Phase Equilibrium Diagrams:-

Phase equilibrium diagram ***is a graphic relationship between temperature and weight ratios of elements and alloys contribute to the built of the diagram.***

Phase diagrams provide information on the following :

- Melting point .
- Casting condition .
- Crystallization condition .
- phase transformations (changes).

Phase is a uniform part of an alloy, and a homogeneous aggregation of mater having a certain chemical composition and structure, and uniform physical and chemical and mechanical properties.
and which is separated from other alloy constituents by ***phase boundary***.

Every one notes that H_2O can exit as a ***gas, a liquid and a solid***. These are three different phases of water .

solvent: component of a solution present in the greatest amount in alloy .

solute: component or element of solution present in lowest concentration in alloy .

Solubility Limit **:-** max. concentration of atoms to be dissolved in the solvent to form a *solid solution.*

example solubility of sugar in water.

For example the salt – water solution have a four possible phases:
- Water vapor (steam)
- Liquid salt solution (sodium chloride in water)
- Crystals of water (ice).
- Crystals of salt (sodium chloride).

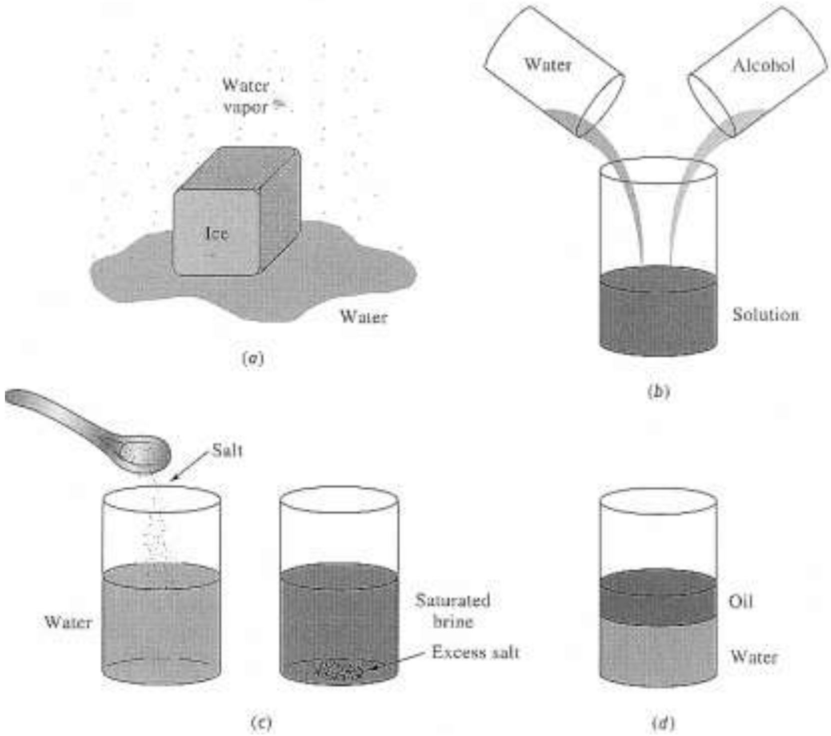


Fig (1) Phases and solubility: (a) The three forms of water-gas, liquid, and solid are each a **phase**. (b) Water and alcohol have unlimited solubility. (c) Salt and water have limited solubility. (d) Oil and water have virtually(practice) no solubility.

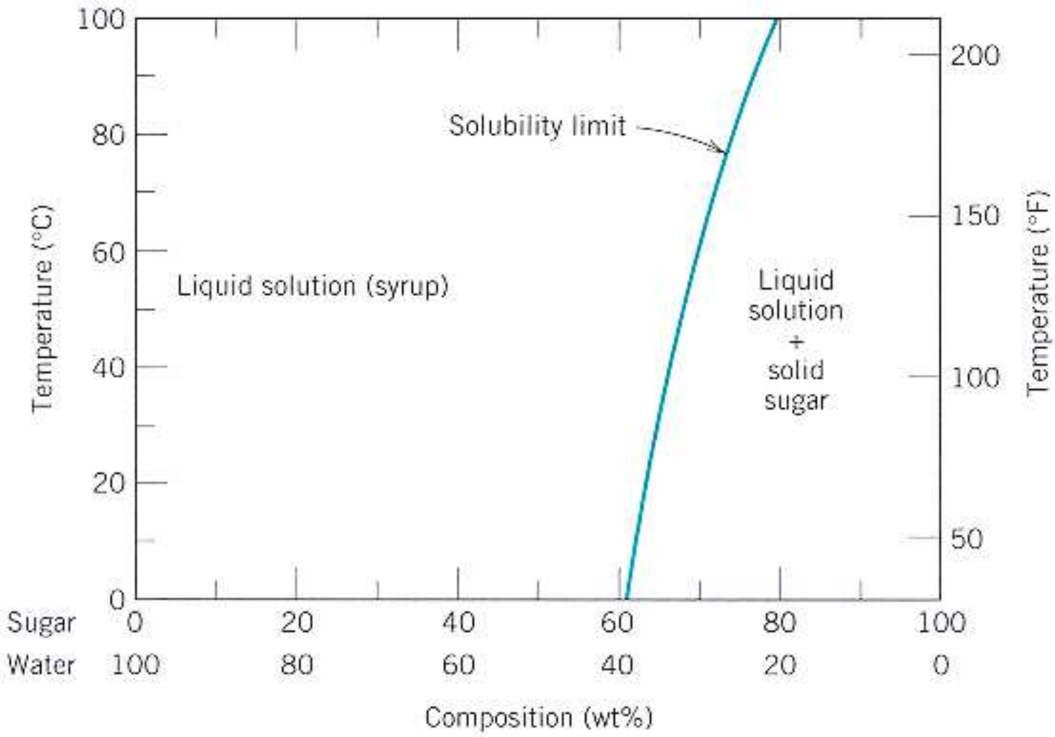


Fig . (2) Solubility limit of sugar – water solution .

All curve from ***three curves*** in the fig. below represent ***case equilibrium of two phases.***

Critical point :at a certain pressure and temperature , it mean , no separate interface between three material phases(gas , liquid , solid).

Triple point : at a certain pressure and temperature , it mean , the three phases may be found in equilibrium at the same time .

From a fig. :-

1- the red curve represent , equilibrium of ice and water vapor(steam).(solid and gas).
2- the blue curve represent , equilibrium of water liquid and water vapor(steam).(liquid and gas).
3- the green curve represent , equilibrium of water liquid and water (ice) .(liquid and solid).

Note :- the hidden green curve applied on water only .(because the water expanded when transform to solid (ice), while all another material converge(تنكمش) when densification.

