MASINDE MULIRO UNIVERSITY
ECE 204 LESSON 3

PHASE DIAGRAMS

As a reminder lets consider the phase diagram for water

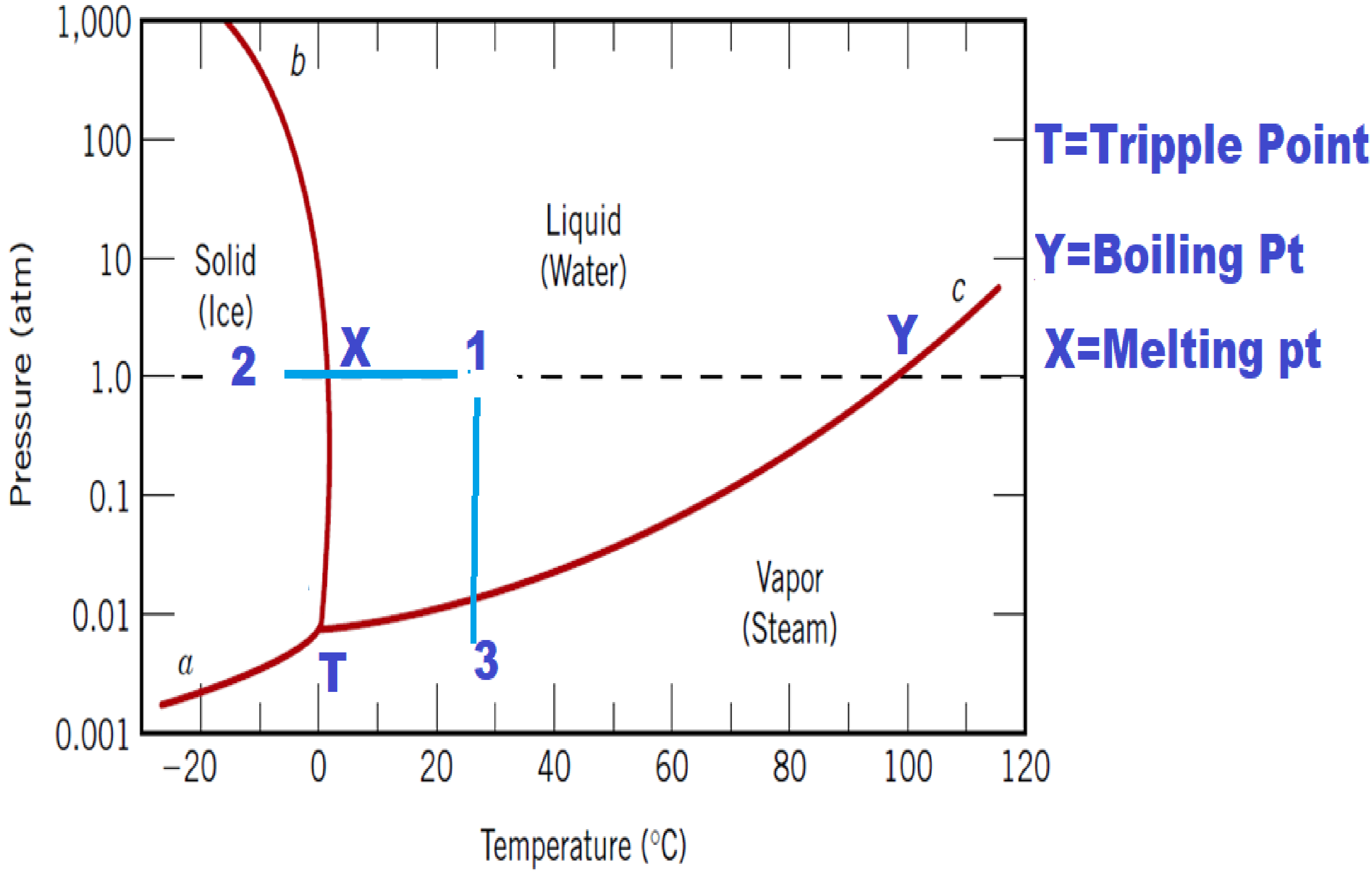


Fig 1: Phase Diagram for water

Adapted from W. D Callister Jr. and D.G. Rothwisch 2010 – pg 281
Material Science and Engineering 8th edition-Online version

With Ref to Fig 1

It can be observed that factors affecting the existence of a phase are Pressure and temperature

At Point 1 (25^oC , 1 atm). H_2O exist as liquid

At Point 2(-20^oC , 1 atm). Ice (solid)

At Point 3 (25^oC , 0.001 atm). Vapour (Steam)

At Triple point (T), Solid , Liquid and vapor are at **equilibrium (Change of Pressure or temp will make it unstable and one phase disappears)**

Such a point is also called invariant point

How do we construct a phase diagram

1 Thermal Analysis

- Plot series of graphs of cooling from the melting temp vs time at constant pressure.

Any change in slope of cooling curve indicates a phase change

2 Metallurgical Method

-Ht samples to different temps.

-wait for equilibrium

- Cool quickly to retain high temp structure

-Examine samples by the help of a metallurgical microscope

-Difficult to apply why? metals do not maintain high temp. Structures when cooled rapidly.

Typical example is the most commonly used metal **steel**

Steel at high temp such as 900^{o}C is called austenite and structure is FCC at room temp it is called ferrite and structure is BCC. But when we cool steel very fast we form a different structure BCT called martensite

Why do we need to study Phase Diagrams (PD)

Gives information about

1) Microstructure which is related to its mechanical properties
2) Melting point of an alloy
3) Helps us in choosing casting temperature
4) Crystallization behavior and final microstructure produced.

TYPES OF EQUILLIBRIUM DIAGRAMS

Type I: Two metals completely soluble in the liquid state and completely soluble in the solid state (ISOMORPHOUS ALLOY SYSTEM)

Formed by substitution solid solution

Obeys Hume-Rothery rules

- ❑Same type of crystal structure
- ❑Differ in atomic radii by less than 8%

Procedure

- **Run a series of cooling curves for various combination or alloys between metals A and B varying in composition from**

  100%A, 0%B to 0%A, 100%B I.e.

-100%A ,0%B

-80%A, 20%B

-60%A,40%B

- Plot on the same axes to show relationship

NOTE:

Each cooling curve is a separate experiment

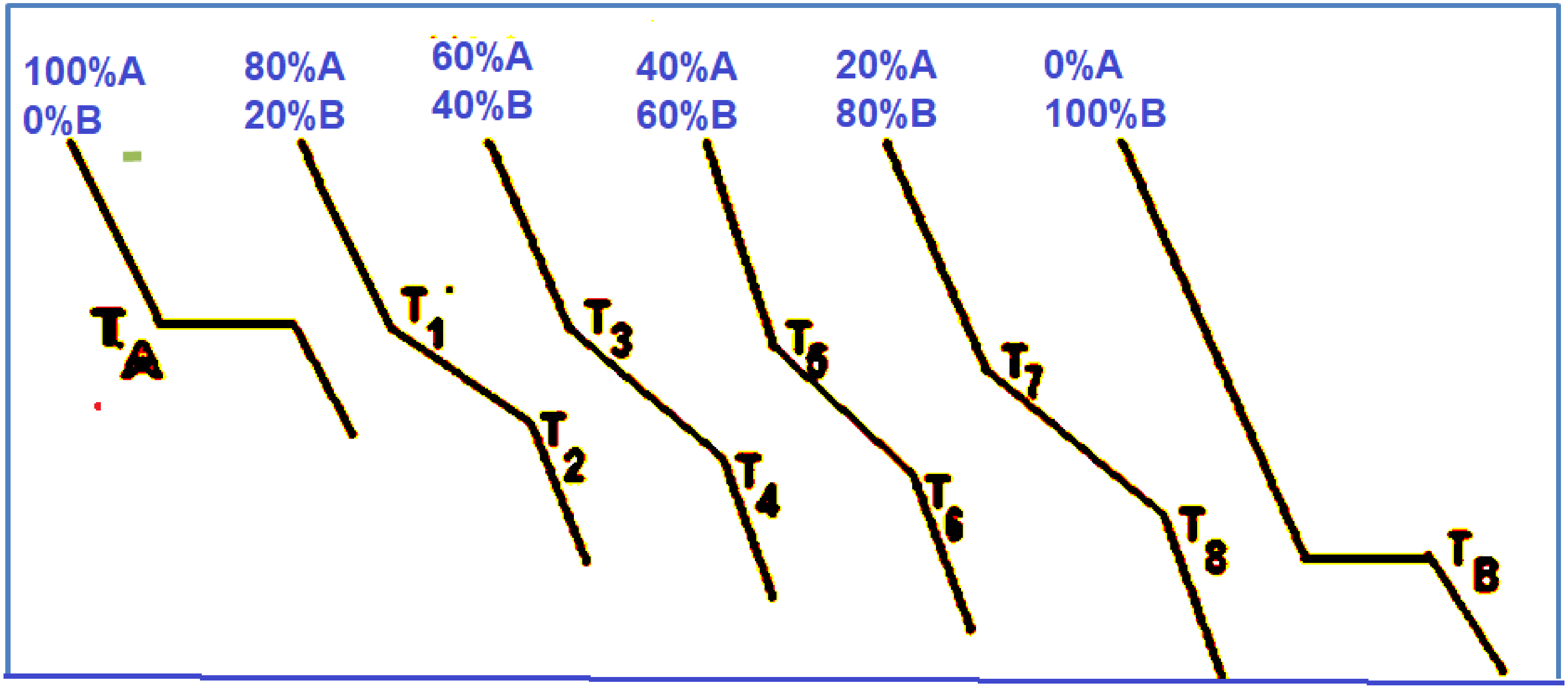


FIG 2: Construction of an Isomorphous Phase Diagram

- For **Pure metals** beginning and end of solidification take place at **a constant temp**.
- For 100% A 0%B solidification begins at T_A and ends at T_A
- For 80% A 20%B solidification begins at T_1 and ends at T_2
- For 60%A,40%B solidification begins at T_3 and end at T_4
- Do this until 0%A,100%B where solidification begins at T_B and end at T_B

