

---

*Chapter*

**VI**

**Mechanisms of crystal growth  
during diffusionless  
transformations**

## VI-1. Introduction

The phase transformation in solid states can be divided into two groups:

- *Diffusional Transformations*

These are transformations that allow a new phase to form by breaking the atomic bonds of the initial phase and the redistribution of atoms inside the solid after they move randomly over long distances. In this type of transformation, diffusion plays an important role.

- *Diffusionless Transformations*

They are also called, athermal transformations, do not require a diffusion of atoms over a long distance but displacements of a large number of the latter, at low amplitude. In these transformations there is no change in chemical composition and they generally propagate independently of time. It is noted that, the displacive transformations can during a very rapid cooling.

In steels, phase transformations on cooling from the austenitic phase are of two types: diffusional transformations generally leading to the formation of ferrite and carbides and displacive or martensitic transformations. The physical mechanism involved in the formation of these new phases depends on the temperature at which the transformation is initiated and this is a function of the cooling rate. Figure VI-1 shows the mechanisms of displacive and diffusional transformation.

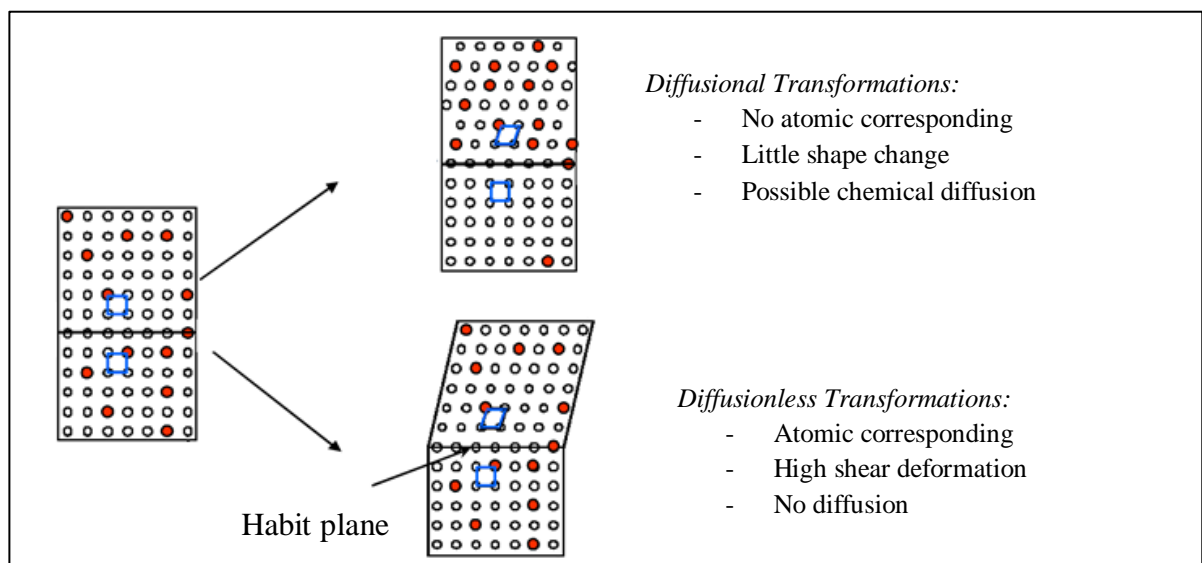


Fig. VI-1- : Illustration of the mechanisms of displacive and diffusional transformation.

## **VI-2. Normal transformation**

The solid-state transformation kinetics are said to be normal, if the time and temperature dependencies of the transformation rate  $V_{tr} = f(T, t)$  are identical to those established during the study of the crystallization process.

During the decrease in temperature (for reactions that occur by cooling) the rate of transformation first increases and then decreases:

- The increase in the transformation rate is linked to the ease of formation of the germs and the acceleration of their growth when the supercooling increases.
- The decrease in the transformation rate during a subsequent increase in supercooling is explained by a drop in the mobility of the atoms when the temperature decreases.

