Chapter IV

Transformations kinetics in materials and alloys in the solid state

Chapter 4: Kinetics of transformations in materials and alloys in the solid state.

IV-1. Introduction

There are two types of phase transformation, depending on the mode of transfer of substance from the initial phase (mother phase):

The first, the most common in practice, is associated with uncoordinated movements of atoms. There is therefore destruction of the lattice of the mother phase and reconstruction of that of the new phase. Phase transformations of this type involve the mechanisms of transfer of substance in a solid medium, that is to say diffusion. When the phase change is accompanied by a change in chemical composition, there is movement of atoms over distances which are large compared to the interatomic distances.

The second corresponds to crystallographic changes, with no change in chemical composition. The corresponding transformations involve movements of atoms over short distances. These displacements are coordinated (so-called *shear structures*): each atom keeps its neighbours. Example: the martensitic transformation of steels, which makes it possible to obtain stainless steel blades which retain their sharpness for a long time, due to their hardness.

It is essential to precede the study of the different types of transformation in alloys in the solid state, with a study of the kinetics of these transformations.

IV-2. General characteristics of solid-state transformations

The general characteristics of the phase transformation kinetics can be summarized as follows:

a- The initiation of reactions is difficult, which results in significant retard in time or in the temperature scale, depending on whether the reaction is carried out at constant temperature or at variable temperature.

b- The initiation of the reactions is subject to the influence of the defects of the crystal lattice and, consequently, to all that modifies the number and the nature of these defects (hardening, etc.)

c- The subsequent evolution of the reactions is most often subordinated to the diffusion of the lattice species of the matrix so that the influence of the temperature on the reaction rate results in fact from its influence on the diffusion coefficients.
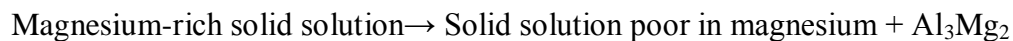
These characters belong to most of the transformations in the solid state which are accompanied by a variation of the number of phases that is to say to the transformations of the

first order. We will see, however, that it is difficult to establish a sharp distinction between transformations of the first order and those of the second order, the appearance or disappearance of a phase in a solid system being able in certain cases to take place from a progressively, both thermodynamically.
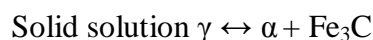
IV-3. Initiation of reactions proceeding by germination and growth

Among all the transformations that can occur in metals or alloys in the solid state, a very important category is represented by those through which a new phase arises within an initially homogeneous single-phase medium. From a purely chemical point of view, this situation can result from very different types of reactions and in particular:

❖ *Precipitation of an intermetallic compound in a supersaturated solid solution*, during a decrease of the temperature. A good example of such a reaction is provided by the precipitation of the compound Al_3Mg_2 by slow cooling of a solid solution Al-Mg, homogeneous at high temperature:

Magnesium-rich solid solution→ Solid solution poor in magnesium + Al_3Mg_2

❖ *Allotropic transformation* of a pure metal by sudden transition from the stability domain of one of the forms to the stability domain of the other form. We can cite as an example the cooling transformation of iron: Fe_γ (CFC) $\rightarrow Fe_\alpha$ (CC).

❖ *Eutectoid transformation* of a solid solution which this time gives birth, not to one but to two new phases. The example of the formation of the eutectoid: $\alpha+Fe_3C$, within the homogeneous solid solution of 0.8% carbon in γ iron below 727°C is well known:

$$\text{Solid solution } \gamma \leftrightarrow \alpha + Fe_3C$$

If we compare these different transformations from a morphological point of view, we see that they proceed in the same way at the beginning. In the alloy, initially heated to high temperature in the average where it exists as a single homogeneous phase, and then cooled to a temperature where this phase becomes unstable, appear after some time in the dispersed state of small crystalline individuals of the new phase. These individuals develop at the expense of the matrix until they completely invade it in the case of an allotropic transformation.

In the case of precipitation within a supersaturated solution, they cease to increase when the latter has reached its new state of equilibrium. It is customary to distinguish two successive stages in this process: germination and growth.

IV-4. Classical theory of germination

The theory that will be developed is based on the evolution of the stability and the possibilities of growth of a germ of the new phase according to the size of this germ.

Germination is the phenomenon by which a new phase begins to form within the parent phase. There are two types of germination: homogeneous germination and heterogeneous germination. Homogeneous germination can theoretically only exist in a perfect crystal; the places where the precipitates form are absolutely indeterminate and are randomly distributed in the matrix. On the contrary, heterogeneous germination occurs on crystal defects.

IV-4-1. Homogeneous germination

When a supersaturated solid solution (the mother phase) is allowed to evolve, concentration fluctuations occur which lead to the formation of clusters of solute at a temperature where the mother phase becomes unstable. The formation of a cluster of radius r (the new phase) produces a modification of the energy of the system. The germ of the new phase only becomes stable when it has reached a certain critical volume which can be evaluated as follows:

- The free enthalpy of initial germ formation < 0 for this germ to be stable.
- The variation of the free enthalpy of the system is the sum of three contributions:

    1-   If ΔGv is the variation of free energy per unit volume, at temperatures where the new phase is stable, the formation of a volume V of this phase leads to a decrease in free energy by a value $V.\Delta Gv$ (indicated by a sign (-) in the equation of ΔG). Note also that ΔGv is zero at the equilibrium temperature T_e.

