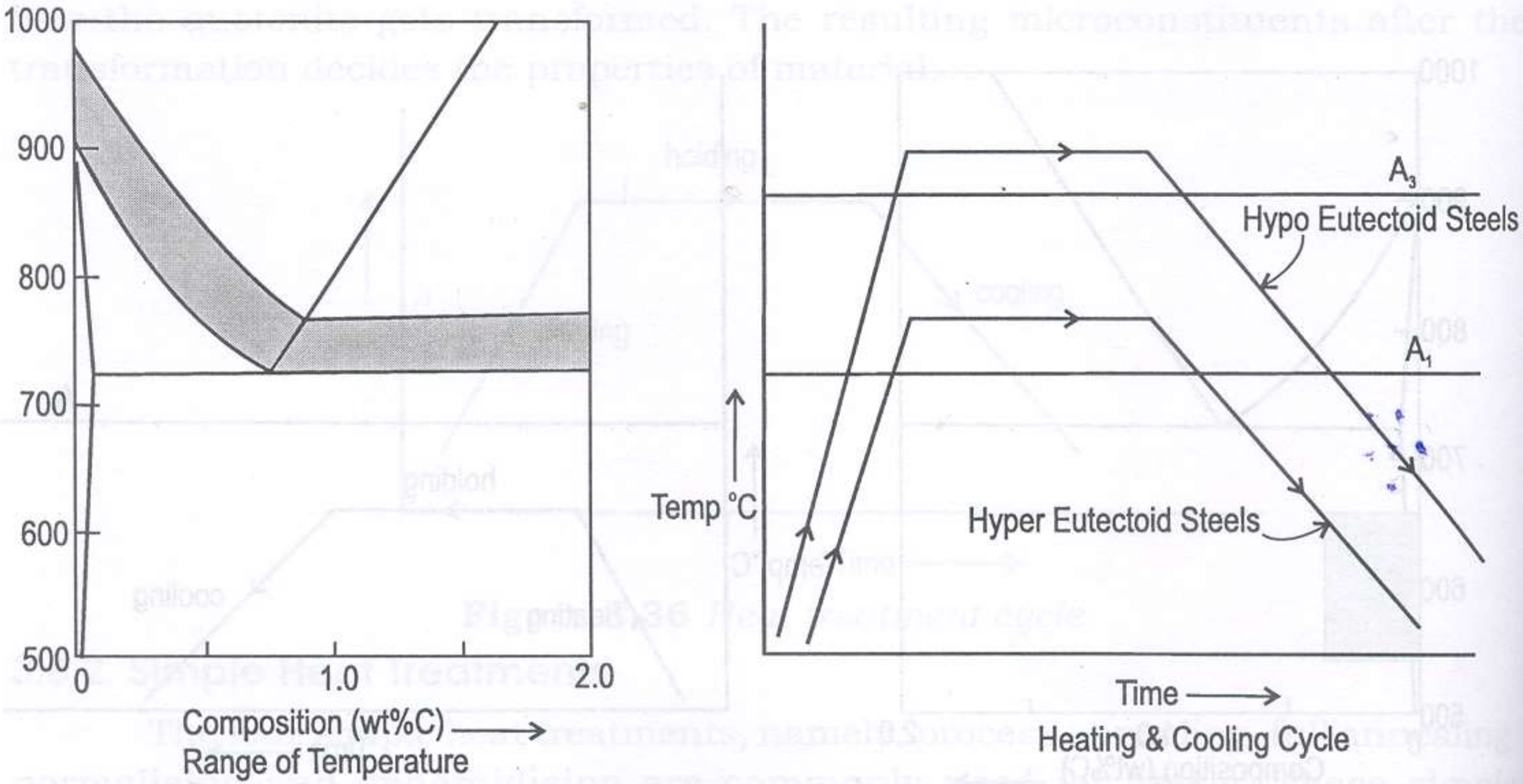


Figure 3.38 *Full Annealing*

Spheroidising

- Process similar to Annealing, but results in a structure consisting of globules or spheroids of Cementite
- Purpose: to improve machinability, reduce hardness and to increase ductility

Spheroidising

- Heated to about 30˚C below the A1 line
- Held at this temp: for several hours
- Very slow cooling in the furnace
- Usually used for High Carbon Steels – considerable fraction of Cementite at room temperature
- Cementite present as lamellae in Pearlite, transforms in to spheroidal grains – reduces surface area of Cementite hence the hardness
- Softest state of steel
- Mic: known as spheroidite

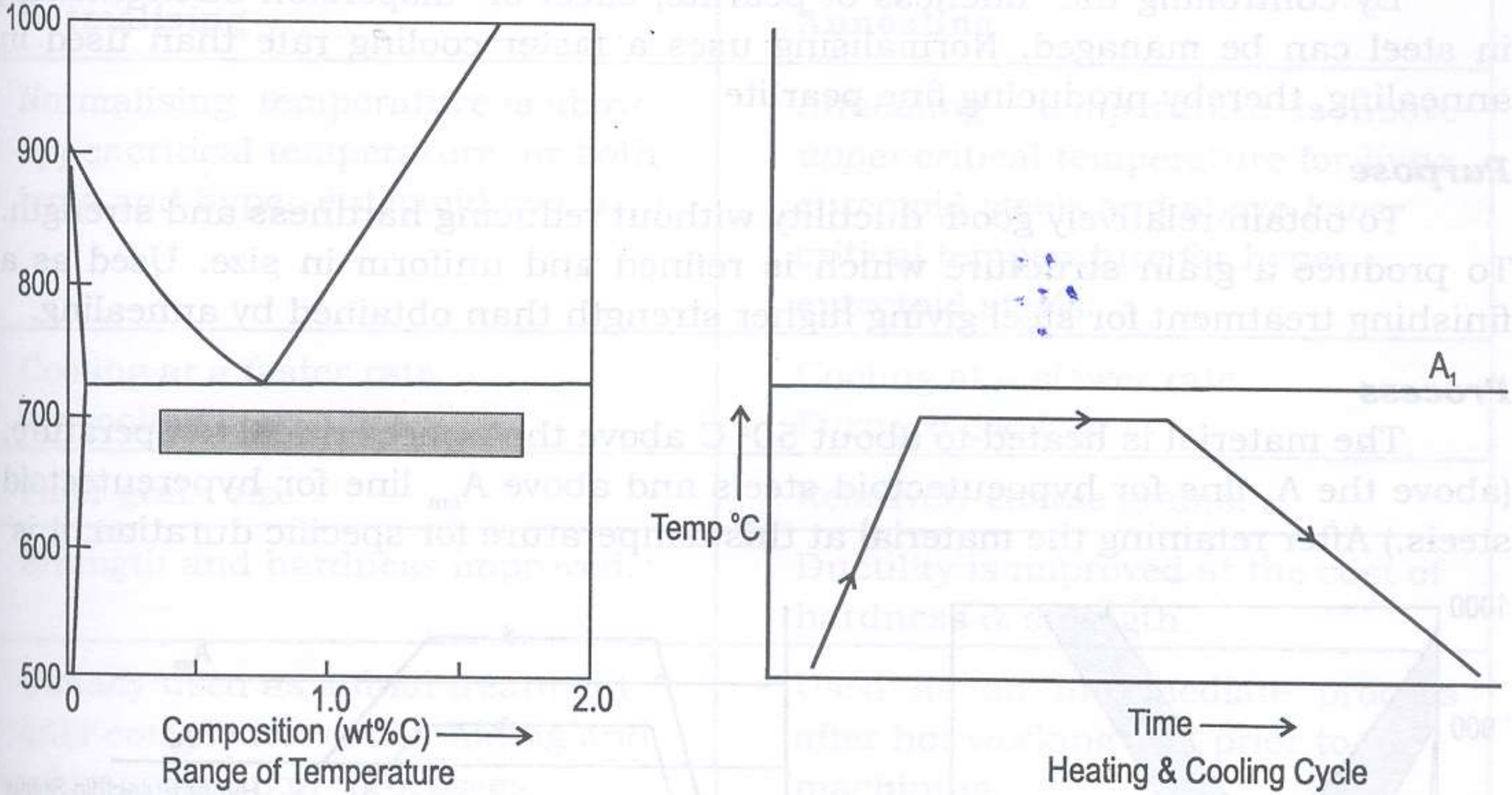


Figure 3.39 *Spheroidising*

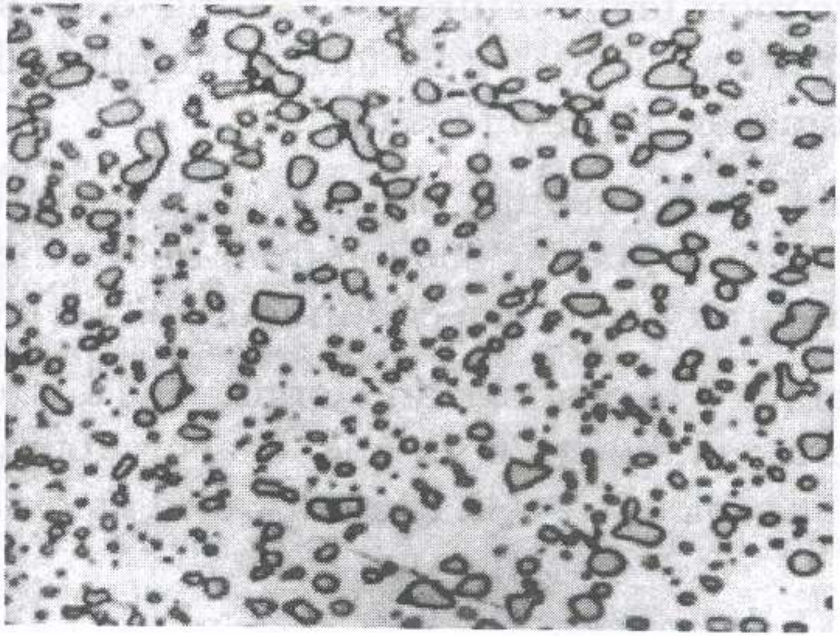


Figure 3.40 *Spheroidite.*

Normalising

Purpose:

