Chapter

VII

Types of diffusional transformations

VII-1. Introduction

One of the phase transformations in the solid state which is of particular interest to researchers today is the precipitation reaction which occurs in certain materials during heat treatment (tempering or aging) and thus gives the material its working properties.

Precipitation processes from supersaturated solid solutions, which involve diffusion phenomena, are generally classified into two main categories: discontinuous and continuous precipitation. In practice, homogeneous precipitation only occurs exceptionally and germination almost always starts on heterogeneities in the initial phase which lower the free enthalpy of nucleus formation by reducing either the surface energy or the strain energy, or even both. These heterogeneities can be impurities, inclusions, dislocations, surfaces, or grain boundaries. It is established that the presence of lattice defects favors the germination of the precipitate, under conditions where this would have little chance of occurring in the absence of these defects. The crystallites of precipitates formed on the defects frequently appear for this reason before the crystallites resulting from the homogeneous precipitation. During discontinuous precipitation, the initial supersaturated phase, in which the solute concentration remains unchanged, coexists with the precipitation products: the latter correspond to the equilibrium phases whose respective compositions are those of equilibrium at the temperature considered. Thus, at the interfaces between regions which have undergone the decomposition reaction and those where the latter has not yet taken place, there is a concentration discontinuity.

VII-2- Definition of precipitation

The precipitation of a supersaturated solid solution is a solid state transformation with an increase in the number of phases. It generally consists of a decomposition of the supersaturated solid solution (the initial matrix) into two new phases:

- The poor matrix
- The precipitated phase

It follows that an alloy, which would be single-phase at a certain temperature, can become two-phase at lower temperatures. The supersaturated homogeneous alloy is relatively soft, its hardness and elastic limit are low. The precipitation of a second phase causes structural hardening which increases the hardness and the elastic limit.

To start a precipitation reaction, it is necessary to go through the following three steps:

- A homogenization treatment to eliminate any segregation in the alloy and to achieve a homogeneous single-phase system. The homogenization temperature is chosen above that of the solubility limit, in the single-phase range.

- Quenching of the homogenized alloy to obtain a single non-equilibrium phase. It is called supersaturated solid solution, since it contains more solute than the equilibrium solid solution at this temperature; in addition another supersaturation in vacancies can be caused.

- Aging at a temperature chosen in the two-phase range, which causes the appearance of one or more phases.

Homogenization treatment to eliminate any segregation in the alloy and to achieve a homogeneous single-phase system. ($T_{homg} > T$ of the solubility limit, in the single-phase domain.

A quenching of the homogenized alloy to obtain a single non-equilibrium phase: supersaturated solid solution (contains more solute than the equilibrium solid solution and supersaturation in vacancies)

Aging at a temperature chosen in the two-phase range, which causes the appearance of one or more phases.
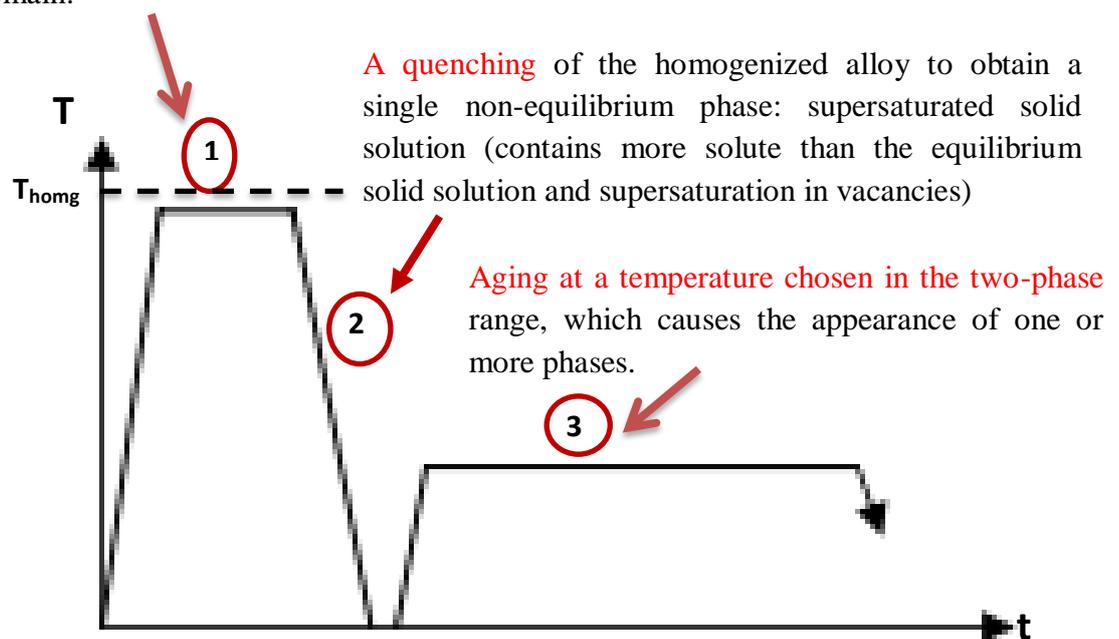
Fig. VII-1- : schematic representation of the precipitation steps

There are generally two types of precipitation as indicated in the introduction:

- ❖ **Continuous precipitation**: during which the supersaturated solid solution begins to deplete in a random and theoretically homogeneous continuous way throughout the matrix. We then observe a single parameter of the lattice whose evolution will be

continuous. Sometimes continuous precipitation appears mainly in grain boundaries and slid planes; it is then called localized or heterogeneous precipitation.

- ❖ **Discontinuous precipitation**: the precipitation is said to be discontinuous when during the transformation two regions appear:
- One where the transformation is complete,
- The other where the solid solution is still supersaturated.

The transformation generally begins on the grain boundaries by developing cells (hence the name cellular precipitation). During this precipitation, the lattice parameter varies discontinuously with two distinct values.

VII-3. Precipitation characteristics

VII-3-1. Composition criteria and sequence of heat treatments for alloys

Consider a binary aluminum-element Al-M alloy (figure VII-2-). Using figure VII-2-, the alloy of concentration X_1 (concentration lower than the solubility limit X_S of the addition element) at a temperature T_1 higher than the solidus temperature T_S for duration sufficient to reach thermodynamic equilibrium and thus obtain total dissolution of the solute atoms M.

- If the alloy is cooled very slowly from the temperature T_1 to a temperature below T_S, the solid solution of M in the aluminum, which retains its face-centered cubic structure (denoted by α), tends to decompose in the form of more or less coarse particles of the stable intermetallic compound Al_xM_y in the solid solution of aluminum poor in M atoms: it is the equilibrium precipitation which leads to a structure close to that of annealing, and which is generally of no interest from the point of view of the hardening of the alloy due to the coarse size of the precipitates (of the micrometer order) and their too low number per unit volume of alloy. Their molar fraction f_m respects the rule of lever arms or rule of inverse segments:

$$f_m = \frac{BA}{BC} \qquad \text{(VII-1-)}$$

Where BA and BC are defined in figure VII-2-, at temperature T_2.