    2-   The creation of an interface of total surface A, causes an increase in the free energy of the seed of a value $A.\gamma$ (γ is the specific energy of interface between the mother phase and the new supposedly isotropic phase).

    3-   When the volume of the germ of the new phase is different (which is generally the case) from the volume initially occupied by the parent phase, the free energy of the germ increases by a value proportional to V due to a stress energy per unit volume of the new phase ΔGc.

The total variation of free energy associated with the formation of a germ of volume V is therefore written in the form:

$$\Delta G = -V\Delta G_v + A\gamma + V\Delta G_c = -V(\Delta G_v - \Delta G_c) + A\gamma \qquad (IV\text{-}1)$$

Assuming that the interface energy does not depend on its orientation, and assuming that the germ has a spherical shape of radius r, the previous equation becomes:

$$\Delta G(r) = -\frac{4}{3}\pi r^3 * (\Delta G_v - \Delta G_c) + \gamma * (4\pi r^2) \qquad (IV\text{-}2)$$

The variation in the free energy of formation of a nucleus is therefore a function of its size r (figure IV-1).
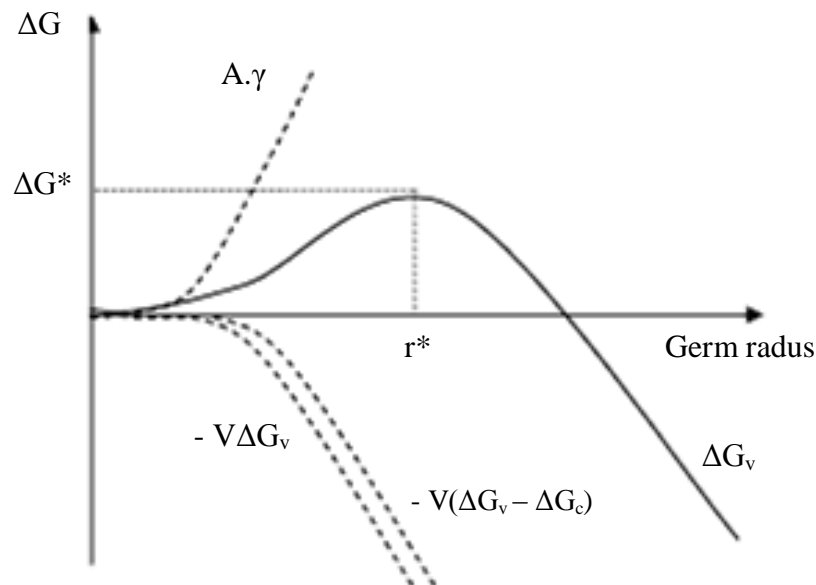

Fig. IV-1 : Evolution of the free energy of formation of a spherical germ as a function of its radius r.

We note that if the size of the germs is small, it is the interface energy which is predominant; the germs are therefore unstable and consequently they disintegrate spontaneously in the matrix. On the other hand, if the germ size is large enough, the driving force is predominant; germs of such size can evolve and become stable. There is therefore a critical germ size threshold beyond which germination can take place, allowing transformation to begin. By differentiation of the equation of ΔG, we obtain the critical size of a germ r*:

$$r^* = \frac{2\gamma}{(\Delta G_v - \Delta G_c)} \qquad \text{(IV-3)}$$

This gives the value of the activation free energy barrier for the formation of a critical germ:

$$\Delta G^* = \frac{16\pi\gamma^3}{3\,(\Delta G_v - \Delta G_c)} \qquad \text{(IV-4)}$$

➤ **Homogeneous germination rate**

Statistically, the number of germs that have a size greater than the critical size is given by:

$$N^* = N_0 \, exp\left(-\frac{\Delta G^*}{KT}\right) \qquad \text{(IV-5)}$$

N_0, being the number of atoms in the matrix per unit volume.

The more atoms there are whose energy is sufficient to cross the energy barrier, the greater is the probability of a germ formed; which means that the germination rate is proportional to $exp\left(-\frac{\Delta G^*}{KT}\right)$ as well as to the rate of diffusion of the atoms to the germs $exp\left(-\frac{\Delta G_D}{KT}\right)$.

In general, the following expression can be written for the germination rate:

$$V_{homo} = W N_0 \, exp\left(-\frac{\Delta G_D}{KT}\right) exp\left(-\frac{\Delta G^*}{KT}\right) \qquad \text{(IV-5)}$$

Where W is a factor that encompasses the vibrational frequency of atoms.

IV-4-2. Heterogeneous germination

Germination in a solid as in a liquid is often heterogeneous; favorable germination sites are structural defects such as dislocations, grain boundaries, inclusions, free surfaces, supersaturation vacancy, etc. All these sites are in a non-equilibrium state, the atoms in the immediate neighborhood are therefore in a higher energy state, thus increasing the free energy of the system. Imagine that the formation of a germ of the new phase leads to the elimination of a defect. Then, the free energy of the whole system decreases by an amount equal to that of the defect ΔG_d. Therefore, the defect energy plays the same role as that of the energy per unit volume, that is to say, a driving role. Therefore, the expression of the variation of free energy associated with the formation of a germ of volume V is written:

$$\Delta G_{\text{hété}} = -V\,(\Delta G_v - \Delta G_c) + A\gamma - \Delta G_d \qquad \text{(IV-6)}$$

An example of this type of germination is ***germination on grain boundaries***:

If we note θ the wetting angle of the particle on the grain boundary (Figure IV-2 (a)), and r its radius of curvature (assuming a geometry of double spherical calotte), if $\gamma_{\alpha\alpha}$ is the joint energy and $\gamma_{\alpha\beta}$ that of the interface between the two phases α (the mother phase) and β (the new phase), then the free enthalpy of creation of the germ in heterogeneous germination is deduced from that obtained in germination homogeneous.