- To obtain relatively good ductility without reducing hardness and strength
- To produce a grain structure which is refined and uniform in size

Normalising

- Hypoeutectoid steels are heated 50 ˚C above A3 line
- Hypereutectoid steels are heated 50 ˚C above Acm line
- soaking for specific duration
- Air cooled at room temperature
- Heating, mic: completely transformed in to Austenite and faster cooling, fine pearlite is formed
- Applied to castings and forgings
- Often called as *air quenching*

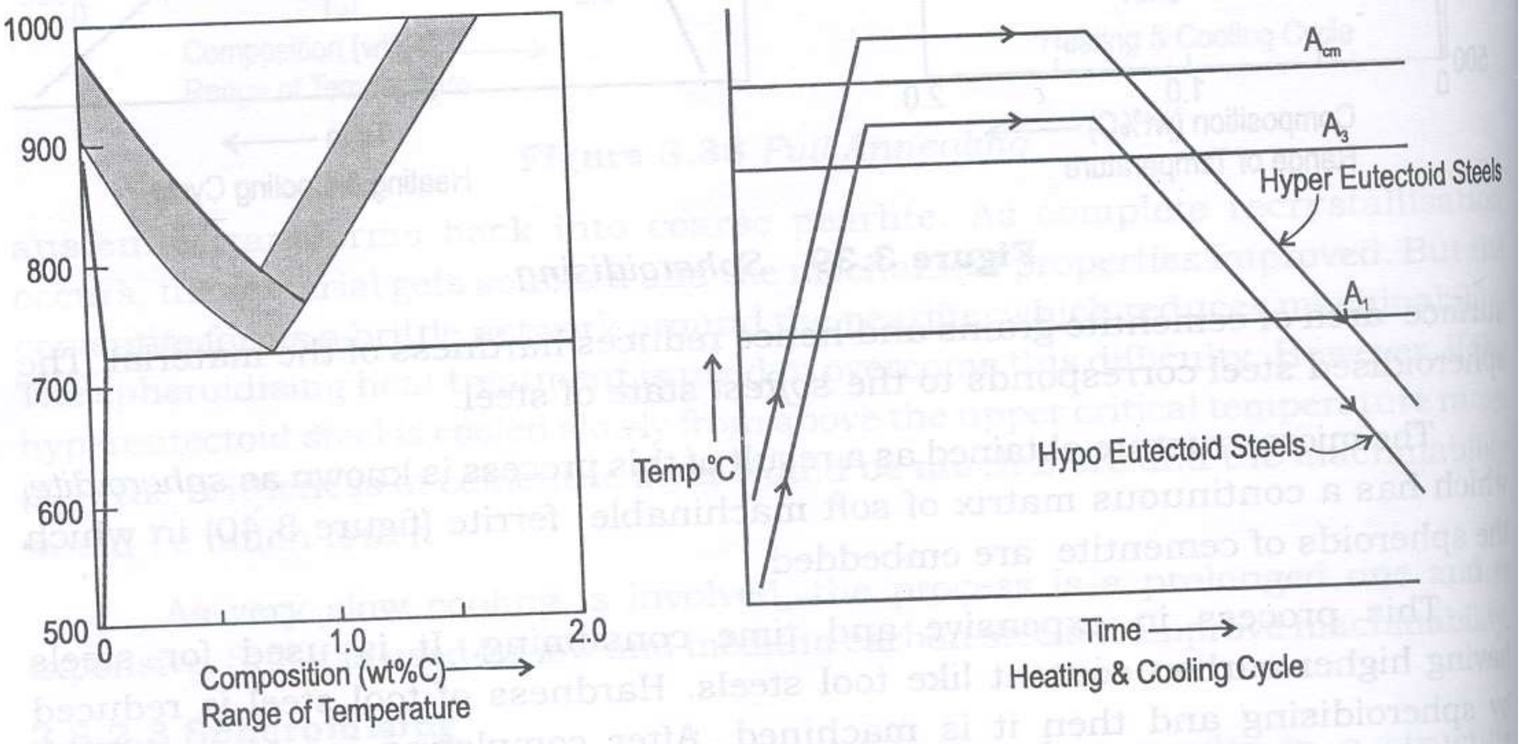


Figure 3.41 *Normalising*

Patenting

- Special HT process fro wire products of meium C content to increase ductility
- Wire is heated above LCT (A1 line)
- Cooled to lower temp using bath of molten lead (500 ˚C)
- Austenite transforms in to <u>very fine pearlite</u> – increases ductility
- The process is given to steel wires prior to drawing or b/w drafts

Quench and Temper treatments

- Quenching increases hardness of steels
- Hardening and Tempering are used together to obtain desired properties

Hardening

- To increase the hardness, strength and wear resistance of steels
- Achieved due to formation of Martensite
- Structural components, dies, knives, cutting tools

- Process
- 1st step is Austenitising
- Hypo – heated above A3 and Hyper heated above A1 only
- Held at this temperature for uniform transformation throughout the thickness
- Quenched in water, oil or brine (@ cooling rate greater than CCR)
- Quenching results in instantaneous transformation of Austenite to Martensite
- FCC Austenite changes to BCT Martensite
- BCT has no close packed slip planes

- Martensite can hold the entire amount of C present in the steel
- Martensite becomes harder as the C content increases
- Two conditions for successful Hardening:
    1. Formation of homogeneous Austenite
    2. Rapid cooling of Austenite to transform into Martensite

       Transformation depends on variables like quenching media, composition of steel and size of component

Effect of Quenching media

- Temperature of the component needs to be lowered to M_s at the earliest
- The rate of extraction by liquid bath is dependent upon HT characteristics of liquid
- Decreasing order of rate of heat extraction

  Brine (NaCl, $CaCl_3$)

  water (For plain C steels with moderate thickness)

  water+oil

  oil (alloy steels with complex shapes)

  molten salt bath

- Agitation of component and circulation of liquid bath

- **Effect of Alloying elements**
- Help to prevent transformation of Austenite to Pearlite or Bainite (Mn, Cr, Ni)
- This leads to uniform hardness throughout the c/s
- **Effect of size**
- For large objects it takes a longer time to achieve the same temperature at the surface than a small specimen
- Longer duration- some Austenite transforms to Pearlite or Bainite

Tempering

- Heat Treatment process which immediately follows hardening
- Hardened steel is very brittle
- Tempering – to reduce brittleness and improve toughness of hardened steel
- It relieves internal stresses developed during quenching

Tempering

- Heating to temperatures below A1 line followed by slow cooling
- Temperature varies from 150 to 680˚C depending on the purpose
- 3 categories: low, medium and high temperature tempering

- When heated to low tempering temperatures (150-250˚C) internal stresses are removed
- Toughness and ductility improved without loss in hardness
- No transformation of martensite
- For cutting tools made of low alloy steels

- When tempered in 300-450˚C the mic: consists of Martensite+fine Pearlite=***Troostite***
- Leads to decrease in hardness and strength with increase in ductility
- Springs, axles, hammers, chisels

- When tempered above 450˚C, ***Sorbite*** is formed
- Imparts high ductility with hardness and strength
- Connecting rods, shafts, gears

