Chapter 2

Equilibrium diagrams

II.1. Crystallization of materials

II.1.1. Principle of crystallization and cooling curves

Crystallization is a process whereby a material changes from a liquid or gaseous state to an ordered solid state with a defined crystalline structure.

A cooling curve is a graph that represents the variation in temperature of a material over time as it cools. They are used to study the solidification of liquids and the crystallization of materials.

Two physical factors influence the nature and composition of the phases present:

(1)- temperature, which plays a particularly important role during casting and in changes to the mechanical properties of alloys;

(2)- pressure, which is usually neglected because it only has an influence at extremely high levels.

Two types of transformations can be found in phase diagrams:

Liquid-solid transformations, which give rise to solidification diagrams.

Solid-solid transformations to predict the properties of an alloy after heat treatment.

II.1.2. Basic concepts

II.1.2.1 Phases and components

Phase: A phase is a region of a material that is chemically and physically uniform. Examples include solid, liquid, and gas phases.

Component: A component is a chemically independent element of a system. For example, in a binary alloy system, the two elements are the components.

II.1.2.2 Gibbs' phase rule

Gibbs' phase rule relates the number of phases (P), components (C), and degrees of freedom (F) in a system: $F = C - P + 2$

Degrees of freedom: The number of independent variables (such as temperature, pressure, and composition) that can be changed without altering the number of phases in equilibrium.

II.1.2. Basic concepts

● **A phase:** This is a uniform part of an alloy, a homogeneous aggregation of matter with a certain chemical composition and structure, and uniform physical, chemical, and mechanical properties. It is separated from the other constituents of the alloy by a phase boundary.

Everyone knows that H2O can exist in gaseous, liquid, and solid forms. These are three different phases of water.

● **A component:** This is a chemically independent constituent of a system. For example, in a binary alloy system, the two elements are the components. We distinguish between:

1- Solvent: a component of a solution present in greater quantity in an alloy.

2- Solute: a component or element of a solution present in lower concentration in an alloy.

If the two components can be mixed regardless of the ratio, they are said to be completely miscible, such as water and alcohol. If they cannot be mixed, such as water and oil, they form two distinct phases and are said to be immiscible.

● **Solubility limit:** maximum concentration of atoms that can be dissolved in the solvent to form a solid solution. Example: solubility of sugar in water.

II.1.2.2 Gibbs phase rule

Gibbs' phase rule **(variance)** establishes a relationship between the number of phases (P), components (C), and degrees of freedom (F) in a system: V= C+ ν−φ (or F = C – P + n)

(n) represents the two intensive variables, temperature and pressure.

This relationship is reduced for binary alloys where only temperature influences the system to the relationship: $V = 3 - \varphi$

If V = 0, the system is invariant (no variable can be modified).

If V = 1, the system is monovariant (one variable can be modified).

If V = 2, the system is bivariate (two variables can be modified), and so on.

II.1.3. Structures of solutions and compounds

- Very few metals are used in their pure state. For example, pure gold (24 karat) is used in jewelry, but also in electronics for electrical contacts due to its resistance to corrosion and good conductivity. A solid solution is a homogeneous mixture of two or more elements in the solid state, where the atoms of the solute are incorporated into the crystal structure of the solvent. In such a mixture:

The solvent (element A) is the primary component and its crystal structure is preserved.

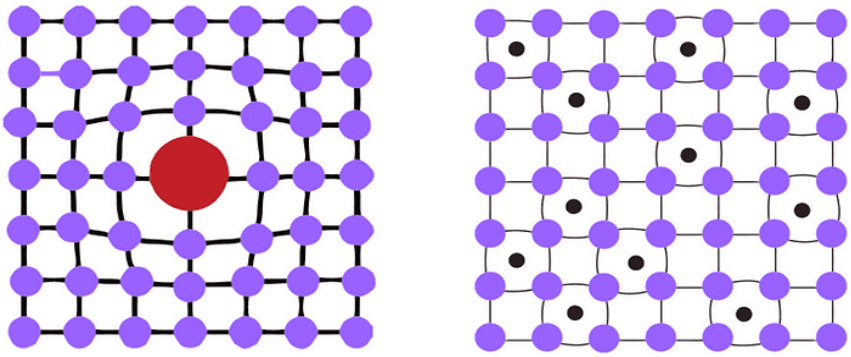
The solute (element B) is the secondary component, which is dissolved in the crystal lattice of the solvent.