- A line joining start of solidification is called **liquidus line**

-A line joining end of solidification is called **solidus line**

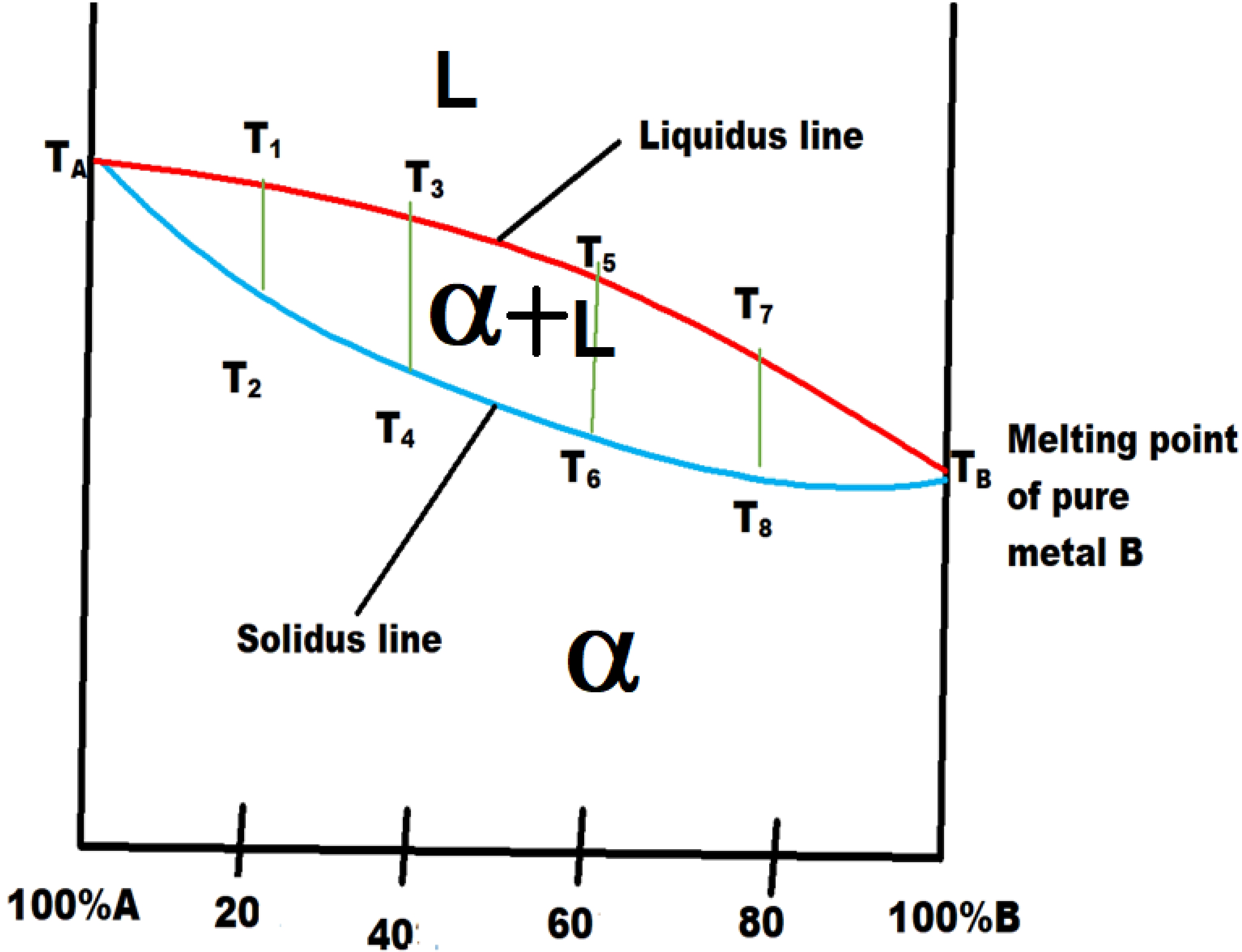


Fig 3: Isomorphous Phase Diagram

DETERMINATION OF CHEMICAL COMPOSITION AND RELATIVE AMOUNTS OF PHASES

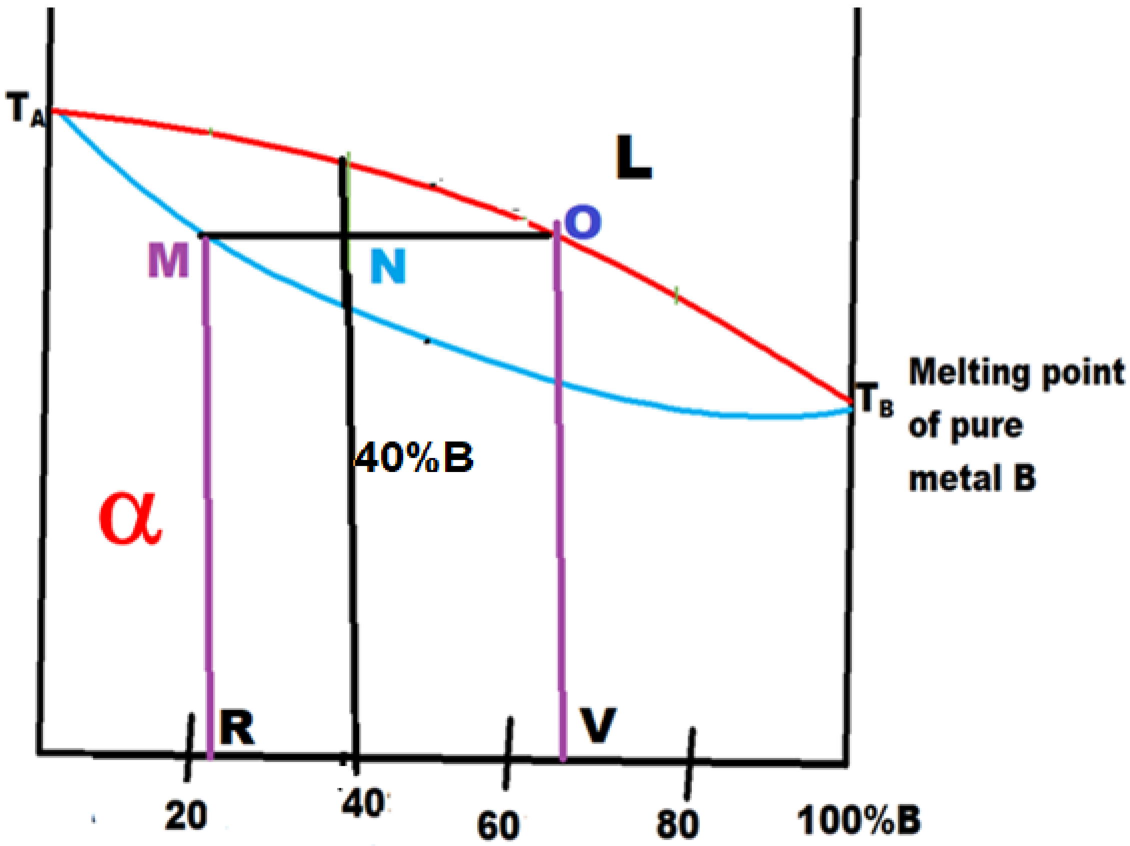


FIG 4: Use of Tie Line

THE LEVER RULE

A TIE LINE IS A HORIZONTAL LINE DRAWN AT THE POINT OF INTEREST

a) DETERMINATION OF CHEMICAL COMPOSITION

Considering point N , We draw a tie line.

- Point O the intersection of tie line with liquidus when dropped gives **Liquid sol. Of composition labelled V(33%A and 67%B)**
- Point M when dropped gives **α- solid solution** of composition **labelled R(78%A and 22%B)**

Relative amount of each phase is determined as follows.

% of Liquid =(NM/MO)x100%

α %=(NO/MO)x100%

CONSIDERING POINT N AS FULCRUM OF A LEVER

Relative lengths of the arm multiplied by **the amounts of the phases present must balance.**

In our case

AN ALLOY OF COMPOSITION 40%B (point N) or **(60%A,40%B)** at temp T consists of a mixture of two phases

One is **α-solid solution** of composition 33%A 67%B OR SIMPLY

67%B

$$\textbf{RELATIVE AMOUNT}= \frac{67-40}{67-22} \times 100\%$$

=60%

and **liquid solution** of comp 78%A 22B

OR SIMPLY 22%B

relative mount

$$\textbf{RELATIVE AMOUNT} = \frac{40-22}{67-22} \times 100\%$$

=40%

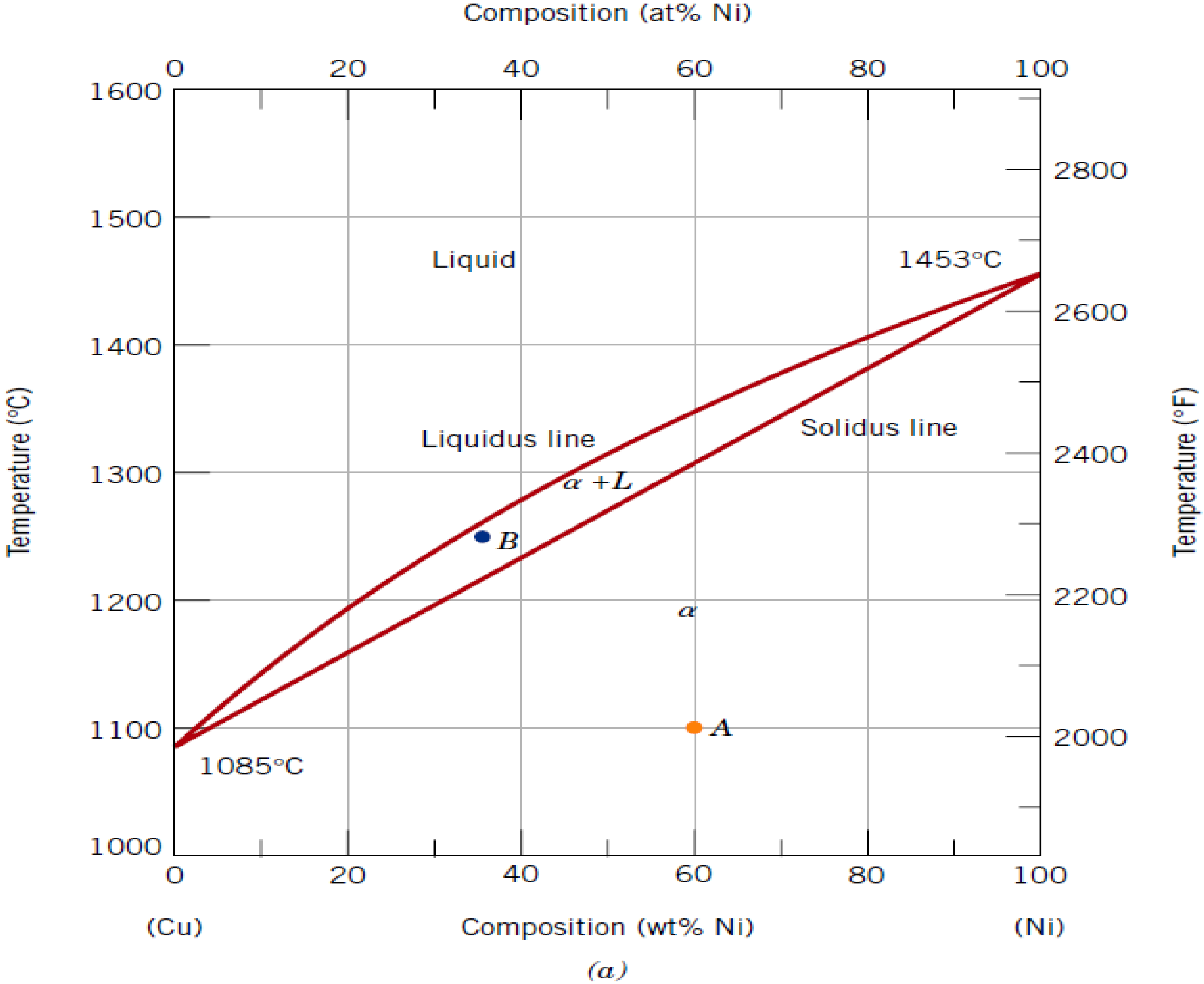


Fig 5 Considering Cu-Ni Phase Diagram Adopted from Calister Jr Pg 288.