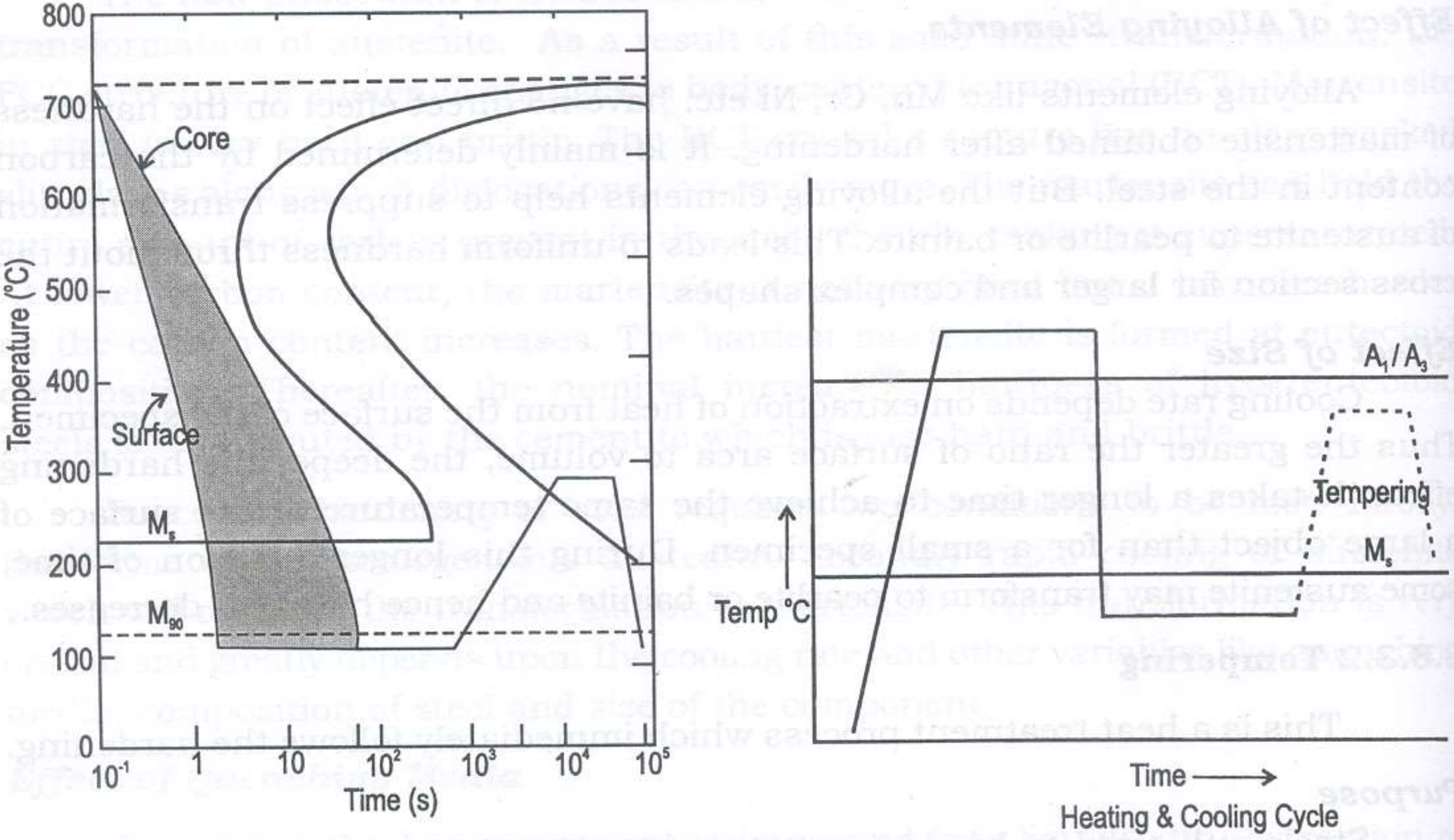


Figure 3.42 *Hardening & tempering*

Isothermal heat treatments

- Quenching – severe internal stresses, quench cracks, warping
- Two special processes:
- Austempering and Martempering
- Also called interrupted quenching processes

Austempering

- In this process Austenite is completely transformed to Bainite
- Also called Isothermal quenching/hardening
- <u>Purpose</u>
- To harden and temper thin sections (springs) with min: distortion
- To obtain uniform hardness, toughness and impact strength

- Process
- Heating above Austenitising temperature
- Quenching in a molten salt bath at const: temp: within lower side of Bainitic range (200-400˚C)
- Holding at this temp: for sufficiently long time and cooling in air
- No transformation on quenching from Austenitic to Bainitic range
- During soaking complete transformation to lower (acicular Bainite)
- It has better mech: properties than tempered Martensite; hence Austempered components rarely need Tempering

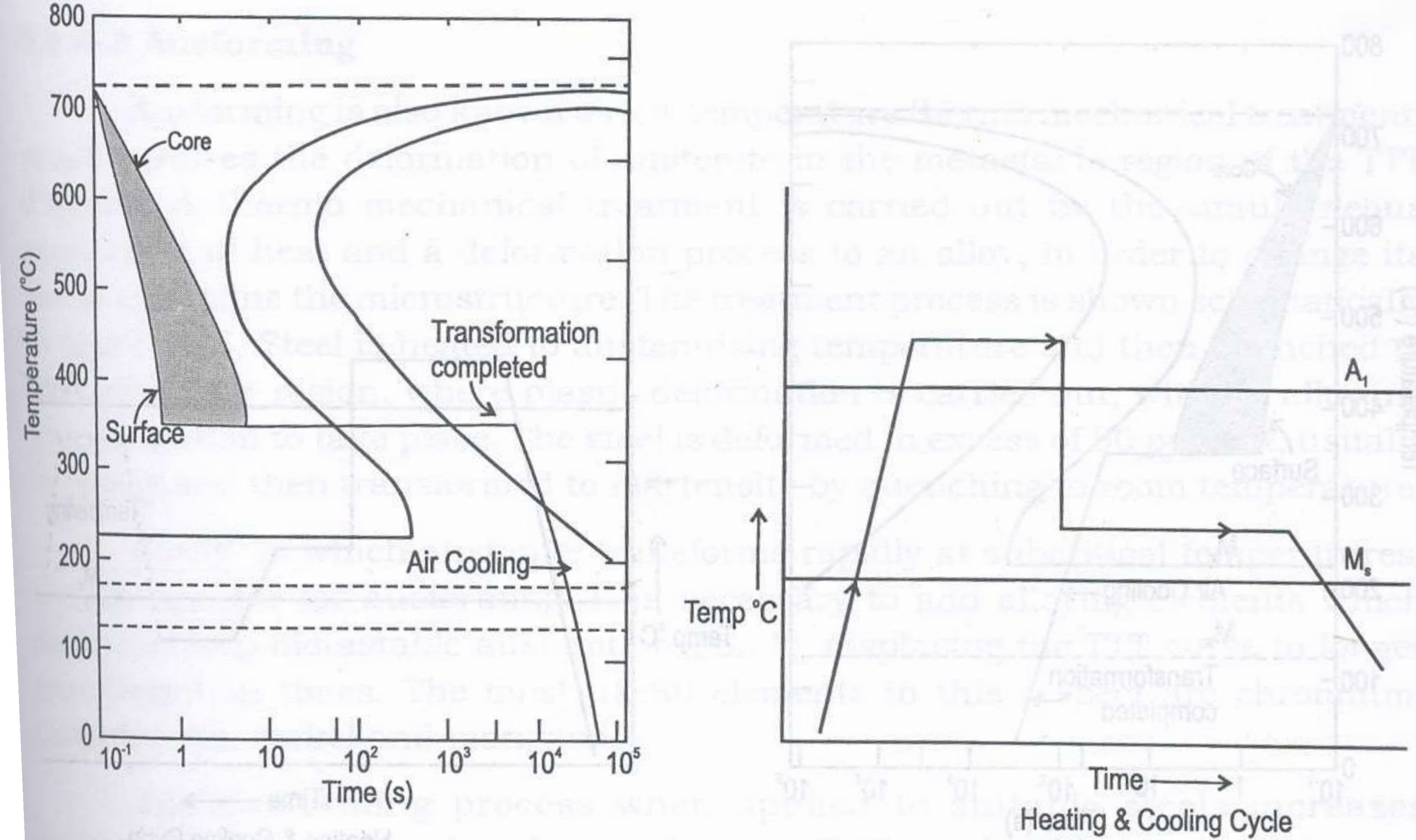


Figure 3.43 *Austempering*

Martempering

- Similar to Austempering, except that the component is slowly cooled through Martensite transformation range
- To minimise distortion, cracking and residual stresses
- Process
- Austenised steel is cooled rapidly to a temperature just above the M_S, with the help of a molten salt bath at const: temperature
- Soaking, and air cooling to room temperature

- Cooling at first stage should be greater than CCR so that no Austenite is transformed
- Soaking ensures uniform temperature
- Second stage cooling prevents large difference in temp: b/w outside and core of section
- Formation of Martensite occurs uniformally throughout, avoiding excessive residual stresses
- Martempering is often followed by Tempering to increase ductility