$\gamma_{\alpha\beta}$: Interface energy α/β
$\gamma_{\alpha\alpha}$: Grain boundary energy
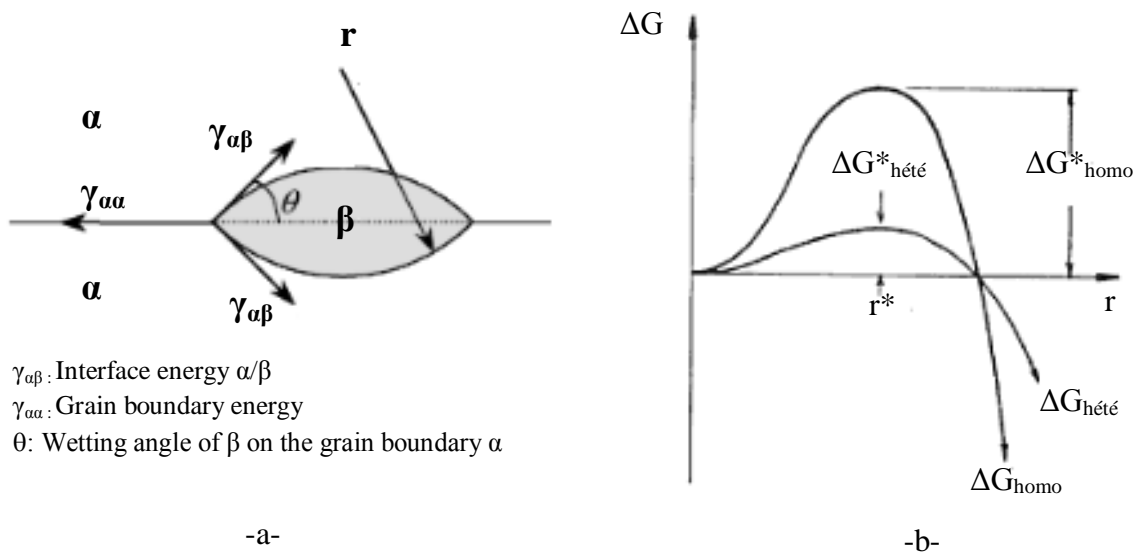θ: Wetting angle of β on the grain boundary α

-a-

-b-

Fig. IV-2: Heterogeneous germination; (a) schema and (b) decrease in the energy barrier to germination, although the critical radius remains unchanged.

➢ **Heterogeneous germination rate**

Germination will take place quickly on heterogeneities. However, their influence on the rate of germination with which the alloy transforms depends on their concentration. For homogeneous germination each atom is a germination site. On the other hand, in the case of germination on the grain boundaries, only the atoms in the grain boundaries can participate in this process. If the concentration of germs on heterogeneous germination sites per unit volume is C_1, the heterogeneous germination rate is given by the following relationship:

$$V_{hetro} = W C_1 \exp\left(-\frac{\Delta G_D}{KT}\right) \exp\left(\frac{\Delta G^*}{KT}\right) \qquad \text{(IV-7)}$$

IV-5. Description of the global behavior of phase transformations by Avrami's theory:

Solid-state phase transformation kinetics that proceeds by a nucleation mechanism generally obeys a transformation law proposed by Avrami. Avrami's treatment gives an equation which makes it possible to calculate the degree of advancement of the phase transformation as a function of time.

The appearance and development of a new β phase within an initial α phase can be imagined as follows:

- Initially, and at time t_0, a gem appears within the mother phase α. This germ constitutes an element of the β phase. It is called the time necessary for the formation of these germs.
- In a second stage, the germs grow at the expense of α phase and contribute to the advancement of the transformation (Fig. IV-3): at t_f the transformation stops where the initial phase is completely transformed into the new phase β. The growth of the new phase does not necessarily proceed at the same rate in all directions of space.

