Chapter

VI

Mechanisms of crystal growth during diffusionless transformations

VI-1. Introduction

Phase transformations in the solid state can be categorized into two main types:

- *Diffusional Transformations*

These transformations involve the formation of a new phase through the breaking of atomic bonds in the initial phase and the subsequent redistribution of atoms within the solid. During diffusional transformations, atoms move over relatively long distances and their movement is essential for the process. In this type of transformation, diffusion is a crucial mechanism.

- *Diffusionless Transformations*

Also known as *athermal transformations*, diffusionless transformations do not require the diffusion of atoms over long distances but involve the displacement of a large number of atoms over short distances. In these transformations, there is no change in chemical composition, and they generally propagate independently of time. It should be noted that displacive transformations can occur during very rapid cooling.

In steels, phase transformations during cooling from the austenitic phase are of two types: diffusional transformations, which generally lead 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 begins, which is a function of the cooling rate. Figure VI-1 illustrates the mechanisms of displacive and diffusional transformations.

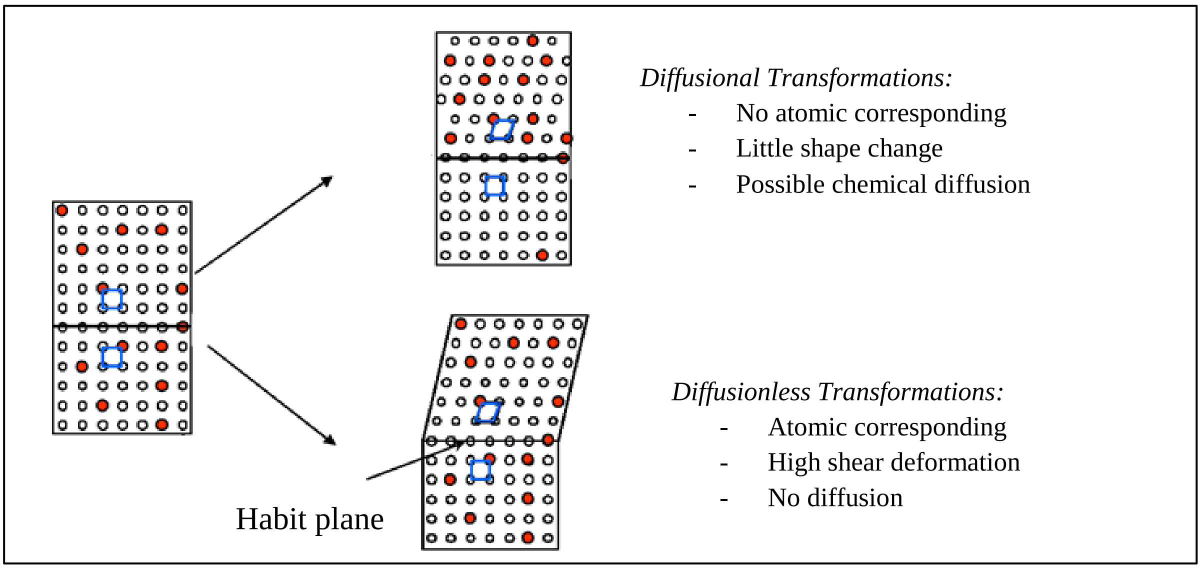


Fig. VI-1- : Illustration of the mechanisms of displacive and diffusional transformation.

VI-2. Normal transformation

The solid-state transformation kinetics are considered normal if the time and temperature dependencies of the transformation rate $V_{tr} = f(T, t)$ match those observed during the study of the crystallization process. During a decrease in temperature (for reactions that occur upon cooling), the rate of transformation initially increases and then decreases:

- The increase in the transformation rate is attributed to the ease of nucleation and the acceleration of growth as supercooling increases.
- The subsequent decrease in the transformation rate with further supercooling is explained by the reduced mobility of atoms as the temperature drops.

VI-3. Martensitic transformation

The term *martensite*, named after the physicist A. Martens, refers to the product formed by the quenching of carbon steel from the high-temperature phase known as "austenite." The term has since been extended to describe products formed through similar mechanisms, even if these products have structures quite different from those of steels (such as certain metal alloys). The structure of the martensite phase results from a transformation of the crystallographic lattice that occurs in the absence of atomic diffusion. This transformation is known as martensitic transformation.