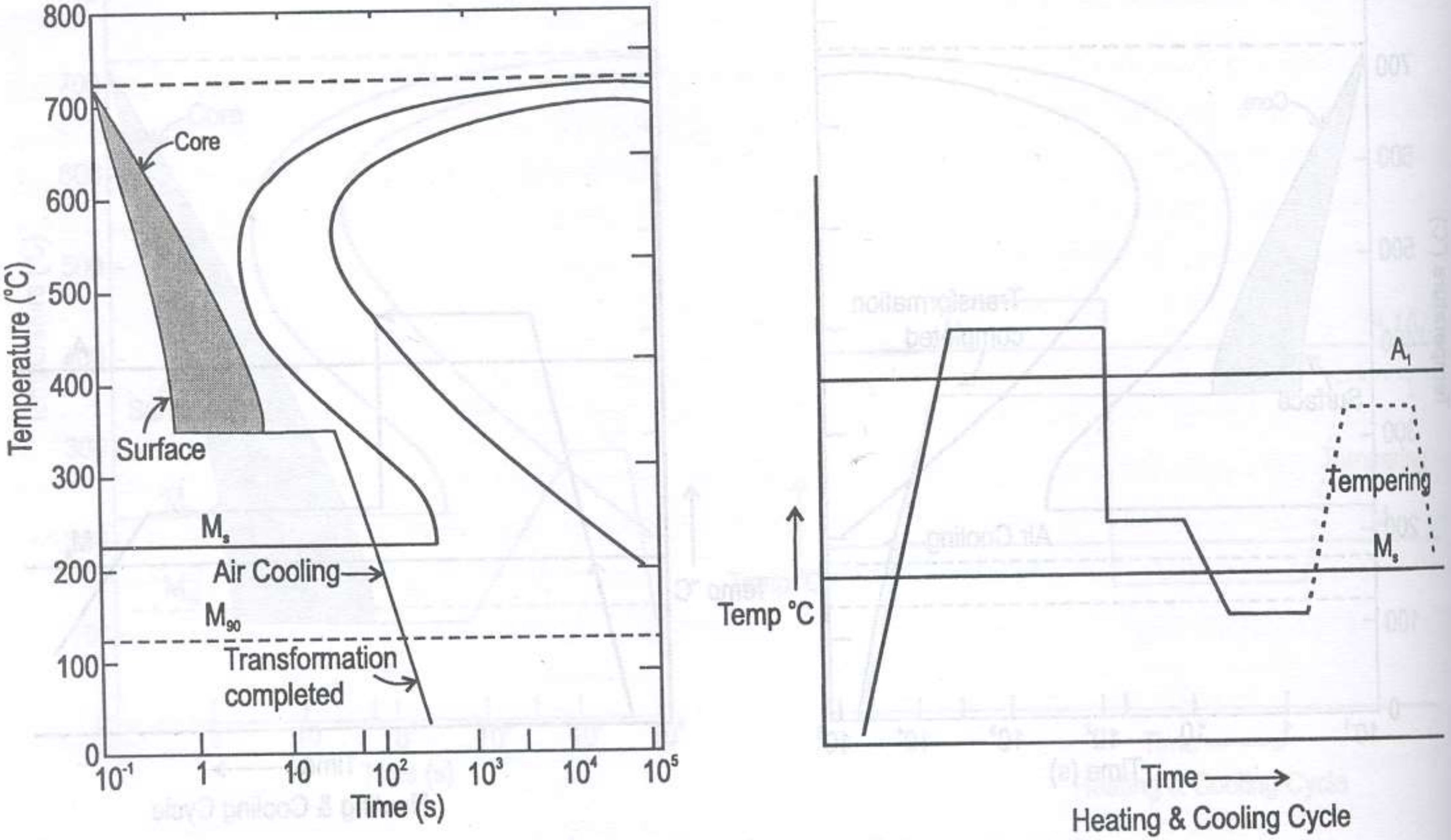


Figure 3.44 *Martempering*

Ausforming

- Involves deformation of Austenite in the metastable region of TTT diagram
- Also known as low temperature thermo mechanical treatment
- Simultaneous application of heat and a deformation process to an alloy, to change its shape and refine its mic:
- <u>Process</u>
- Heated to A1 line and quenched to metastable region
- Plastically deformed (rolling), without allowing transformation
- Then quenched to room temp: to form Martensite

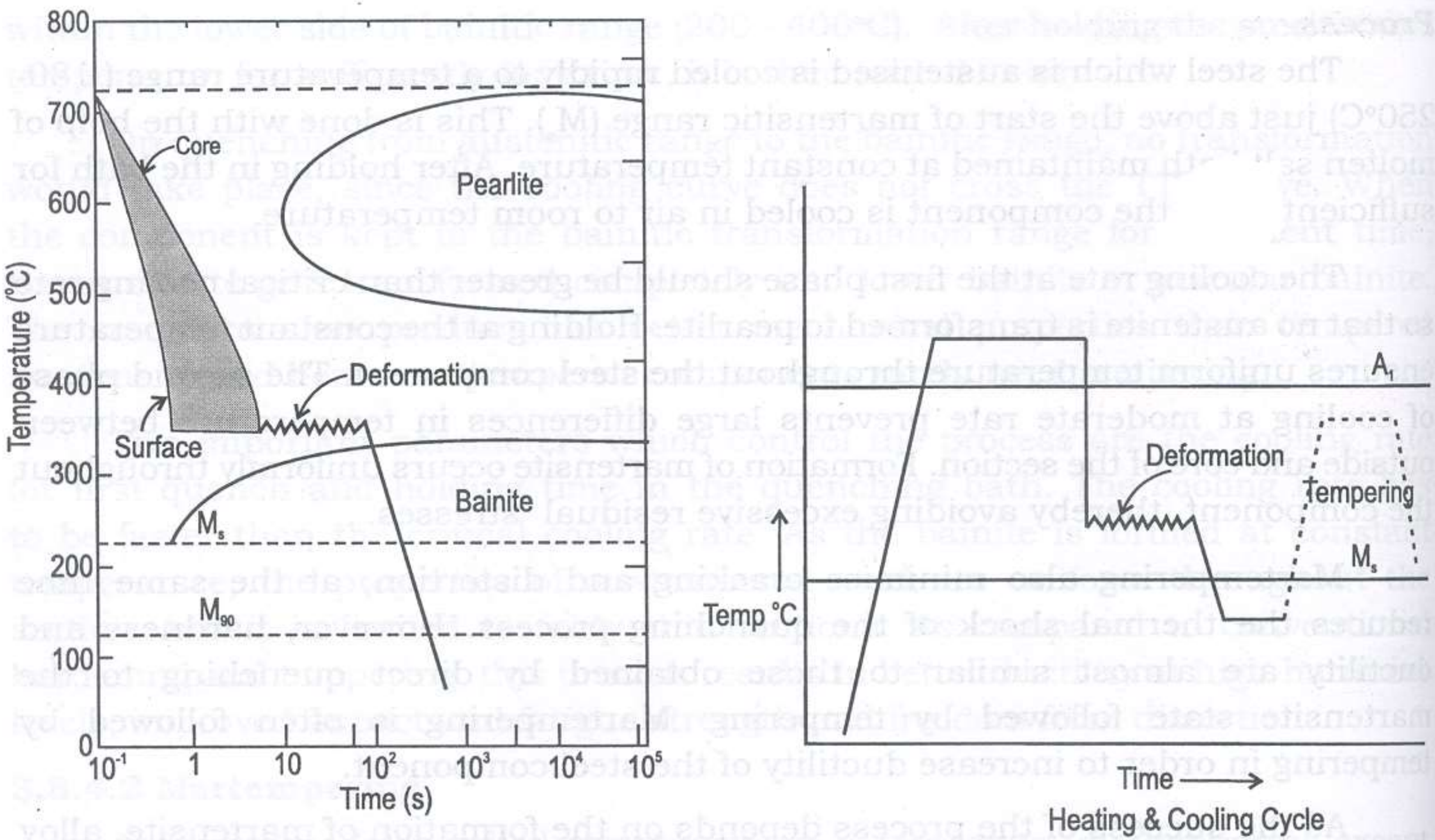


Figure 3.45 *Ausforming*

- Some steels (with rapid transformation) are not suitable
- Alloying elements (Mn,Ni,Cr) added to develop a deep metastable region by displacing TTT curve to longer transformation times
- Ausforming – improved strength without affecting ductility and toughness
- 12% Cr steels – Tensile strengths of over 3000 MPa can be obtained

Table 8.2 *Summary of various heat treatment processes.*

Process	**Initial Microstructure**	**Type of cooling**	**Final Microstructure**	**Physical properties**
Annealing	Austenite	Furnace Cooling	Coarse pearlite	Low strength, high ductility
Normalising	Austenite	Air Cooling	Fine pearlite	Medium strength & ductility
Hardening	Austenite	Quenching	Martensite	Hard & brittle, high strength
Tempering	Martensite	Any cooling rate depending on need	Tempered martensite	To eliminate the brittleness of martensite
Austempering	Austenite	Interrupted quench	Bainite	Intermediate between pearlite & martensite
Martempering	Austenite	Interrupted quench	Tempered martensite	Hard, ductile

Hardenability

- Ability of the steel to develop a hardened layer across the c/s
- The hardenability of a metal alloy is the depth up to which a material is hardened after putting through a heat treatment process
- A measure of thickness of steel that can be hardened by quenching
- Hardness decreases with distance from the surface of a hardened specimen due to decreased Martensitic content
- A material is said to have hardenability when decrease in hardness towards the centre is very low