The growth of the new phase takes place freely during the first times of the transformation. This behavior changes at a certain conversion rate, when the growing phases come into contact with each other. By taking this characteristic into account and based on the laws of germination and growth, we obtain a general equation which gives the conversion rate (volume fraction f) as a function of the transformation time:

$$f = 1 - \exp{(-Kt)^n} \qquad\qquad (IV-8)$$

This is Avrami's equation, n varies from 1 to 4 depending on the type of transformation, and K is a function of the germination and growth processes which are strongly dependent on temperature. Knowing K as a function of the temperature, the time required to reach a determined conversion rate (1, 50, 90%, etc.) at a given temperature is calculated.
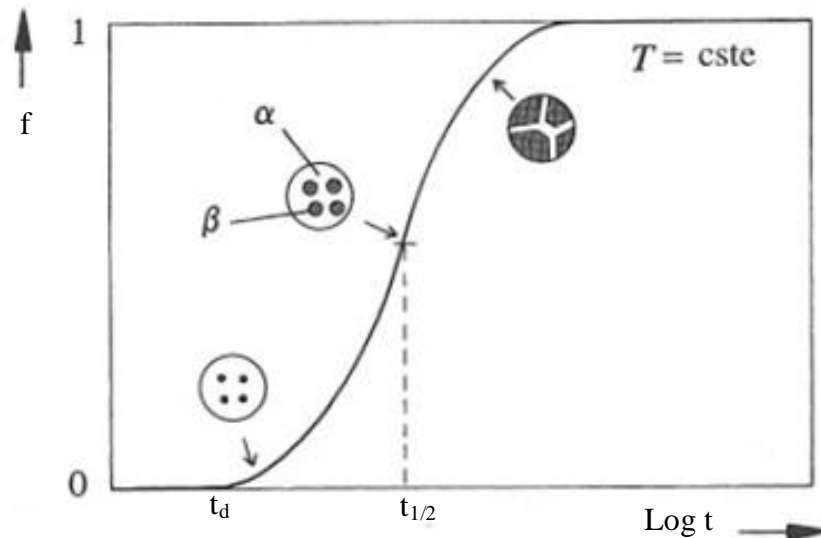
Fig. IV-3- : Isothermal variation of the volume fraction f of the transformed phase as a function of the logarithm of time t according to the Avrami equation. f is the fraction of β transformed at t and (1-f) is the fraction of the untransformed α phase.

IV-6. Diagrams TTT (Transformation/Time/Temperature)

From Avrami's expression, we can plot the fraction transformation (f) curves as a function of time and temperature (TTT diagrams). In general, two values of the conversion rate are chosen, which can still be determined experimentally and characterize the start (1% conversion) and the end of the reaction (99% conversion rate). This curve is illustrated in Figure IV-4-(a). This figure shows how we determine, at the temperature $T=T_1$ included in the transformation interval, the value of t_d and t_f. Curve IV-4- (b) establishes the relationship between the TTT diagram and the isotherm at temperature $T=T_1$. These TTT diagrams make it possible to establish the type of heat treatment that should be applied to a material to obtain a given structural state. Although such diagrams can in principle be obtained for any phase transformation, they are difficult to determine experimentally for the crystallization of metals and metal alloys because of the rapidity of transformation.

TTT diagram reading is very simple. For example, let's select a temperature $T_1 < T_e$ and analyze the progress of the transformation. After rapid cooling (quenching) of the material from $T > T_e$ down to the temperature T_1 (solid line in figure IV-4 (a)), the material is maintained at a constant temperature (T_1). The transformation starts practically at time $t=t_d$. The transformation proceeds gradually at a faster and faster rate because the transformation rate is proportional to the transformed volume and, as shown in Figure IV-4 (b). Then, it gradually slows down as the growing grains rub against each other.

Practically it stops when the transformed volume is equal to 99% ($t=t_f$). The dashed curve in diagram IV-4- (a) therefore represents, the end of isothermal transformation as a function of the transformation temperature.

A typical example of solid-solid transformation represented by the TTT diagrams is the eutectoid transformation of steels containing 0.8% mass. C. From austenite, ferrite and iron carbides (cementite) are formed (Fig. IV-5-).
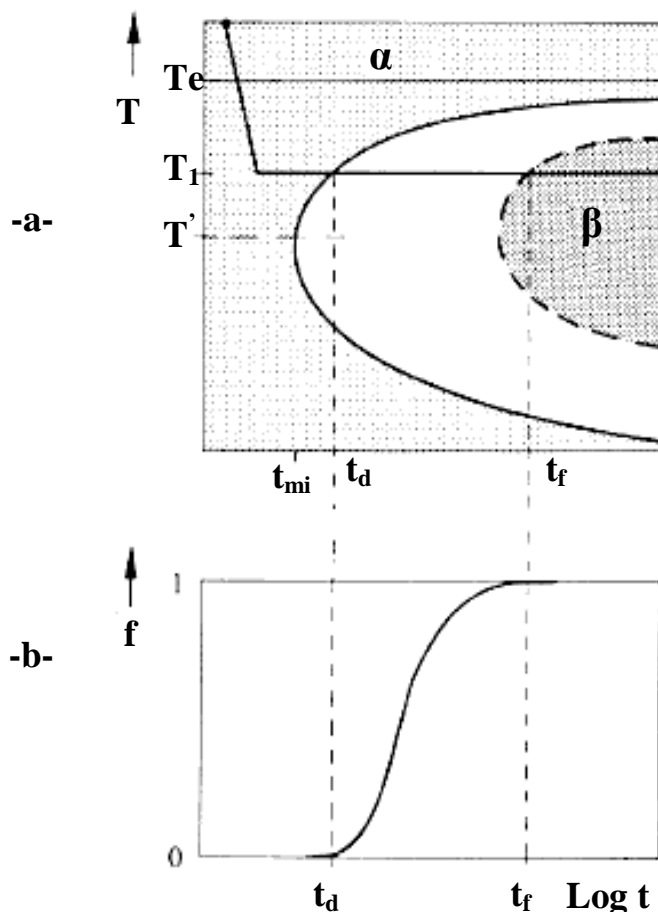
Fig. IV-4: Schematic appearance of the TTT diagram of a phase transformation.