There are two types of solid solutions:

Substitutional solid solution (substitution): The solute atoms replace the solvent atoms in the crystal lattice. This occurs when the solute and solvent atoms have similar sizes and chemical properties (e.g., copper and nickel in the Cu-Ni alloy).

Interstitial solid solution (insertion): The solute atoms occupy the interstitial spaces (vacancies)

between the solvent atoms in the crystal lattice. This occurs when the solute atoms are much smaller than the solvent atoms (e.g., carbon in iron to form steel).



(a) (b)

Figure II.1. Substitution (a) and insertion (b) solid solutions

II.1.4. Cooling curve

A cooling curve is a graph that shows the change in temperature of a material over time as it cools. They are used to study the solidification of liquids and the crystallization of materials.

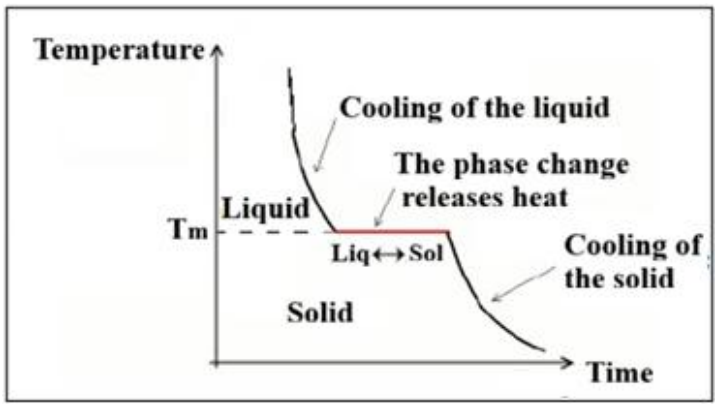


Figure II.2. Typical cooling curves

- The presence of a horizontal plateau in the cooling curve indicates the crystallization of the material.
- The position of the horizontal plateau indicates the melting or crystallization temperature of the material.
- The length of the horizontal plateau is proportional to the amount of material that has crystallized.

II.1.5. Crystallization of a pure metal

The crystallization of a pure metal is a solidification process that occurs when the liquid metal is cooled below its melting temperature. This process involves the formation and growth of metal crystals, which are regular, repetitive structures of metal atoms.

When a pure molten metal is cooled under constant pressure, the phase change always occurs at a fixed temperature.

The curve has a constant slope during the cooling of the liquid. At the melting temperature, the curve has a horizontal plateau because the latent heat of fusion is released. The curve then continues with a constant slope during the solidification of the material.

The cooling curve of a pure metal has a plateau. This plateau corresponds to the period of coexistence of the liquid metal and the solid crystals already formed. This isothermal plateau is more pronounced when cooling is slow and the alloy mass is larger.

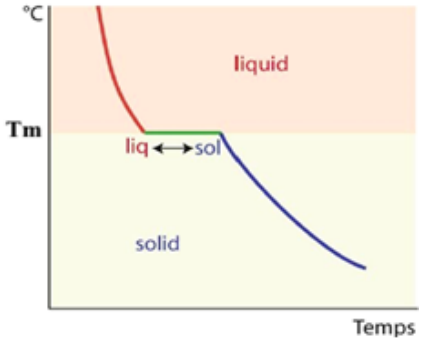


Figure II.3. Cooling curve of a pure metal

II.1.6. Crystallization of an alloy

To produce an alloy, defined proportions of different constituents are melted and mixed, then the mixture is cooled. When studying alloys, the solidification curves become much more complex. They then comprise several sections of curves connected by inflection points (Figure II.4).