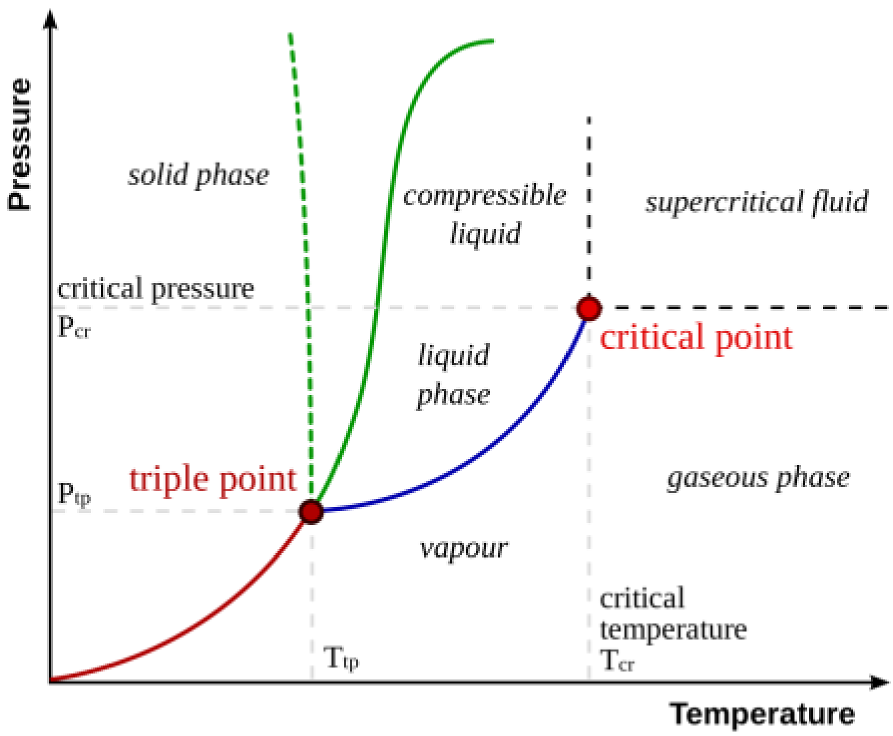


Fig (3) Temp. press. relationship of material .

Alloying systems :

There are many types of alloying systems which they are:

1- Binary system
It means that alloying have two metals only.

Binary Alloy: when tow metals or a metal and a small amount of a non-metal are mixed in their molten states and allowed to cool the result is a binary alloy.

2- Ternary system
It means that alloying have three metals only.

3- Multi system
It means that alloying have three and more than that metals.

In general, ***binary alloys*** can be classified into the following types.

1- ***Simple eutectic type***
   The two components are soluble in each other in the ***liquid state*** but are completely insoluble in each other in the ***solid state***.
2- ***Solid solution type***
   The two components are completely soluble in each other both in the ***liquid state and in the solid state***.
3- Combination type
   The two components are completely soluble in the ***liquid state***, but are only ***partially soluble in each other in the solid state***.

Thus this type of alloy combines some of the characteristics of both the previous types, hence the name 'combination type' phase equilibrium diagram.

Let's now consider these three types of binary alloy systems and their phase equilibrium diagrams in greater detail.

1) Eutectic type:-
In general case, consider for studying a two components presents which are referred to as metal A and metal B, with the phase diagram as shown in figure 1.

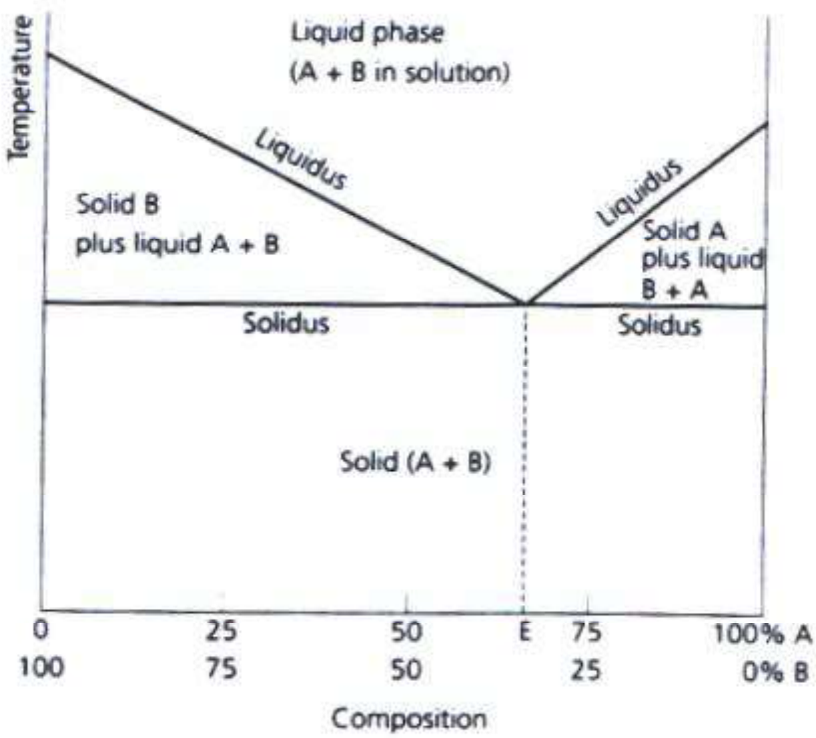


Figure 4. Phase equilibrium diagram (eutectic type).

This point on the diagram is called the *eutectic*, the temperature at which it occurs is the *eutectic temperature,* and the composition is the *eutectic composition.*

Eutectic : this is the particular composition of two substances which freeze simultaneously at the same temperature .

Eutectic temperature: - It is the melting temperature of any alloy with the eutectic composition.

OR: - The temperature at which the liquid and the solid are in equilibrium.

In practice, few metal alloys from simple eutectic type phase diagrams. As an example of eutectic are ***carbon steels***.

2- Solid solution alloy is a phase, where two or more elements are completely soluble in each other.

Depending on the ratio of the solvent (matrix) metal atom size and solute element atom size,

for example :- gold- silver alloy , cupper- nickel alloy.

Two types of solid solutions may be formed: ***substitution or interstitial***.