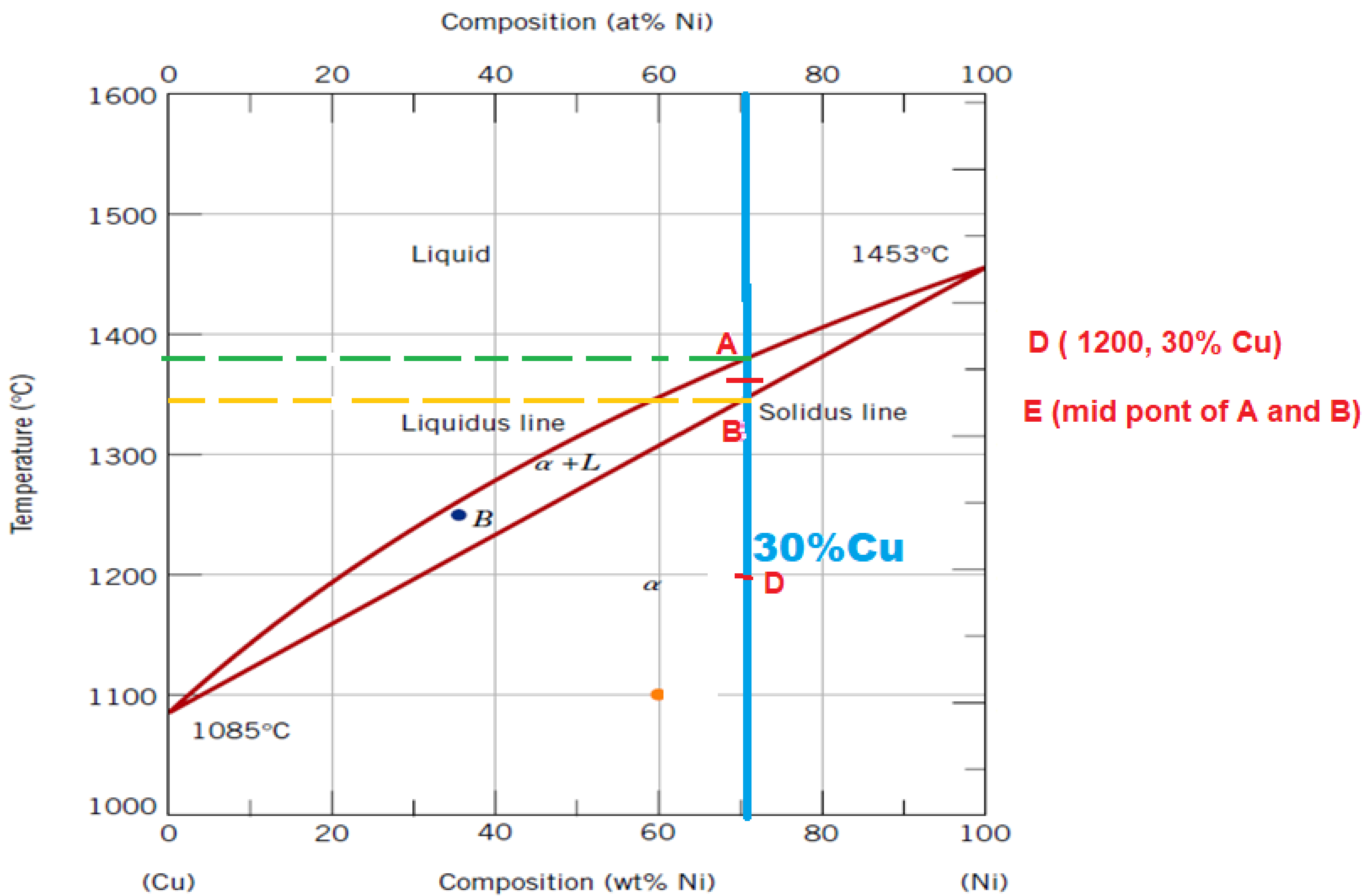


Fig 6: Consider A atypical isomorphous diagram Cu-Ni

Cooling to room temp 30%Cu (or 70%Ni)

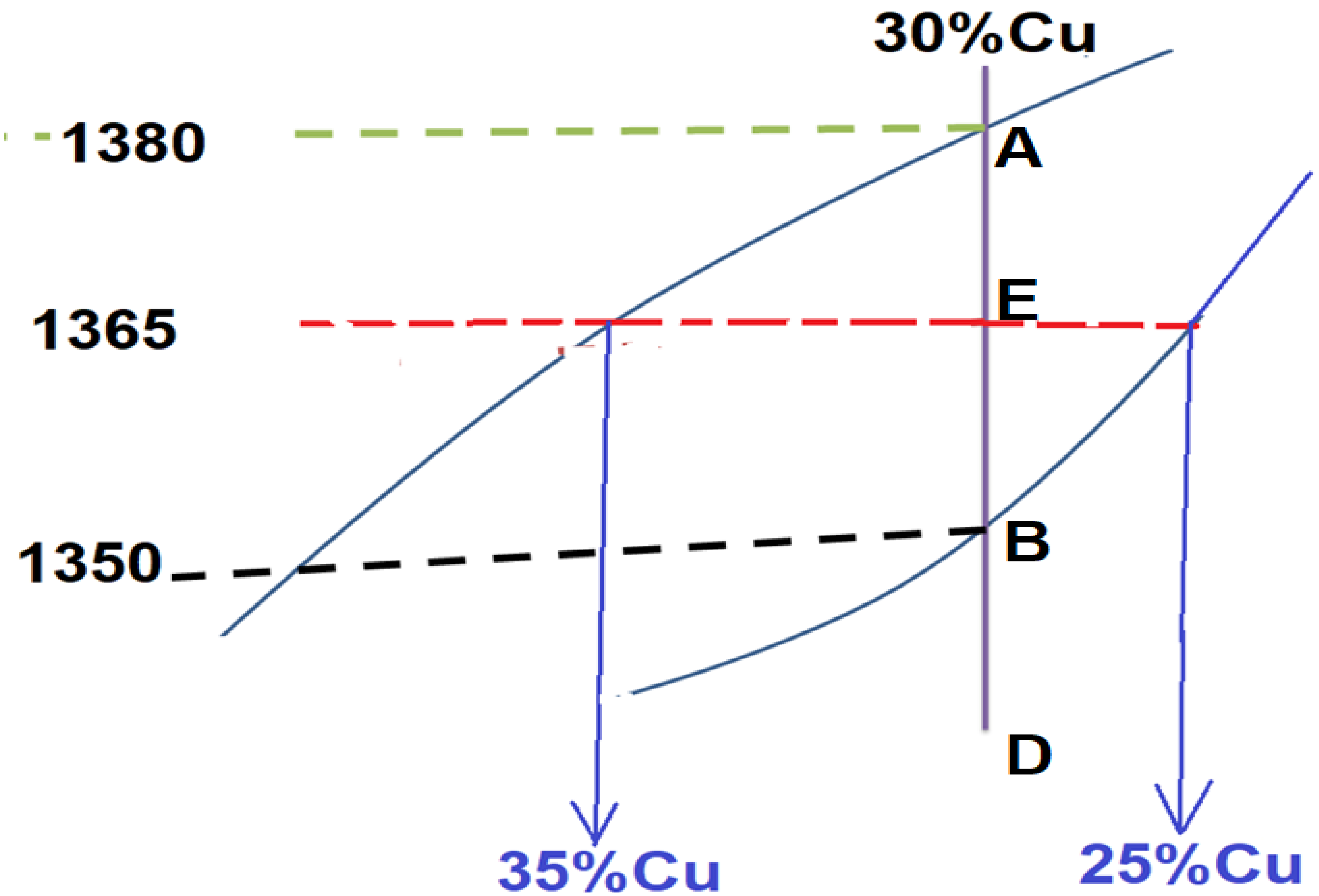


Fig 7: Magnified 2-phase zone

Ni-Cu Phase Diagram M.Pt of Ni=1452°C and that of Cu=1083 °C. cooling an alloy with 30% Cu from the molten state to 1200 °C.

TEMP	point	Phases	Composition	Relative amounts
1500°C	See diag.	L	30%B	100%L
1380°C	A	L-solution	>30%Cu	Essentially 100%L
		α-solid solution	20%Cu	Negligible α-solid
1365°C	E	L-solution	35%Cu	$\frac{35-30}{35-25} \times 100\%$ =50%
		α-solid solution	25%Cu	=50%
1350°C	B	L-solution	41%Cu	Negligible L
		α-solid solution	>30%Cu	Essentially 100% α-solid
1200°C	D	α-solid solution	30%B	100% α-solid

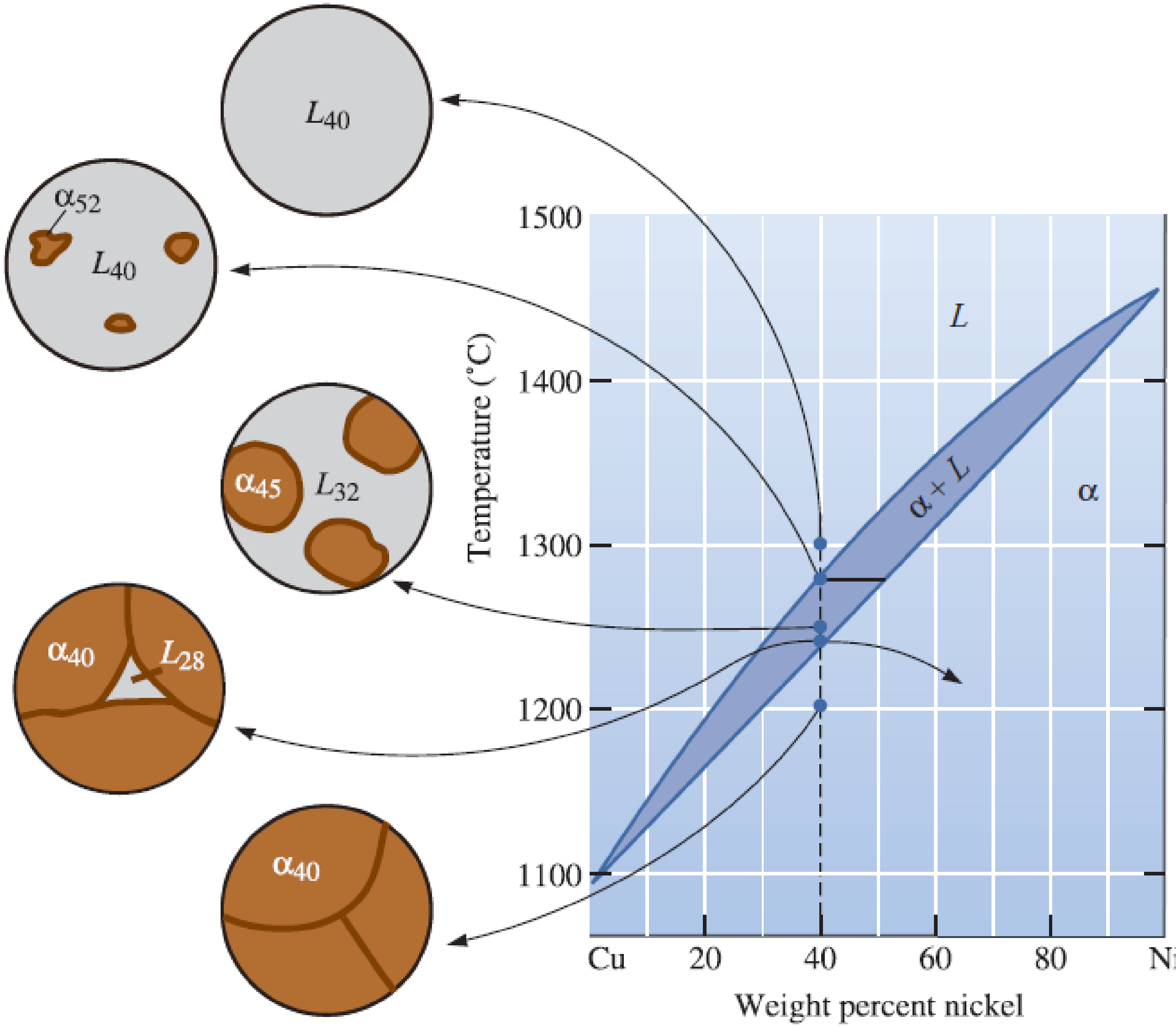


Fig 8: Change in Structure of Cu-40% NI alloy

From a PD we can

1 Determine phases present

2 Properties of phases

Note : microstructures depends on

1 Alloying elements present

2 Conc. of the elements

3 History of the ht treatment process undertaken

EXERCISE 1

Metals X and Y forms an isomorphous alloy system. If the melting point of metal X is higher than that of metal Y.

Using a suitable scale,

i) sketch the phase diagram
ii) Selecting any composition of your choice determine the composition of the phases present and their relative amounts as you cool from the molten state to room temperature.