When studying the solidification of a binary alloy, the curve reveals two inflection points :

- The first corresponds to the start of solidification (appearance of the first solid crystal in the liquid). This is the liquidus point.
- The second corresponds to the end of solidification (disappearance of the last traces of liquid). This is the solidus point.
- Solidification occurs within the solidification interval $\Delta T = (T_L - T_S)$
- The value of ΔT depends on the nominal composition C_0 of the mixture.

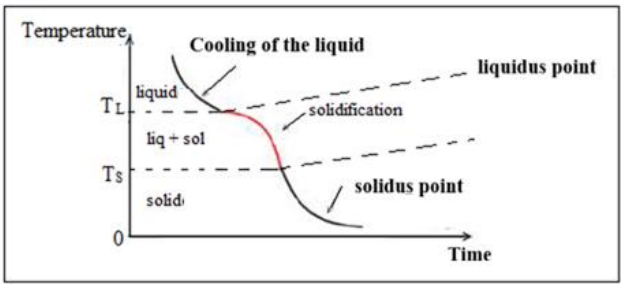


Figure II.4. Cooling curve of a two-component alloy

II.2. Binary equilibrium diagrams

The phase equilibrium diagram is a graphical relationship between temperature and the weight ratios of the elements and alloys that contribute to constructing the diagram.

Phase diagrams provide information on the following:

- Melting point.
- Casting conditions.
- Crystallization conditions.
- Phase transformations (changes).

Two types of transformations can be found in phase diagrams:

- The study of liquid-solid transformations produces solidification diagrams.
- The study of solid-solid transformations makes it possible to predict the properties of an alloy after heat treatment.

II.2.1. Principle of diagram construction

Consider all alloys formed from two metals, A and B, whose composition varies continuously from 0% B and 100% A to 100% B and 0% A (Figure 4 (a)).

The points of change of state for these constituents are found on the temperature axes corresponding to each of the pure substances. The diagram is divided into domains, corresponding to the presence of a single phase (single-phase domain) or two coexisting phases (two-phase domain), depending on the coordinates of the constituent point of the mixture.

In the thermal analysis curve diagram (Figure 4 (b)), curve 1 corresponds to pure A and therefore has a horizontal plateau for the change of state. The same is true for curve 2, which corresponds to pure B. The other curves correspond to the cooling of liquid A-B mixtures and show changes in slope at the start of crystallization and the disappearance of the last drop of liquid.

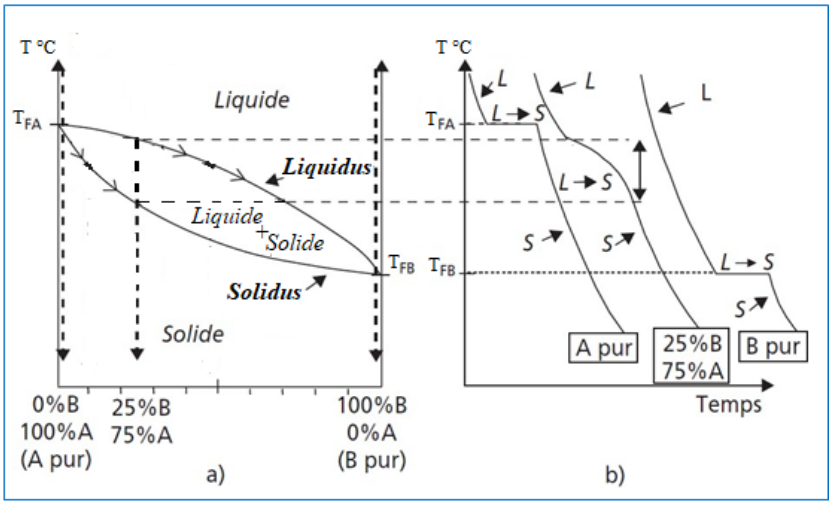


Figure II.5. Construction of a phase diagram

a) Phase equilibrium diagram Binary A-B.

b) Thermal analysis curves of different mixtures.