- The quenching operation consists in cooling the alloy sufficiently quickly after dissolution to prevent the decomposition of the solid solution with the formation of these coarse equilibrium precipitates. Quenching also makes it possible to trap the very numerous vacancies that are stable at high temperature. Immediately after

quenching to room temperature T_2 (Fig. VII-2-), a solid solution supersaturated with solute M and vacancies is obtained where the solute atoms are randomly positioned at the nodes of the face-centered cubic lattice of aluminum (Fig. VII-3-a-) and form a substitute solid solution.
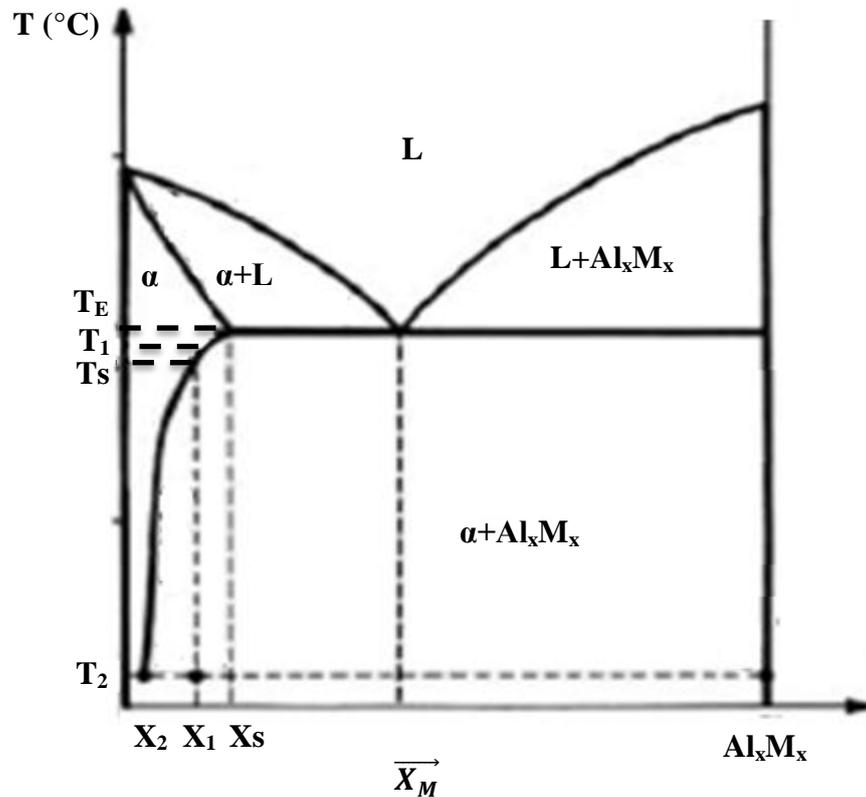
Fig. VII-2- : Principle of heat treatments for hardening aluminum alloy by precipitation in a binary phase diagram.

After dissolution and quenching, hardening by precipitation then results from the decomposition of this supersaturated solid solution into the main addition elements. During the aging of the alloy at room temperature or at low temperature after quenching, the supersaturated solid solution is therefore metastable. During this phase, called *maturation* or *natural ageing*, the alloy gradually and spontaneously hardens and the solid solution decomposes to give rise to the formation of small clusters of solute atoms (the *Guinier-Preston zones* or *GP zone*) in very high density: this is pre-precipitation.

These clusters of atoms are always located at the nodes of the aluminum matrix lattice and consist of small portions of crystallographic planes of the aluminum lattice enriched in solute atoms (figure VII-3-b-). These GP zones introduce elastic distortions into the matrix

lattice. The local chemical enrichment in solute and the elastic deformations which result from it explain that in certain cases this precipitation is facilitated by the presence of structural defects - such as dislocations - which favor a higher diffusion of solute atoms or accommodate fields of adapted elastic deformation.
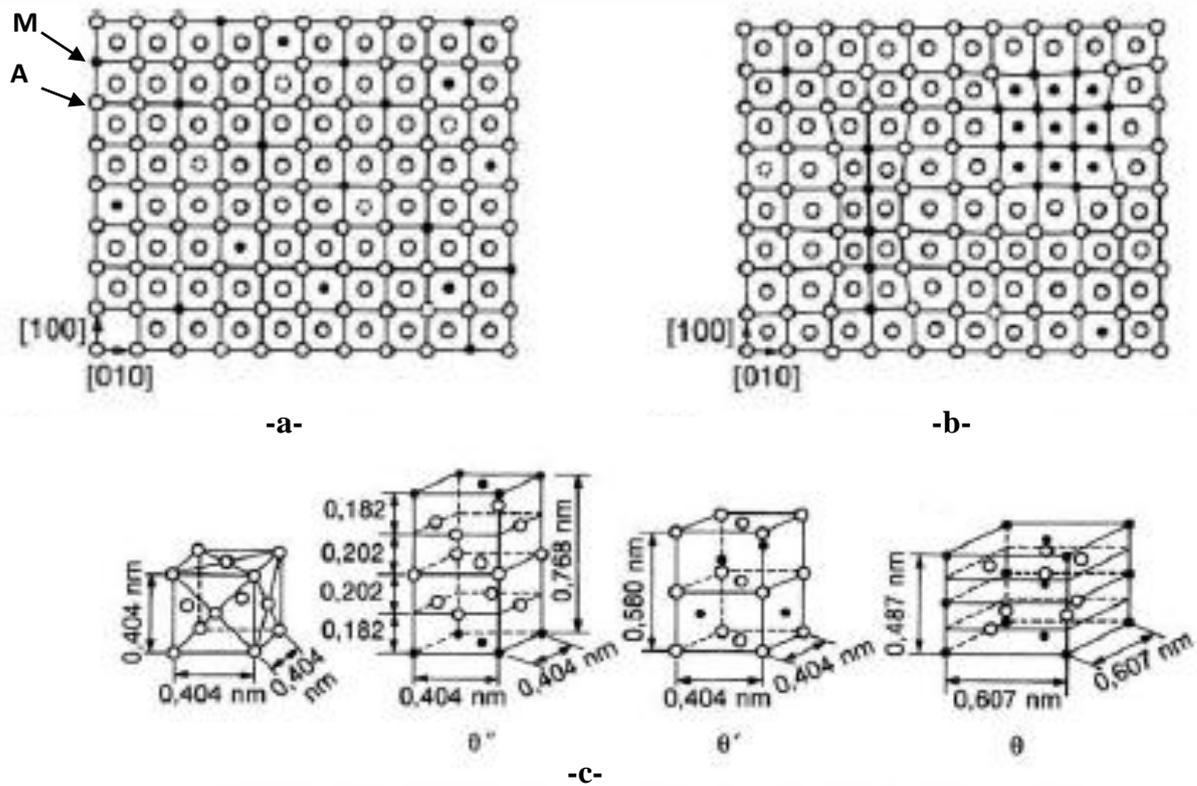
Figure VII-3- : Different steps of the precipitation sequence of the Al-Cu system (*B. DUBOST et al, Techniques de l'Ingénieur, traité Matériaux métallique, la fiche M240, 1991*).