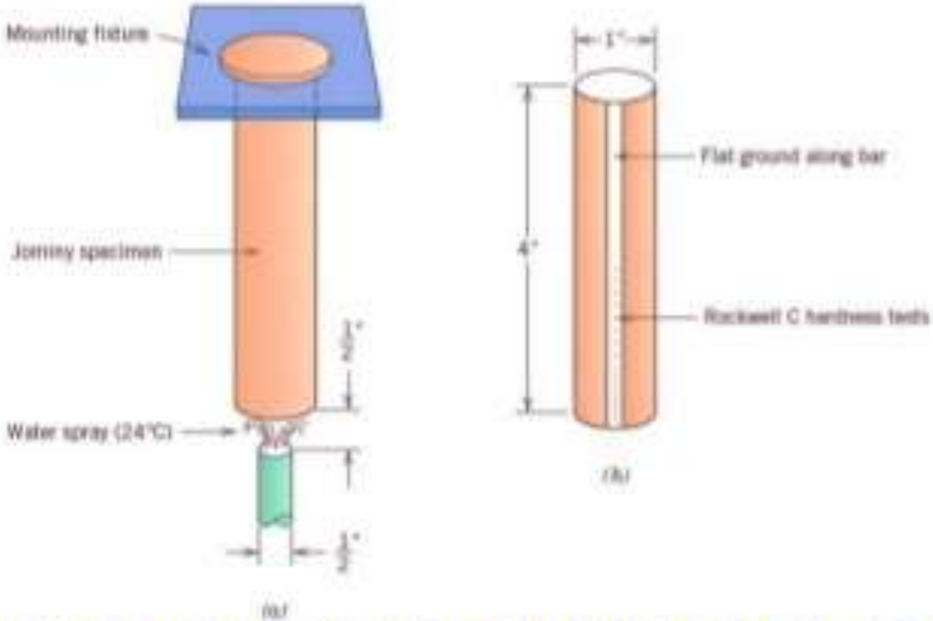
- Hardenability of steel is expressed as the diameter of the bar that will form a structure composed of 50% Martensite at the centre when it is severely quenched
- Ideal critical diameter
- A good hardenability means even thicker sections can be uniformly hardened
- Effect of Alloying elements on Hardenability

- *Don’t confuse hardness and Hardenability.*
- ***Hardness*** *is a material property.*
- ***Hardenability*** *is a way to indicate a material’s potential to be hardened by thermal treatment.*

Jominy – End Quench Test

- A method to determine hardenability of steel
- A standard specimen (25.4mm,100mm) is heated above A1 temperature for a specified period of time
- Fixed on a fixture; lower end is quenched by a jet of water @ specified flow rate
- Results in different rates of cooling along the length

JOMINY END QUENCH TEST



Schematic representation of Jominy End-Quench Test

- Surface hardness (HRc) measured along the length
- A curve is plotted b/w hardness and distance from quenched end
- Jominy curve or hardenability curve

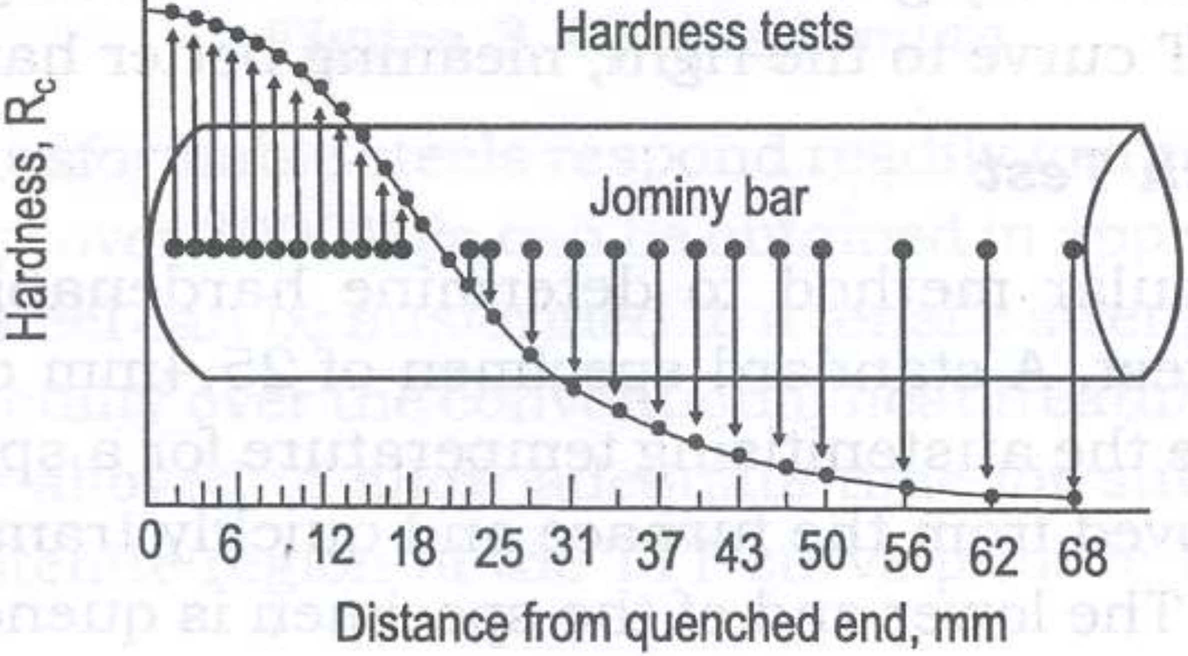


Figure 3.47 *Jominy curve*

- If quench rate for a given part is known, hardness can be prdicted
- Can be used to determine hardenability of different steels
- Jominy distance – a measure of hardenability
- Mass effect

Surface Hardening

- Some materials need different properties for surface and interior
- Gears, cranks, camshafts, rolls – Hard wear resistant surface and tough shock resistant interior
- Chemical processing equipments – corrosion resistant surface with enough strength
- Decorative fittings require good surface finish with adequate strength
- Surfaces of such components are given appropriate treatments to develop desired properties

Surface treatments - classification

- **Mechanical treatments** – shot blasting, Burnishing (pressing b/w rolls) – residual compressive stress developed
- **Providing protective coatings** – painting, plating, metal spraying, metal cladding
- **Changing the chemical composition** – surfaces of components are brought in contact with suitable materials – C, N etc allowed to diffuse into the surface
- **Giving heat treatment to the surface** – surface alone is heat treated to change the properties while interior un affected
- “Case” and “core”

- **Diffusion methods (case hardening)**

  - Carburising
  - Cyaniding
  - Nitriding
  - Carbonitriding

- **Selective Hardening methods**

  - Flame hardening
  - Induction hardening
  - Laser hardening
  - Electron beam hardening

Case Hardening

- Some m/c parts require a tough core with hard wear resistant case
- This can be done by spreading into the surface excess of C or N at high temperature – Carbides or Nitrides formed
- Gears, shafts, axles, cutting tools

Carburising

- Spreading the surface of a steel component with C to the desired value
- Up to 1.2% C is added
- Process: Heating the steel in contact with a C rich substance above critical temperature for a long duration
- C penetrates into the steel to form a solid solution on the outer surfaces
- MS can be converted to High carbon steel
- Based on C rich substance used:
    - solid or Pack carburising
    - Gas carburising
    - Liquid carburising

Pack carburising

- Solid substances such as coke, coal, charcoal, carbonates of Barium, Calcium, sodium etc are used
- Steel object is placed in a closed chamber surrounding solid powder and heated
- C rich fumes - C spreads in to the surface
- 0.1 mm penetration takes place in 1 Hour