This solidification diagram consists of:

Y-axis: **temperature**

X-axis: **mass percentage composition**

■ Phases: * A liquid phase: **L** * A solid phase: **α**

■ There are three domains:

□ Liquid (**L**)

□ Liquid (**L**) + solid (**α**)

□ Solid (**α**)

Liquidus: the line separating the L and α+L phase domains is called the liquidus. Above this line, the phase is liquid for all temperatures and compositions.

Solidus: the line separating the α and α +L domains is called the solidus. Below this line, the phase(s) is (are) solid for all temperatures and compositions.

II.2.2. Determination of phase quantities (inverse segment rule)

Consider an alloy with nominal composition C_0 heated to a temperature T. If we take a representative point (C_0 , T) in the single-phase region, the alloy then contains a single liquid phase with a proportion equal to 100%. If we take a representative point (C_0, T) in the two-phase domain, Figure 5, the alloy contains two phases, liquid and solid, with compositions $C_L$and $C_{(S)}$,whose proportions $f_S$and $f_L$are determined by the lever arm rule. In fact, conservation of mass allows us to write the following two relationships:

$$f_S + f_L = 1 \qquad f_S C_S + f_L C_L = C_0$$

These relationships can be used to determine the proportions present as a percentage:

$$f_s = \frac{C_L - C_0}{C_L - C_s} x100 \qquad f_L = \frac{C_0 - C_S}{C_L - C_s} x100$$

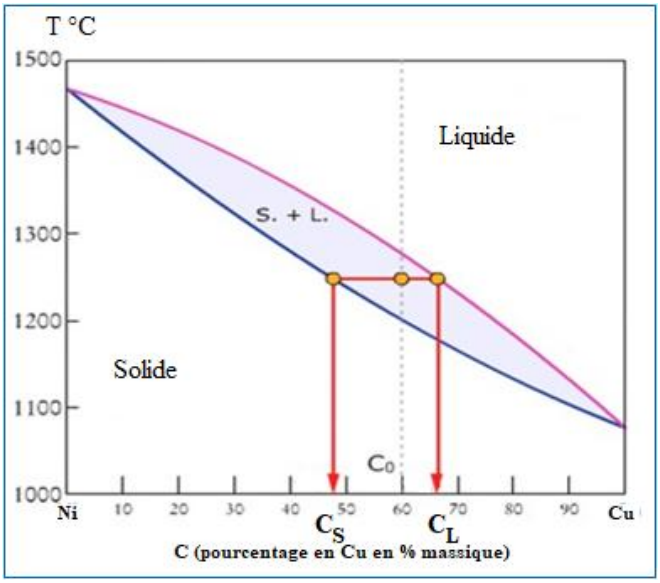


Figure II.6. Ni-Cu diagram with total miscibility

II.3. Types of equilibrium diagrams

II.3.1. Binary diagram with complete miscibility

A continuous solid solution is said to exist when a binary diagram shows complete mutual solubility for the entire concentration range.

This type of diagram is characterized by solidification delimited by the solidus and liquidus curves. Between the liquidus and the solidus, the alloy is in a two-phase state (liquid + solid) (Figure II.7). There are two types of diagrams with total miscibility:

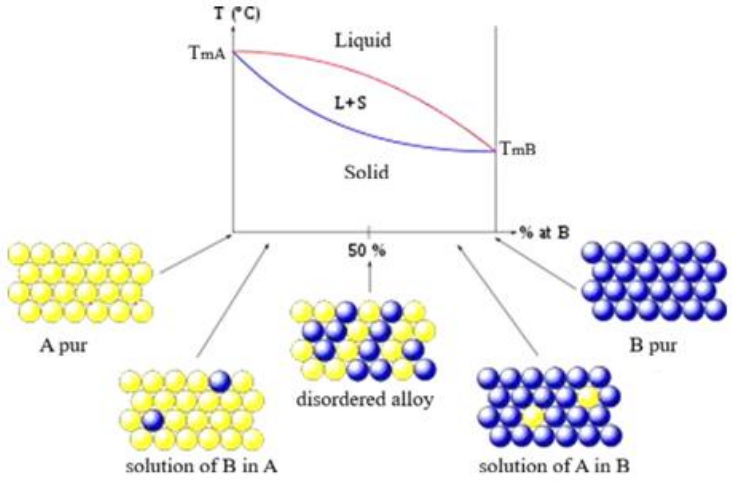


Figure II.7. Schematic illustration of a binary diagram with complete miscibility

a- Single-spindle diagram (lens-type phase diagram)

This is a characteristic of binary alloy systems with complete solid solubility (i.e., total miscibility in the liquid and solid states). This occurs when the two components have:

1. Similar crystal structures (e.g., FCC and BCC);
2. Comparable atomic sizes (atomic radius difference generally less than 15%);
3. Similar electronegativities and bonding characteristics.

Examples of such systems:

Cu-Ni. **(**Figure II.8.).

Ag-Au (both FCC, similar radii).

Cu-Pd (FCC, complete solid solubility).

Ir-Pt (both FCC, high melting point metals).

Ag-Pd (FCC, widely used in jewelry and catalysis).

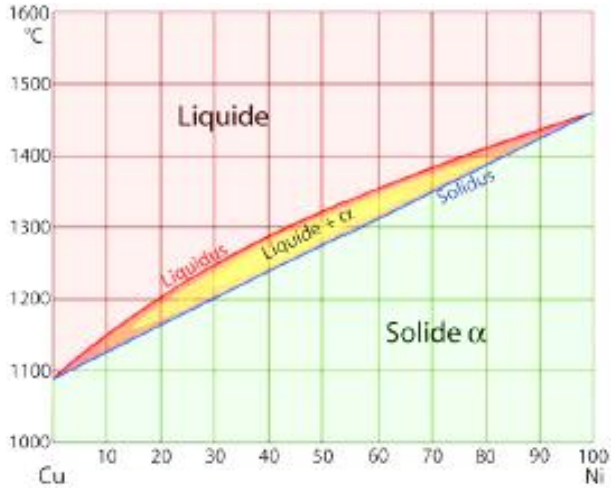


Figure II.8. Copper-nickel phase diagram with one spindle

b- Two-spindle diagram (Phase diagram with a minimum or maximum)

- Phase diagram with a minimum (most common)

The liquidus and solidus curves meet at an intermediate composition, forming a minimum melting point.

Examples: Au-Cu, Fe-Cr, Cu-Mg, Ni-Pd.

- Phase diagram with a maximum (rare)

The liquidus and solidus curves meet at an intermediate composition, forming a maximum melting point.

Examples: V-W, Nb-Ti.

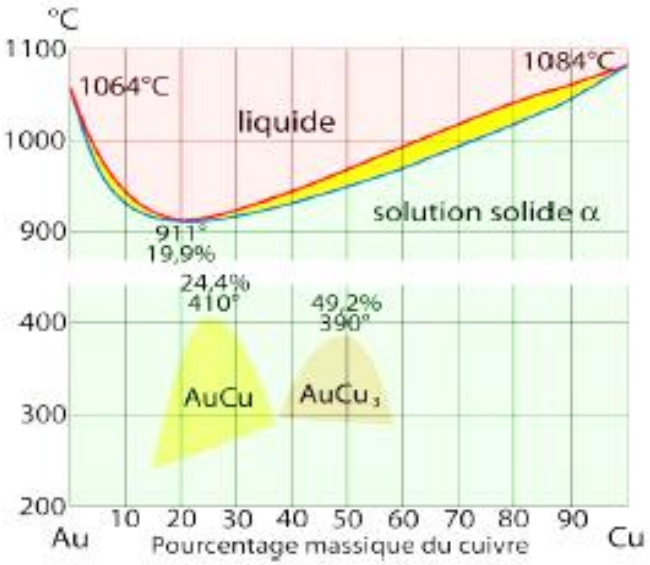


Figure II.9. Gold-copper phase diagram with two spindles

II.3.2. Equilibrium diagram of two partially miscible metals

This is obviously the most common case in binary alloys. Two types of transformations can occur: diagrams with a eutectic point and diagrams with a peritectic point.