Submit on or before 14/5/2020

Type II—Two Metals Completely Soluble in the Liquid State and Completely Insoluble in the Solid State

NOTE:

1 In this type of phase diagram, solids exist as solid A and solid B

2 Technically, no two metals are completely insoluble in each other. However, in some cases the solubility is so restricted that for practical purposes they may be considered insoluble

Raoult's Law:

States that the freezing point of a pure substance will be lowered by the addition of a second substance **provided the latter is soluble in the pure substance when liquid and insoluble when solidified**

- As more of element **B** is added to **A** the temperature of solidification is **lowered**
- A line joining beginning of solidification has a minimum point indicated as **Eutectic point (E)**

CONSTRUCTION OF EUTECTIC PHASE DIAGRAM

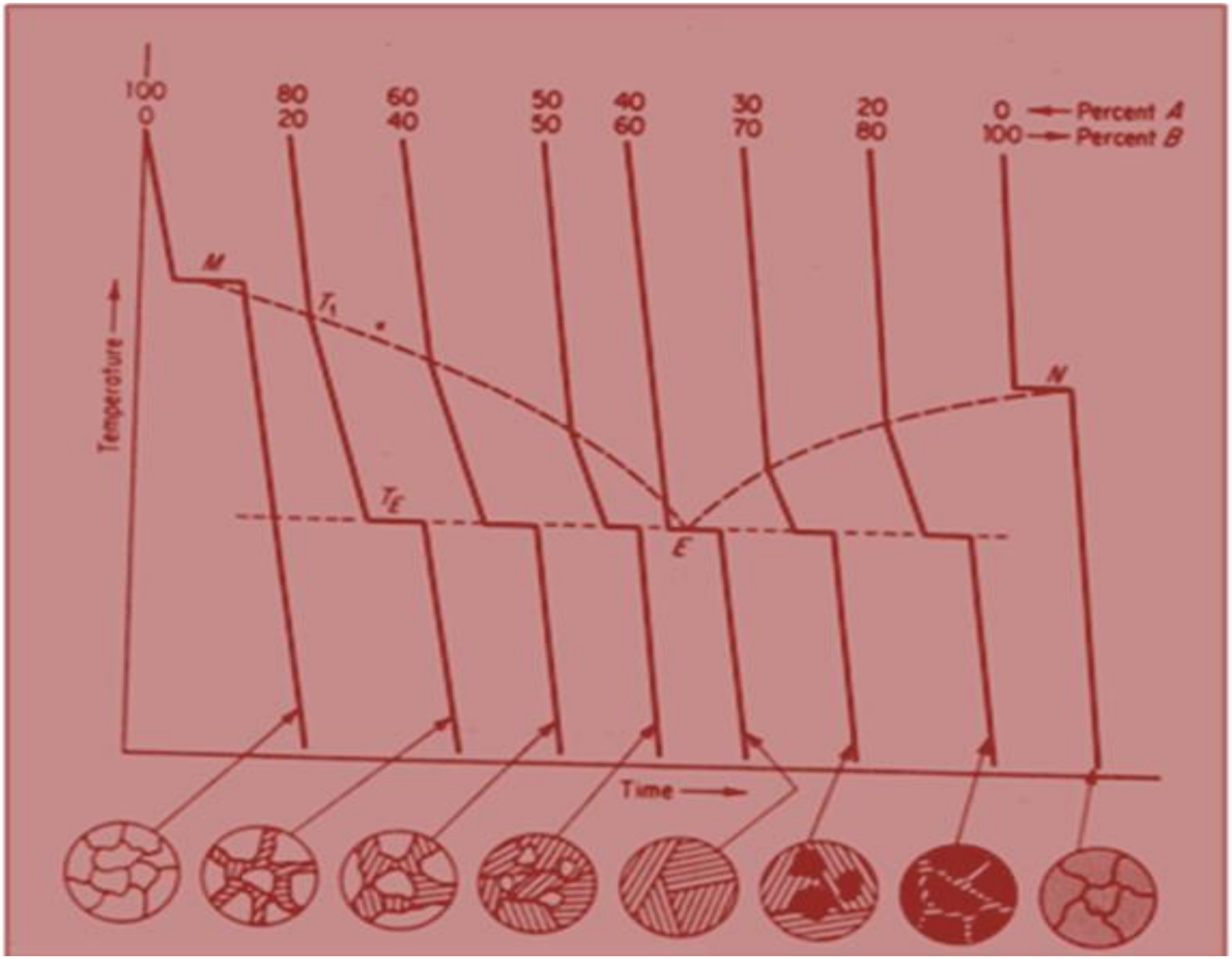


Fig 8: Construction of a eutectic Phase diagram

EUTECTIC PHASE DIAGRAM

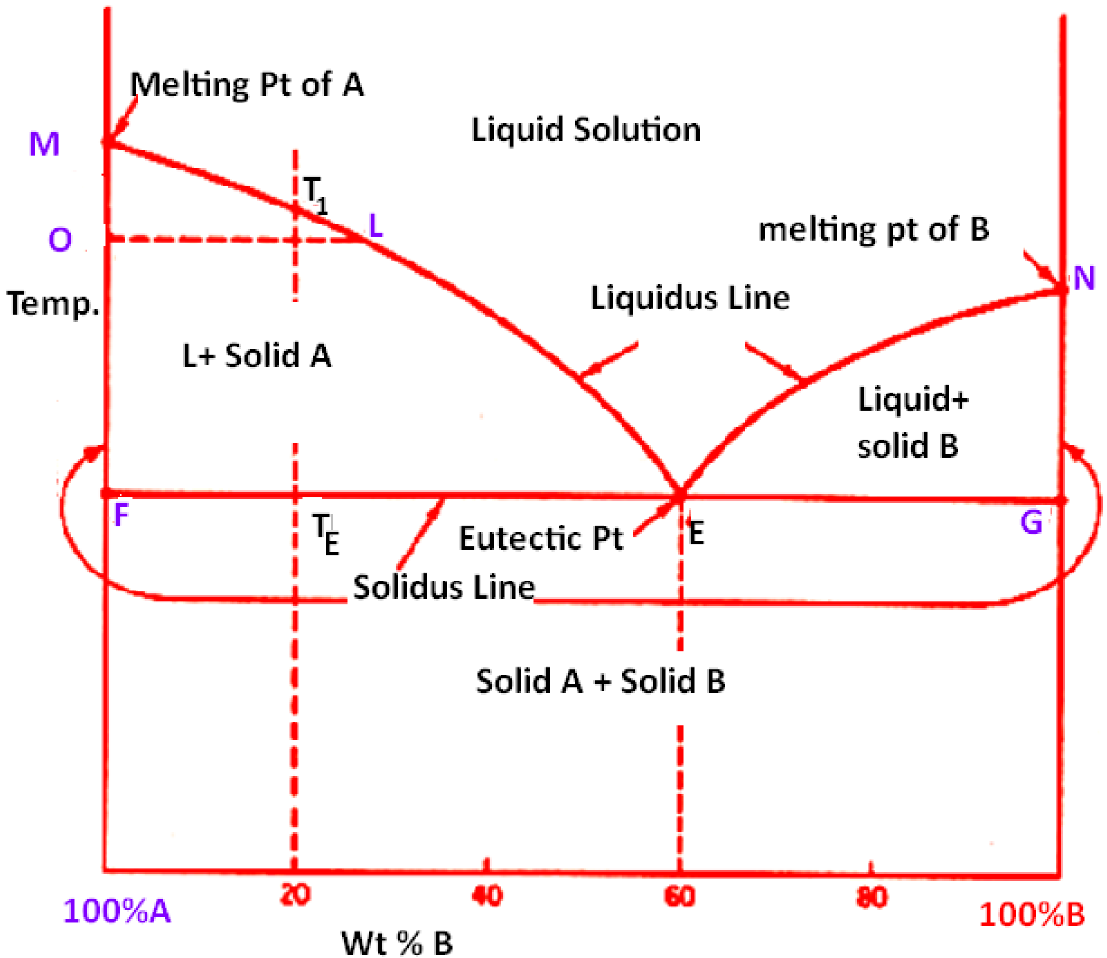


Fig 9:A fully drawn and labelled eutectic phase diagram

- **The actual phase diagram may now be constructed by transferring the breaks on the cooling curves to a plot of temperature vs. composition**
- **The melting points of the two pure metals, points *M* and *N*, are plotted on the vertical lines that represent the pure metals.**

- **For an alloy containing 80%*A-20%B* the beginning of solidification is T_1 and the end of solidification T_E as shown. The same procedure is followed for the remaining alloys**

- **The upper line on the phase diagram connecting the two melting points, MEN - is called the liquidus line (shows the beginning of solidification).**

E is known as the ***Eutectic point.***

T_E Eutectic temperature

*From diagram Pt E (40%A-60%B) the composition at the minimum temp is termed **eutectic composition.***

MFGN-Solidus Line

-**The remaining three areas are two-phase areas.**

-**Every two-phase area on a phase diagram must be bounded along a horizontal line by single phases hence to determine phases present,**

-**Draw a tie line and read the values at the end of the tie line (Gives us the phases that exists in the 2 phase region)**

- **In the Eutectic Diagram,**

to determine the phases that exist in the two-phase area such as MFE

-Draw a tie line *OL* .

NOTE: This line intersects the liquidus at *L,* which means that the liquid is one of the phases

The line intersects the left axis at point O. (The left axis represents a single phase the pure metal *A* which when below its melting point is solid)

Therefore. the two phases existing in the area *MFE* are liquid and solid *A.*

- The two phases that exist in area *NEG.* are liquid and solid B

- Since the two metals are assumed to be completely insoluble in the solid state, when freezing starts the only solid that can form is a pure metal.
- In this phase diagram, every alloy when completely solidified must be a mixture of the two pure metals.

NOTE:

1 Alloys to **the left of** the **eutectic composition** are referred to as ***hypoeutectic*** *alloys* and **those** to the **right** as ***hypereutectic*** *alloys.*

2 During solidification of eutectic composition, C_E , nothing occurs until T_E is reached and at that constant temp all liquid changes to eutectic microstructure.

- (This behaves is like that of a pure metal with constant melting temp.)
- **Solidification occurs by forming alternate layers of the constituents existing at the end s of the tie-line**

Type III: Two Metals partially soluble in the solid state but completely soluble in the Liquid state

- Since most metals show **SOME SOLUBILITY** in the solid state **this is the most common of all the phase diagrams hence the most important**
- Since the metals are partially soluble in the solid state **a solid solution is formed.**

α is the solid soln. of metal B in A

β is the solid sol. of metal A in B

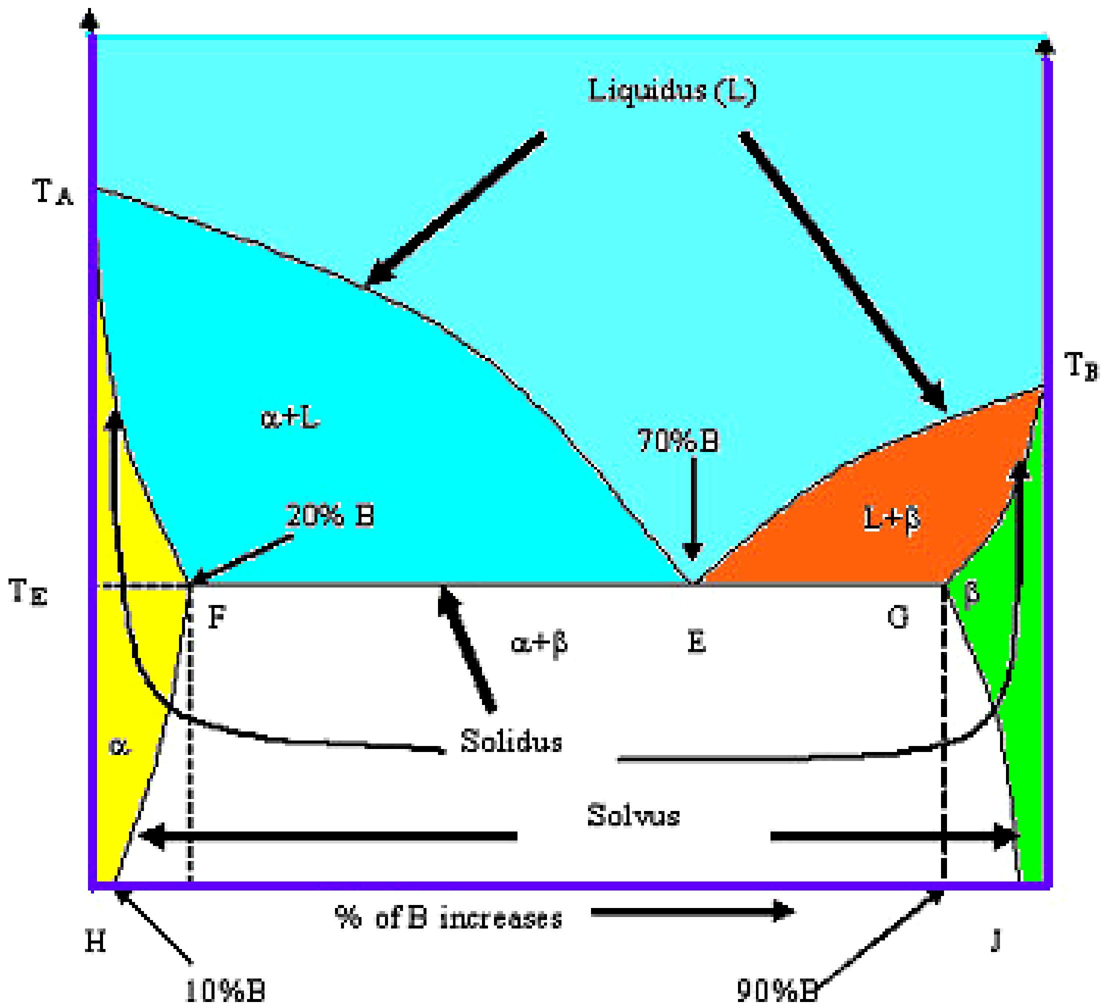
- Alloys of such a system will finally form solid solutions and not pure metals. Examples are :