    (a)- α-substitution solid solution

    (b) GP zones formation

    (c) Lattice of metastable intermetallic compounds θ'' and θ' and equilibrium intermetallic compound θ-Al_2Cu

Subsequent heating at a moderate temperature (100°C), called tempering, further accentuates the decomposition of the solid solution by the dissolution of the GP zones previously formed and by the precipitation of very numerous (10^{16} to 10^{17}/cm^3) and very fine particles (average size between 2 and 50 nm) which further harden the alloy to its maximum mechanical strength. These precipitates are metastable intermetallic compounds (transition precipitates), which now have their own crystal lattice and chemical composition (figure VII-3-c-).

Precipitation of the equilibrium intermetallic compound in the poor matrix as much as possible in solute is most often possible only during an over-tempering treatment carried out at properly high temperature (generally greater than 160°C) for a period of treatment exceeding that which leads to the relative maximum hardening. The relative softening of the alloy is then governed by the coalescence of the precipitates, the largest of which (with a size of the order of a micrometer) then become visible in optical microscopy at high magnification: the microstructure therefore tends to approach that of the annealed state, the most stable from the thermodynamic point of view, which is reached in practice after maintaining a few hours between 250 and 400°C.

VII-3-2. Precipitation sequence in quenching aluminum alloys

For thermodynamic and kinetic reasons, we note that the quenching of supersaturated solid solution almost never gives rise directly to the precipitation of the intermetallic phase of stable equilibrium. The hardening of alloys at room temperature then during tempering generally results from a sequential decomposition of the solid solution α and a progressive depletion in solute of the latter follow the schematic steps:
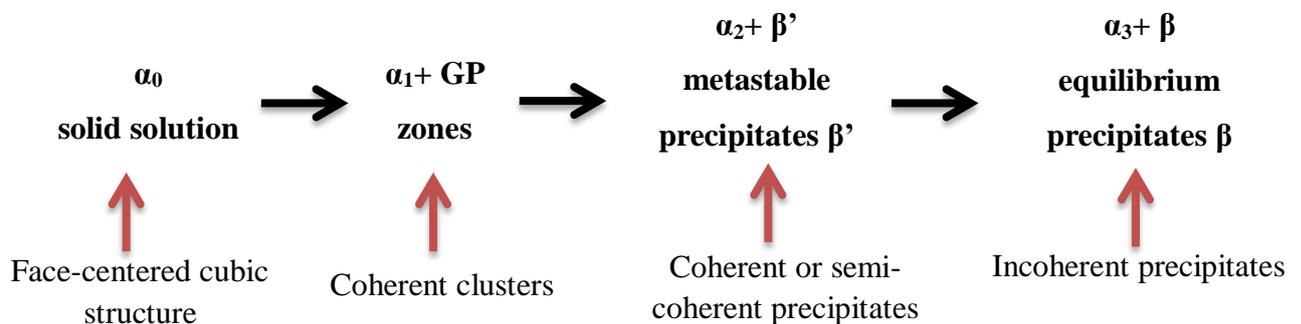
For the structural hardening to be important, the formation of a high density and a homogeneous distribution of clusters and/or metastable precipitates in the matrix are sought.

VII-4. Types of precipitation in metal alloys

VII-4-1. Continuous precipitation

It is a reaction in which the atoms are transported towards the germs of precipitates by diffusion over large distances from the initial phase, so that the solute composition of the latter is modified in a continuous manner towards its equilibrium value.

The experimental characteristic for such transformation is the continuous variation of the parameter of the crystal lattice of the matrix up to a limiting value which corresponds to the equilibrium state. Precipitation begins with the appearance of germs at the expense of the G.P zones which will therefore tend to disappear completely and give way to metastable or stable phases. The passage from the initial state to the final state is generally done by a succession of intermediate stages which were indicated in the previous paragraph for aluminum alloys.

❖ **Guinier-Preston zones (G.P)**

It was Guinier and Preston who suggested in 1938 the existence of zones enriched in dissolved atoms forming small domains coherent with the matrix. These so-called Guinier-Preston zones (G.P zones) are responsible for the first stage of hardening.

Contrary to the mechanism of precipitation of the two metastable and stable phases, which is generally done on heterogeneities structures, the formation of the G.P zones is done in a homogeneous way; its mechanism has been widely studied for aluminum-based alloys where it has been established that these zones form at sufficiently low temperatures, and that vacancies play a predominant role in their formation. Indeed, being in excess after quenching at sufficiently low temperatures, and before reaching their equilibrium limit at these temperatures, the excess vacancies allow a diffusion of the solute atoms which group together very quickly in the form of coherent zones having a definite shape and structure.
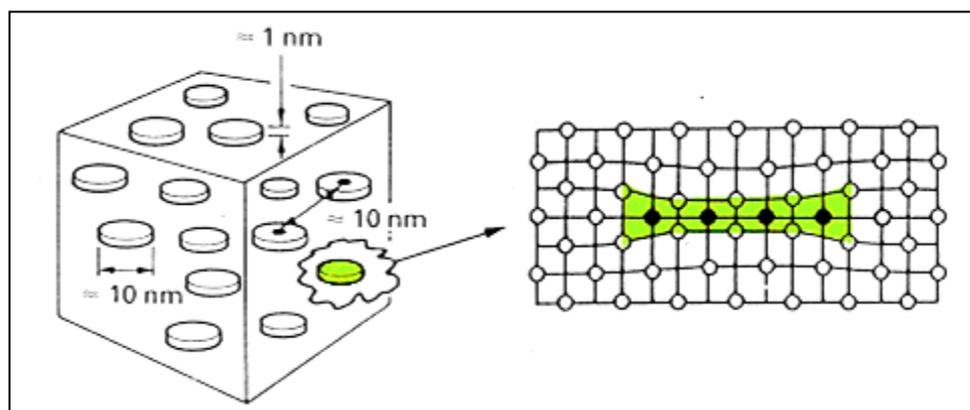
Figure VII-4- : Guinier-Preston zones (G.P)

