KINETIC THEORY OF PHASE TRANSFORMATIONS

B.Ya. Lyubov

Translated from Russian

This book contains a theoretical analysis of the kinetics of phase transformations in solid metals and alloys. Two types of phase transformations are considered: without diffusion, i.e. taking place without change in the chemical composition of the phase; and with diffusion, i.e. where diffusion plays an important part.

Aimed at a wide circle of metallurgists and metal physicists, this book may also be useful for students and research workers specializing in the area of physical metallurgy.

FOREWORD

The theory of phase transformations occupies an especially important place in today's science of metals and alloys. On the one hand it allows the selection of a regime of thermal processing that will produce a definite structural state of matter and thus yield material needed for practical use. On the other it makes it possible to eliminate undesirable changes in metal articles in use under the action of high temperatures, large stresses, irradiation and so on.

There is now a huge accumulation of data on the thermodynamic characteristics of phases and the kinetics of phase transitions in different systems. But there has been practically no systematic analysis of these data using the theory of the processes occurring in phase transformations.

This book attempts a systematic account of the factors determining the kinetics of individual processes occurring in metastable solid metals and alloys, assigning them their relative roles in the overall kinetics of phase transformation at different temperatures, compositions of alloys and pressures.

There is a theoretical analysis of the kinetics of phase transformations in solid metals and alloys. Two types of phase transformations are considered: without diffusion, i.e. taking place without change in the chemical composition of phase and consequently not connected with diffusional redistribution of components; and with diffusion, in which diffusion processes play an important part. Special attention has been paid to analysis of the effect of heterogeneous structure and concentration on the course of the processes in question.

In Chapter I some features of transformations in solid matter are explained on the basis of further development of the classical theory of nucleation and growth of centers of new phase. Strong interatomic interaction in solid bodies produces considerable stresses in the system, in the center of the new phase-matrix, and is responsible for the cooperative nature of transformation. There is a detailed examination of the effect of the circumstances mentioned on the development of phase transformations in metals. An estimate has been made here of the effect of pressure on the conditions of phase equilibrium in metals and the kinetics of diffusionless phase transformations. Some space is devoted to consideration of temperature conditions on the interphase boundary depending on the form of the crystal of

· new phase and characteristics of the kinetics of its growth.

Chapter II presents the theory of growth of centers of new phase during decomposition of ideal solid solutions. There is a detailed analysis of the relative contribution of processes occurring on the phase boundary and realized in their volume. Along with the description of the physical features of the processes there is a discussion of the techniques used in the solution of the special problems of the mathematical theory of diffusion posed by these processes.

Chapter III considers the effect of structure and concentration stresses and the effect of the chemical interaction of atoms of different types on the local properties of a solid solution (possibility of the appearance and stabilization of segregations of atoms of the dissolved substance) and on the kinetics of phase transition.

Chapter IV deals with the overall kinetics of the processes of phase transformations and their dependence on temperature, composition (in particular, addition of a third component to a binary alloy) and high hydrostatic pressure. A comparison is made with the effect of change in composition and pressure on the kinetics of decomposition of a solid solution.

The examples of calculations and the various discussions in the text relate to the study of processes of interest in the working out of optimal methods of thermal processing of steel. The present monograph is mainly concerned with the analysis of phase transformations in solid interstitial solutions (System Fe-C). But many of the results presented of course have a wider range of application.

In discussing the problems taken up the author has made use mainly of the results of research by himself and students and associates close to him. It was not possible to take in the whole of contemporary theory of phase transformations in metals and alloys. Besides, the interpretation of individual aspects of the theory presented does not agree with the generally accepted one: it represents strictly the author's point of view.

Valuable help in the preparation of the manuscript for the press was rendered by the research scholars V.S. Gerasimenko, G.M. Butnikova and V.A. Shumakov, to whom the author expresses his deep gratitude.

B.YA. LYUBOV

CONTENTS

Chapter I

DIFFUSIONLESS PHASE TRANSFORMATIONS

A study of the processes occurring in metals and alloys during various thermal treatments is one of the chief tasks of the physics of metals [1]. To begin with we will confine ourselves to consideration of the problems in the simpler case of pure metals. During the process of heating or cooling of a metal capable of existing in different phases temperatures may be obtained above or below which the initial phase becomes unstable and must reduce to a new phase that is stable under the given conditions. The aim of our analysis will be to determine the factors that influence the kinetics of such phase transitions and the laws governing processes of this type.

We will be considering transitions in the solid state.[1] In studying such processes it is essential to take into account the principal features of solid crystalline matter: the anisotropy of its properties and the possibility of appearance of considerable stresses in the region occupied by the new phase as well as in the matrix volume, which are capable of exerting considerable influence on the phase transitions in question.