  -Pb-Sn

  -Al- Si

  -Cu-Ag

  -Pb-Sb



TA=Melting Point of Pure Metal A
TB =Melting point of pure metal B
α=Solid solution of metal B in Metal A
β= Solid Solution of metal A in Metal B
TAETB= Liquidus Line
TAFEGTB=Solidus Line
Line FH and GJ=Solvus line
E=Eutectic Point

Fig 10: Eutectic diagram with Partial Solubilities

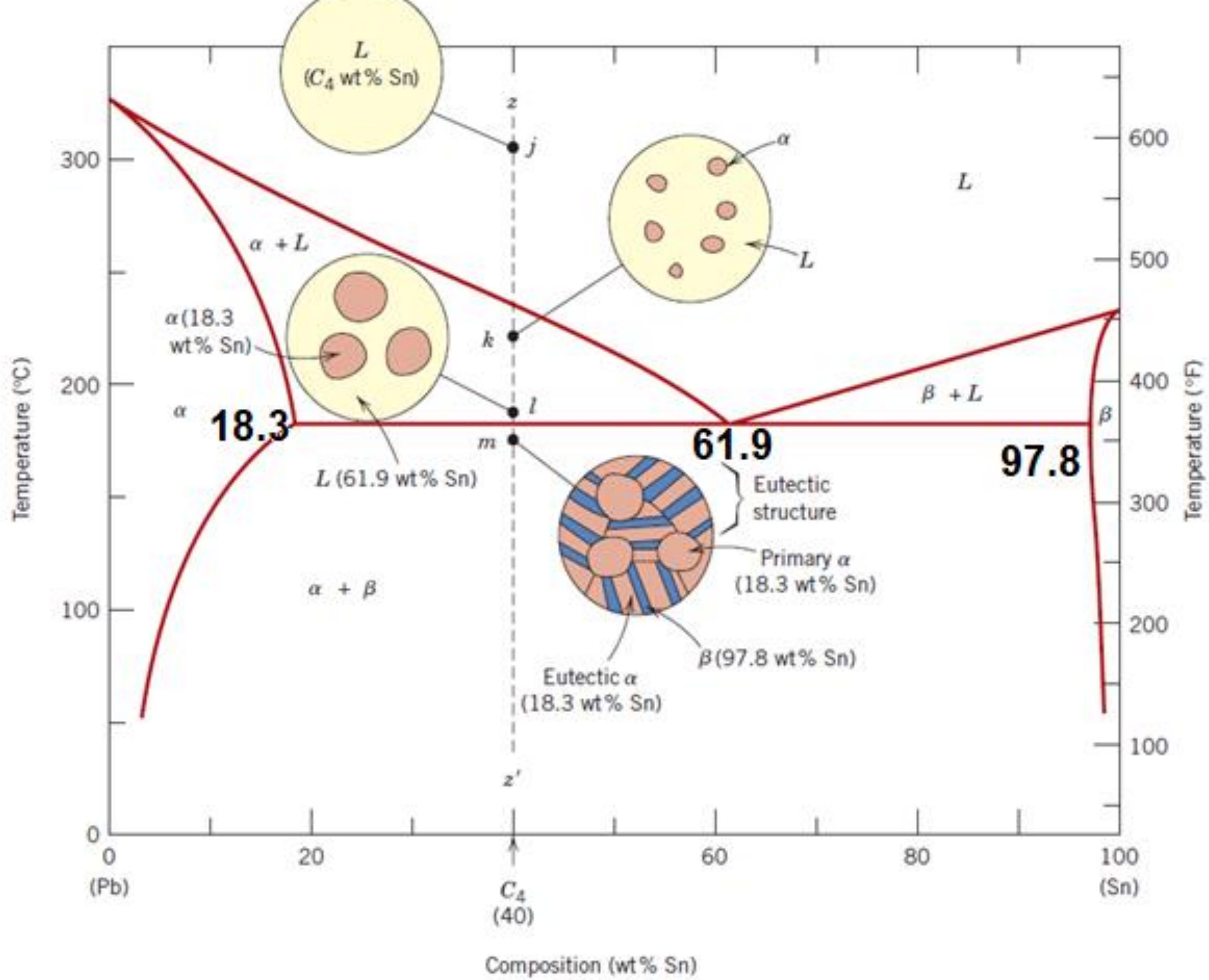


Fig 11: Diagram for Pb-Sn alloy
Source :Calister Jr pg. 280

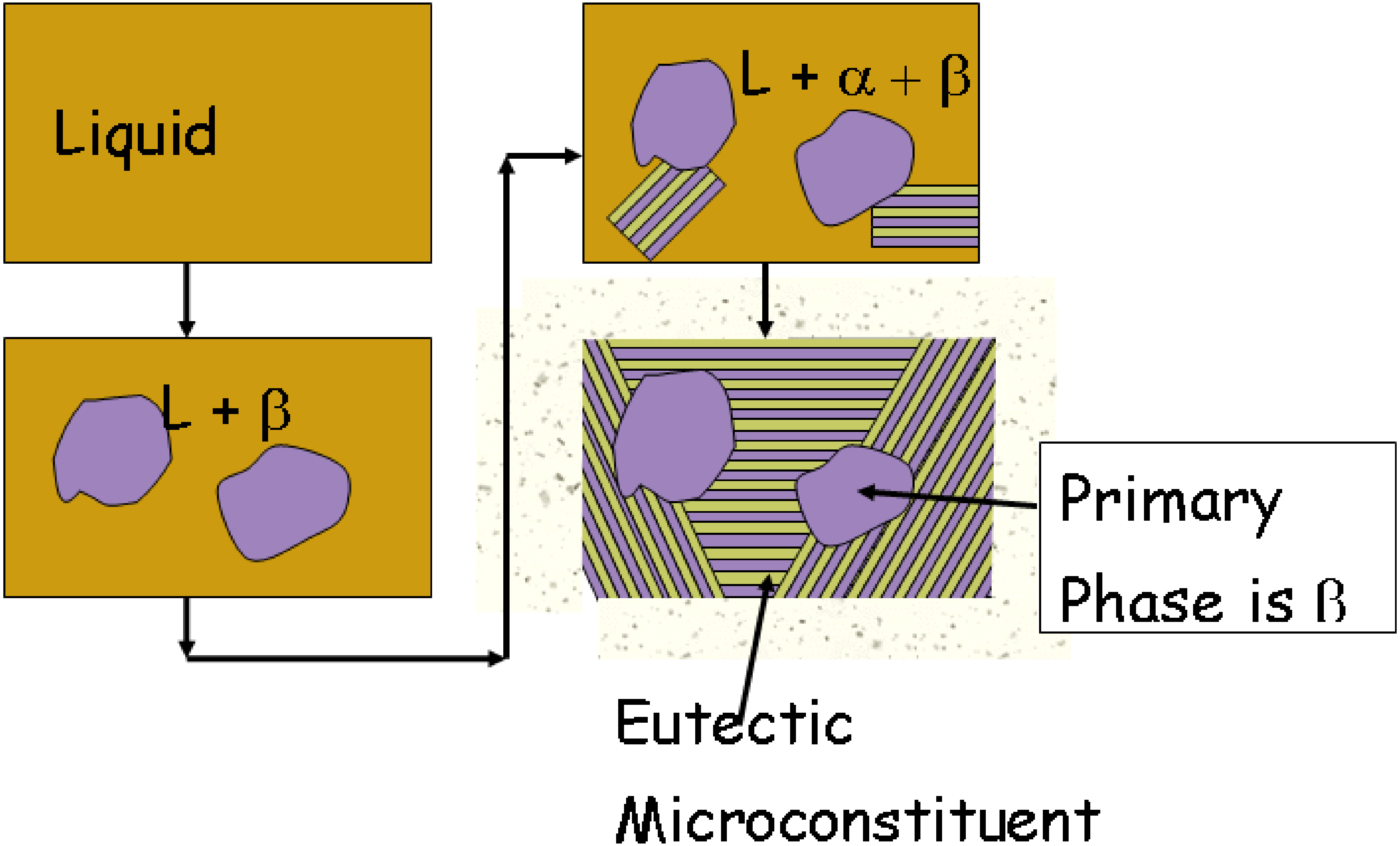


Fig 12: Microstructure of a hypereutectic constituent

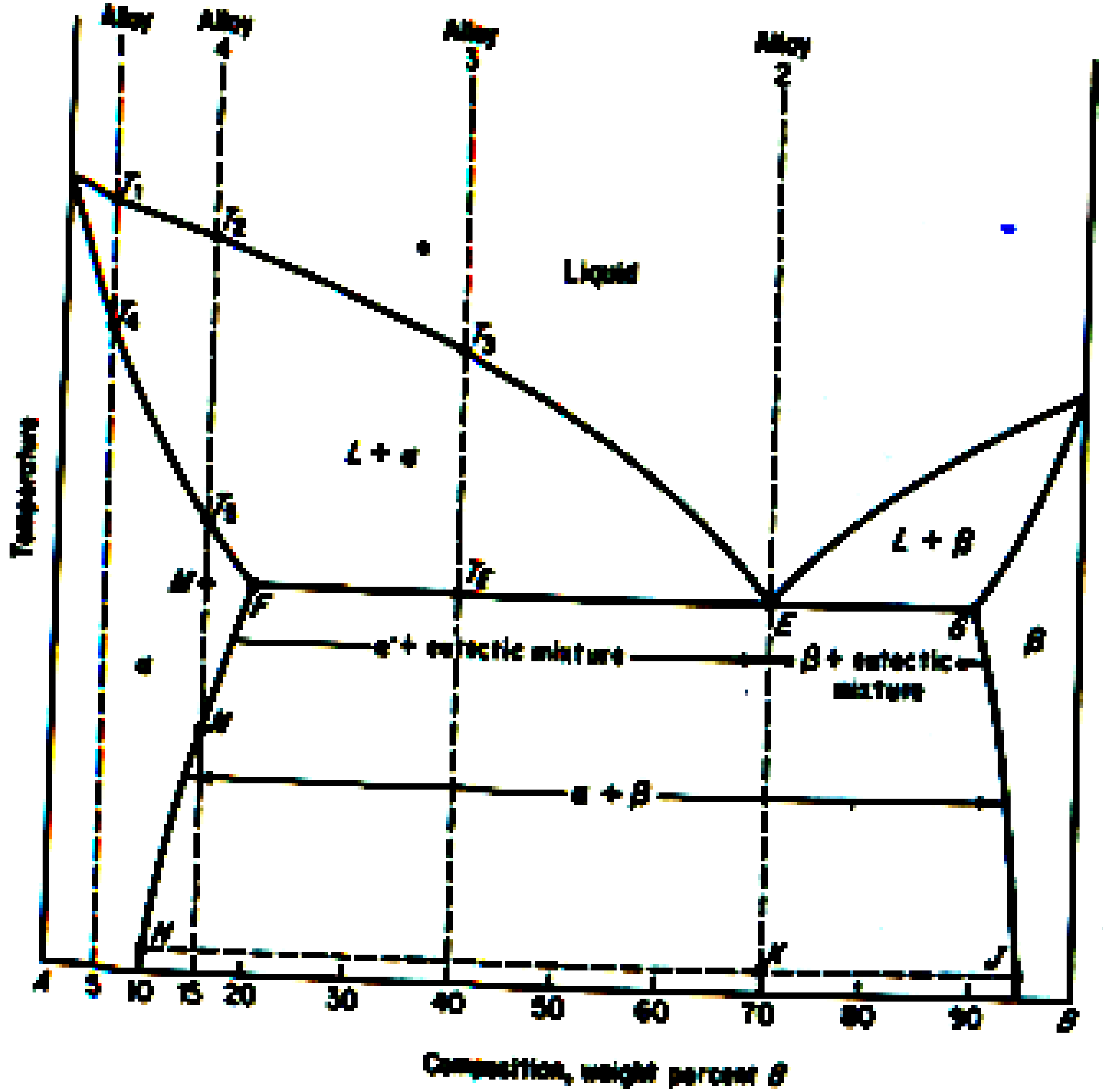


FIG 13: Cooling Specific compositions for a Partial Solubility Alloy

EXERCISE: submission 2 Weeks time

Melting point of pure silver Ag-960

Melting point of pure copper Cu-1083

Cu dissolves a maximum of 8%Ag and silver a max of 8.8%Cu at Eutectic Temp

Eutectic temp (T_E)=779 , Eutectic composition =28.1%Cu

At room temp Ag dissolves 2%Cu and Cu dissolves 0%Ag

Draw the phase diagram on a graph paper and use it to answer the following questions

Cool the following Alloys, Stating the chemical composition, relative amounts and sketching the microstructure at various appropriate temperature zones (join point using straight lines)