The martensitic transformation is a first-order transformation that occurs without diffusion, through the shearing of entire groups of atoms. This process is externally manifested by the appearance of an acicular microrelief on the surface of a metal cut. As such, the martensitic transformation is classified as a displacive phase transformation in the solid state. During these transformations, atoms maintain their relative positions, with each atom retaining the same neighbors and not moving more than an interatomic distance. The progression of the transformation is driven by the movement of the interfaces between the phases, at a rate limited by the speed of sound in the material. In martensitic transformations, lattice distortion (deformation) is more significant than atomic rearrangement.

Martensitic transformation induces transformation strain. Specifically, directly above each martensite wafer, the metal surface exhibits tilting, and any straight line drawn on the surface of the austenite will show bending as it passes through the martensite crystallites after transformation (see Figure VI-2-(a) and VI-2-(b)). The measured transformation strain is a plane-invariant strain characterized by a large shear component and a small expansion directed normal to the invariant plane. The rate of transformation is described by:

$$Y = 1 - exp[-\alpha M_s - T] \tag{VI-1-}$$

α: coefficient and $T < T_{Ms}$

The M_f point designates the temperature below which martensite no longer forms. While M_f cannot be precisely determined, it is often approximated as $M_f = M_s - 215°C$. Martensite is carbon-saturated compared to equilibrium ferrite; it is a solid solution of carbon within a centered quadratic Q.C lattice of the ferrite, where c/a=1+0.045 x (% Carbon) by mass (Fig. VI-3-).

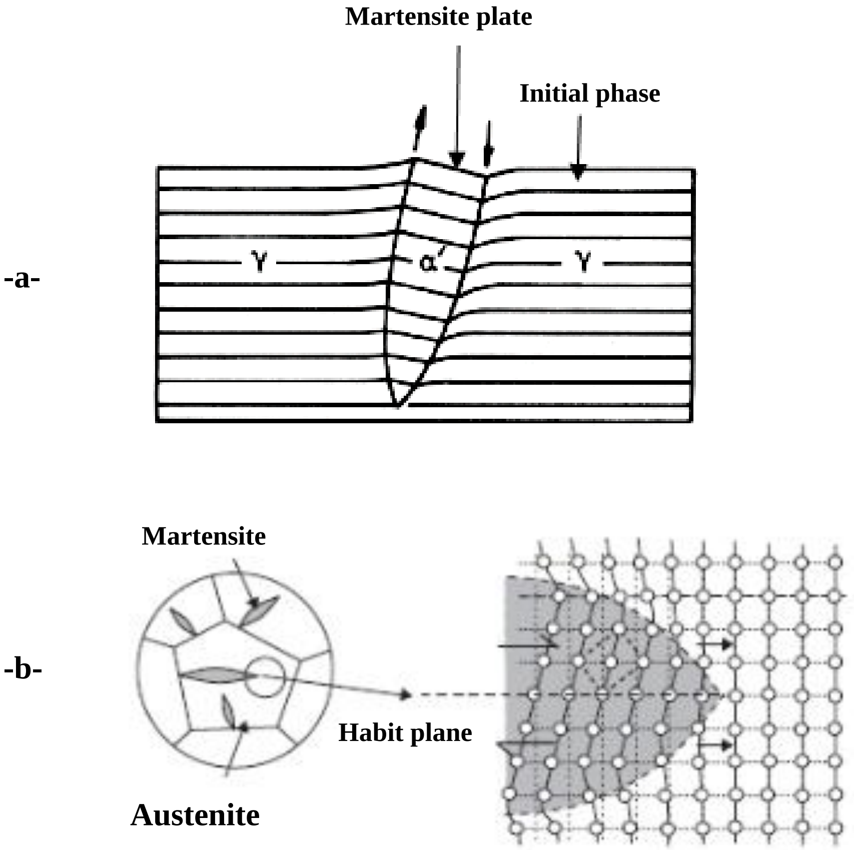


Fig. VI-2-: (a) Formation of Martensite α' from initial phase γ
(b) Simplified schematic representation of the martensitic transformation mechanism in iron.