(a) Phase transformation curves as a function of time and temperature for two values of the conversion rate characterizing the start (1% conversion) (t_d) and the end of the reaction (99% conversion rate) (t_f): t_{min} corresponds to the minimum time for the transformation to actually start.

(b) Relationship between the TTT diagram and the transformation isotherm at temperature $T=T_1$.
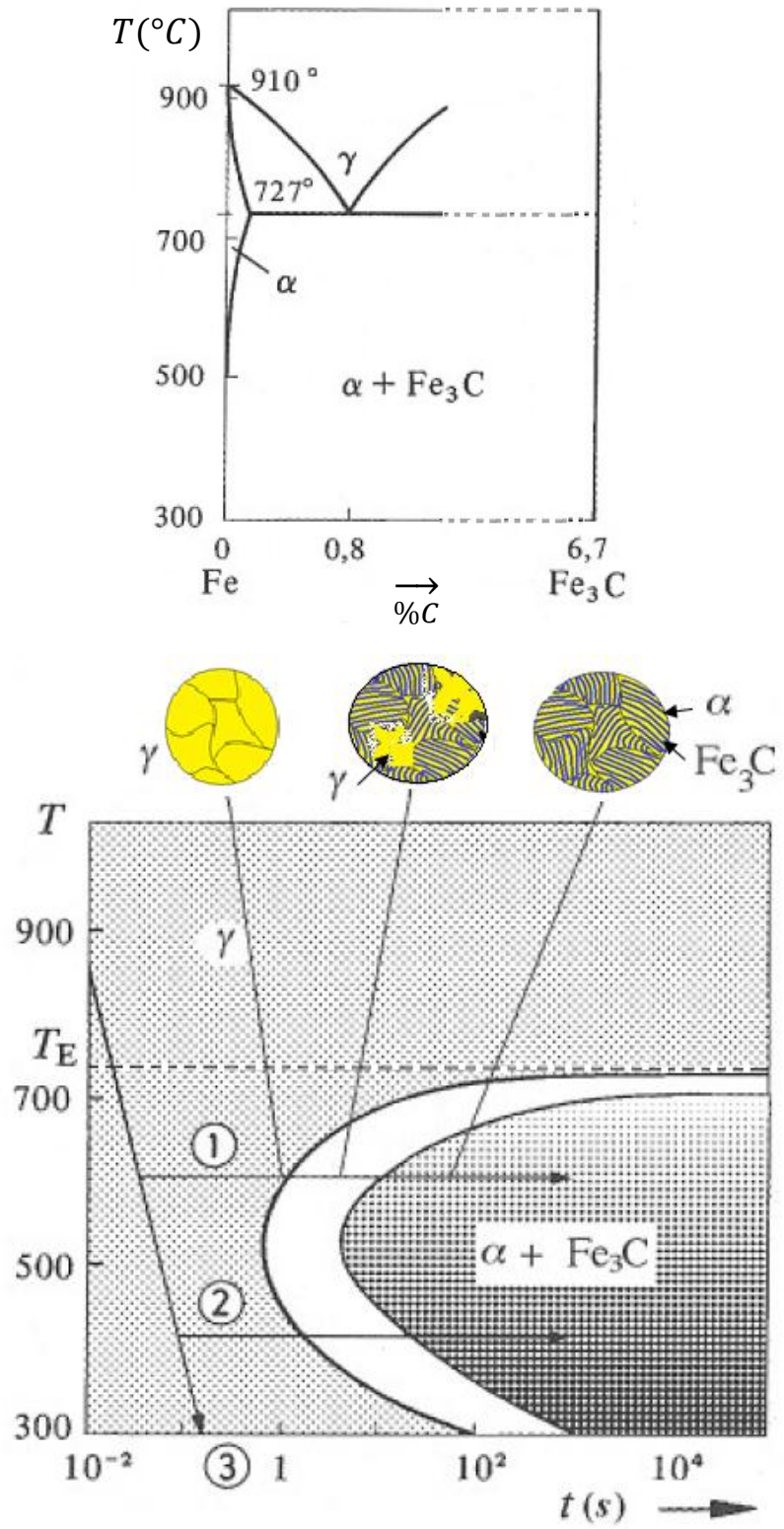
Fig. IV-5- : Part of Fe-Fe3C system phase diagram (a), TTT diagram of the eutectoid transformation in this system (b).

IV-7. Spinodal decomposition theory

The previous theory attributed to the existence of a positive energy of creation of the interfaces the origin of the barrier responsible for the lateness in germination. A different analysis of the phenomenon has been known for a number of years and we will briefly describe it.

IV-7-1. Spinodal decomposition definition

Spinodal decomposition is a phase transformation phenomenon that occurs when a continuous solid solution cools below a critical temperature.

Figure IV-6(a) shows a phase equilibrium diagram of A-B binary system. Above the critical temperature and below the melting temperature, this system is in the form of a continuous solid solution α.

Below T_c, an isothermal reading of the diagram at temperature T', indicates that it is divided into three zones according to the value of x (composition in element B).