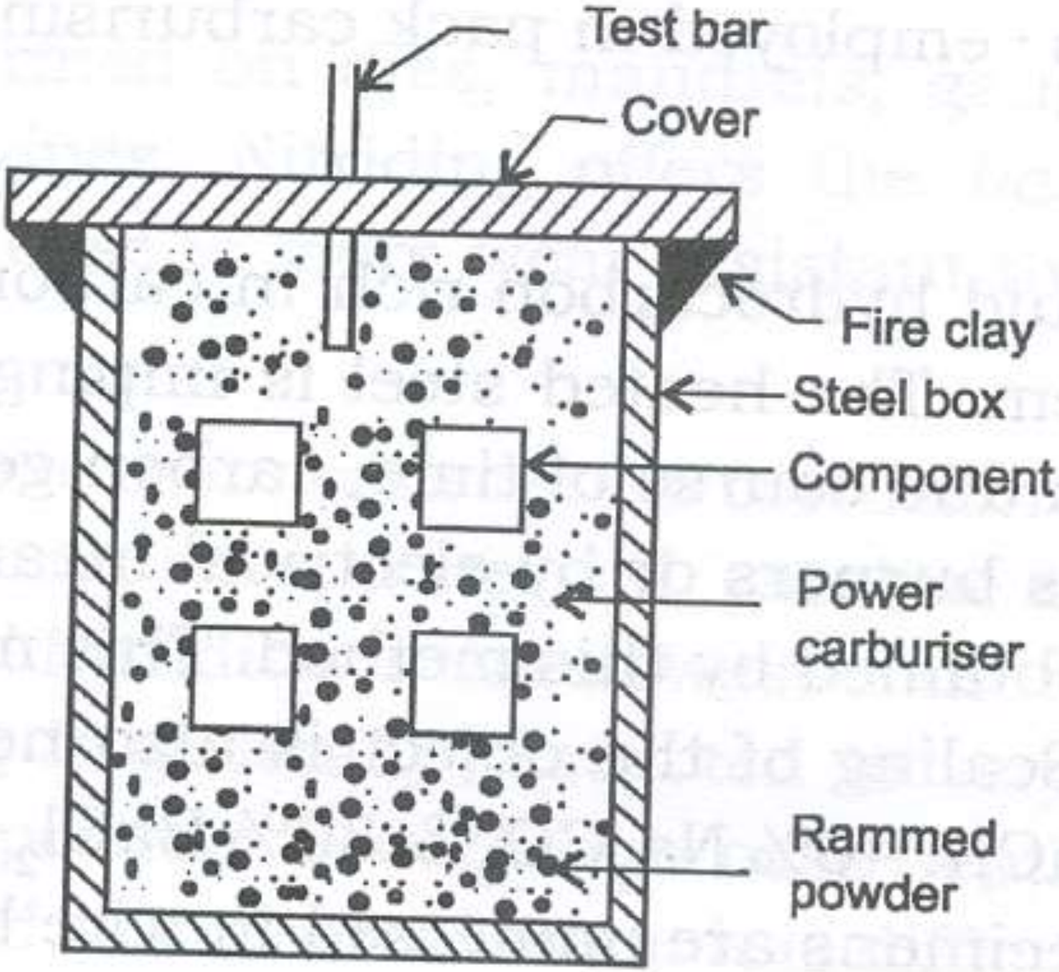


Figure 3.48 *Pack carburising process*

- Heating range in the furnace 870-980˚C for 5 – 10 Hrs.
- Steel gets Austenised, and can absorb C up to 1.2%
- The carbonaceous material will release CO which combining with Fe form Fe_3C

Gas carburising

- Component is heated in furnace which is filled with C rich gas (methane, propane, butane, CO)
- Hydrocarbons decompose and gets deposited on steel surface
- Thickness of hardened case depends on rate of gas flow and time of contact
- Heated to Austenitic range to get full C penetration
- Faster; and the depth can be more accurately controlled
- Expensive; hence For large quantities of parts only

Liquid carburising

- A liquid Hydrocarbon rich in C is used
- The heated steel is impinged by jets of liquid
- C gets deposited on the steel – 0.1 to 0.5mm depth
- Bath is prepared with 20-50% NaCN, 40%Na_2CO_3 and 30% $BaCl_2$ or NaCl heated to 850-950˚C
- Liquid – fast heat transfer and C is added rapidly
- Salt baths are relatively small chambers; hence for small parts only

Nitriding

- Most effective for those steels which contain stable nitride forming elements (Al, Cr, Mo, V,W)
- Heating of steel to about 650˚C and holding in an atmosphere of $NH_{3.}$
- Anhydrous NH_3 gas is passed into the furnace at about 550˚C, where it dissociates in to nascent nitrogen and hydrogen
- N penetrates into the steel and forms very hard nitrides on the surface
- Steel is allowed to cool in the furnace
- 21-100 Hrs depending on case depth and size

- Improves corrosion resistance, very high hardness, needn’t be machined
- Portions which are not to be nitrided should be covered (tin)
- Dies, parts of pumps and IC engines
- Nitriding gives the hardest surface
- Slowest process – restricted to very thin cases
- Expensive and time consuming process

Cyaniding

- In the process MS absorbs C and N to obtain a hard surface
- The parts are immersed in a liquid bath of NaCN (800-960˚C) with concentration varying between 25% to 90 %
- Measured amount of air is passed
- NaCN reacts with O_2 in the air and is oxidised
- C and N thus formed diffuse into the steel and give a thin wear resistant layer of Carbonitride phase

- 30-90 minutes
- After cyaniding, parts are quenched in water or oil
- For a case depth from 0.5 to 2 mm –gigh temp (950^0C), bath containing 8%NaCN, 82% BaCl and 10% NaCl- 2-6 hrs for completion
- Low temperature tempering
- Used where fast and thin but a hard case is required

Carbonitriding

- For improving wear resistance of MS, plain C steel
- Carried out in a gas mixture (800-870˚C) consisting of a carburising gas and ammonia
- C and N are diffused at the same time in to the surface of the steel in Austenitic-Ferritic condition
- N is more effective than C
- N content in steel depends on NH3 content and temp
- Quenched in oil followed by tempering (150-180˚C)
- Better properties than Carburising
- Time for Heat Treatment longer

Selective hardening processes

1. Flame Hardening

- some areas of a component is heated above critical temperatures by oxy-acetylene flame and simultaneously quenched by spraying water
- depth case depends on temperature of flame, heating time, temperature of cooling water…
- For local hardening of components such as gear tooth, cams, cutting tools

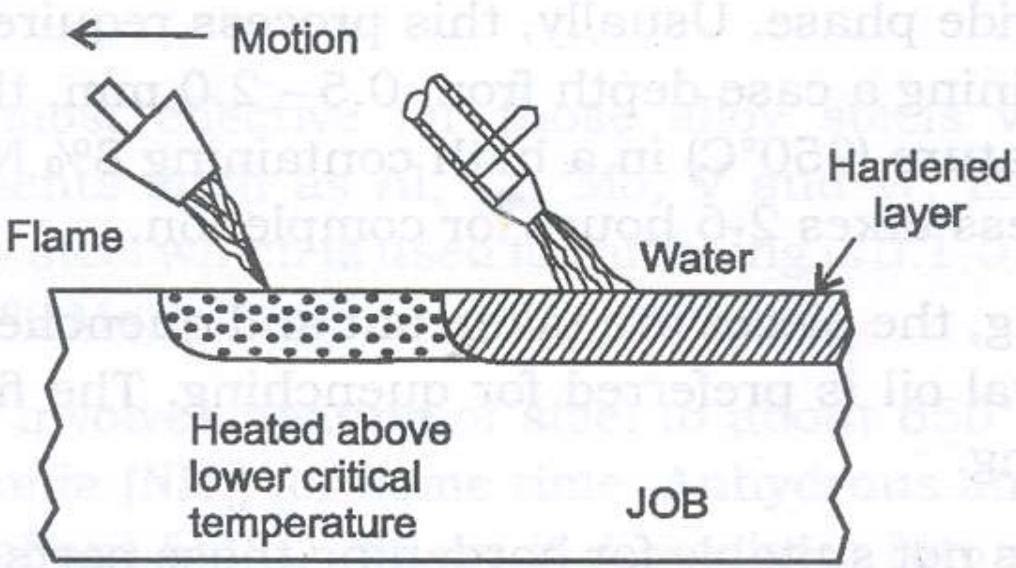


Figure 3.49 *Flame hardening*

- Features
- Slightly oxidising flame, and torch is adjusted not to exceed 850˚C
- Torch is moved so that uniform heating
- For better results C content of steel should be 0.3-0.6%
- Tempering to relieve the stresses

- Advantages
- Rapid and efficient method (depth-6mm)
- Zone hardening possible
- Large, heavy parts can be hardened

- Disadvantages
- Control of depth difficult; not suitable for thin sections
- No C or N is added to the surface; low Carbon steel can’t be hardened. Medium C steels are commonly used

Induction hardening

- To get a hard and wear resistant surface with a soft core in steel
- Job to be hardened is placed in an induction coil having several turns of Cu wire
- A high frequency current is passed through a Cu block which acts as primary coil of transformer; an alternating mag: field and an AC is induced
- This AC produces heating effect on job surface (750-800)
- Followed by Quenching
- Rapid; depth 0.8mm in 1-5 seconds

- Advantages
- Fast
- No warm up time required
- Irregular shapes and interior surfaces can be hardened
- Thickness can be varied by varying current, time
- No skilled operator is needed
- Cleaner process
- Disadvantages
- No C or N is added to the surface; more expensive steel is needed

Laser hardening

- A variant of flame hardening
- A phosphate coating is applied over the steel to facilitate absorption of Laser energy
- Exposure to Laser causes the outer layer to be heated (900-1400)
- Parts are self quenched and tempered
- Depth 0.1-1.5mm
- Greater depth requires larger volume of material

Electron Beam Hardening

- Similar to Laser beam hardening; source is a beam of electrons
- Beam is manipulated using electro magnetic coils
- Austenising, rapid cooling by self quenching
- Can be hardened very precisely both in depth and loacation
- w/p thickness should be 5-10 times austenising depth
- Low distortion and energy consumption

Strengthening mechanisms

- Strength is related to mobility of dislocations
- Easy dislocation movement – easy to deform – lower mechanical strength
- Introducing obstructions to dislocation movement material can be strengthened
- Single phase materials: grain size reduction, solid solution strengthening, work hardening
- Multi phase materials: precipitation hardening, Dispersion hardening

Grain size reduction

- As moving dislocations reach near grain boundary, difficulty in moving forward to next grain
- It is due to different atomic arrangements in neighboring grains
- When grain size reduced total grain boundary area will be larger; more obstructions to dislocation motion
- ie, a fine grained material has high strength and hardness