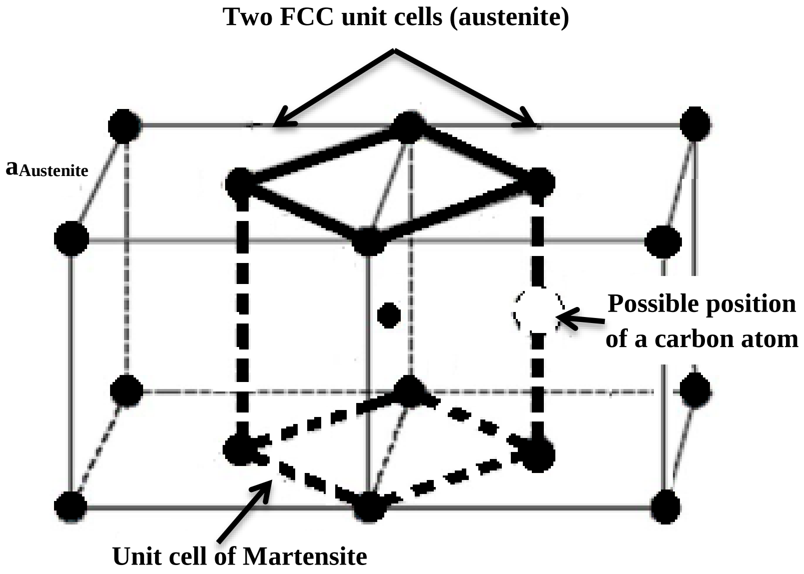


Fig. VI-3-: Schematic representation of the unit cell of martensite

- **Habit plane (adjoining plan)**

The interface between the initial phase and the martensite, on the macroscopic scale, is known as the invariant plane, also referred to as the *habit plane* or the adjoining plane. An invariant plane is characterized by two key conservation properties: its orientation remains unchanged by the transformation, and the relative atomic positions within this plane are preserved (i.e., distances and angles are conserved).

VI-3-1. General characteristics of martensitic transformation

The martensitic transformation has the following main characteristics:

1. It is a solid-state phase change resulting from homogeneous crystal lattice deformation. This deformation is not due to atomic diffusion but rather to a collective and cooperative movement of atoms over distances relatively small compared to the lattice parameters.
2. The transformation occurs almost instantaneously, with a rate comparable to the speed of sound in the solid.
3. The martensitic transformation results in changes to both the shape (shear) and volume of the specimen. For shape memory alloys, the volume change is minimal, while the shear is significant.
4. To minimize the energy between the formed martensite and the remaining austenite, martensite domains typically take the shape of flattened platelets. Martensite forms

preferentially on specific crystallographic planes, known as the limit plane, adjunction plane, or habit plane. These planes are associated with the shear of martensite. The domains formed generally exhibit a flattened platelet shape.

Figure VI-4 illustrates the various forms of martensite in steels as an example.

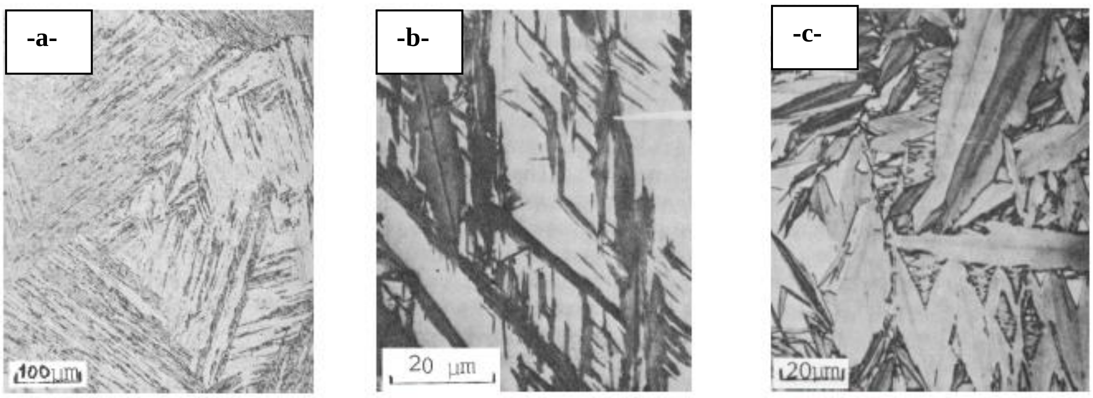


Fig. VI-4- : Different martensite morphologies in iron alloys: (a) low C (lath), (b) medium C (plate), (c) Fe–Ni (plate). *(D. A. Porter, K. E. Eastorting. Phase transformation in metals end alloys, second edition, Chapman et Hall, London, (1992))*