ECE class answer question 1 and SRT group question 2

Question1

i) **Choosing any hypereutectic comp cool from liquid to room temperature**

ii) **28.1%Cu cool from liquid to room temperature**

Question2

i) **Choosing any hypoeutectic comp cool from liquid to room temperature**

ii) **28.1%Cu**

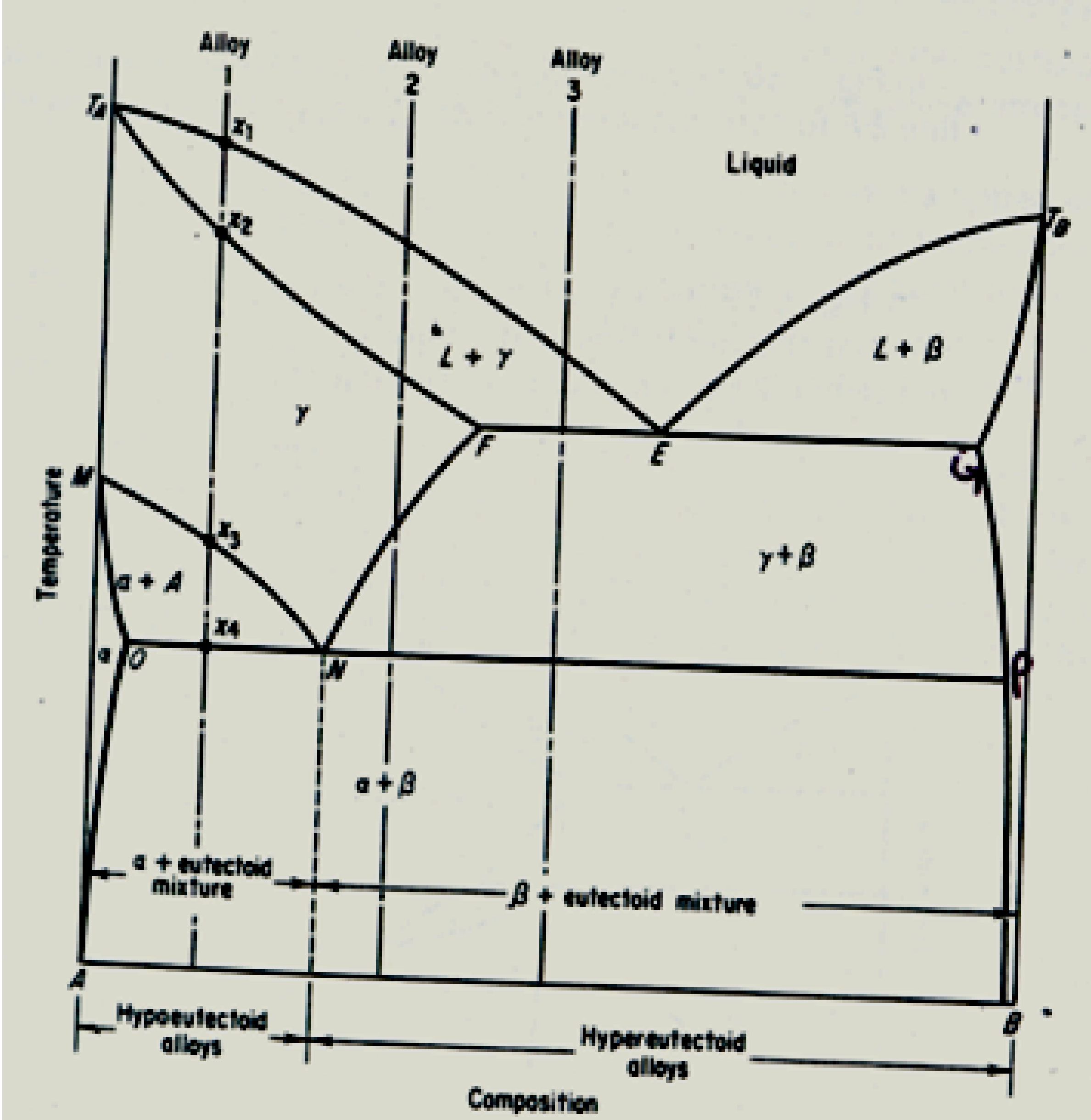


Fig 14: Eutectoid Phase diagram

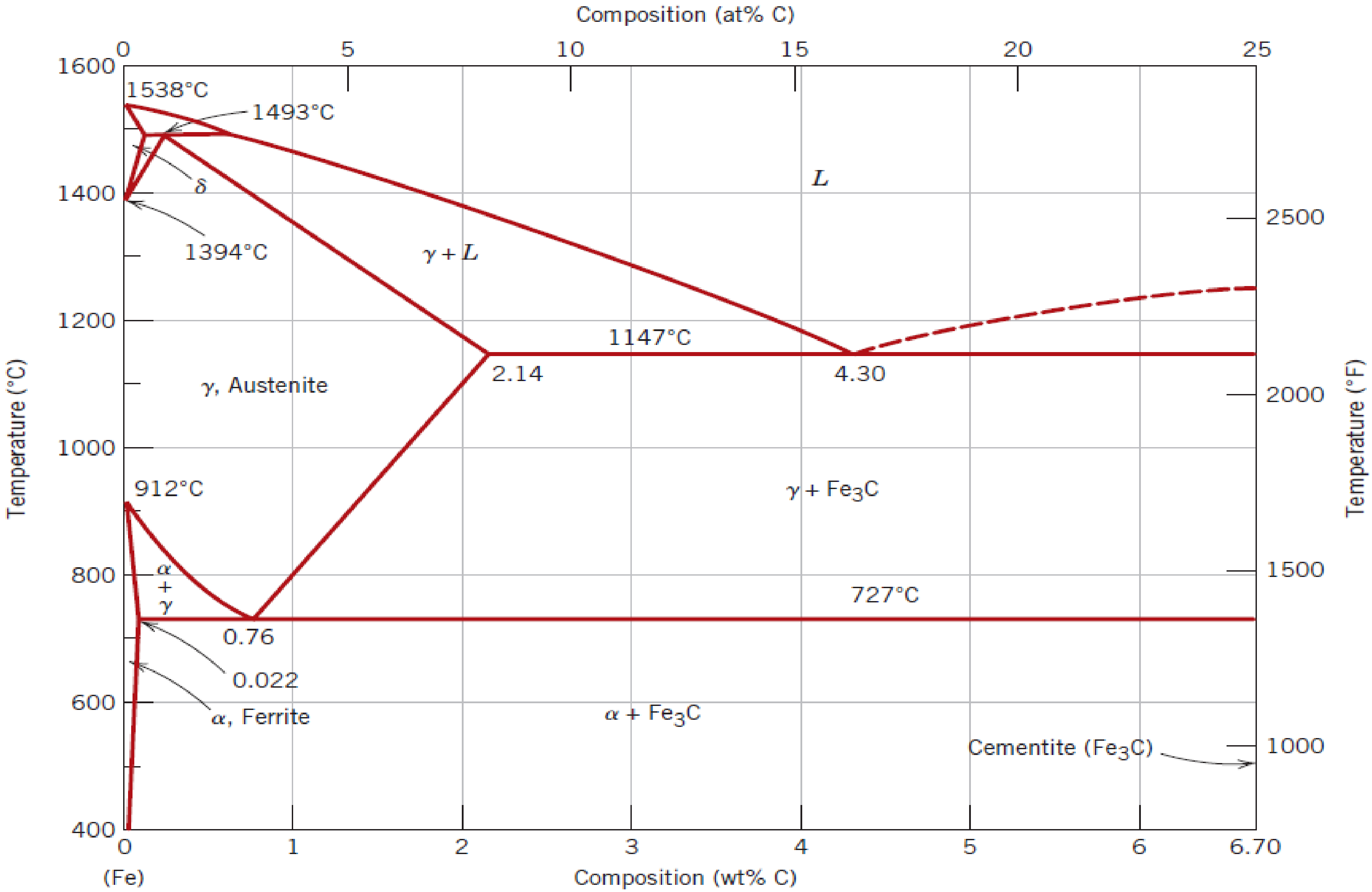


Fig 15: The Fe-Fe_3C Phase diagram
Source: Calister Jr. Pg. 290

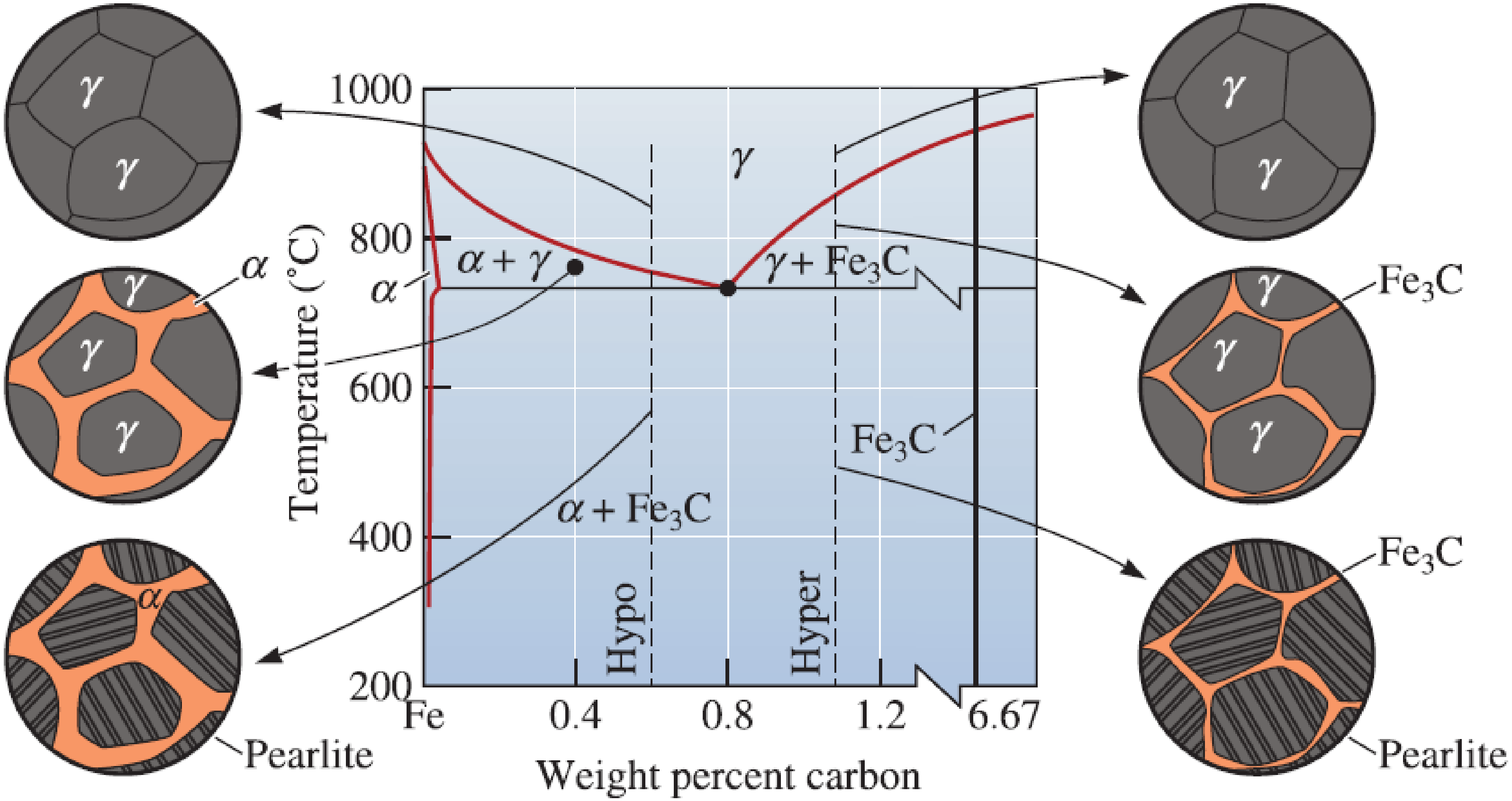


Fig 16: Cooling of Hypoeutectoid and hypereutectoid steel

Source: Engineering materials by Donald Askeland 6th edition

Fe-Iron Carbide Diagram

This is the most important commercial phase diagram

and provides the major scientific basis for

the IRON and STEEL industries.

- **Ferrite (a-Solid solution)**
- -It is BCC in structure
- -Is a soft and ductile phase
- -Dissolves only 0.008% Carbon at room temperature
- - Is the softest substance in the diagram
- -Can contain a maximum of 0.02%C

Cemntite (Fe_3C)

- **Consists of 6.67%C**
- **This is an extremely hard brittle phase of complex crystal structure**
- **It dissolves in Ferrite interstitially. It is the hardest substance found in the Fe-C phase diagram**

NOTE

Fe=56, C=12

Fe_3C=56x3+12=180

C=12/180

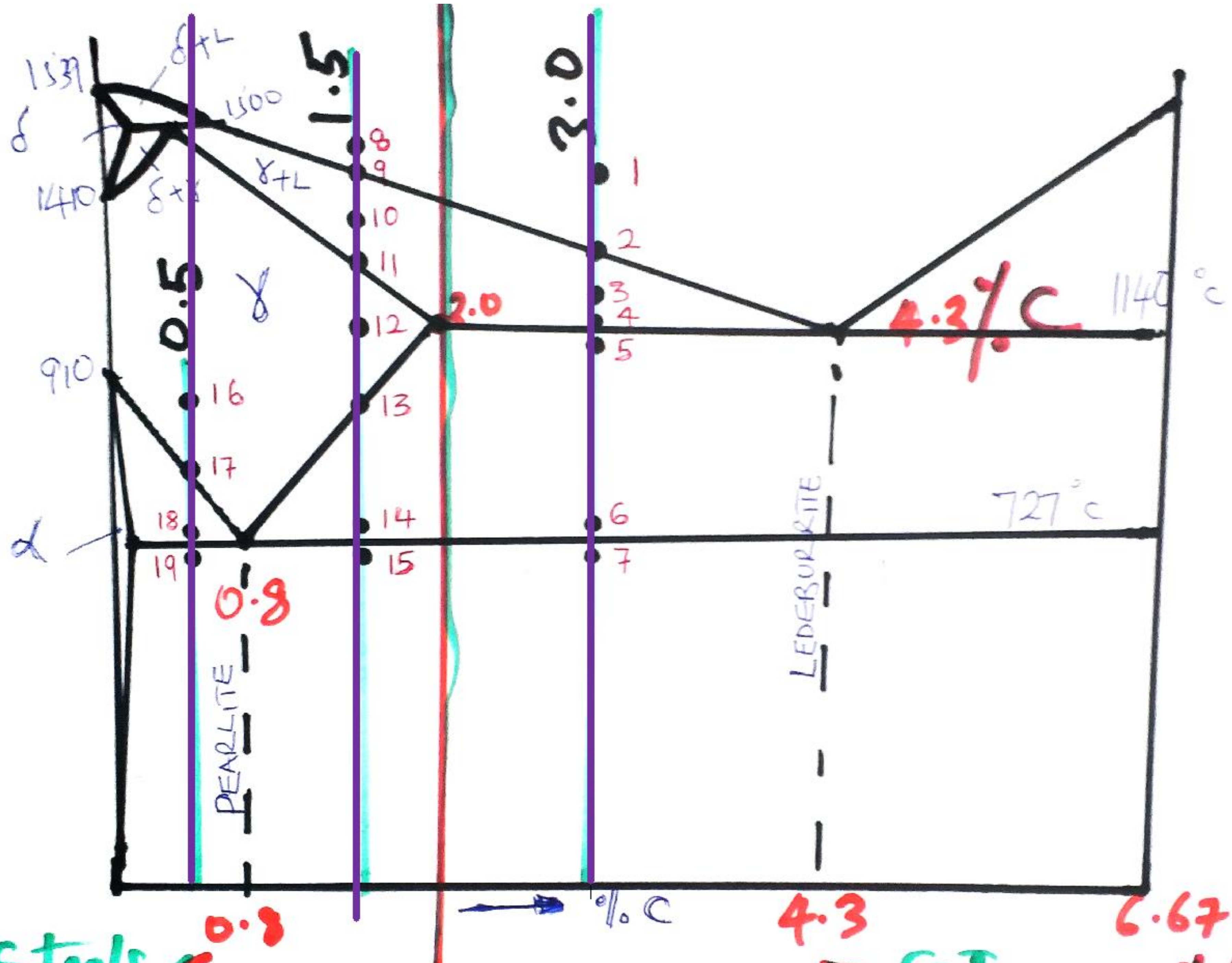
=6.67%

implies that 100%Fe_3C=6.67%C

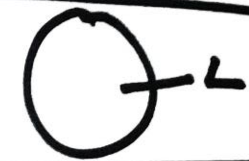
- **Austenite (γ-Solid solution)]**
- -This is an interstitial solid solution of carbon in iron
- - It is slightly harder and less ductile than ferrite
- -Can contain a maximum of 2%C -It is unstable at room temperature