By their size effect, these precipitates are the center of a deformation field (Fig. VII-5-). The dislocation is therefore attracted or repelled by the particles. The dislocation therefore bends between the particles and sufficient stress must be applied to overcome the elastic interactions and thus allow its sliding. But, in doing so, the dislocation shears the precipitate: when it enters or leaves a particle, it creates a small interface of width b (Fig. VII-5-a-), which requires work equal to the change of cohesive forces. The necessary yield is very high and can even grow with the diameter of the particles up to a critical value of the latter, where the Orowan mechanism comes into play which applies each time the circumvention of the particle becomes easier than its crossing (Fig. VII-5-b-).
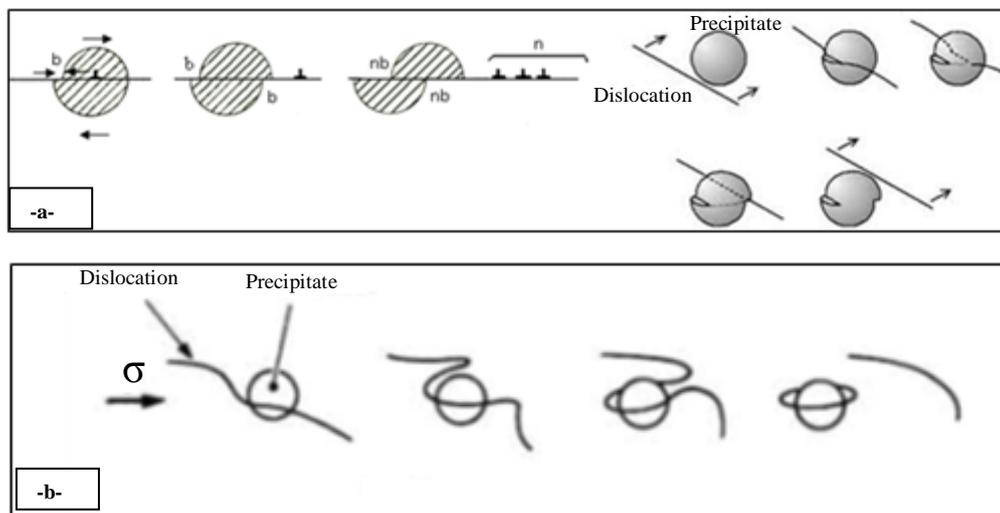
Fig. VII-5- : (a) Shearing of a coherent precipitate.

(b) Dislocation line bends around the precipitate: (Orowan mechanism)

VII-4-2. Discontinuous precipitation

Discontinuous precipitation, which is one of the discontinuous reactions that can be called reactions with two migrating phase boundaries, is a heterogeneous reaction in the solid state, controlled by diffusion at the boundaries which constitute a transport circuit for solute; it is triggered preferentially on the joints of strong disorientation. During this reaction, α' supersaturated solid solution is replaced by a cellular structure composed of two phases (α + β).

$$\alpha' \longrightarrow \alpha + \beta$$

Where: α': The supersaturated matrix.

α: the same phase but with a different concentration

β: equilibrium precipitate (of the second phase).

Since the discovery of discontinuous precipitation by Agreew et al in 1930 in Ag-Cu alloys, the understanding of this reaction has evolved enormously. However, many very important questions about her are still ambiguous. Indeed, it is still impossible to say exactly which mechanism controls its process in a well-defined alloy or which discontinuous reaction occurs in one alloy and not in another. In addition, until now the criterion according to which this reaction in the solid state occurs is still difficult to establish, due to the fact that this reaction has several factors that can promote it.

✓ **Different types of discontinuous precipitation**

❖ **Interfacial precipitation**

The precipitation product exhibits a cellular structure containing alternating lamellae behind a reaction front which is identical to an incoherent grain boundary (Fig. VII-6-). For isothermal annealing, the interlamellar distance remains approximately constant, but in their work Gust et al have shown that in certain zones the interlamellar distance of precipitates formed isothermally does not have a constant value but varies according to a Gaussian distribution. In this type of reaction, the transport of the material is ensured by the interfacial diffusion along the reaction front which is a grain boundary of strong disorientation.

-a-   -b-
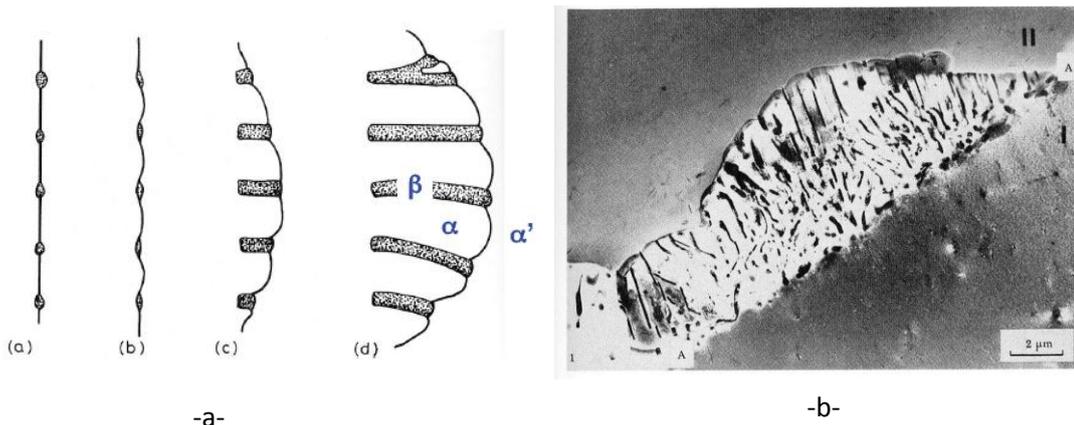
Fig. VII-6-: (a)- Schematic representation of an interfacial type precipitation reaction

(b)- Cellular precipitation of $Mg_{17}Al_{12}$ in the Mg-9 at. % Al alloy annealed for 1 h at 220°C *(D. A. Porter, K. E. Eastorting. Phase transformation in metals end alloys, second edition, Chapman et Hall, London, (1992)).*

Dislocations play a big role in the germination and growth processes of precipitates, as they form preferential regions for precipitation. This second type of precipitation differs from the first type by:

- The precipitated particles are not lamellar but small platelets of well-defined crystallographic structure.
- Volume diffusion of the solute element

Precipitation on dislocations occurs in systems where the specific volume of the initial matrix and that of the reaction product are very different. It is assumed that in the process of precipitation of the β-particle the dislocations produced act as new nucleation sites. This type of precipitation on dislocations does not occur frequently. However, in several solid solutions, both types can be observed simultaneously.

❖ **Precipitation at interphase boundaries**

The problem of precipitation from interphase boundaries has been the subject of numerous theoretical studies. The idea that an immobile interphase boundary can provide favorable sites for the particles germination of a new phase at low temperature is well accepted.