VI-3-2. Thermodynamic aspect of martensitic transformation

Before delving into the details of the martensitic transformation from a thermodynamic perspective, we will define the key characteristics, including the transformation temperatures and the extent of the transformation. The transition from the initial phase to the martensitic phase, and vice versa, is temperature-dependent. Four critical temperatures characterizing the transformation process are defined as follows:

M_s: The start temperature of the direct transformation (austenite → martensite).
M_f: The end temperature of the direct transformation.

The direct martensitic transformation during cooling (austenite → martensite) begins at the temperature M_s (martensite start) and becomes complete at the temperature M_f (martensite finish). Since the transformation occurs without diffusion, the initial phase and the martensitic phase differ only in their crystallographic structures. Thus, the system can be considered as consisting of two solid phases with different crystallographic structures but identical chemical compositions.

The study of the variation in free enthalpy of these two phases, excluding deformation energies and surface energies, is illustrated in Figure VI-5. This can be expressed by the following relation:

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

G_M: the free energy of martensite
G_A: the free energy of austenite

In Figure VI-4, which presents Gibbs free energy as a function of temperature, it is evident 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., at temperatures below the critical temperature T_0. At T_0, the difference in the chemical free energy, $\Delta G_{A\to M}$, between the two phases becomes zero, establishing a thermodynamic equilibrium such that:

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

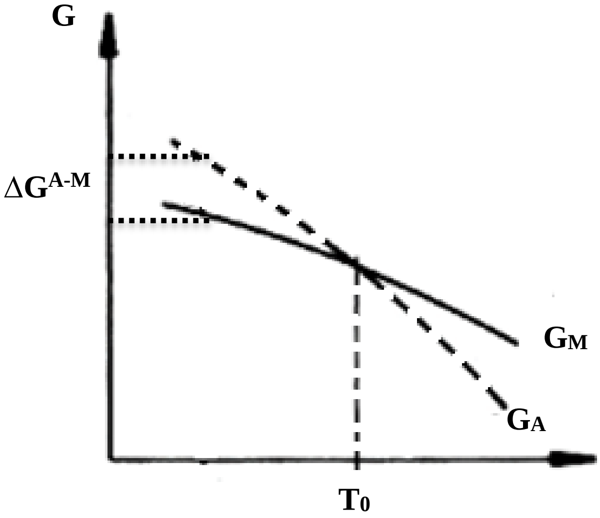


Fig. VI -4- : Gibbs energy of austenite and martensite as a function of temperature

However, in reality, the two phases are not entirely independent of each other; the martensitic transformation occurs through a mechanism of nucleation and growth. This implies the presence of interface energy between the two phases. The energy required to move this interface contributes to the overall energy balance, creating an energy barrier that influences the progression of the transformation.

VI-4. Massive transformation

The martensitic mechanism assumes the absence of atomic redistribution, indicating a non-diffusional nature of the transformation in solid solutions. However, in complex component alloys, transformations can also occur without the redistribution of components between phases. This type of transformation is referred to as massive.

The immediate result of such a transformation is a single-phase state. In classic cases, during normal kinetics, the grains appear as massive blocks without distinct shapes or clear lines of separation. This characteristic led to the term "massive transformations."

