
Chapter

III

General classification of phase transformations and new phase germination problems

III-1. Introduction

Phase transformations occur when the temperature, pressure and type of the components number of the system (the chemical composition of the alloy) vary. Great importance is given to phase transformations due to temperature variations: precipitation and order in solid solutions.

A transformation of phases, complete or partial (stopped at an intermediate stage) ensures the optimal properties of the material. These properties are determined not only by the composition of the phases and their properties, but also by the microstructure of the alloy, i.e. the size, morphology, dispersion and distribution of the phases as well as the basic crystallographic structure of the alloy or the grain substructure. The interest of certain heat treatment operations consists precisely in forming the appropriate structure.

In general, the temperature of the final operation of the heat treatment is higher than the temperature of use of the material, and consequently the material retains its structure and its properties as long as possible.

The problem of studying phase transformations is made difficult by the fact that the mechanism and the kinetics of a phase transformation of the same type (allotropic transformation, precipitation, order of the solid solution,.....etc) can be very different.

The analysis of phase transformations in alloys requires the consideration of a combination of various mechanisms that occur one after the other or simultaneously.

The theory of phase transformations in the solid state uses the same laws as those highlighted and well-studied during the study of the process of crystallization; however, two specific factors of transformations in a crystalline medium must still be taken into account:

❖ *Elastic energy factor*

During the formation of the new phase in a crystalline medium, in addition to the variation of the free energy in volume $V \cdot \Delta G_v$ and the interface energy $A \cdot \gamma$, the variation of the free energy of the system ΔG must necessarily include the energy of the elastic stress field. The elastic energy factor together with the interface energy determines the morphology, orientation and distribution of new phase particles during their formation and growth.

❖ *Factor limiting the mobility by atoms diffusion in the crystal and the possibility of the cooperative movement of all the atoms:*

Limiting the mobility of atoms makes it possible to obtain metastable and absolutely unstable states using the usual means of modern technology (temperature and pressure).

A sudden change in pressure over a wide range (a few tens or hundreds of atmospheres) at low temperature or a high cooling rate under conditions of limited mobility of the atoms make it possible to achieve very high supercooling; which completely changes the course of the phase transformation.

The cooperative character of displacement of the atoms (or for a weak development), gives a mechanism of the transformation of the particular crystallographic structure called martensitic. The kinetics of martensitic transformations differs greatly from the kinetics of other phase transformations.

III-2. General classification of phase transformations

The basis of classification of phase transformations can be the comparison of the crystallographic structure and the chemical composition of the phases in the initial state with the phases produced from the transformation. In this respect the transformation occurs by the formation of the new phase (or several new phases), which differs by:

- The crystalline structure, i.e. the coordination of the atoms in the lattice (eg: allotropic transformation in metals and alloys, ordering),
- The chemical composition during the conservation of the coordination of the atoms in the lattice (demixing of the solid solution),
- Structure and composition (precipitation of supersaturated solid solutions).

If the phase transition accompanies an abrupt change in a property. If we take into account the requirement of thermodynamic stability, very close to the transition point, the variation of the thermodynamic potential of the system must be infinitely small; this is possible in two cases:

- When an infinitely small amount of the new phase appears with a definite difference in its properties from those of the initial phase,
- At an infinitely small variation of any property in the all volume.

The appearance of the domain of the new phase with other properties must lead to the birth of a surface energy. Therefore very small domains of the new phase are not advantageous. Such a transition is called *a first-order phase transition*.

If the phase transition occurs by a gradual variation of internal parameters (e.g., concentration distribution, displacement of atoms, or other features of atomic structure), such that at the point of the transition the difference between the parameters of each phase an infinitely small amount, the transition belongs to *the second-order phase transitions*. During this last type of transition, in principle metastable states are not possible.

III-3. New phase germination problems

The need for supercooling for the formation of the new phase is due not only to the loss of energy for the formation of the contact surface between the old and the new phase, but also to overcome the elastic resistance of the medium.

A more detailed analysis of the first order phase transition shows that under given conditions, the passage of the system, through the intermediate states, towards the state of equilibrium (by considering, for example, the continuous variation of the degree of differentiation of the constituents or the homogeneous shear during the deformation of the lattice), can lead to the rise of the free energy. The passage of such barrier of potential can be represented by the fluctuation formation of critical germs.

On figure III-1- we present the variation of the free energy of the system according to a given parameter X for a transformation of the first order (a) and the second order (b).

The origin of the calculation is taken to be the free energy level of the initial phase β . The diagram reproduced in this figure is suitable, for example, for the thermodynamic analysis of the precipitation process of a supersaturated solid solution (the ordinate axis will then give the mean variation of the free energy of the system and the abscissa axis that of the composition of the solid solution).

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

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- At the phase transition point ($T_3 = T_0$) the equilibrium of the phases means the equality of the free energies (or the thermodynamic potentials) of the phases for a difference of the determined structural parameters (x' and x'').
- For $T < T_3$ the initial phase is not stable with respect to large variations of the parameter X . The cooling leads to the decrease of the energy barrier during the variations of the atomic structure which transform the β phase into α phase.
- Up to the temperature $T > T_5$, the system remains stable with respect to small fluctuations of the parameter x .
- At $T_c = T_5$ there is a loss of stability of the initial system with respect to the infinitely small variations of the parameter X . The temperature T_c is called the absolute loss temperature of the initial phase stability.

In the case of 2nd order phase transitions, the parameter X can be, for example, the degree of order in the case of order-disorder transformations; each intermediate structure therefore has a smaller free energy throughout the volume and there are no metastable states.

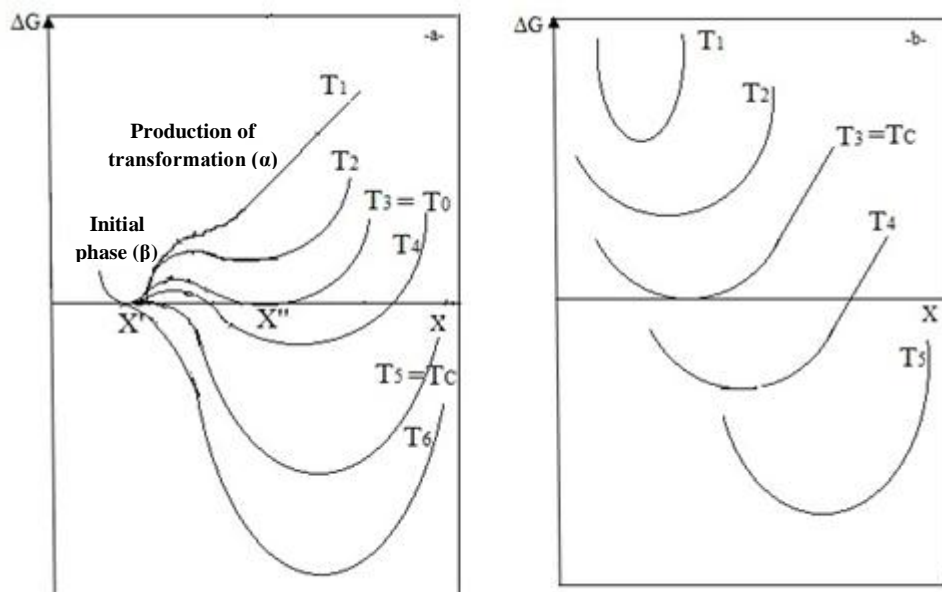


Fig. III-1- : Variation of the Gibbs free energy ΔG as a function of a thermodynamic parameter for two systems, one with a 1st order transition (a) and the other with a 2nd order transition (b).