II.3.2.1. Diagrams with eutectic point

In this type of diagram, there is an invariant point whose temperature is lower than the melting temperature of the two constituents. One of the advantages of these eutectic alloys is that they can be used in brazing.

The example shown here is the binary silver-copper alloy (Figure II.10).

At point E, or the eutectic point, equilibrium is established between three phases: one liquid phase and two solid phases. At this point, a liquid simultaneously transforms into two solid phases: $Li \Leftrightarrow \alpha + ß$

The main properties of eutectics :

* the eutectic temperature is the lowest temperature at which a liquid phase can be observed;

* The eutectic temperature is lower than the melting temperatures of each of the pure substances.

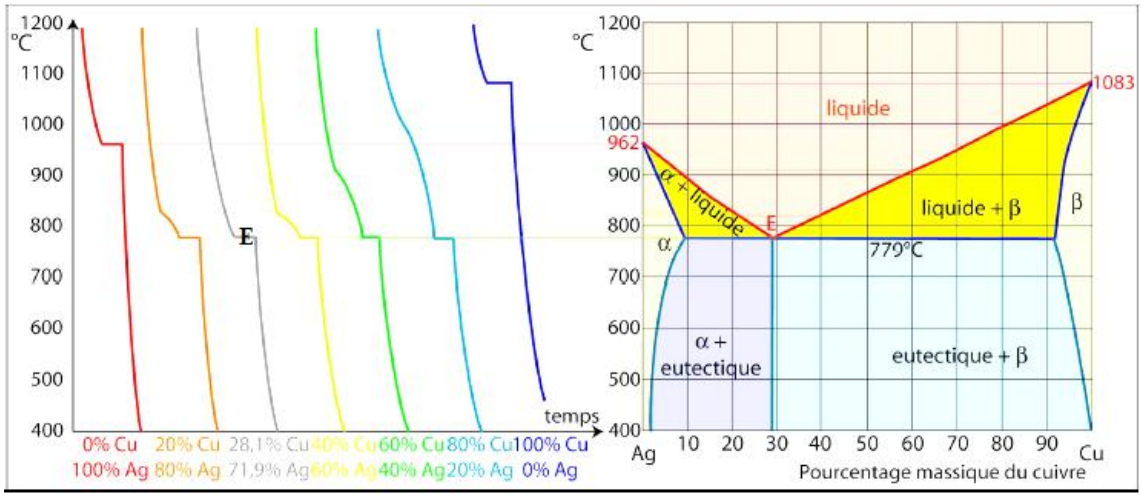


Figure II.10. Construction of a phase diagram with eutectic point

II.3.2.2. Diagrams with a peritectic point

In a peritectic transformation, a liquid phase and a solid phase transform into a single solid phase of defined composition. The peritectic point is invariant at a fixed temperature with equilibrium between the three phases. ß + L ⇔ α

The upper part of the phase diagram for the silver-platinum alloy (Figure II.11) illustrates the typical appearance of a peritectic transformation. The peritectic point is located at 1185°C for a composition of 55%m platinum and 45%m silver.

At this composition, just above 1185°C, two phases coexist: a solid β phase with a composition of C_β= 86% Pt and a liquid phase with a composition of C_L= 32% Pt. At 1185°C, these two phases abruptly transform into a single solid α phase with a composition of C_α= 55% Pt.