- **<u>Substitution Solid Solutions:-</u>**

If the atoms of the solvent metal and solute element are of similar sizes (not more, than 15% difference), they form **substitution solid solution,** where part of the solvent atoms are substituted by atoms of the alloying element as shown in figure 2. for example . copper and nickel

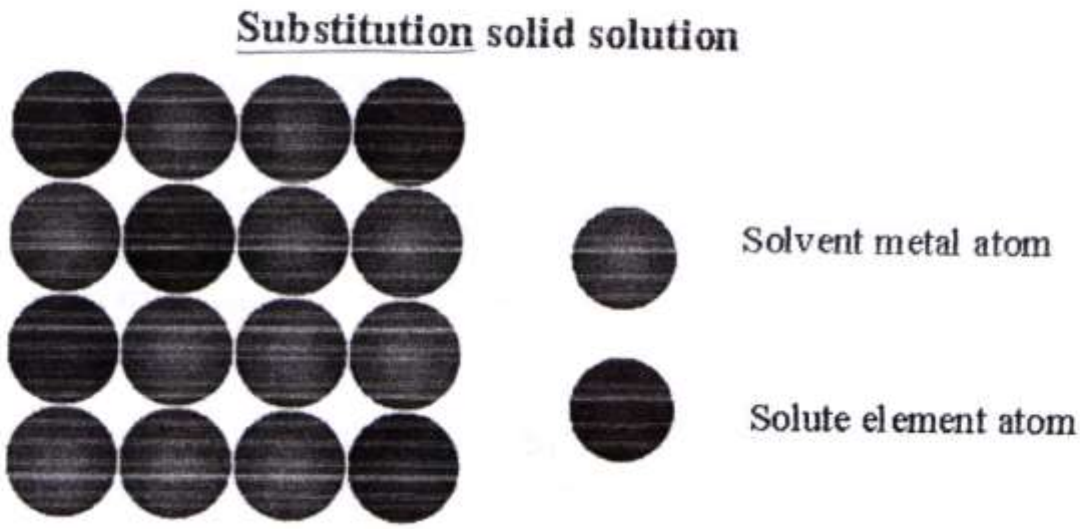
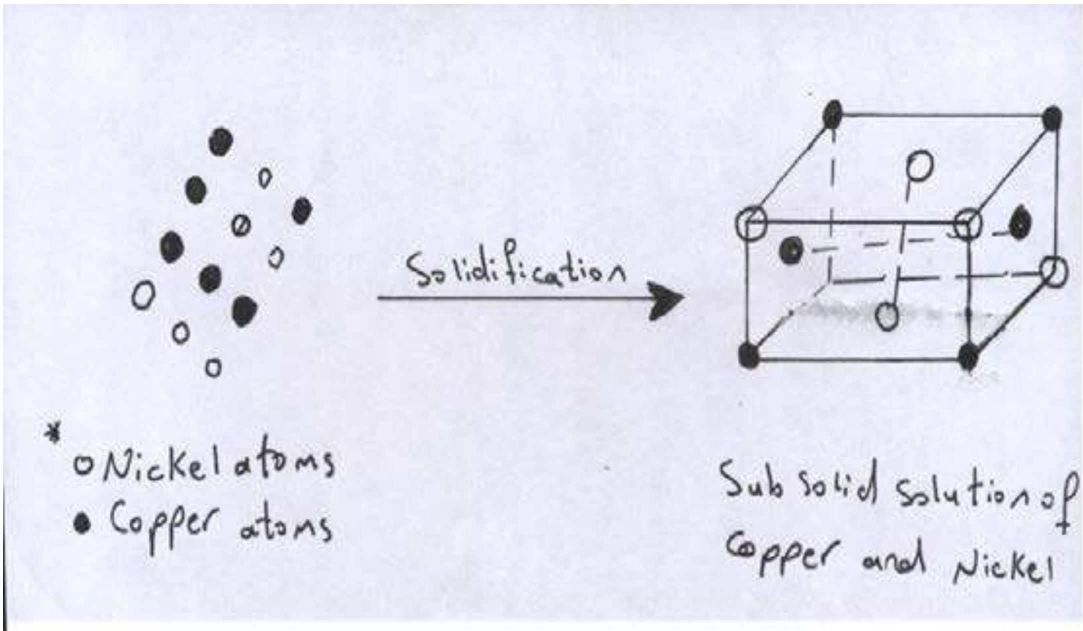


Figure 5. Substitution solid solution.

Some substitution solid solutions may form ordered phase where ratio between concentration of matrix atoms and concentration of alloying atoms is close to simple numbers like $AuCu_3$ and AuCu.



Figure(6) explain formation of a Substitutional Solid Solution alloy.

- **<u>Interstitial solid solution</u>**

The atoms of the added element inter the interstices of the parent lattice. In other words, they fit into the spaces between the atoms of the parent metal this is of less common occurrence and is only possible if the atoms of the added element are small compare with those of the parent metal. *Good example is that of carbon in iron to form that various step solid solutions.*

If the atoms of the alloying elements are considerably smaller, than the atoms of the matrix metal, **interstitial solid solution** forms, where the matrix solute atoms are located in the spaces between large solvent atoms as shown in figure 7.

