Chapter III

General classification of phase transformations and issues related to new phase nucleation.

III-1. Introduction

Phase transformations occur when temperature, pressure, or the chemical composition of the system (i.e., the number and type of components) change. Phase transformations driven by temperature variations are particularly significant, including phenomena such as precipitation and ordering in solid solutions.

A phase transformation, whether complete or partial (stopping at an intermediate stage), is crucial for achieving optimal material properties. These properties are influenced not only by the composition and characteristics of the phases but also by the alloy's microstructure. This includes factors such as the size, morphology, dispersion, and distribution of the phases, as well as the basic crystallographic structure or grain substructure. The purpose of certain heat treatment processes is precisely to develop the desired microstructure.

In general, the temperature of the final heat treatment operation is higher than the temperature at which the material will be used. As a result, the material retains its structure and properties for as long as possible.

The study of phase transformations is challenging because the mechanisms and kinetics of phase transformations of the same type (such as allotropic transformations, precipitation, or ordering in solid solutions) can vary significantly.

The analysis of phase transformations in alloys requires considering a combination of various mechanisms that may occur either sequentially or simultaneously.

The theory of phase transformations in the solid state relies on the same principles established in the study of crystallization processes. However, two specific factors must also be considered when dealing with transformations in a crystalline medium:

❖ *Elastic energy factor*

During the formation of a new phase in a crystalline medium, the change in the system's free energy (ΔG) must account for not only the volume energy variation $V.\Delta G_v$ and the interface energy $A\gamma$, but also the energy associated with the elastic stress field. The elastic energy factor, together with the interface energy, influences the morphology, orientation, and distribution of the new phase particles during their formation and growth.

❖ **Factor limiting the mobility of atoms through diffusion in the crystal and the potential for cooperative movement of all atoms:**

Limiting the mobility of atoms allows for the achievement of metastable and even absolutely unstable states using conventional techniques such as temperature and pressure.

A sudden change in pressure over a wide range (several tens or hundreds of atmospheres) at low temperatures, or a high cooling rate under conditions of limited atomic mobility, can achieve extremely high supercooling. This, in turn, significantly alters the course of the phase transformation.

The cooperative movement of atoms, or its weak development, leads to a type of phase transformation known as martensitic transformation. The kinetics of martensitic transformations differ significantly from those of other phase transformations.

III-2. General classification of phase transformations

The classification of phase transformations can be based on comparing the crystallographic structure and chemical composition of the phases in the initial state with those produced by the transformation. In this context, the transformation occurs through the formation of one or several new phases, which differ in:

- **The crystalline structure**, which refers to the arrangement of atoms in the lattice (e.g., allotropic transformations in metals and alloys, ordering).
- **The chemical composition**, while maintaining the same atomic lattice coordination (e.g., demixing of a solid solution).
- **Structure and composition** (e.g., precipitation from supersaturated solid solutions).

If a phase transition is accompanied by an abrupt change in a property, then, considering the requirement for thermodynamic stability, the variation in the thermodynamic potential of the system must be infinitesimally small near the transition point. This can occur in two cases:

- When an infinitesimally small amount of the new phase appears, with a distinct difference in properties compared to the initial phase.
- When there is an infinitesimally small variation in any property throughout the entire volume.

The formation of a new phase with different properties leads to the development of surface energy. Therefore, very small domains of the new phase are not favorable. This type of transition is known as a first-order phase transition.

If the phase transition occurs through a gradual variation in internal parameters (e.g., concentration distribution, atomic displacement, or other aspects of the atomic structure), such that at the transition point the difference between the parameters of each phase is infinitesimally small, the transition is classified as a *second-order phase transition*. In this type of transition, metastable states are, in principle, not possible.

III-3. New phase nucleation problems

The need for supercooling to form a new phase arises not only from the energy required to create the interface between the old and new phases but also from overcoming the elastic resistance of the medium.