- ✓ a single-phase zone consisting of an A-rich phase α1 for $0 < x < x_1$,
- ✓ a two-phase zone comprising two phases for $x_1 < x < x_4$,
- ✓ a single-phase zone consisting of a B-rich α_2 phase for $x_4 < x < 1$.

The phenomenon of isomorphic demixing of the continuous solid solution for $x1 < x < x_4$ is explained with the help of figure IV-6 (b). The latter shows the variation of the molar free enthalpy of the system in the form of a continuous solid solution as a function of the composition, at the temperature T'.

For the two solid solutions to be in equilibrium with each other, the chemical potential of compound A must be the same in the solid solution α_1 and in the solid solution α_2. It is the same for the chemical potential of constituent B. The rule of the common tangent to the curve of free molar enthalpy of phase makes it possible to locate the compositions of the solid solution α1 saturated by B (x_1) and of the solid solution α_2 saturated by A (x_4) in equilibrium with each other.

The range of the points x_1 and x_4, obtained at different temperatures, define in the equilibrium diagram a curve serving as a boundary between the single-phase domains and the two-phase domain. The domain where the two solid solutions α_1 and α_2 coexist is also called the *miscibility gap*.

In addition to its three domains, the molar free enthalpy curve of the continuous solid solution also has two points of inflection x_2 and x_3 which become remarkable if one is interested in the mechanism of transformation of the single-phase system into a two-phase system.

In the domain between the two inflection points x_2 and x_3 for which $\partial^2 G/\partial X^2 < 0$ the single-phase solid solution is unstable and decomposes spinodally. In the composition ranges x_2-x_1 and x_4-x_3 the single-phase solid solution is metastable and, subject to sufficient activation energy, will decompose into solid solutions by a mechanism of germination and growth.
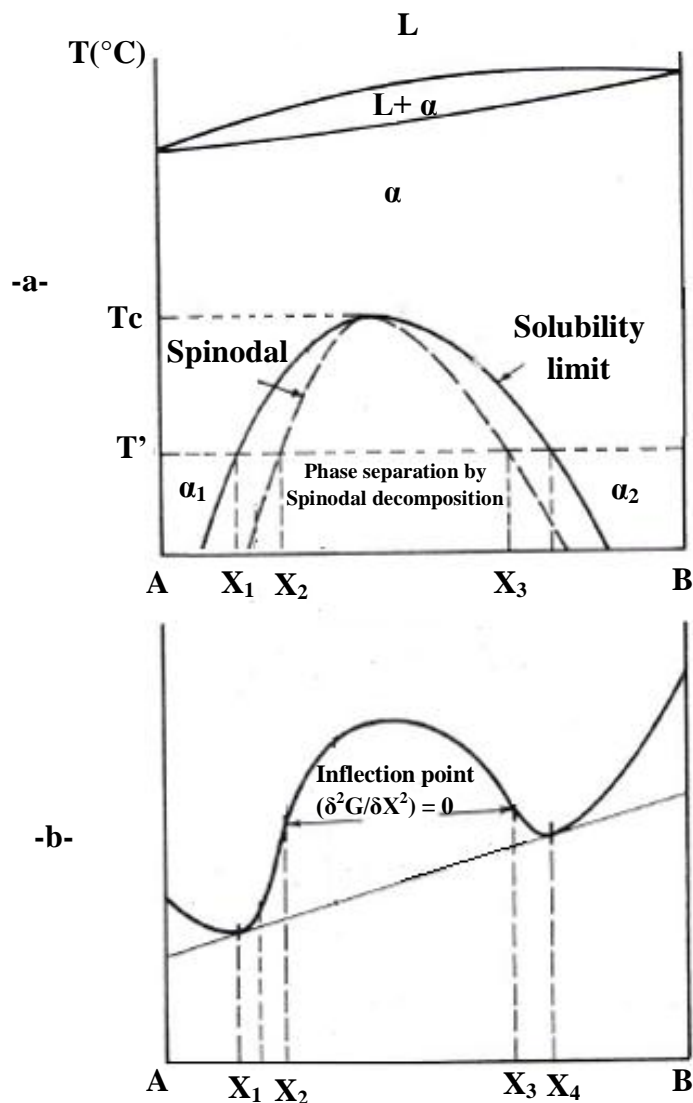
Figure IV-6: (a) Phase diagram of a binary system with a miscibility gap
(b) Variation of the free enthalpy of a solid solution at temperature T'.