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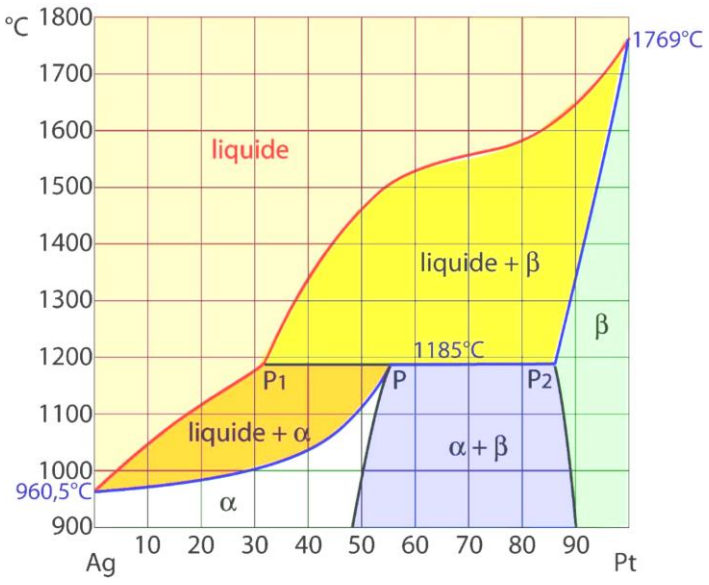
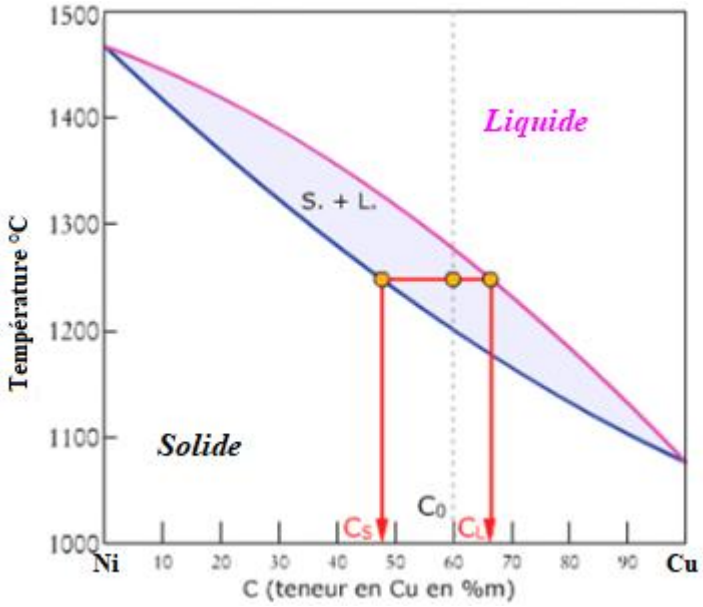


Figure II.11. Phase diagram of the Ag-Pt alloy with peritectic points

Exercise

Consider an alloy containing 60% copper and 40% nickel. At a temperature of 1250°C, the alloy is in the two-phase region. The composition of the liquid phase is 67% copper, while that of the solid phase is 48% copper.

Calculate the solid fraction f_S and the liquid fraction f_L of this alloy.



Ni-Cu diagram with total miscibility

Solution

Conservation of mass allows us to write the following two relationships:

$$f_S + f_L = 1 \qquad f_S C_S + f_L C_L = C_0$$

C_0 : nominal composition,

C_S: composition of the solid phase,

C_L : composition of the liquid phase.

f_S: solid proportions.

f_L : liquid proportion.

These relationships can be used to determine the proportions *(inverse segment rule)* expressed as a percentage:

$$f_s = \frac{C_L - C_0}{C_L - C_s} x100 \qquad f_L = \frac{C_0 - C_S}{C_L - C_s} x100$$

Or: $f_L = 100 - f_s$

The proportion of solids f_S is then:

$$f_S = \frac{67-60}{67-48} \times 100 = 36\%$$

The proportion f_L of the liquid can then be deduced: $f_L = 100 - 36 = 64\%$