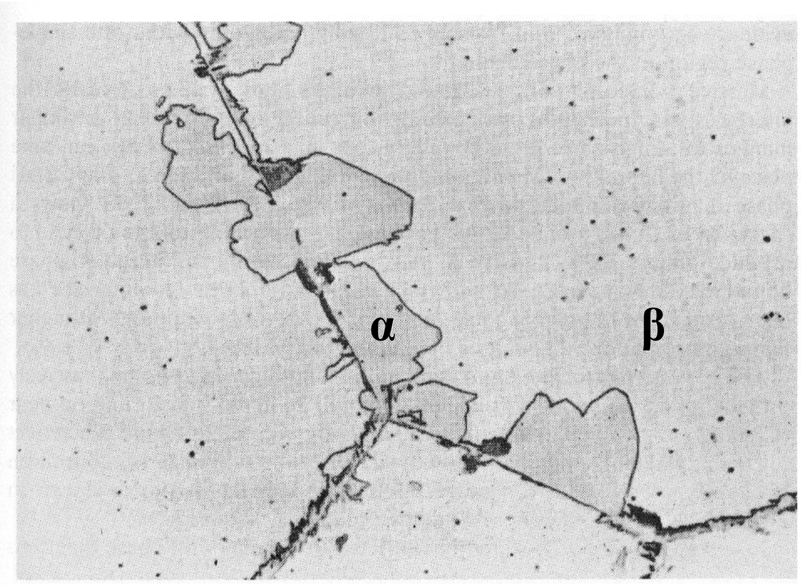


Fig. VI- 5- : Formation of the α phase by massive transformation at the grain boundaries of the β phase in the Cu-38.7% Zn alloy, quenched from 850°C. *(D. Hull, K. Garwood, the mechanism of phase transformations in metals, institue of metals. London (1956)*

The following table outlines the differences between the two types of transformations: diffusional and diffusionless.

Displacive transformation (or martensitic)	**Diffusive transformation**
- Atoms migrate over interatomic distances. - Atoms migrate by bond breaking and local rearrangement. - Atoms move individually and are not necessarily cooperative. - The rate of transformation is influenced by temperature and is typically governed by diffusion kinetics. - The transformed volume depends on both temperature and time. - The composition can change due to atomic diffusion. - The transformed phase may not always maintain crystallographic relationships with the initial phase.	- Atoms migrate over distances ranging from 1 to 10^6 interatomic distances. - Atoms move from site to site through activated thermal diffusion. - Atom movement is random. - The rate of transformation strongly depends on temperature and typically cannot occur below 0.3 to 0.4 T_f (where T_f is the melting point). - The transformed volume depends on both time and temperature. - Diffusion allows for composition changes in alloys. - There may be some crystallographic relationships between the phases.

Practice exercises

Exercise 1:

Calculate the volume percentage change resulting from martensite formation in a 1% C steel.

Exercise 2:

Sketch a diagram demonstrating the Bain model of homogeneous deformation during martensitic transformation of FCC → BCC. Supposing that $a_\gamma = 3.56$ Å, $a_\alpha = 2.86$ Å and the ratio $c/a = 1.1$

- Calculate the maximum movements of atoms during the martensitic transformation.

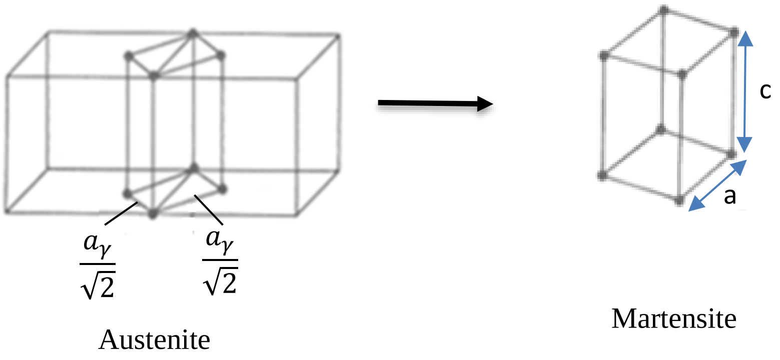
Answers

Answers for Exercise 1

$c/a = 1 + 0.0467 \times (\%\ \text{carbon})$

Answers for Exercise 2

Diagram of the Bain deformation:



Movements of atoms can be calculated as follows:

$c/a = 1.1$ and $a_\alpha = 2.86$ Å, so $c_\alpha = 3.15$ Å

$\frac{a_\gamma}{\sqrt{2}} = 2.52$ Å

Movement of atoms along the vertical direction is: 3.56 – 3.15 = 0.41 Å

Movement of atoms along the horizontal direction is: 2.86 – 2.52 = 0.34 Å