IV-7-2. Mode of decomposition

To explain the mode of decomposition, we rely on the molar free enthalpy curve of the single-phase binary system, at a temperature T, for an average concentration Xi of element B, located in the domain of spinodal decomposition (Fig. IV- 7).
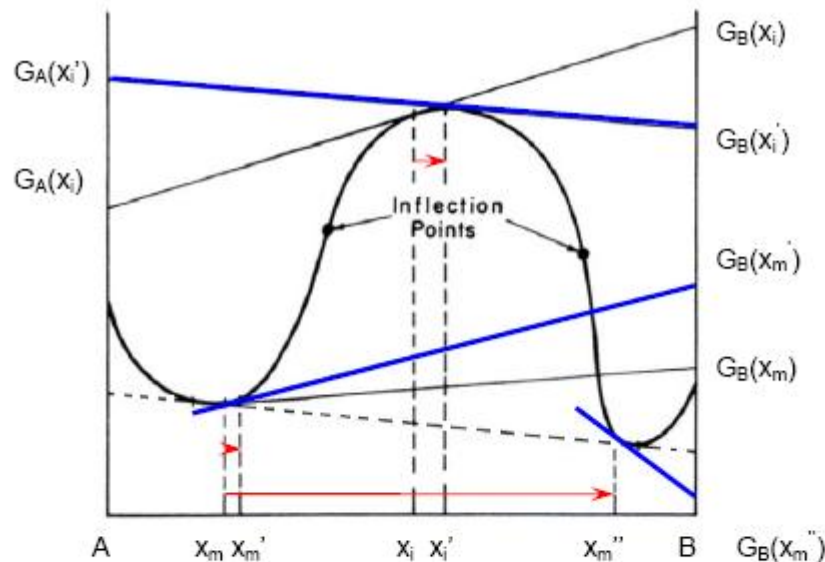

Figure IV-7: Variation of chemical potential as a function of composition in the miscibility range.

We consider, at a point of the solid solution, the appearance of a small fluctuation in composition passing from Xi to Xi', locally generating a composition gradient. To the element B concentration gradient is linked a chemical potential gradient which induces a flow of matter B directed in the direction of decreasing chemical potentials.

In figure IV-7, the material with the composition Xi presents the chemical potentials GA(Xi) and GB(Xi) for the constituents A and B respectively, the material with the average composition Xi' presents the chemical potentials GA(Xi') and GB(Xi').

If we place ourselves in the domain of Spinodal decomposition, we note that a fluctuation in concentration from Xi to Xi' (increase in the concentration of B) results in a reduction in the chemical potential of constituent B (and an increase in the chemical potential of component A). According to Gibbs' law, the B constituents adjacent to the zone where the composition fluctuation has occurred will diffuse towards the latter zone in the unusual direction of increasing concentrations while the A constituents will move away from it. It then appears in the material zones increasingly enriched in B and other zones increasingly poor in

B (fig. IV-8 (a)-stage II). The phenomenon self-propagates to lead to Spinodal decomposition (fig. IV-8 (a)-stage III).

In the metastable range, at temperature T, the decomposition mechanism is different from that of a Spinodal decomposition. We see that a small fluctuation in composition (transition from X_m to X_m+dX_m) (fig. IV-7 and IV-8(b)-stage I), induces a variation in chemical potential from $G_B(X_m)$ to $G_B(X_m')$, with $G_B(X_m') > G_B(X_m)$. The flows of matter then being directed classically in the direction of decreasing concentrations (fig. IV-7 and fig. IV-8(b)-stage II), in the end, this fluctuation in composition disappears (fig. IV-7 and IV -8(b)-stage III).

Still in the metastable domain, in the case of a large fluctuation in composition, such as for example the passage from X_m to X_m'', $G_B(X_m'')$, the chemical potential of B for the composition X_m'' is lower than $G_B(X_m)$, the composition fluctuation will therefore increase and cause the germination and growth of the two solid solutions of respective compositions X_1 and X_4 (fig. IV-7 and IV-8 (c)).
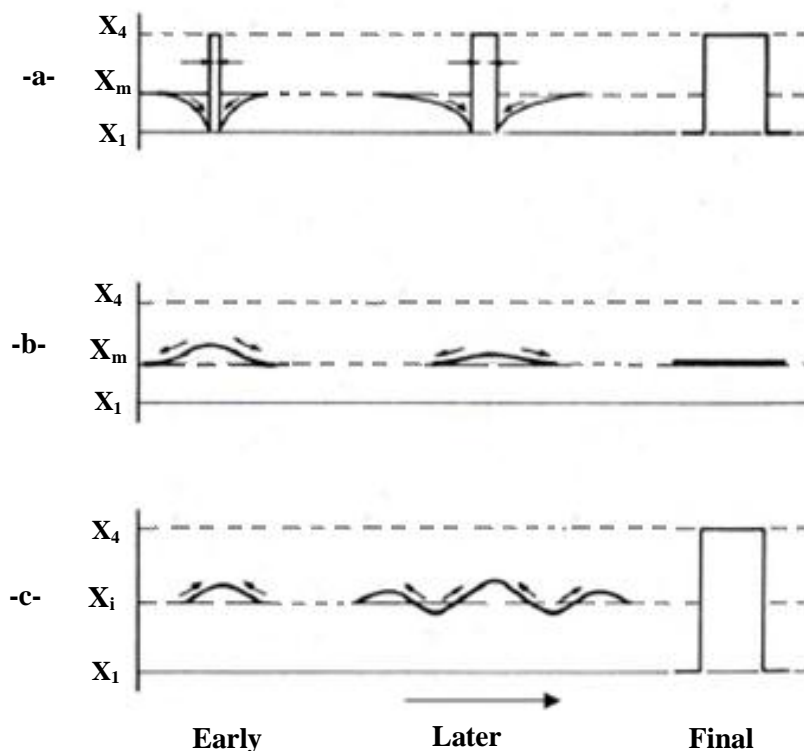

Figure IV-8: (a) Progression of a small fluctuation in the Spinodal decomposition gap,
(b) Disappearance of a small fluctuation from the metastable phase,
(c) Germination and growth of a large fluctuation from the metastable phase.