## **VI-3. Martensitic transformation**

The term martensite, from the name of its inventor the physicist A. Martens, designates the product resulting from the quenching of carbon steel from high temperature called "austenite". Subsequently the term extended to products obtained by similar mechanisms, even if these products have structures very different from those of steels (certain metal alloys). The structure of the martensite phase results from a transformation of the crystallographic lattice occurring in the absence of atomic diffusion. This transformation is called martensitic transformation.

The martensitic transformation is a first-order transformation that takes place without diffusion by a process of shearing of whole groups of atoms, which is manifested externally by the appearance on the surface of a metal cut of an acicular microrelief. Therefore, the martensitic transformation is part of the transformations of displacive phases in the solid state. In these transformations the atoms keep their respective places such that each atom always has the same neighbors, it does not move over a distance greater than an inter-atomic distance. The progression of the transformation is done by the displacement of the interfaces between the phases concerned, with a rate limited by that of the sound in this material. In martensitic transformations, the distortion (deformation) of the lattice is predominant compared to the atomic rearrangement.

Martensitic transformation produces transformation strain. In fact, directly above each wafer, the surface of the metal shows tilting and any straight line drawn on the surface of the

austenite shows a bending when passing through the martensite crystallites after transformation (figure VI-2-(a) and VI-2-(b)). The transformation strain measured is a plane-invariant strain with a large shear coefficient and a small expansion directed normal to the invariant plane. The rate of transformation is described by:

$$Y = 1 - \exp[-\alpha M_s - T] \quad (\text{VI-1-})$$

$\alpha$ : coefficient and  $T < T_{Ms}$

The  $M_f$  point designates the temperature below which martensite no longer forms.  $M_f$  cannot be strictly determined and it is often considered that  $M_f = M_s - 215^\circ\text{C}$ .

Martensite is saturated with carbon compared to an equilibrium ferrite: It is a solid solution of carbon insertion in a centered quadratic lattice Q.C of the ferrite where  $C/a = 1+0.045\%$  C by mass (Figure VI-3-).

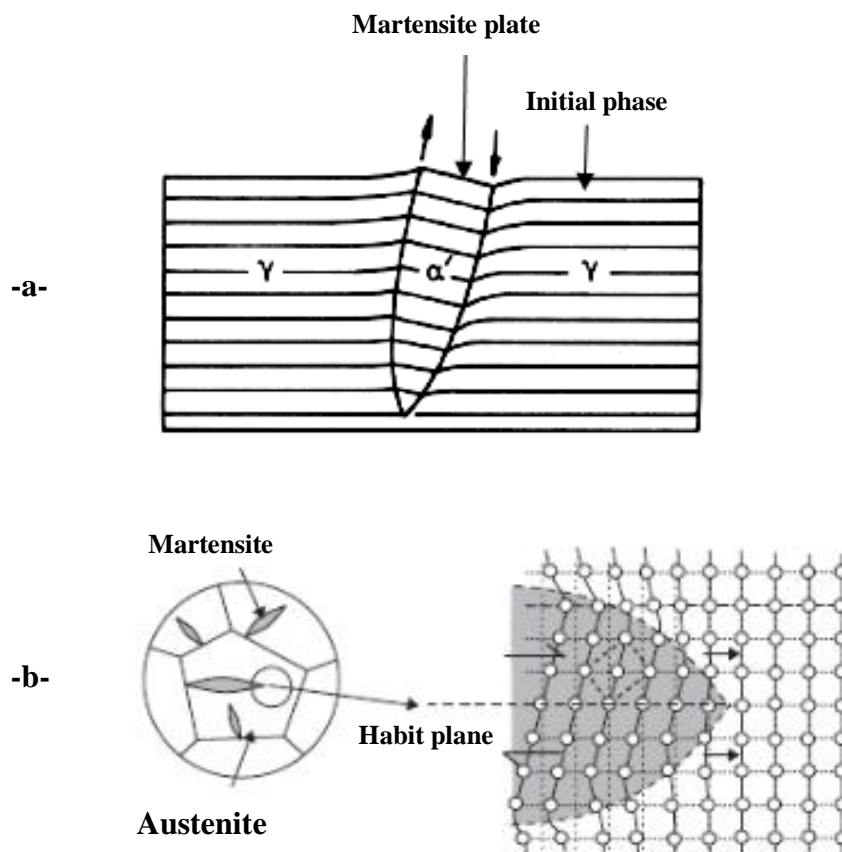


Fig. VI-2-: (a) Formation of Martensite  $\alpha'$  in initial phase  $\gamma$

(b) Simplified schematic representation of the martensitic transformation mechanism of iron.