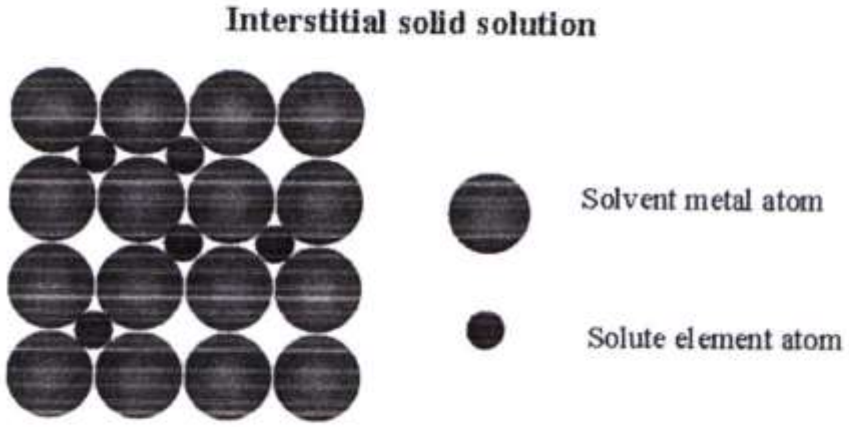
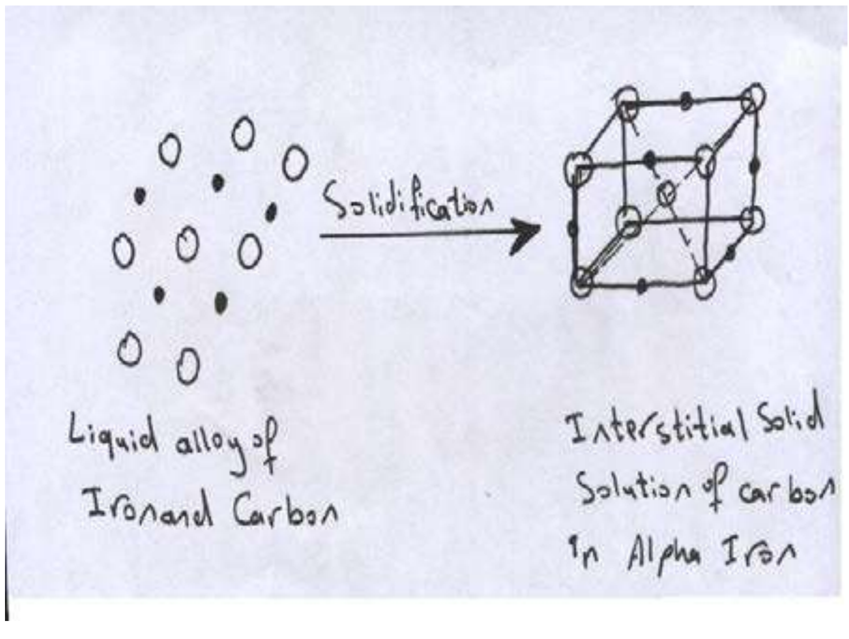
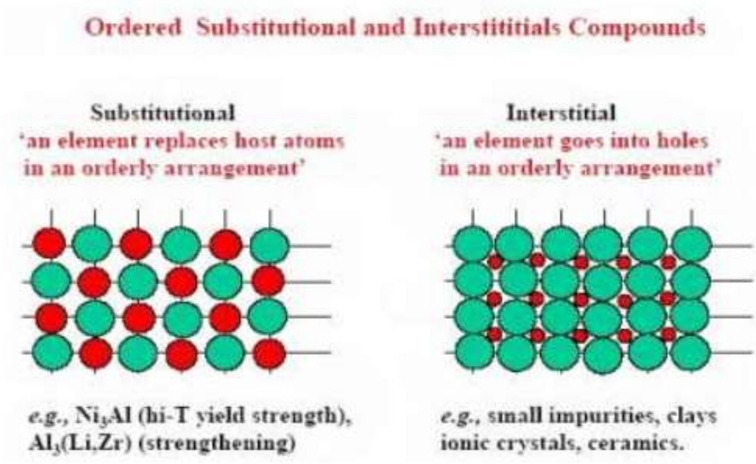


Figure 7. Interstitial solid solution.



Figure(8) explain formation of an interstitial solid solution



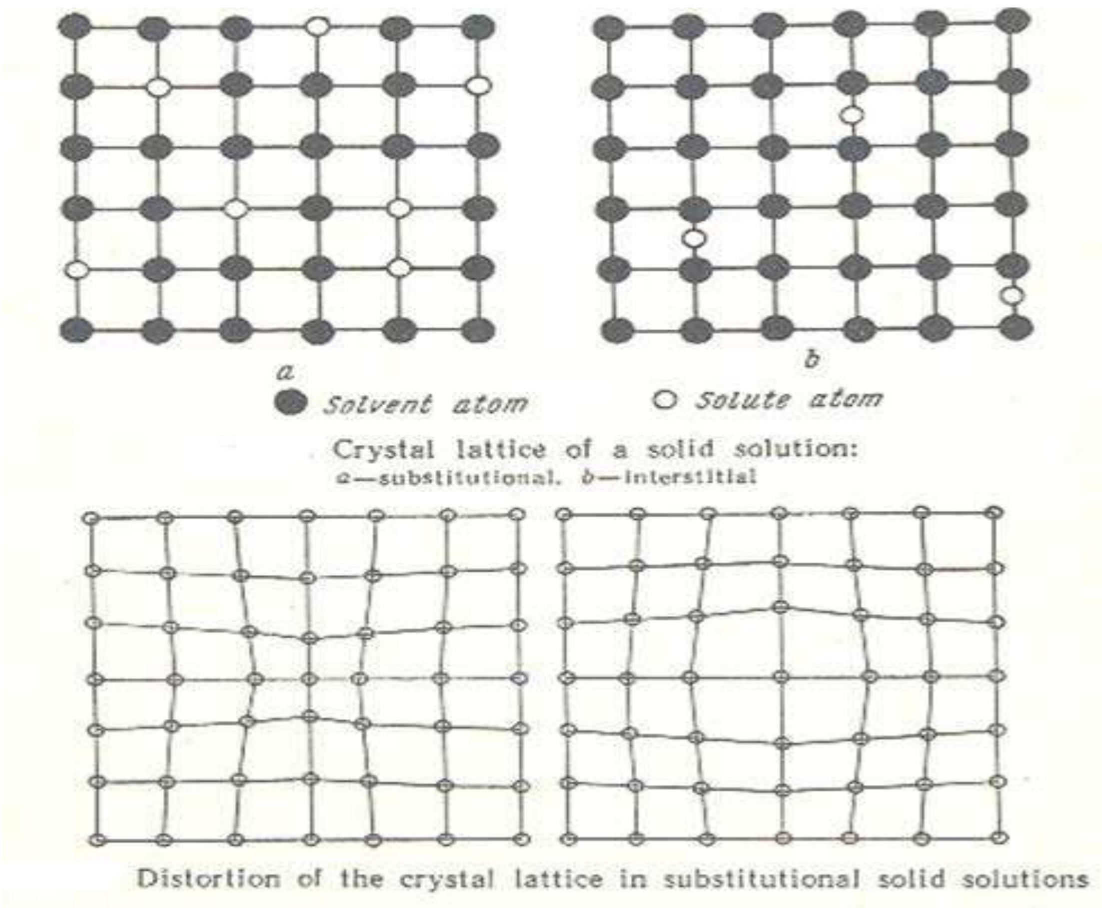


Fig (9-10) **Substitution** and interstitial solid solution and distortion.

In certain alloys containing 3 metals not as ternary alloy, both types of solid solution may co-exit.

<u>For example, in austenitic manganese steel there is a substitution solid solution of manganese in iron and also an interstitial solid solution of carbon in iron.</u>

Solid solution formation usually causes increase of <u>electrical resistance</u> and <u>mechanical strength</u> and <u>decrease of plasticity</u> of the alloy.
For example ,on solid solution :- copper-nickel alloys is shown below.