The displacements of an atom in a solid crystalline substance cannot be considered to be independent[2] of the other atoms in the lattice (autono-

---

[1]From the thermodynamic point of view phase transitions are divided into two classes:

1) Phase transitions in which thermodynamic functions such as energy, free energy, etc. change in a discontinuous way. These transitions are accompanied by emission or absorption of definite amounts of the heat of phase transformation. A typical example of phase transition of this first kind is the change in the aggregate state of matter and the conversion of one crystalline modification into another; and

2) Phase transitions during which all the thermodynamic functions are continuous but the heat capacity, compressibility and volume coefficient of thermal expansion are discontinuous. In this case the heat of the phase transition is zero. An example of such phase transformations is the conversion of a ferromagnet into a paramagnet.

Special note should be made of the fact that the possibility of realization of metastable states (i.e. the existence of a phase in conditions under which another phase would be more stable) is characteristic only of phase transitions of the first kind. In the present chapter we will consider a phase transformation in a metastable state at a temperature below (supercooling) the temperature of phase equilibrium.

[2]By "displacements of an atom" we understand displacements from the equilibrium position that are considerably larger than the amplitude of its thermal oscillations.

1

mous). A shift of the given atom from its equilibrium position in the lattice of the crystal brings about a change in the position of neighboring atoms. Thus the displacement of an atom in a solid substance is a collective process connected with energy changes involving a large or small group of such particles. In the usual thermodynamic theory, which is confined to a study of the conditions of equilibrium of different phases capable of coexisting in the given system, every phase is regarded as homogeneous in composition, relative position and energy states of atoms and the interphase boundaries are taken as planes. Actually a real polycrystalline metal has lattice defects of various types [2]. Besides, as a result of thermal motion the atoms of crystals situated at the lattice points continuously oscillate about their mean positions, corresponding to the correct geometrical structure. The energy and consequently the amplitude of such oscillations increase with rising temperature. At a sufficiently high temperature[1] all the atoms are displaced from their positions of equilibrium to various extents at any given moment. The higher the temperature the more "distorted" is the crystal lattice. As a result, at high temperatures anisotropy has insignificant influence on the processes in question and the independence of the displacements of atoms increases. When the temperature decreases the influence of interatomic interactions begins to be more clearly felt and very rapid phase transitions may become possible [3]. In principle a situation is even possible where the individual displacements of atoms in the classical sense are obliterated, so that the process may be treated from the point of view of quantum mechanics, which provides for investigation of the behavior of particles with wave properties during passage through potential barriers (tunnel effect[2]) [4, 5]. This effect is especially clear at very low temperatures (near absolute zero).

The change in the role of interatomic interactions in the kinetics of processes taking place in solid metals during a change in temperature is con-

---

[1]High and low temperatures are relative concepts—they are to be related to some temperature which is characteristic for the given substance (Debye temperature, fusing temperature, etc.). In our discussion temperatures close to the equilibrium temperature of the coexistent phases will be called high and correspondingly temperatures much lower than the equilibrium temperature of the coexistent phase will be called low.

[2]In the simplest case the tunnel effect consists in allowing non-zero probability to the penetration of a particle through a potential barrier [a region where the potential energy $U(x)$ of the particle exceeds its total energy E]. For a particle in the classical sense such a thing is not possible since

$$E = \frac{mv^2}{2} + U(x) = \frac{p^2}{2m} + U(x),$$

where m is the mass of the particle; v is the velocity; p is the momentum. Consequently inside the barrier $[U(x) > E]$ the particle must have an imaginary value of momentum. Therefore the tunnel effect has an essentially quantum character and cannot be described by means of concepts of classical mechanics.

firmed by the presence in them of two types of phase transformation. For the usual changes in the structural form of existence of a polymorphic metal a new phase appears in the form of equiaxial crystals: the maximum rate of growth of the latter is of the order of a few centimeters per second, there being no clear interrelation between the geometro-crystallographic characteristics of the initial and new phase. Transformations of this type are observed in iron, tin, manganese, plutonium and other elements. In iron, cobalt, uranium and some of their alloys a different type of transformation is observed which we will call the martensite type. Under experimental conditions crystals visible in the phase appearing in this case are characterized by the laminated form; strictly oriented correspondence of lattices of the coexisting phases; and a high rate of growth ($\sim 10^5$ cm/sec), the rate of growth depending very little on temperature. These peculiarities of crystal growth during martensite transformation are the result of a process taking place in an elastic medium under conditions of strong interactions between atoms. The considerable stresses arising as a result of transformation exert a very strong influence on the thermodynamic motive force of the process and in particular explain the existence of hysteresis [6]. The interactions of atoms during a change in the structural state of the metal introduce an element of order in their displacement, making the process a collective one [3, 7, 8] which accounts for the high speed of the phase transition.