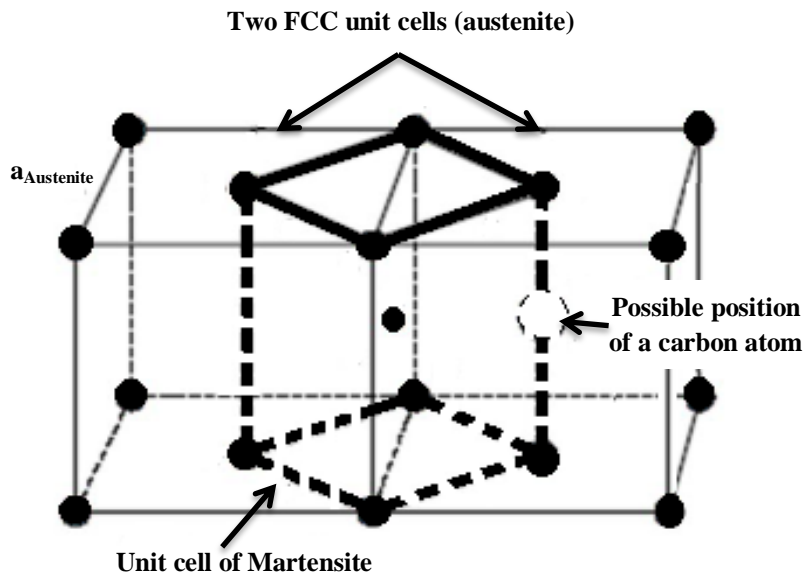


Fig. VI-3-: Schematic representation unit cell of martensite

#### ❖ Habitat plane (adjoining plan)

The interface between the initial phase and the martensite, on the macroscopic side, is an invariant plane also called the *habitat plane* or the adjoining plane. An invariant plane is characterized by two conservation properties: its orientation is not changed by the transformation, and the relative atomic positions in this plane are not modified by the transformation (conservation of distances and angles).

#### VI-3-1. General characteristics of martensitic transformation

The martensitic transformation has the following main characteristics:

1. It is a solid-state phase change due to homogeneous crystal lattice deformation; this deformation is not due to a diffusion movement of atoms but to a collective and cooperative movement of atoms over relatively small distances compared to the lattice parameters.
2. The transformation is almost instantaneous, with rate comparable to that of sound in a solid.
3. Martensitic transformation causes a change in the shape (shear) and volume of the specimen. For shape memory alloys, the variation in volume is low and the shear is high.

4. In order to minimize the energy between the martensite formed and the austenite still present, the domains of martensite formed have the shape of flattened platelets. The germination of martensite always takes place on a particular crystallographic plane and the equivalent planes, which are called limit plane or adjunction plane or even habitat plane. This plane is that of martensite shear. The domains formed have the shape of flattened platelets.

Figure VI-4- shows the different forms of martensite in steels as an illustrative example.