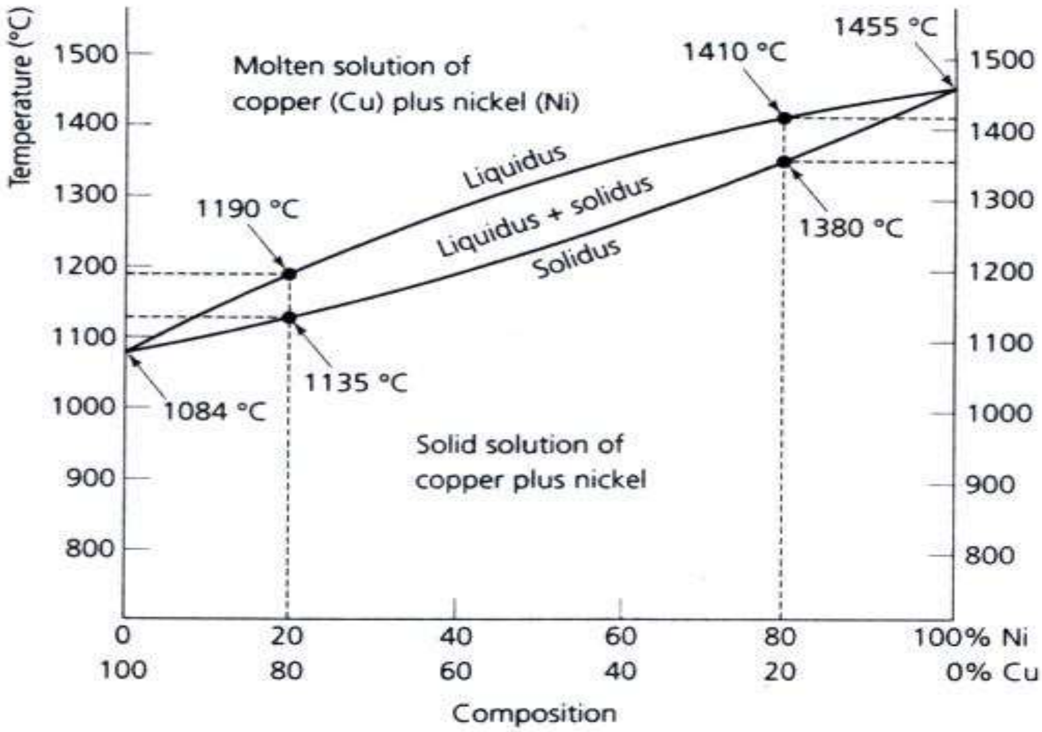


Figure (9) . Copper-nickel phase equilibrium diagram.

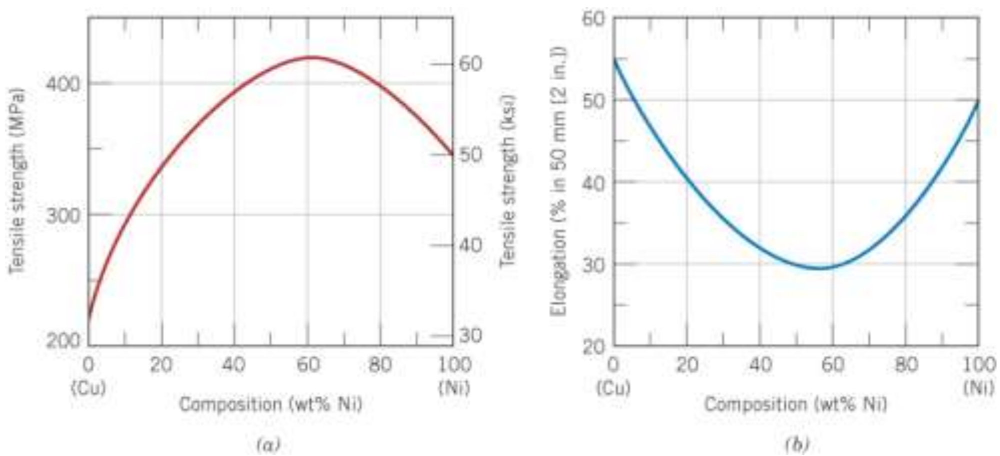


Fig.(10) some a mechanical properties of (Ni-Cu) alloy.

Factors Effecting in solubility of solid solution alloys:-

1- Similarity the space lattice of solvent metal and soluble element.
2- Atomic diameters for solvent and soluble must be converges .
3- Chemical composition must be near of solvent and soluble.
4- Frequency (HZ/Sec) must be near of solvent and soluble.
5- Type the charges of solvent and soluble.

Cooling Curves:-

1- Pure metals

If a pure metal is allowed to cool slowly from liquid to room temperature and the temperature drop is plotted against time the resultant cooling curve will be as show in fig.(11) below

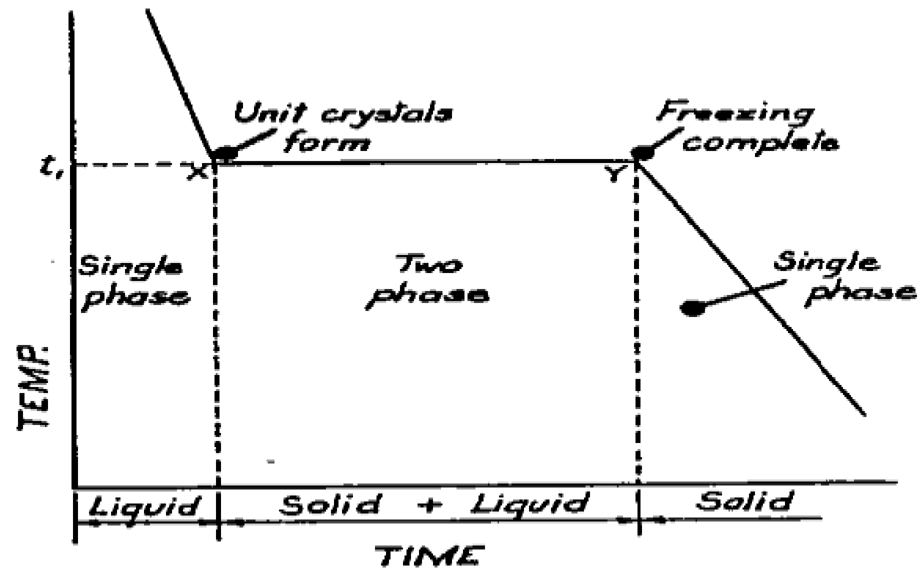


Fig. 1.

As the temperature of the metal falls the movement rate of the atoms drops. The "loss" in kinetic energy is given off as heat.

At temperature t,(X), unit crystals form and freezing begins. The temperature remains constant while freezing continues. With freezing complete at Y the temperature falls steadily to room temperature.

ALLOYS

(A) COMPLETE SOLID SOLUBILITY

For TWO metals which exhibit complete solid solubility the cooling curve for any composition will be as shown in Figure 2. All compositions will be single phase in their solid state.