- **Pearlite (0.8%C)**
- -This is the structure formed from the eutectoid reaction
- - Is composed of alternate layers of ferrite and Cementite
- -It has a very fine plate-like (lamellar) mixture of ferrite and Fe_3C
- It has a hardness and ductility values between those of ferrite and Cementite

Ledeburrite (4.3 % C)

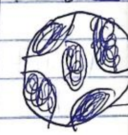
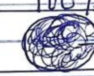
- This is the Eutectic mixture
- It occurs only in cast irons
- Consists of colonies of Pearlite in a continuous network called a matrix of Cementite



1539
1500
1410
910
δ
δ+L
δ+γ
γ+L
γ
α
0.5
1.5
2.0
3.0
2.0
4.3% C
1140 °c
727 °c
0.8
PEARLITE
LEDEBURITE
% C
0.8
4.3
6.67
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

Point	Phase	Comp	R. A	App. micro
1	L	3%C	100%L	
2	L	>3%C	Essentially 100%L	
	γ	~1.3%C	Negligible γ	
3	L	3.6%C	$\frac{3-1.7}{3.6-1.7}\times 100 = 68.4$	
	γ	1.7%C	$= 100-68.4 = 31.6$	
4	Just above T_E L	4.3%C	$\frac{3-2}{4.3-2}\times 100 = 43.4\%$	
Just below	γ	2.0%C	56.6%	
5 Just below				

Line B (1.5% C)

Point	Phases	Comp. of phases	Relative Amounts	Appr. Sketch
8	L	1.5% C	100% L	
9	L	> 1.5% C	Essentially 100% L	
	γ	~0.75% C	Negligible γ	
10	L	2.2% C	$\frac{1.5-1.1}{2.2-1.1} \times 100 = 36.4\%$	
	γ	1.1% C	= 63.6%	
11	L	< 3% C	Negligible L	
	γ	< 1.5% C	Essentially 100% γ	
12	γ	1.5%	100% γ	
13	γ	< 1.5%	Essentially 100% γ	
	Fe_3C	6.67% C	Negligible Fe_3C	
14 Just above TED	γ	0.8% C	γ = 88.1%	
	Fe_3C	6.67% C	$\frac{1.5-0.8}{6.67-0.8} \times 100 = 11.9\%$	
15 Just below TED	α	0.02	α = 77.7%	
	Fe_3C	6.67%	$\frac{1.5-0.02}{6.67-0.02} \times 100 = 22.2\%$	