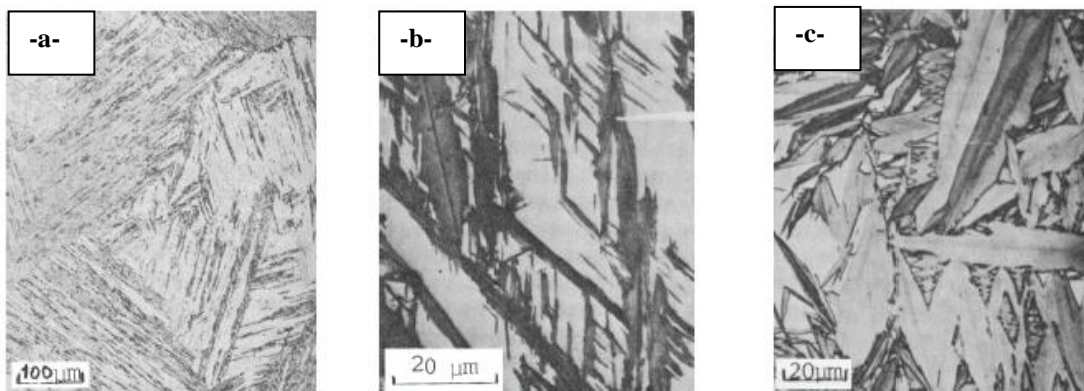


Fig. VI-4 : Different martensite morphologies in iron alloys: (a) low C (lath), (b) medium C (plate), (c) Fe–Ni (plate). (D. A. Porter, K. E. Eastoring. *Phase transformation in metals and alloys*, second edition, Chapman et Hall, London, (1992))

### VI-3-2. Thermodynamic aspect of martensitic transformation

Before going into the details of the martensitic transformation, on the thermodynamic side, we will define the most important common characteristics, i.e. the transformation temperatures and the spread of the transformation.

The passage from the initial phase to the martensitic phase and vice versa depends on the temperature. Four critical temperatures characterizing the transformation process are thus defined:

$M_s$ : Start temperature of the direct transformation (austenite  $\rightarrow$  martensite)

$M_f$ : End temperature of the direct transformation

The direct martensitic transformation on cooling (austenite  $\rightarrow$  martensite) begins at the temperature  $M_s$  (martensite start), it becomes complete at the temperature  $M_f$  (martensite finish). As the transformation is without diffusion, that is to say the initial phase and the

martensitic phase, being different only by their crystallographic structure, we therefore consider a system consisting of two solid phases of different crystallographic structures but of identical chemical composition.

The study of the free enthalpies variation of these two phases, in the absence of deformation energies and that of the surface, schematized by figure VI-5-, can be stated by the following relation:

$$\Delta G_{A \rightarrow M} = G_A - G_M \quad (\text{VI-2-})$$

$G_M$ : martensite free energy

$G_A$ : the free energy of austenite

In figure VI-4- which presents the Gibbs energy as a function of temperature, it can be seen that the martensitic transformation occurs when the free energy of martensite ( $G_M$ ) is lower than the free energy of austenite ( $G_A$ ), i.e. for temperatures below the critical temperature  $T_0$ . At  $T_0$  the difference in the chemical free energy  $\Delta G_{A \rightarrow M}$  of the two phases becomes zero and a thermodynamic equilibrium is established such that:

$$\Delta G_{A \rightarrow M} = G_A - G_M = 0 \quad \text{at } T = T_0 \quad (\text{VI-3-})$$

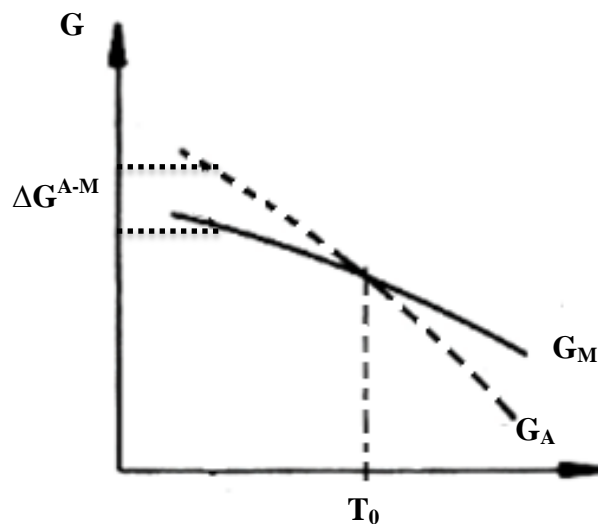


Fig. VI -4- : Gibbs energy of austenite and martensite as a function of temperature

However, in reality the two phases are not independent of each other; the martensitic transformation takes place by a mechanism of germination and growth. This indicates that there is interface energy between the two phases; the energy necessary for the displacement of this interface is added to the energy balance which constitutes an energy barrier leading to the spreading of the transformation.