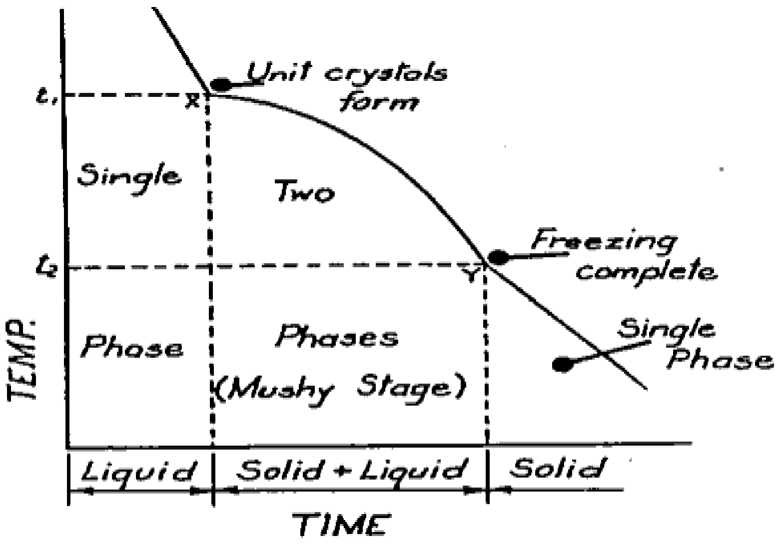


Fig. 2.

At t_1 (X) unit crystals containing atoms of both metals form in liquid.

As solidification proceeds from X to Y the temperature drops from t_1 to t_2. From X to Y two phases are present solid and liquid.

At Y freezing is complete and the structure will be single phase.

This type of alloy system is not common, occurring only between metals with the same crystal structure and similar sized atoms.

The most important alloy of this type is copper-nickel. Others with less practical value are:

Copper with platinum or gold.
Gold - silver.
Bismuth with tin or antimony.

Solid solutions are either substitutional or interstitial. These will be covered later.

(B) COMPLETE SOLID INSOLUBILITY

Figure 3 shows the cooling curve for a particular alloy composition which exhibits complete solid insolubility (2 phases).

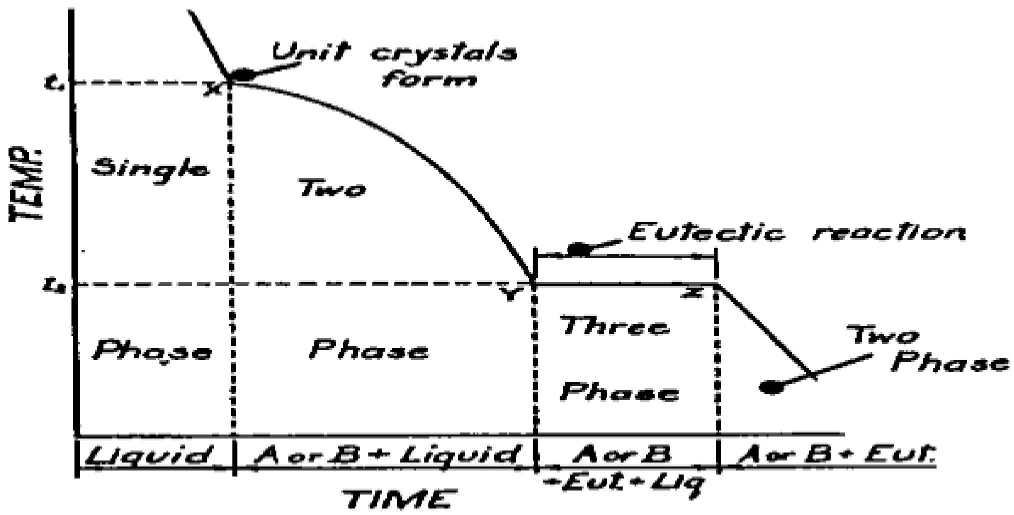


Fig. 3.

At t_1(X) unit crystals of the major constituent, metal A, form in a liquid mix of the two metals.

As solidification proceeds from X to Y the temperature drops from t_1 to t_2 and dendrites of metal A develop in the liquid mix in which the concentration of metal A steadily falls.

At t_2(Y) the eutectic reaction begins and proceeds at constant temperature to complete freezing at Z. From Y to Z there are three phases present, metal A or metal B plus liquid plus eutectic

Once solid the structure will be two phase, either metal A or metal B plus eutectic.

It should be noted that this type of alloy in its solid state exhibits varying amounts of eutectic depending on the composition. For a particular composition the solid state will be all eutectic.

Once again, examples of this alloy type are rare, bismuth-cadmium and tin-zinc being the most important.

Lever Rule

The **lever rule** is a ***tool used to determine weight percentages of each phase of a binary equilibrium phase diagram . It is used to determine the percent weight of liquid and solid phases for a given binary composition and temperature that is between the liquidus and solidus.***

$$W_l + W_\alpha = 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$C_\circ = W_\alpha C_\alpha + W_l C_l \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$From\ eqution\ (1)$

$$W_\alpha = 1 - W_l \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Sub. (3) in (2)

$$C_\circ = W_\alpha C_\alpha + W_l C_l$$

$$C_\circ = (1 - W_l) C_\alpha + W_l C_l$$

$$C_\alpha - W_l C_\alpha + W_l C_l = C_\circ$$

$$C_\alpha - C_\circ = W_l C_\alpha - W_l C_l$$

$$C_\alpha - C_\circ = W_l (C_\alpha - C_l)$$

$$W_l = \frac{C_\alpha - C_\circ}{C_\alpha - C_l} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (5)$$

and by using same method

$$W_l = 1 - W_\alpha \text{..........................(4)}$$

Sub. (4) in (2)