In copper-based alloys, only two works have been devoted to the study of discontinuous precipitation from interphase boundaries. Manna et *al.* investigated for the first time the possibility of inducing discontinuous precipitation from interphase boundaries, comparable to that occurring at grain boundaries.

In their studies on a Cu-15% mass. In, Hamana and Boumerzoug have shown that the eutectoid phase can be obtained; a subsequent annealing at 400°C can lead to a discontinuous precipitation from the eutectoid/matrix interphase boundaries, comparable to that observed at the grain boundaries.

VII-5. Precipitation mechanisms

VII-5-1. Precipitation by germination and growth

According to the classical theory of Gibbs extended to the transformations of phases in the solid state by Turnbull and Fischer, germination, the initial stage of precipitation, supposes the formation, from the matrix, of stable germs, rich in solute (of composition very

different from that of the solid solution) and have a defined interface with the matrix. The germ can result from statistical fluctuations of composition of sufficient size (of the order of a nanometer) within the solid solution with very rapid formation kinetics in the presence of vacancies in supersaturation (homogeneous precipitation), or form preferentially on the lattice defects or pre-existing interfaces between different grains or particles (heterogeneous precipitation). The subsequent growth of germs and precipitates is governed by the diffusion of solute atoms towards the germs, which is thermally activated at tempering temperature as long as the solid solution is supersaturated. The proposed precipitation mechanisms include consideration of thermodynamic factors and kinetic effects and apply to most precipitation hardened aluminum alloys.

❖ Thermodynamics of germination

Thermodynamically, germination is only possible after dissolution and quenching if it is accompanied by a reduction in the overall free energy of the system initially consisting of the homogeneous solid solution. This quantity (Gibbs free energy) includes first of all a term of chemical order of molar free energy of germ formation, then thermodynamic barriers opposing the formation of this germ. Figure VII-7- gives the free energy curves formation of the different phases as a function of the concentration X of the addition element at the temperatures T_H (high temperature) and T_B (low tempering temperature). In this figure, the phase equilibrium diagram of the system results from the minimization of its free energy in the whole range of considered temperatures.

- The curve G(α) gives the variation of Gibbs free energy molar of the solid solution α as a function of the solute concentration, as well as that of the GP zones because the latter have the same crystalline structure as the matrix. The curve presents a double concavity with an absolute minimum in the vicinity of the solute concentration at equilibrium X_s (at low values of X) and a relative minimum close to the average solute concentration in the vicinity of the GP zones (for a range of higher values of X).
- G(β') and G(β) represent the respective free energy curves of the metastable phase β' (transition precipitate) and that of the equilibrium phase β (stable phase) as a function of the concentration X as an addition element M.

Any mode of decomposition of low amplitude in two phases represented by A and B (at the temperature T_H) is impossible, thermodynamically, inside the domain where the curvature of G(x) is positive (figure VII-7-b-) because it would lead to an increase in the free energy of

the system in algebraic value. The only mode of decomposition of the initial solid solution decreasing the free energy of the system (and therefore thermodynamically favorable) is then a demixing into a strongly poor solid solution (close to the concentration at equilibrium) and clusters very rich in solute atoms. The latter can then consist of GP zones (with a concentration located beyond the second point of inflection J_1 or J_2 on the G(α) curve, in the part with positive curvature, or precipitates of metastable β' phase or of stable β phase with lower molar free energy. The compositions of the solid solution and of the associated GP zones or precipitates are then given by the abscissa of the contact points of the tangent common to the two parts with positive curvature of the curve G(x) (figure VII-7-b and VII -7-c).

VII-5-2. Precipitation by Spinodal decomposition

This mode of precipitation, the theory of which was established by Cahn, generally affects alloys with a high volume fraction of precipitates (for example copper alloys) but is also likely to account for the structural hardening of certain aluminum alloys in systems Al-Zn and Al-Ag. On the Gibbs free energy molar curve, shown at low temperature in Figure VII-8-, its concentration is between those of the inflection points I and J (the curve connecting I to J is the Spinodal curve). The Spinodal decomposition is then possible inside the domain where the curve G(α) is convex (negative curvature) and for any temperature leading to a portion of the curve such that $\partial^2 G(α)/\partial x^2 < 0$.

A continuous and progressive decrease in the chemical free energy of the system, thermodynamically favorable, is obtained by the demixing of the initial solid solution into two components, one of which is increasingly poor in solute and the other is increasingly enriched in solute (such as the respective concentration phases given by the abscissas of segment MP based on the part of the curve G(α) with negative curvature). Precipitation, which then initiates from random fluctuations in the concentration of the solid solution, occurs throughout the grain. Unlike precipitation by germination and growth, there is no germination energy barrier. The differences in composition, very small at the start of the demixing in the alloy, tend to increase as the decomposition progresses, the solute migrating towards the precipitate by short-distance diffusion going up the gradient of concentration until the final composition of the precipitate X_p (figure VII-9-). This results in a microstructure characterized by an apparently periodic modulation of the distribution of precipitates in the matrix (homogeneous precipitation).
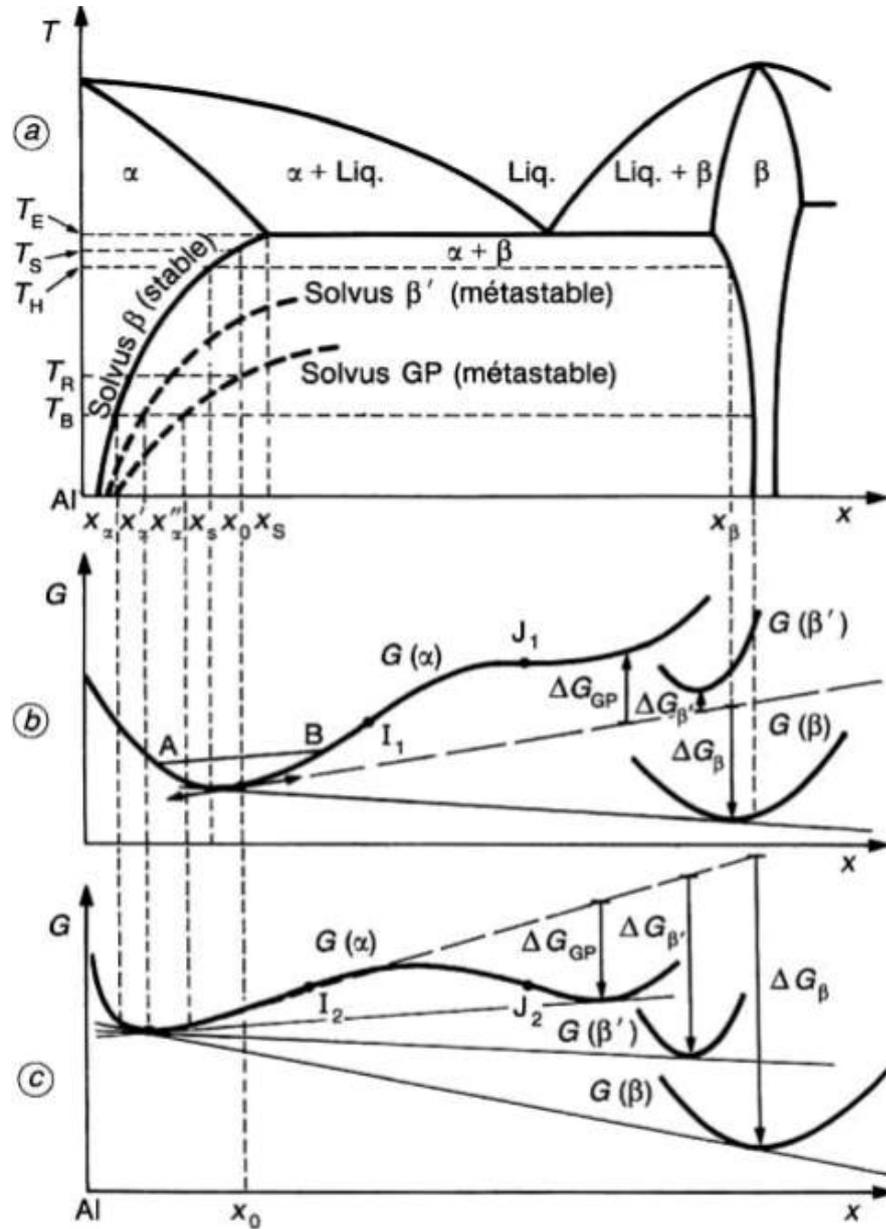
(a) Diagram of equilibrium phases and metastable phases
(b) Molar free energy G at a high temperature T_H
(c) Molar free energy G at low temperature T_B