#### VI-4. Massive transformation

The martensitic mechanism assumes the absence of any atomic redistribution, i.e. a non-diffusional nature of the transformation in solid solutions. However, normal transformation in complex component alloys can also occur without redistribution of components between phases. This type of transformation is said *to be massive*.

The immediate result of such transformation is the single-phase state. Indeed, in the classic cases, during a normal kinetics the grains have an aspect of massive blocks without form and without any simple line of joint; it is what gave place to the name of massive transformations.

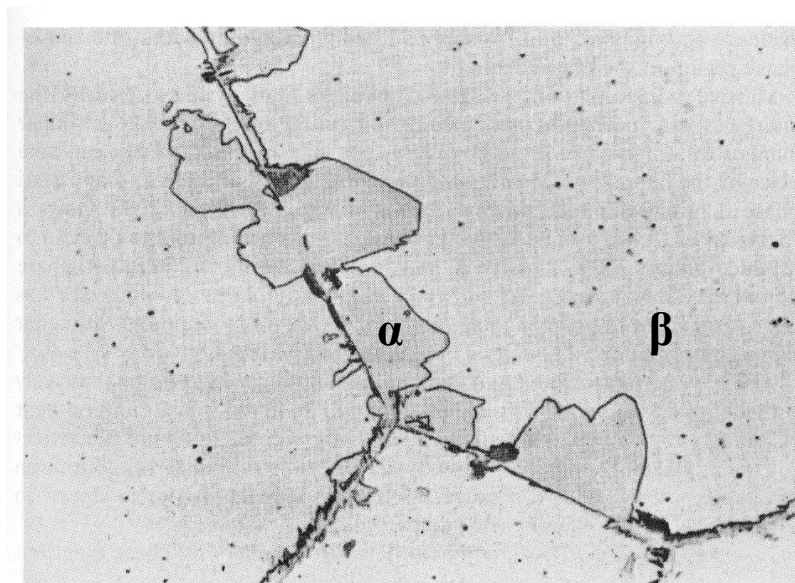


Fig. VI- 5- : Formation par transformation massive de la phase  $\alpha$  au joints de grain de la phase  $\beta$  dans l'alliage Cu-38,7% mass Zn trempé depuis 850°C (D. Hull, K. Garwood, *the mechanism of phase transformations in metals*, institue of metals. London (1956)



The following table shows the differences between the two types of transformations; diffusional and diffusionless:

<b>Displacive transformation (or martensitic)</b>	<b>Diffusive transformation</b>
<ul style="list-style-type: none"> <li>- Atoms migrate over the interatomic distances.</li> <li>- Atoms migrate by bond breaking and local rearrangement.</li> <li>- Atoms move cooperatively.</li> <li>- The rate of transformation is that of the vibrations of the crystal (independent of the temperature).</li> <li>- The transformed volume depends only on the temperature.</li> <li>- The composition does not change (the atoms do not have time to diffuse and remain where they are).</li> <li>- Martensite and initial phase always have crystallographic relationships.</li> </ul>	<ul style="list-style-type: none"> <li>- The atoms migrate over distances of 1 to <math>10^6</math> interatomic distances.</li> <li>- The atoms go from site to site by activated thermal diffusion.</li> <li>- Atoms move randomly</li> <li>- The rate of transformation strongly depends on the temperature and it cannot occur below 0.3 to 0.4<math>T_f</math>.</li> <li>- The transformed volume depends on time and temperature.</li> <li>- Diffusion allows composition changes in alloys.</li> <li>- There are sometimes crystallographic relationships between the phases.</li> </ul>

**Practice exercise**

**Exercise 1:**

Calculate the volume percentage change with martensite formation for a 1% C steel.

**Exercise 2:**

Determine the approximate length change when a 1% C steel transforms to martensite.

**Exercise 3:**

- Schematize the microstructure of Fe-0.5% C steel obtained following water quenching from 950°C.
- According to the TTT diagram below of this alloy, give the proportion of each phase

Diagramme TTT d'un alliage Fe-0.5%C