$$C_\circ = W_\alpha C_\alpha + (1 - W_\alpha)\, C_l$$

$$W_\alpha C_\alpha + C_l - W_\alpha C_l = C_\circ$$

$$C_\circ - C_l = W_\alpha C_\alpha - W_\alpha C_l$$

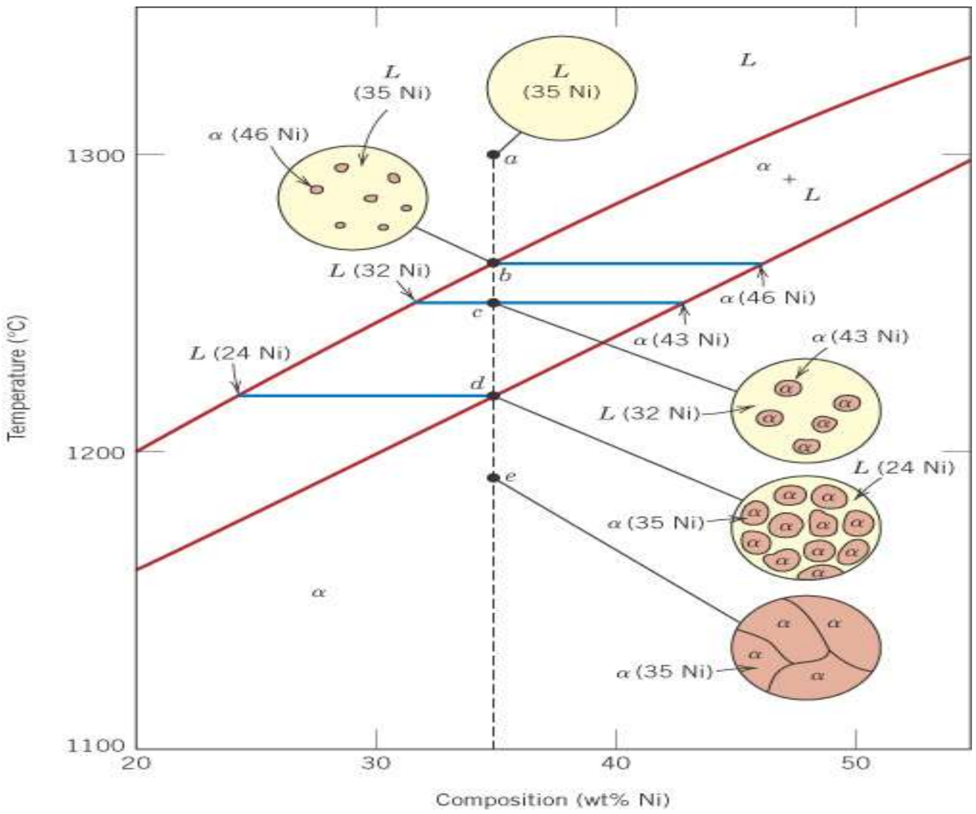
$$C_\circ - C_l = W_\alpha (C_\alpha - C_l)$$

$$W_\alpha = \frac{C_\circ - C_l}{C_\alpha - C_l}$$

W_α : *percentage of wieght ratio of solid*

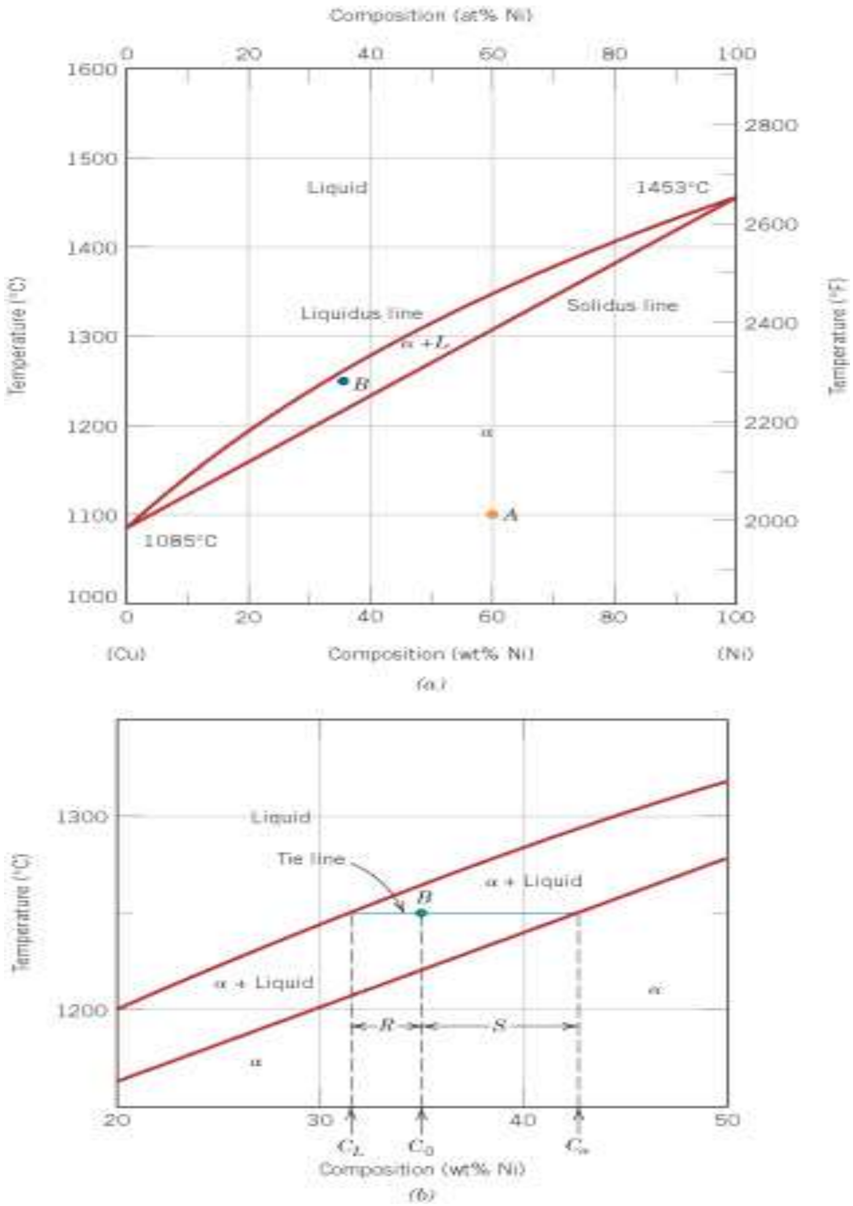
W_l : *percentage of wieght ratio of liquid*

C_α , C_l : ***concentrations of solid, liquid , repectively***



Examples :-

1- At point B (35 wt% Ni, 1250ºC) on figure 10.3b, what are the mass fraction liquid and the mass fraction solid?



Ans.

$$W_l = \frac{C_\alpha - C_\circ}{C_\alpha - C_l} = \frac{\mathbf{42.5 - 35}}{\mathbf{42.5 - 31.5}} = \mathbf{0.68\ kg}.$$

$$W_\alpha = \frac{C_\circ - C_l}{C_\alpha - C_l} = \frac{\mathbf{35 - 31.5}}{\mathbf{42.5 - 31.5}} = \mathbf{0.32\ kg}$$

Example Problem:

2- Calculate the amount of each phase present in 1 kg of a 50 wt.% Ni- 50 wt.% Cu alloy at a) 1400°C b) 1300°C c) 1200°C.

Ans.

a) For a 50 wt.% Ni- 50 wt.% Cu alloy at 1400°C, we are in the liquid (L) region of the phase diagram. Therefore, we have 1 kg of liquid (L).