IV-8. Insufficiency of previous theories

In the exposition of the preceding theories, we have been led to neglect several factors whose importance should not be underestimated. This observation singularly limits the validity of the quantitative conclusions that a student, unfamiliar with the difficulties of the kinetics of reactions in the solid state, could be tempted to draw from what preceded. This is why it is particularly instructive to detect these simplifications, and to research how they can influence the mechanism of the transformations in each particular case.

It should be noted first of all that the two approaches are only apparently contradictory. If the first indeed attributes a decisive importance to the interfacial energy while the second neglects it in the simplified form in which we have presented it, it is possible to also introduce this energy into the spinodal theory by operating a translation of the spinodal curve below the previous one. The difference between these two curves, which can vary according to the temperature, represents the elastic deformation energy due to the differences in parameters between enriched and impoverished regions.

It should then be noted that the classical theory, if it introduces from the outset the concept of interfacial energy, neglects the fact that this energy can vary considerably, for the same pair of associated phases, according to various factors among which we will cite The following :

- Morphology of the dispersed phase within the original matrix,
- Orientation relationship between the two adjoining crystal lattices,
- Constraints resulting from variations in volume resulting from processing.

Practice exercise

Exercise 1:

We consider the germination of a new phase β in the form of a sphere of radius r, in an infinite matrix of another phase α. If the germination is done on the grain boundaries as shown in Figure 1.

- What is the type of germination in this case?
- Give the relation which makes it possible to calculate the free enthalpy of germination in this case, if it is considered that the interfacial energy (γ) of α phase is isotropic and equal to that of the β phase.
- Calculate the critical radius value r*.
- Calculate the wettability angle of the β phase particle on the grain boundary (θ) if $\gamma_{\alpha/\beta}=$ 500 and $\gamma_{\alpha/\alpha}=$ 600 mJ/m^2
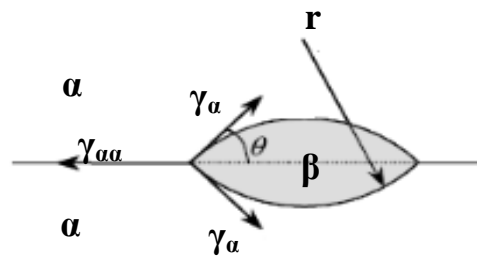- Evaluate the factor f(θ) for this germ.

Figure 1

Exercise 2:

The isothermal transformation diagram in Fig. 2 relates to a eutectoid steel (A: austenite, B: bainite, P: pearlite, M: martensite).

- Determine the final microstructure of a small sample having undergone the time-temperature treatments described below. In each case, the initial temperature of the sample was 845°C and was maintained long enough for the sample to acquire a complete and homogeneous austenitic structure.

(a) Rapid cooling to 350°C, hold at this temperature for 104 seconds, then rapid cooling to room temperature.

(b) Rapid cooling to 250°C, hold at this temperature for 100 seconds, then rapid cooling to room temperature.

(c) Rapid cooling to 650°C, hold at this temperature for 20 seconds, rapid cooling to 400°C, hold at this temperature for 10^3 seconds, then rapid cooling to room temperature.
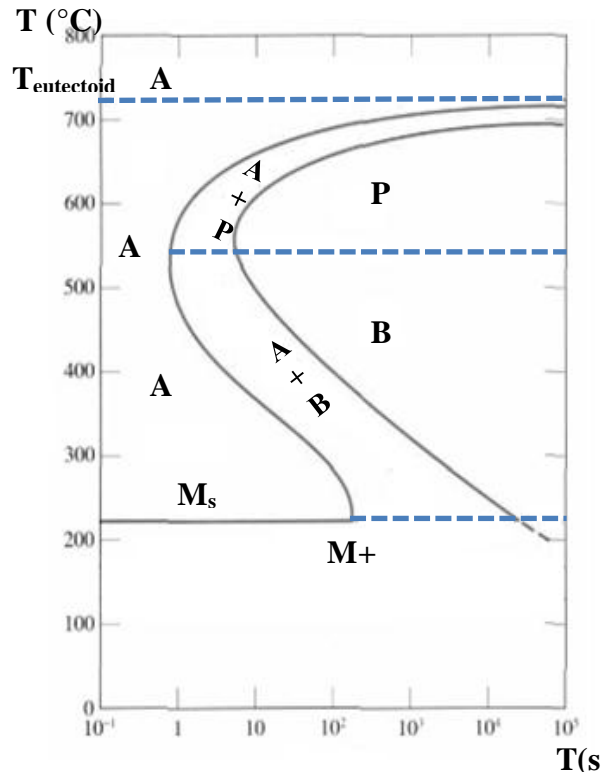

Figure 3

Exercise 3:

Solid-state phase transformation kinetics that proceeds by a nucleation mechanism generally obeys a transformation law proposed by Avrami. Avrami's treatment gives an equation that allows calculating the degree of advancement of the phase transformation as a function of time.

1-If f_1 and f_2 are the fractions recrystallized at a given temperature at time t_1 and t_2, respectively,

- Derive a relation for n in the Avrami equation.

2- For copper, the fraction recrystallized at 135°C is indicated in the following table:

Recrystallized fraction	t (s)
0.10	300
0.50	540

- Determine n and K in the Avrami equation