Fig.VII -7- : Al-M system phase diagram construction schema *(B. Dubost et al, Techniques de l'Ingénieur, traité Matériaux métallique, la fiche M240, 1991).*
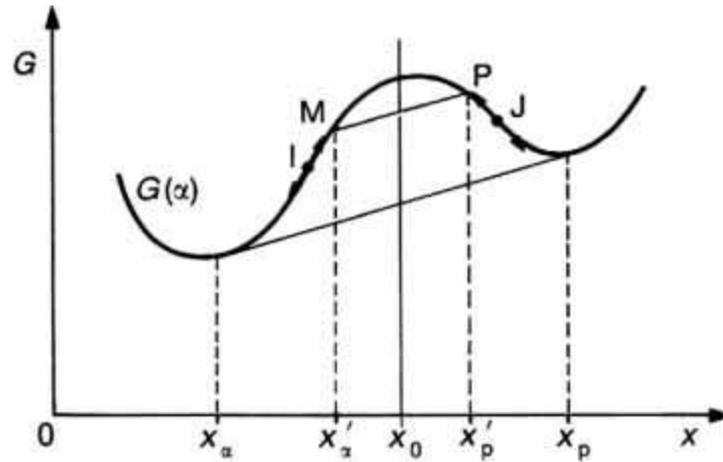
Fig. VII-8- : Free energy curve G at low temperature of an alloy of concentration x_0 *(B. Dubost et al, Techniques de l'Ingénieur, traité Matériaux métallique, la fiche M240, 1991).*
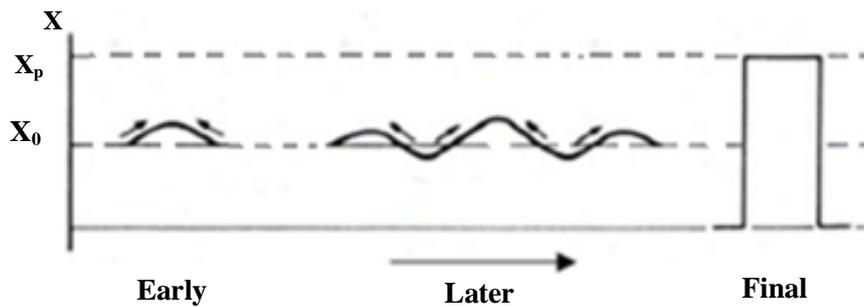
Fig. VII-9- : Evolution of the concentration profile x of the solute of an alloy precipitated by spinodal decomposition depending on the stage of maturation

VII-6. Experimental methods for studying structural precipitation

VII-6-1. Metallography

Optical microscopy, due to its insufficient resolving power, is only used in practice for the visualization of coarse precipitation on samples that have been polished and then possibly attacked by specific solution reagents (Fig. VII-10-). The images obtained are those of attack figures, rich in information on the distribution of the coarsest phases such as the phases out of solution (phases not dissolved during the homogenization treatments after elaboration of the alloy), the precipitated phases at the grain boundaries.
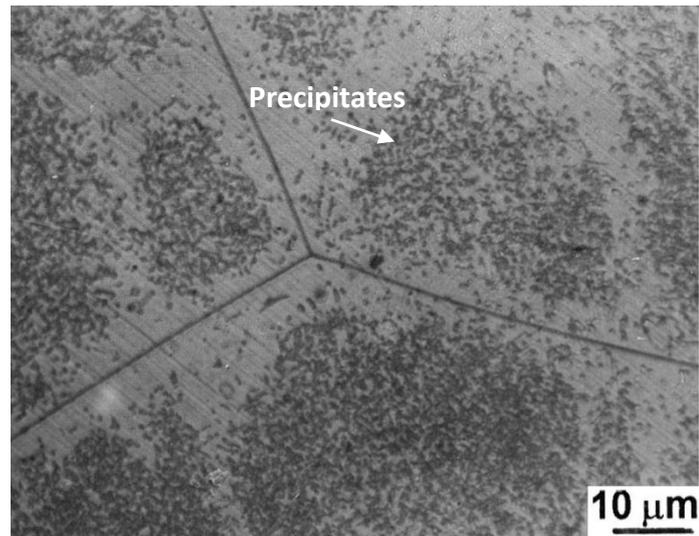
Fig. -10-: Microstructure of Al–12 wt.% Mg alloy homogenised 17 h at 430°C, quenched then aged during continuous heating at a rate of 2°C/min to 280°C *(D. Hamana et al., Journal of Alloys and Compounds 320 (2001) 93–102)*