Transformations of the normal type which are characteristic for high temperatures depend little on the concrete geometro-crystallographic characteristics of the transforming phase. Besides, for high temperatures the processes of relaxation of stresses connected with the structural changes during phase transition may take place intensively. Therefore for an analysis of polymorphic transformations of such a type in time under isothermal conditions we may use the usual theory of phase transformations, developed, for example, to describe the processes of crystallization from the uncondensed phase. This theory is based on the concept of the distribution function at the given time t of the formations of the new phase with respect to the number of atoms contained in them $n : Z(n, t)$ [9, 10]. The equation from which $Z(n, t)$ may be determined takes into account both its change due to fluctuation and the effect of a directed decrease or increase in the sizes of the formations of new phase under the influence of purely thermodynamic factors. For such a treatment the change in the dimensions of one formation is taken as independent of the presence of others, i.e. the conditions corresponding to the start of the process are analyzed.

Of special interest in the detailed investigation of the kinetics of the phase transition is the explanation of the dependence of the speed of nucleation of centers of new phase (s, n, c) I and the rate of their growth (r, g, c) v on a quantity indicating how far the conditions under which the pro-

cess occurs depart from equilibrium conditions. This dependence must include the kinetic coefficients which reflect the concrete atomic-molecular mechanism of the process.

External forces also influence the kinetics of the change in size, form and position of the crystals of new phase. In particular the conditions of phase equilibrium and rate of growth of particles of new phase change considerably when subjected to hydrostatic pressure. The extent of this influence is naturally related to the magnitude of the volume effect of the transformation. Calculation of the elastic energy of the stress field due to the transformation allows us to estimate hysteresis during transformation [11]. In calculating the stress field around the precipitation of new phase the following circumstances have the deciding role, as shown by A.L. Roitburd [12, p. 235]:

a) The crystallographic changes in volume and form of the regions in which the transformation has taken place. These determine the contribution of the inelastic part of the deformation to its overall magnitude.

b) The degree of coherence of the lattices of the new phase and matrix. For the case of complete coherence the entire problem of determination of stresses in the matrix and the center of new phase falls within the scope of the theory of elasticity. The condition for complete coherence of the phase boundary is the requirement that neighboring atoms of the initial matrix remain neighboring atoms after the transformation, even if they are in different phases.

c) The form of the crystal of new phase. This determines the geometrical characteristics of the problem, which in turn are related to the nature and magnitude of the stresses arising during the transformation.

Stresses caused by changes in the crystal lattice during transformation and those associated with the presence of defects of the dislocation type [2] would be called structural stresses.

As can be seen from the foregoing discussion, in the development of the theory of diffusionless phase transformations, i.e. in the case of structural rearrangement taking place in metals and alloys without change in composition, a very important part is played by the temperature conditions under which the process takes place. What we have said above applies to phase transformations taking place in isothermal conditions. However, the actual temperature on the phase boundary is determined by the ratio of the intensities of heat liberation during the transformation and its removal in the coexistent phases.

We will begin the analysis of the factors determining the course of the above-mentioned processes with a consideration of the thermodynamic motive forces of diffusionless phase transformations.

1. Thermodynamic stimuli of diffusionless phase transformations

Phase transformations of the type we are considering reduce to formation in isolated zones of a metastable phase with new positions of the atoms characteristic of a stable state under the given conditions. If the dimension of such a zone exceeds a certain critical value we will consider it to be a center of new phase, the smaller zones being called nuclei, and the zero of any dimension, new phase formations.

The centers of new phase are capable of increasing their size under the influence of the thermodynamic stimulus of transformation.[1] The last is determined by the sum of energy changes due to the appearance of regions occupied by the new phase. When external forces and internal sources of structural stress not related to transformation are absent (for example, dislocation of their system in the initial matrix), the formation of a center of new phase leads to the following changes in the free energy of the system:

1) ΔF_V—the gain in free energy F as a result of the appearance of a crystal of volume V of the new phase having less than the initial value of F under the given conditions. Usually

$$\Delta F_V = \Delta F_0 \cdot V,$$

where ΔF_0 is the change in free energy per unit volume;

2) ΔF_S—the loss in free energy as a result of the appearance of the phase boundary or the transitional region in between, in which the location of atoms undergoes a change from that characteristic of the old phase to that corresponding to the new. Atoms situated at the interface boundary have energy states which do not correspond to equilibrium in any of the coexistent phases. Therefore they possess excess energy.