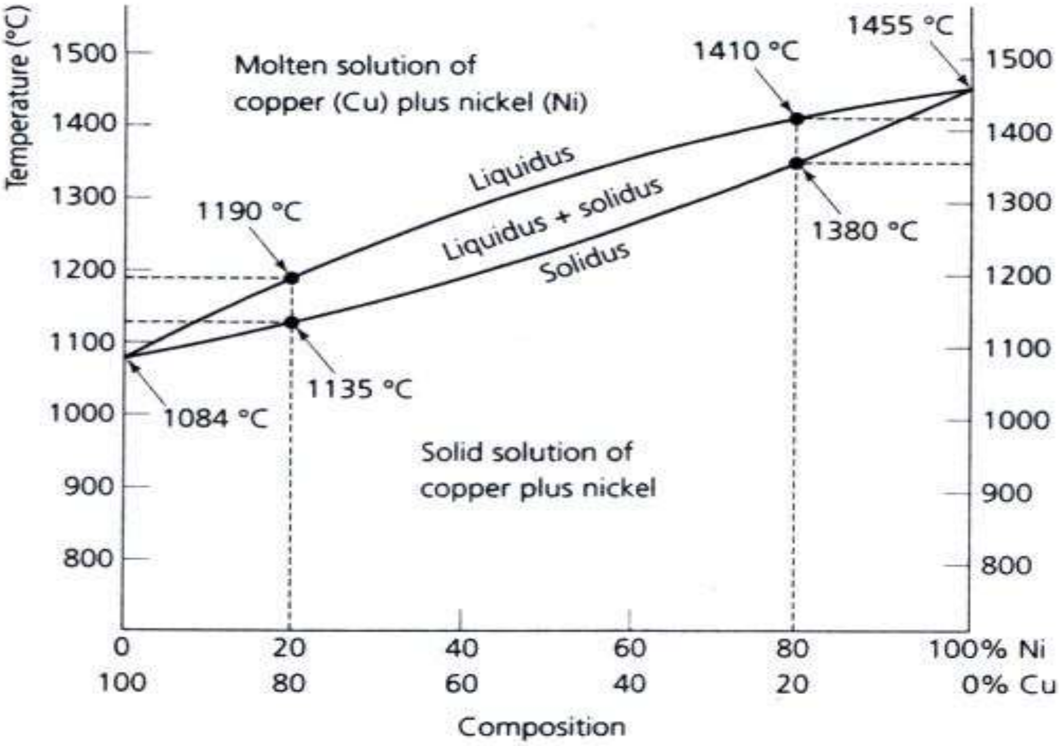
b) For a 50 wt.% Ni- 50 wt.% Cu alloy at 1300°C, we are in the solid + liquid (α+L) region of the phase diagram. Here we must use the lever rule to calculate the mass fraction of each phase.

if we draw a tie line across the α+L region at 1300°C, the endpoints are at about 45 wt.% Ni and 60 wt.% Ni. Therefore, the mass fractions are:

$$W_l = \frac{C_\alpha - C_\circ}{C_\alpha - C_l} = \frac{\mathbf{60-50}}{\mathbf{60-45}} = \mathbf{0.67\ kg}.$$

$$W_\alpha = \frac{C_\circ - C_l}{C_\alpha - C_l} = \frac{\mathbf{50-45}}{\mathbf{60-45}} = \mathbf{0.33\ kg}$$

c) For a 50 wt.% Ni- 50 wt.% Cu alloy at 1200°C, we are in the solid (α) region of the phase diagram. Therefore, we have 1 kg of solid (α).



3) Phase equilibrium diagrams (Combination type):

Many metals and non-metals are neither completely soluble in each other in the solid state nor are they completely insoluble. Therefore they form a phase equilibrium diagram of the type shown in figure 5.
In this system there are two solid solutions labelled α and β. The use of the Greek letters **α, β, γ,** etc., in phase equilibrium diagrams may be defined, in general, as follows:

1- A solid solution of one component A in an excess of another component B, such that A is the solute and B is the solvent, is referred to as solid solution α.

2- A solid solution of the component B in an excess of the component A, so that B now becomes the solute and A becomes the solvent, is referred to as solid solution β.

3- In a more complex alloy, any further solid solutions or intermetallic compounds which may be formed would be referred to by the subsequent letters of the Greek alphabet. That is, γ, β, etc.

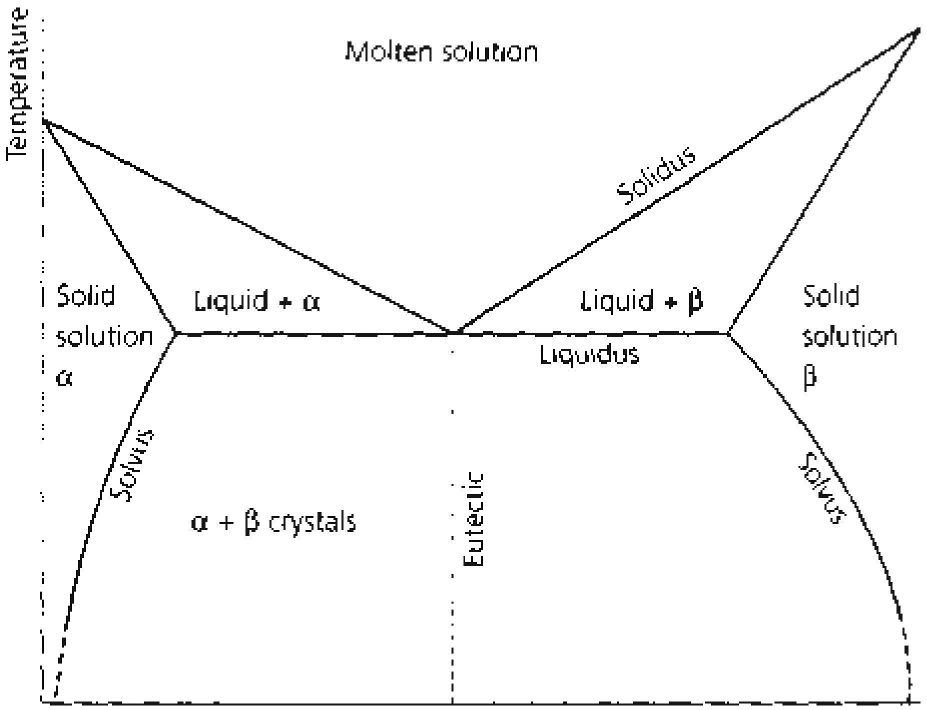


Figure 5. Combination type phase equilibrium diagram.