Scanning electron microscopy on polished sections, according to the chemical contrast resulting from the differences in atomic number accessible in backscattered electron imaging, makes it possible to access similar information with increased spatial resolution while avoiding chemical attack. These two techniques can be easily coupled with devices for analyzing the contrasts and morphologies of the image. The volume fractions of precipitates and the geometric parameters of size, shape and distribution can then be determined quantitatively in an objective manner.
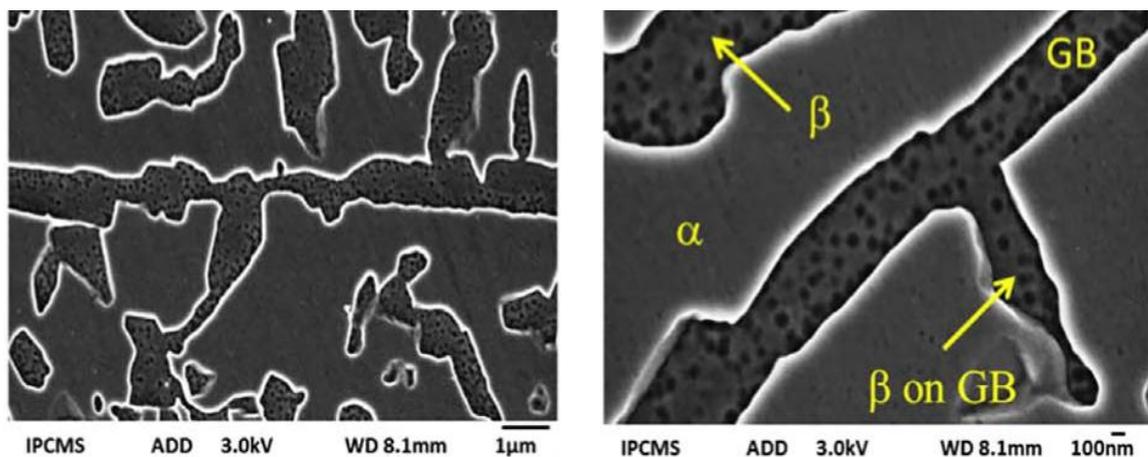
Fig. -11-: SEM images of Al-12 wt% Mg alloy homogenized for 17 h at 430 °C quenched and aged for 21 h at 250 °C *(C. Amrane et al., Materials Characterization 134 (2017) 49–54).*

Transmission electron microscopy allows precise crystallographic (crystallographic structure, orientation relationships between phases), geometric (morphology, size and distribution of phases in the privileged range of very high magnifications) and chemical (main elements) characterization of phases present in the alloy. The spatial resolution in image is sufficient to visualize in certain cases the planes and the columns of atoms constituting the microstructure by interferences of the diffracted electron beams. The spatial resolution in crystallographic analysis (by electron diffraction) or chemical analysis (by energy analysis of X photons emitted by the sample or by energy analysis of transmitted electrons) reaches a few nanometers. These resolution levels are necessary for the characterization of the vast majority of precipitates appearing in quenching aluminum alloys. However, they turn out to be insufficient in certain cases such as the study of the first stages of the pre-precipitation of Al-Mg-Si, Al-Zn-Mg, Al-Cu-Mg alloys. Transmission electron microscopy, which is based on electron diffraction, is particularly well suited to the study of the orientation relationships of precipitates with respect to the matrix and to that of structural defects (dislocations, elastic distortions lattice, characterization of grain boundaries, etc.).
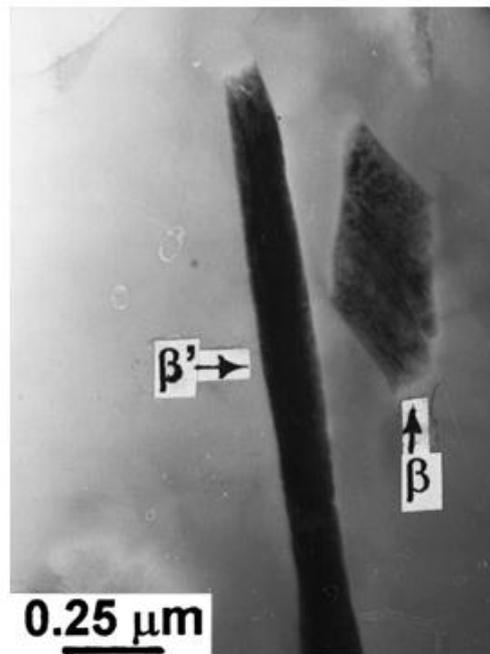
Fig. -12-: TEM micrographs of Al–12 wt.% Mg alloy homogenized 17 h at 430°C, quenched and aged 1 h at 250°C illustrating different particles of β' and β phases *(D. Hamana et al., Journal of Alloys and Compounds 320 (2001) 93–102).*

VII-6-2. X-ray and neutron diffraction

The richness of the relationships existing between the crystallographic structure and the precipitation parameters make diffraction methods (including electron diffraction) tools of choice for the microstructural study of metallic alloys. These techniques are used for the crystallographic characterization and, in some cases, for the determination of the morphology, the volume fraction and the size of the precipitates present in the studied system.
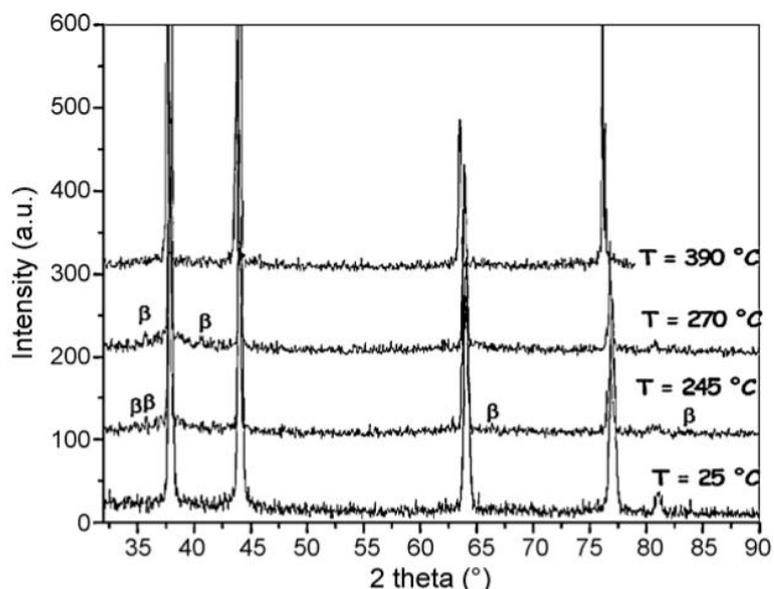
Fig. -13-: Sequence of X-ray diffraction patterns recorded during heating with a heating rate of 2°C/min of an Al–12 wt. % Mg alloy homogenized at 430°C for 17 h and quenched in ice water, then compressed to reduce their thickness to 16% *(A. Hayoune and D. Hamana, Materials Science and Engineering A 527 (2010) 7261–7264).*

VII-6-3. Macroscopic physical methods

They exploit macroscopic variations of physical properties (electrical, thermal, dimensional, etc.) of the material according to its state of structural separation.