Work hardening

- Almost all ductile materials become stronger when deformed plastically by cold working
- This increase in strength - Work hardening or strain hardening
- During deformation dislocations interact each other
- This creates barriers to moving dislocations
- Also when deformed dislocation density increases
- Hence less mobility, strong material
- Strain hardening rate is more in metals with cubic structure than HCP metals
- Annealing relieves the effect of strain hardening

Solid solution hardening

- Pure metals can be strengthened by alloying with impurity atoms to form a solid solution
- Presence of impurity atoms induces lattice strains within the material
- Hence dislocation movement is restricted
- Greater loads are needed to initiate and continue dislocation movement
- ie, presence of impurities enhances mech: properties

Precipitation hardening

- By the formation of extremely small, uniformly distributed particles of a second phase within the original matrix phase
- Accomplished by appropriate heat treatments
- Small particles of second phase are made to precipitate within the matrix – hence the name
- Strength develops with passage of time - Age hardening
- Suitable alloys: Al-Cu, Al-Si, Mg-Al

Dispersion hardening

- Fine particles of one phase are introduced to another phase which is weaker and ductile
- Soft phase – matrix, hard phase – precipitate or dispersed phase
- Dispersed particles should be small enough to impose obstacles
- Dispersion hardening is achieved through phase transformations (eutectic, eutectoid)

Strain hardening

- During deformation severe distortion of crystal lattice – heat generation
- Part of work done (10%) is stored as internal energy
- More work is done at grain boundaries – more int: energy exist in the region
- Hence the int: energy of the deformed metal is very high
- Hence there will be an increase in resistance to further deformation – strain (work) hardening
- Effect of Dislocation density

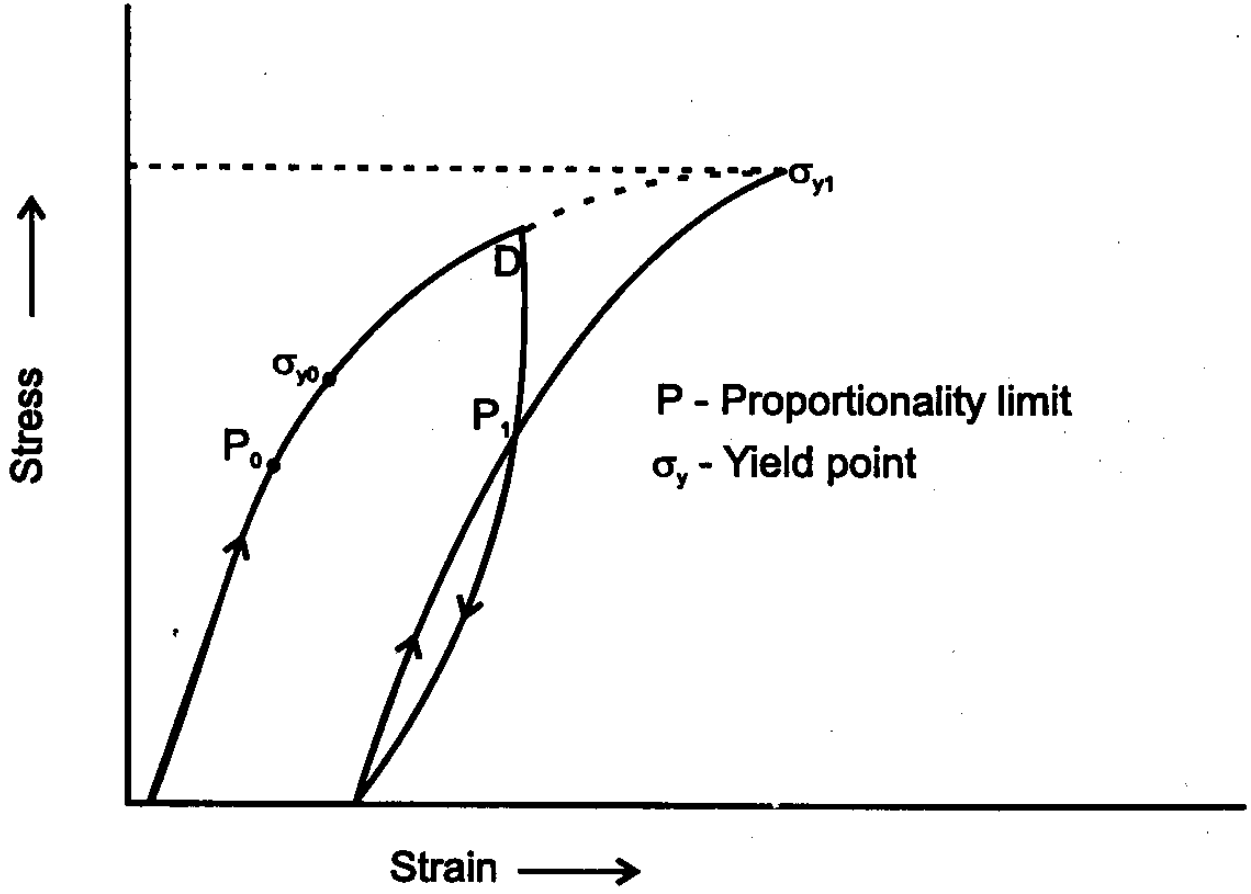
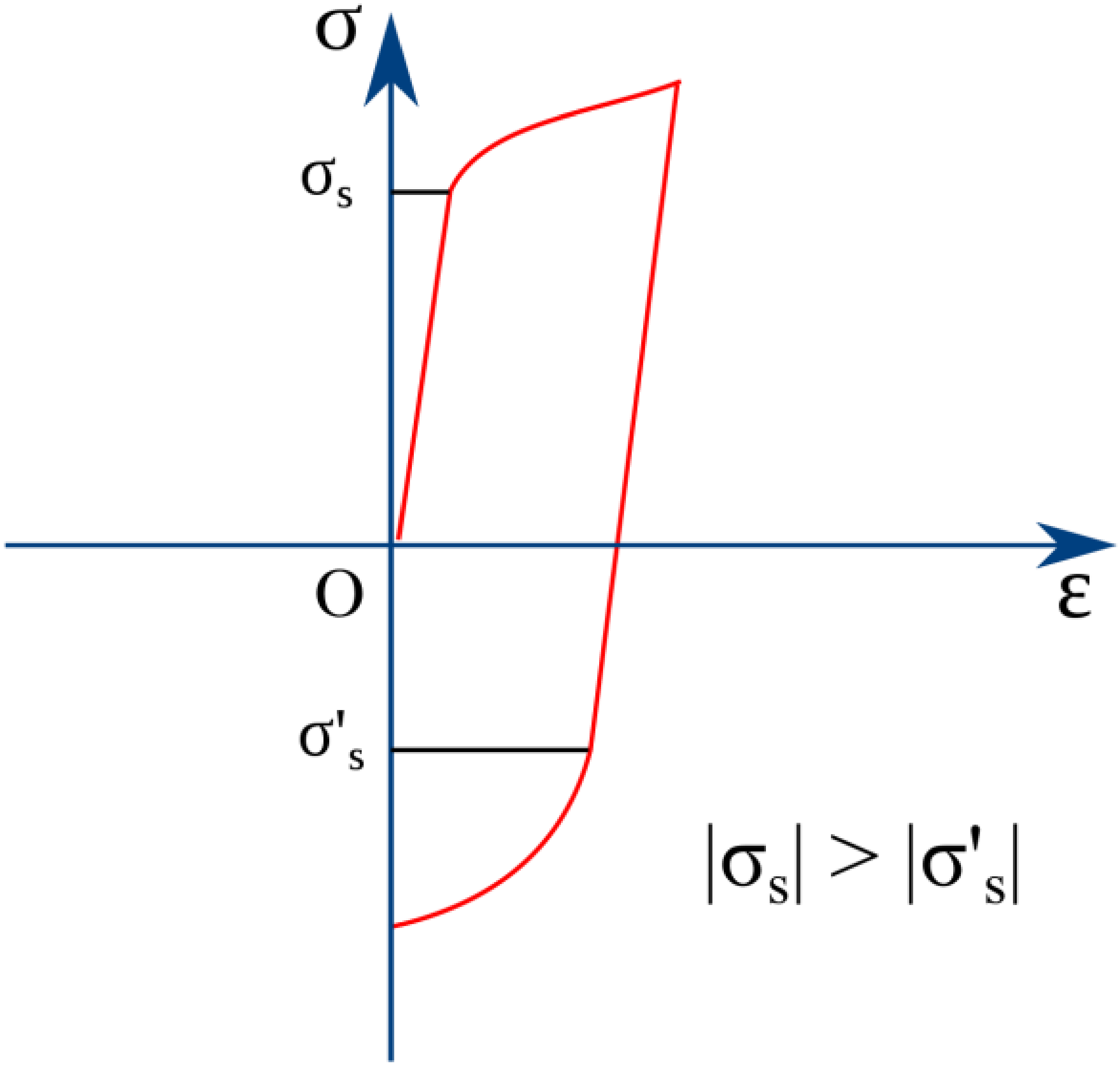