A more detailed analysis of first-order phase transitions reveals that, under certain conditions, the system's transition through intermediate states towards equilibrium (considering factors such as the continuous variation in the degree of differentiation of constituents or homogeneous shear during lattice deformation) can result in an increase in free energy. This potential barrier can be conceptualized as the formation of critical nuclei through fluctuations.

In Figure III-1, we show the variation in the free energy of the system as a function of a given parameter X for a first-order transformation (a) and a second-order transformation (b).

The origin of the calculation is set at the free energy level of the initial phase β. The diagram shown in this figure is suitable, for example, for the thermodynamic analysis of the precipitation process in a supersaturated solid solution. In this context, the vertical axis represents the change in the free energy of the system, while the horizontal axis represents the composition of the solid solution.

- In the domain of stable existence (e.g., at temperatures T_1 and T_2 for the high-temperature phase β), the phase remains stable with respect to both weak and strong fluctuations in the parameter X (the composition).

- At the phase transition point ($T_3 = T_0$), equilibrium between the phases is characterized by the equality of their free energies (or thermodynamic potentials) despite differences in specified structural parameters (x' and x'').
- For $T < T_3$, the initial phase is unstable with respect to large variations in the parameter X. Cooling reduces the energy barrier associated with changes in the atomic structure, leading to the transformation of the β phase into the α phase.
- Up to the temperature $T > T_5$, the system remains stable with respect to small fluctuations in the parameter x.
- At $T_c = T_5$, there is a loss of stability of the initial system with respect to infinitesimally small variations in the parameter X. This temperature T_c is referred to as the absolute temperature at which the stability of the initial phase is lost.

In the case of second-order phase transitions, the parameter X can represent, for example, the degree of order in order-disorder transformations. In such transitions, each intermediate structure has a lower free energy throughout the volume, and no metastable states are present.
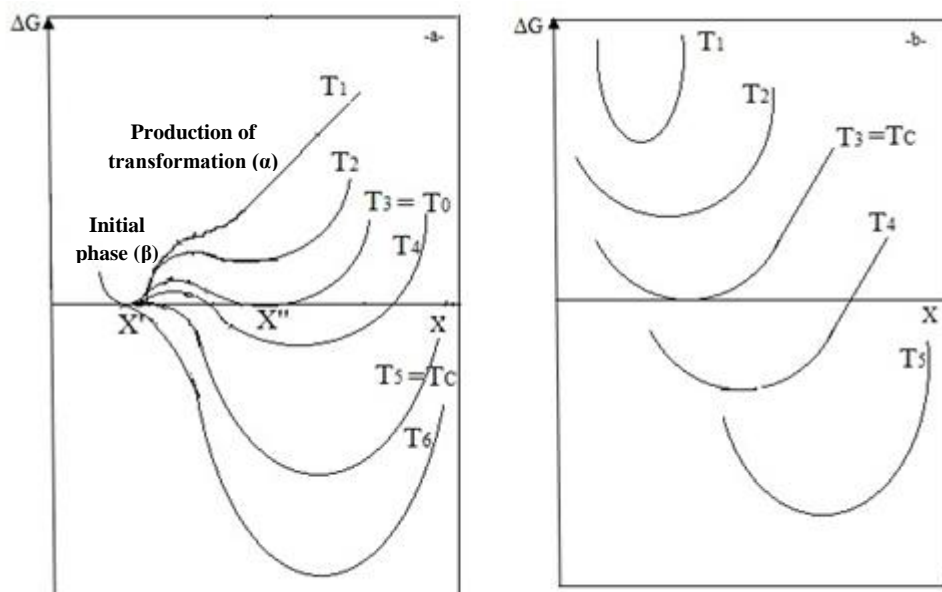

Fig. III-1- : Variation of the Gibbs free energy (ΔG) as a function of a thermodynamic parameter for two systems: one exhibiting a first-order transition (a) and the other exhibiting a second-order transition (b).