Differential calorimetric analysis (DSC) is a very sensitive calorimetric method which allows the direct measurement of the heat released or absorbed by an alloy sample, during an exothermic (precipitation) or endothermic (dissolution of precipitates or GP zones) caused by a rise in temperature at an imposed rate or by a controlled isothermal segment (Fig. VII-14-). This technique can allow, after calibration, a quantitative determination of the mass fraction of phases formed in the matrix by homogeneous or heterogeneous precipitation. It also makes it possible to accurately determine the phase transformation temperatures, which are also

studied by differential thermal analysis and which are essential for defining the conditions for dissolving the alloys.
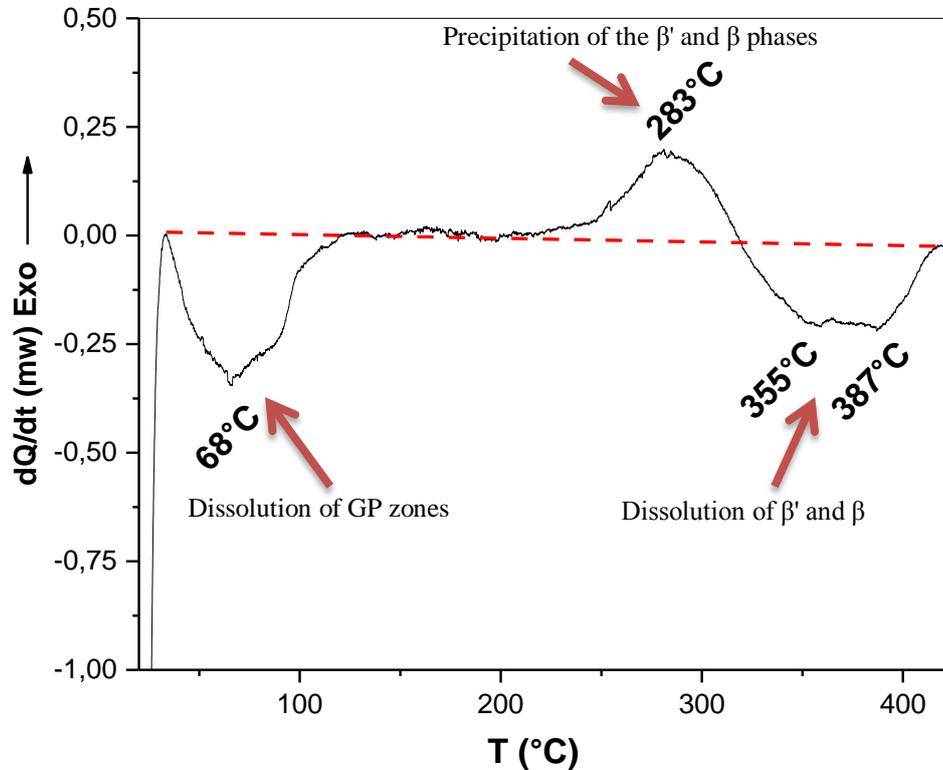
Fig. -14-: DSC curves of the Al-12wt. % Mg alloy homogenized then water quenched

Differential dilatometry makes it possible to follow the kinetics and phase transformation ranges during heat treatments by measuring dimensional variations (contractions or expansions) induced by the maturing or tempering of the alloys (Fig. VII-15) The effects are however generally weaker on industrial light alloys (in particular, those of the ternary systems Al-Cu-Mg and Al-Mg-Si) than on the constituent binary alloys (Al-Cu, Al-Mg, Al-Si), due to the compensation of the individual effects inherent in the deviations of atomic radii of the different types of solute atoms relative to that of the aluminum matrix and the precipitation of different types of metastable phases.
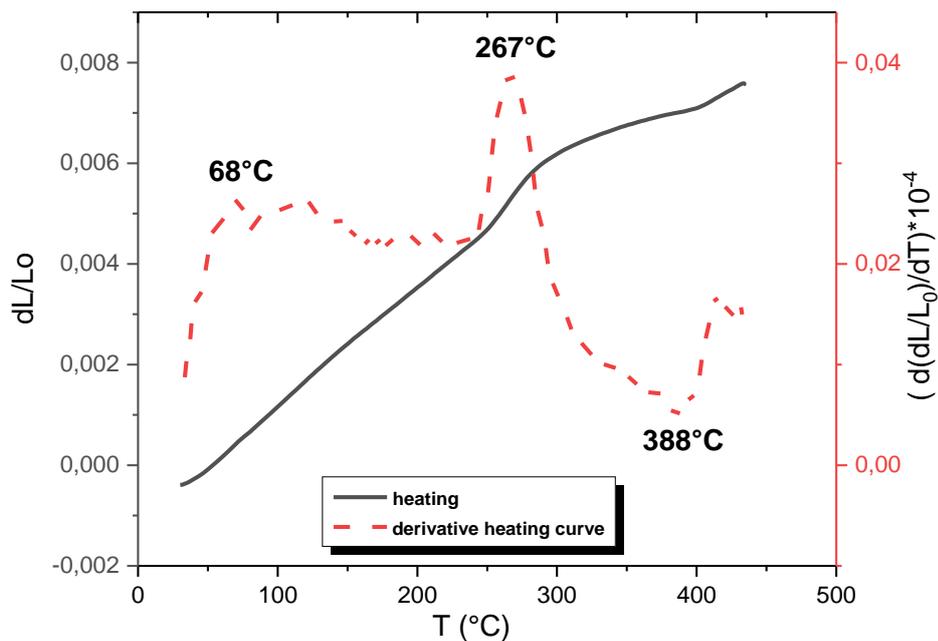
Fig. -15-: Derivative of the heating segment of an alloy Al-12 wt. % Mg homogenized 17 h at 430°C then water quenched

The electrical conductivity and, conversely, the electrical resistivity are governed by the state of progress of the decomposition of the solid solution. Solute concentration has an order of magnitude greater effect than precipitate volume fraction on these transport properties. The measurement of the surface electrical conductivity and that of the electrical resistivity at room temperature are commonly used in industry as a non-destructive and rapid means of checking the state of quenching and tempering in semi-finished products (unfinished parts) in aluminum alloys intended respectively for aeronautical and electrical applications. The electrical resistivity increases first rapidly then slowly during maturation under the effect of the formation of GP zones, probably by diffusion of electrons by the clusters of atoms formed. It then decreases progressively during tempering correlatively to the depletion of the matrix in solute, to reach its minimum value after extensive overtempering or annealing. Finally, the electrical resistivity depends on the surface of the precipitates and therefore on their form factor (ratio of the large dimension to the small dimension).

Practice exercise

Exercise 1:

The heat treatment sequence used industrially for the Al-12 wt. % Cu alloy is given in Figure 1.

1- What happens during the high temperature plateau?
2- Why do we quench the alloy after the first stage?
3- Is the quenched alloy then in equilibrium?

Figure 1