Figure 3.50 *Strain hardening*

Bauschinger effect

- Dislocation pile ups and back stress
- If the direction applied stress is reversed, slip (deformation) occurs in the opposite direction
- Dislocations piled up earlier would be supporting the movement now
- As a result deformation would be initiated at a lower applied stress
- This lowering of yield stress when deformation in one direction is followed by deformation in the opposite direction – Bauschinger effect
- During cold working yield stress in tension increases due to strain hardening
- When the same material is subjected to compressive loading yield stress will be much lower than previous case


σ
σ_s
O
ε
σ'_s
|σ_s| > |σ'_s|

Cold and hot working

- Mechanical working: process of effecting shape changes in materials by applying external force
- Changes in structure and properties takes place
- Cold and hot working

- Cold working
- If the grains of a material are in distorted condition at the end of plastic deformation – cold worked
- Properties dependant on lattice structure will be affected
- Tensile strength, yield strength, ductility

- Hot working
- Mechanical working done above recrystallisation temperature
- Below this temperature strain hardening
- But during or after hot working will anneal itself and remain soft and ductile

Recovery, Recrystallisation & Grain growth

- Annealing is a process by which cold worked lattice structure is changed back to a strain free structure
- Heating to desired temperature and slow cooling
- Transformations: 3 stages
- Recovery
- Recrystallisation and
- Grain growth

Recovery

- A low temperature process
- Property changes don’t cause change in mic:
- Atoms move nearer to positions of equilibrium; internal mechanical stresses are reduced
- Principal effect is relief of internal stresses due to cold working
- Mech: properties remain unchanged but electrical conductivity increases
- Also called stress relief annealing

Recrystallisation

- As temp: reaches upper temp of recovery stage, the vibrational energy of atoms increases
- Atoms break loose from strained lattice and form new unstrained crystals
- New crystals have same composition and lattice as that of un deformed metal
- The cluster atoms from which new grains are formed – nucleus
- These nuclei grow in size until whole material has a structure of unstressed crystals – Recrystallisation

Recrystallisation

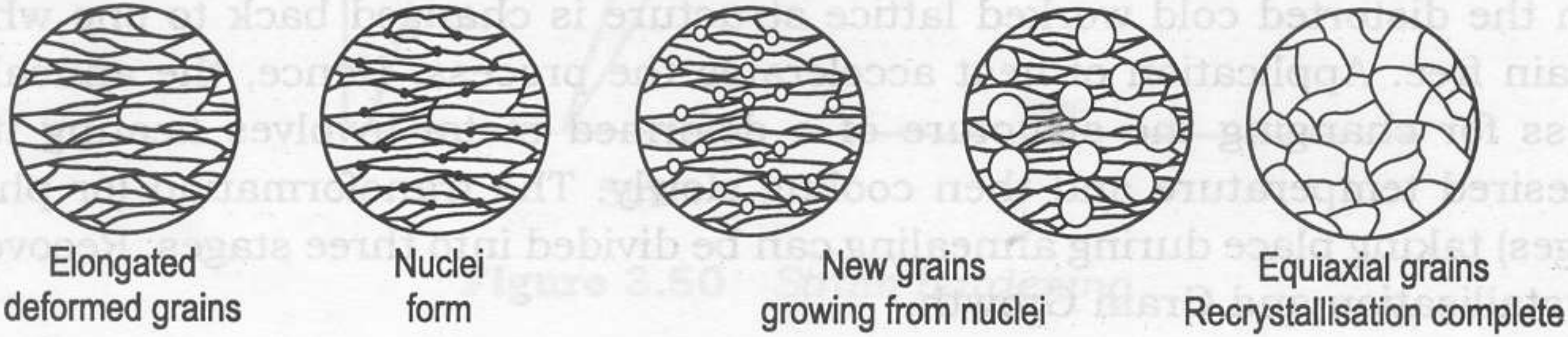


Figure 3.51 *Progress of recrystallisation process*

- Thus recrystallisation – nucleation of strain free garins – their growth until elongated grains is completely transformed to strain free grains
- Change in structure – complete release of internal energy, reduction in strength, hardness and brittleness along with increase in ductility and malleability
- Recrystallisation range – 0.3 to 0.5 Tm

Factors affecting recrystallisation

- Amount of cold work
- Time of annealing
- Annealing temperature
- Composition
- Initial grain size
- Temperature of deformation
- Amount of recovery prior to recrystallisation

Grain growth

- After recrystallisation if metal is kept at high temperature the strain free fresh grains continue to grow and becomes coarse – Grain growth
- Because larger grains have lower free energy compared to smaller grains
- As temp increases rigidity of lattice decreases and rate of grain growth is more rapid
- If rapid nucleation and slow grain growth – fine
- Slow nucleation and rapid growth - coarse

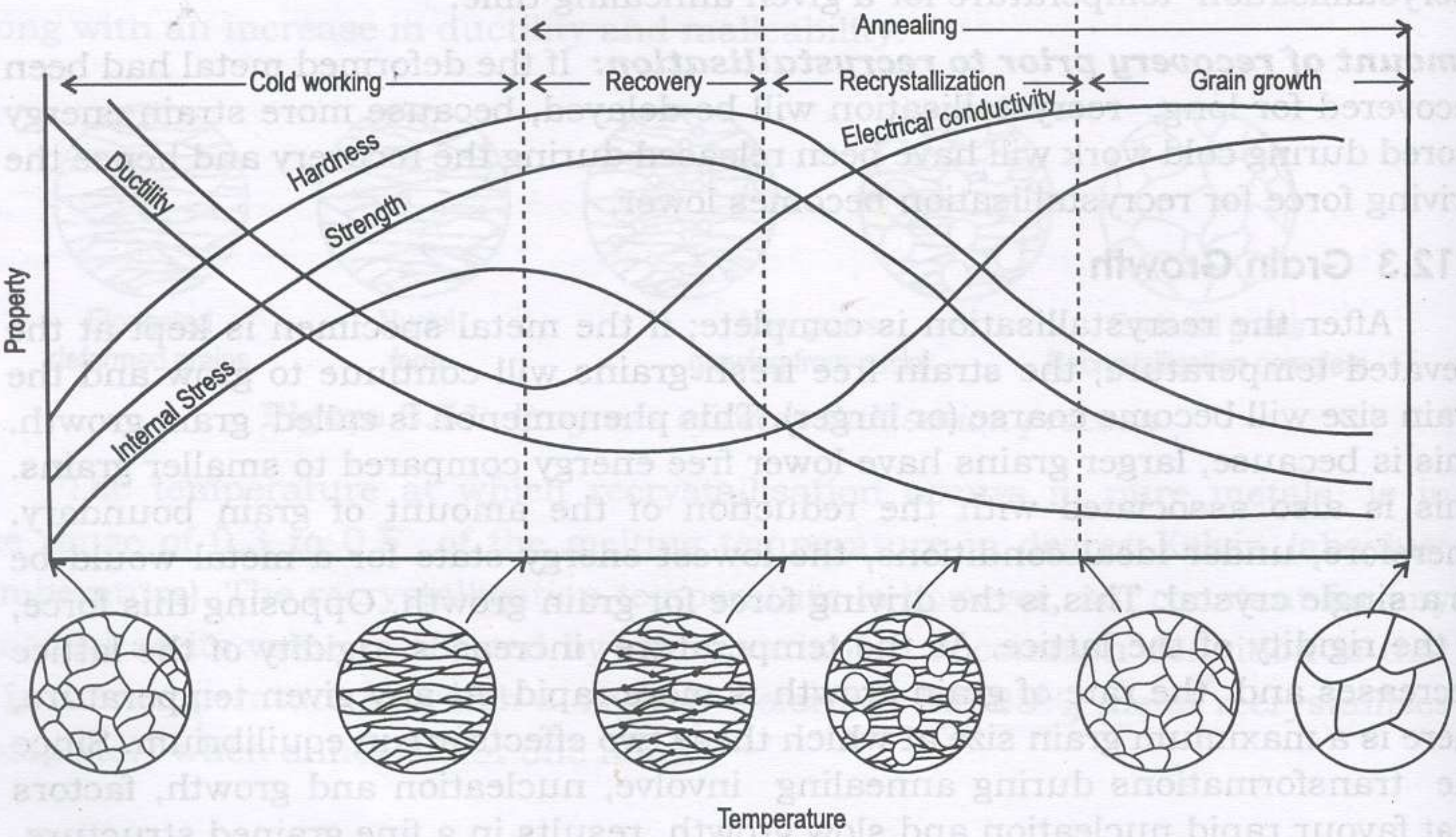


Figure 3.52 *Microstructural and property changes during cold working and subsequent annealing.*

Factors governing grain growth

- Degree of prior deformation: favors nucleation and decreases the final grain size
- Time at temperature: favors the grain growth and increases the final grain size
- Annealing temperature: lower the temp above recrystallisation temp finer the final grain size
- Heating time: faster heating rate to recrystallisation temp finer grain size
- Insoluble impurities: greater the amount of impurities, finer the grain size

Thanks…