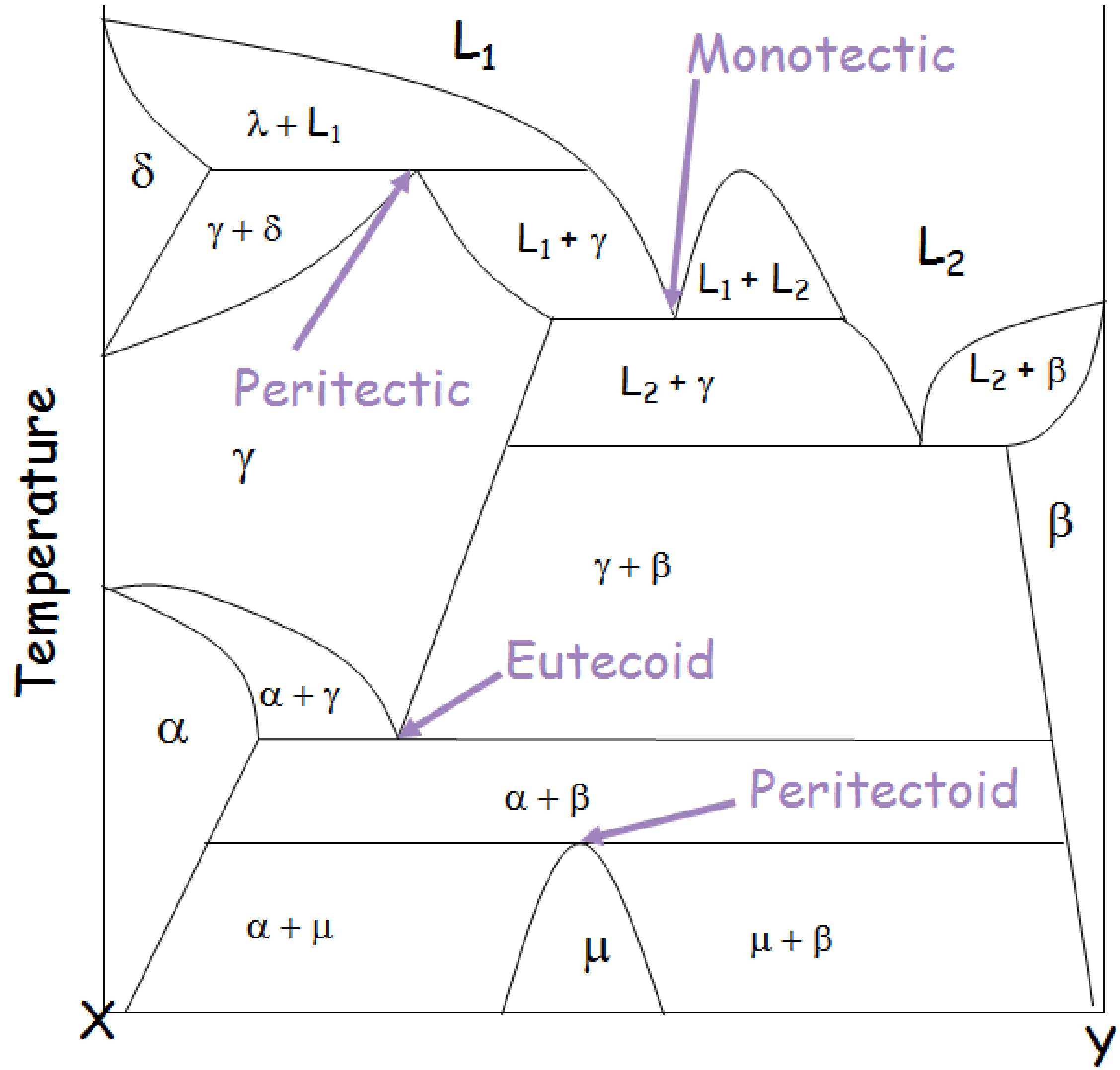
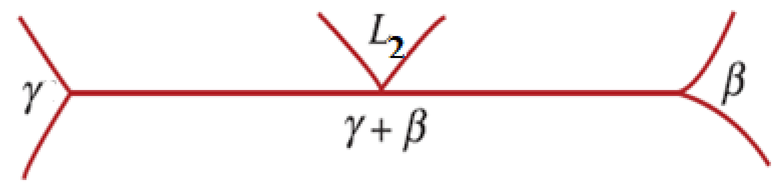
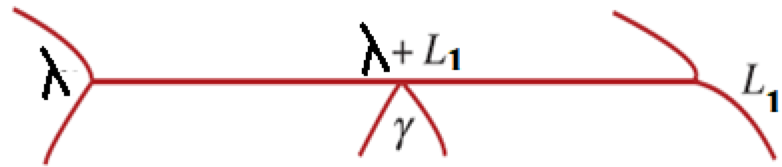
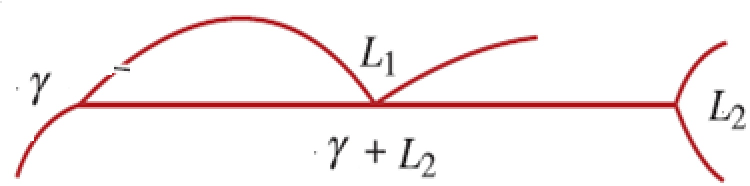
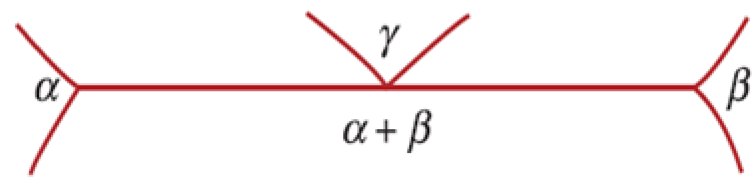
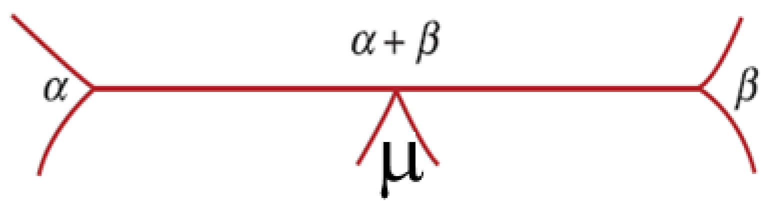


Fig 17: Binary phase diagram with other invariant points

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

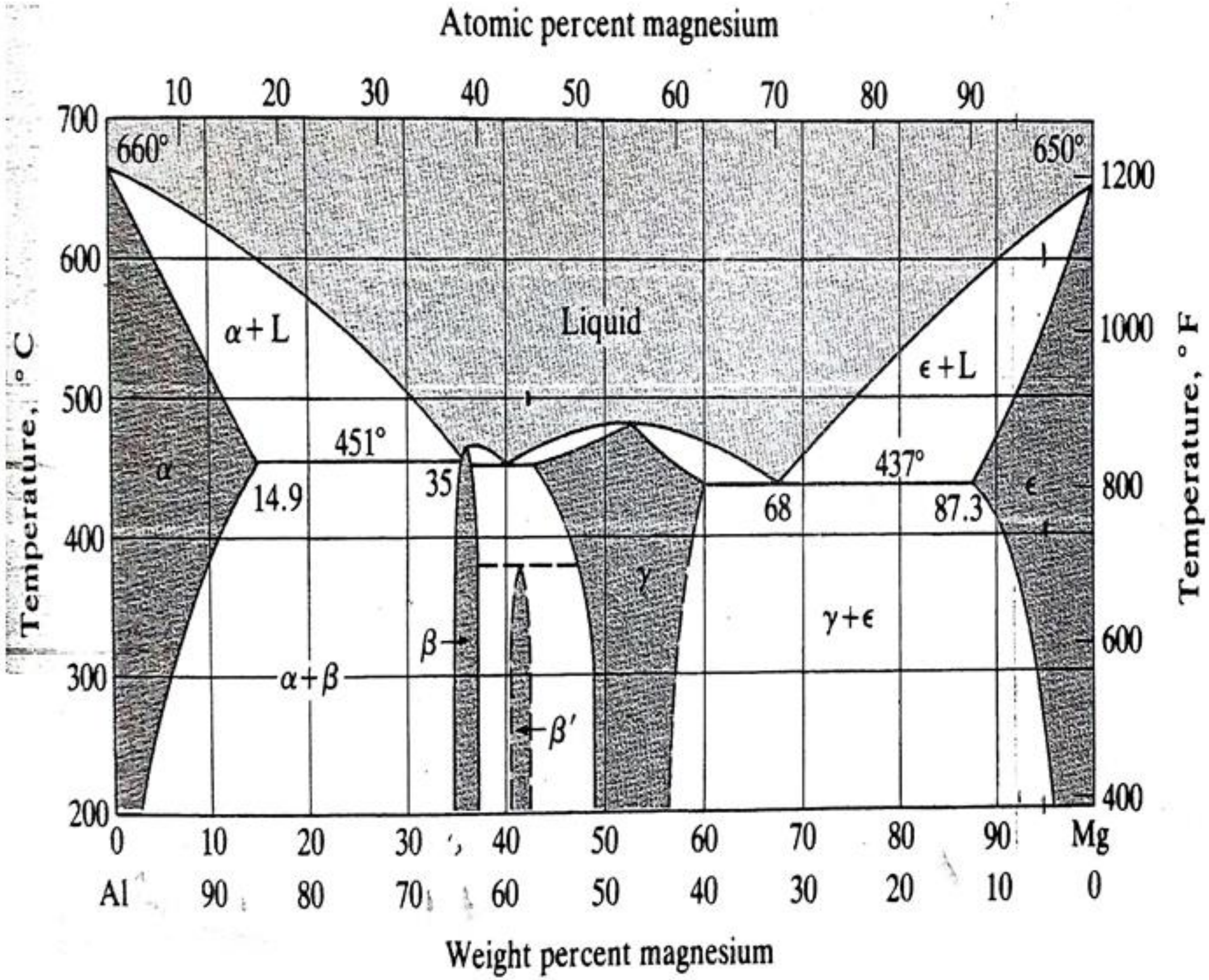


Fig 19: Al-Mg Phase Diagram

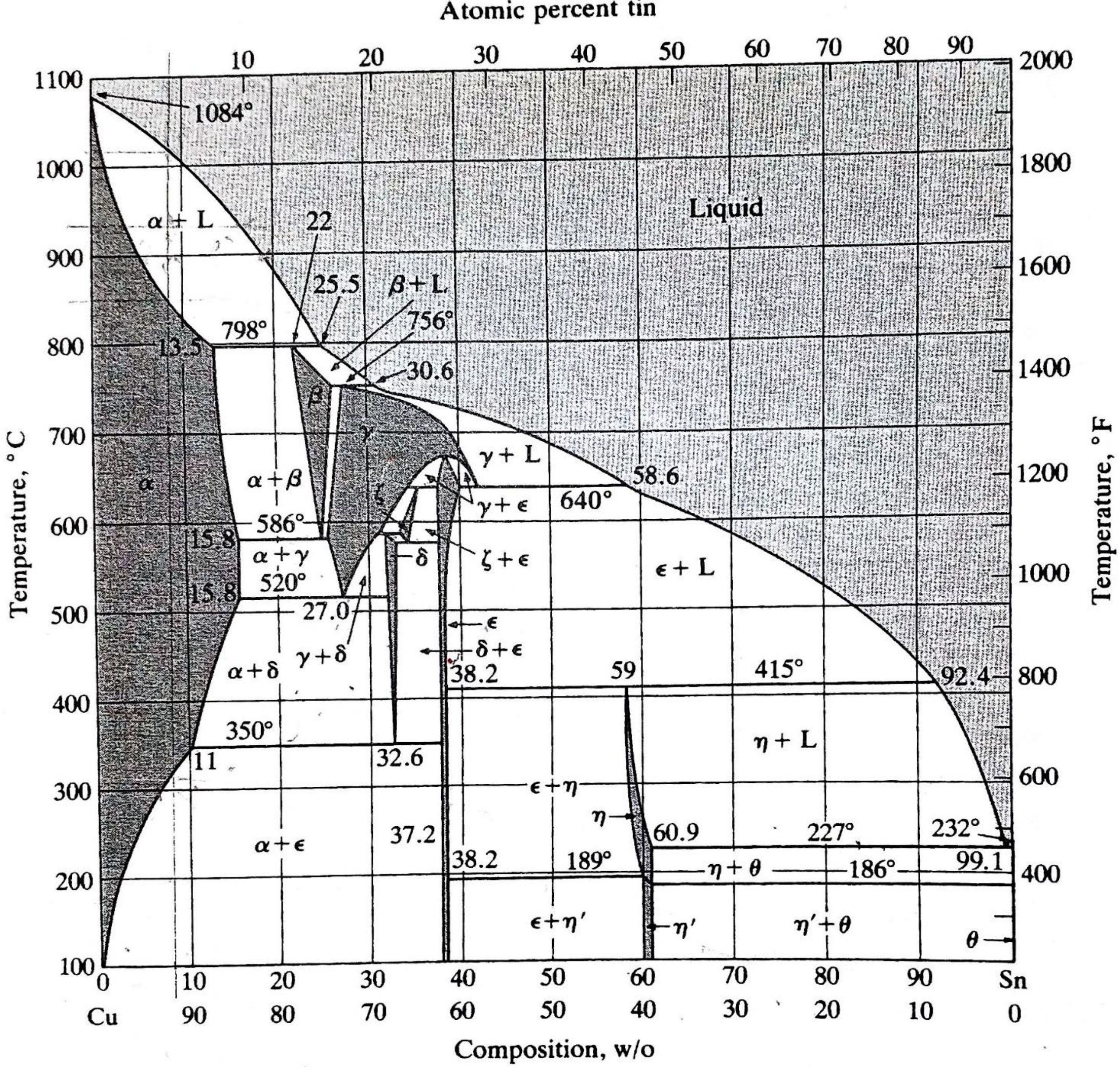


Fig 20 Cu-Sn Phase diagram

Homework

Revise the work on phase diagrams in these reference materials.

1 Material Science and Engineering, An Introduction by William D Calister,Jr and David G Rethwisch 8th edition John Wiley & Sons Inc., 2010.

2 The Science and Engineering of Materials by D.R. Askeland, Pradeep P Fulay and Wendelin J Wright : 6th Edition,2010 Cengage Learning, USA

This is the end of our lesson today