3) ΔF_E—the loss in energy on creation of structural stress fields. Under the condition that the lattices in the center of the new phase and the matrix are coherent, i.e. their·interface boundary is replaced by the transitional region, we may include ΔF_S in ΔF_E [13].

Thus the total change in the freè energy of the system during the formation of the center of new phase containing n atoms equals

$$\Delta F(n) = -\Delta F_V + \Delta F_S + \Delta F_E. \tag{1}$$

The quantity ΔF_0 is very much dependent on temperature. From the condition $\Delta F_0 = 0$ the condition for phase·equilibrium in the case of a

---

[1]Such stimuli arise during a deviation of temperature from the temperature of phase equilibrium and for the given temperature corresponding to a metastable state, if the dimension of the center of new phase is not equal to the critical value. The quantitative expression for the effect of thermodynamic stimuli is the "thermodynamic motive force of the phase transformation process."

plane contact boundary can be obtained.

We will illustrate how ΔF_0 is computed with the example of polymorphic transformation of iron. As is known from reference [14], in the solid state pure iron may be in α (bcc lattice) and γ (fcc lattice) modifications. The α-iron exists in a stable state in two temperature ranges: below 910°C and in the range from 1,390 to 1,535°C. This shows that the free energy of γ-iron (F^γ) at temperatures lower than 910°C is more than that of α-iron (F^α), and $\Delta F_0 = F^\gamma - F^\alpha > 0$ (Fig. 1) (the computations are made for unit volume).
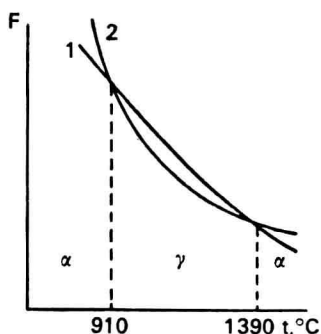

Fig. 1. Free energy of α-phase (*1*) and γ-phase (*2*) of iron for different temperatures. Graph.

Our chief interest will be in the phase transformations $\text{Fe}_\gamma \rightleftarrows \text{Fe}_\alpha$ in the temperature range below 910°C. The value of ΔF_0 may be computed with high accuracy from the data on the heat capacity of α and γ phases of iron for different temperatures. In Table 1 are presented results of computations of the dimensionless quantity $(V_{\text{Fe}} \cdot \Delta F_0)/RT$ (V_{Fe} is the atomic volume of iron) carried out by K. Zener [15] and also by B.M. Mogutonov and I.A. Tomilin [16].

The dependence of $(V_{\text{Fe}} \cdot \Delta F_0)/RT$ on T is shown graphically in Fig. 2. Analytically this dependence for $T < 1,050°K$ may be represented with sufficient accuracy for our purposes by the formula

$$\frac{V_{\text{Fe}} \cdot \Delta F_0}{RT} = 0.538 - 0.000698\,(T-273). \qquad (2)$$

The value of ΔF_S is related to the formation of the phase boundary and depends directly on the magnitude of specific inter-phase tension σ. The value of σ under conditions of normal polymorphic transformation cannot be independently determined at present. It may be of the order of a few hundreths of J/m² (a few tens of erg/cm²) [17]. The value of σ is determined by indirect methods (see Chapter IV).

Finally, the quantity ΔF_E has to be calculated by the methods of the mechanics of deformable bodies
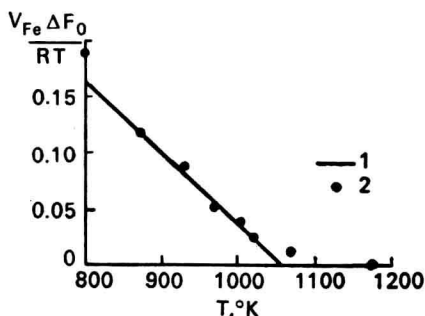

Fig. 2. Dependence of $(V_{\text{Fe}} \cdot \Delta F_0)/RT$ on temperature:

1—according to formula (2); *2*—data calculated in references [15,16].

Table 1. Values of $V_{Fe} \cdot \Delta F_0/RT$ for different temperatures

T° K	According to K. Zener [15]	According to B.M. Mogutnov and I.A. Tomilin [16]
200	—	3.29
373	1.24	—
400	—	1.26
473	0.83	—
573	0.543	—
600	—	0.536
673	0.362	—
773	0.222	—
800	—	0.194
873	0.12	—
923	0.08	—
973	0.05	—
1,000	—	0.0374
1,023	0.0264	—
1,073	0.0135	—
1,123	0.0061	—
1,183	0	0

for each concrete case [18].

The motive force of the process of the growth of the center of the new phase is the quantity $[d\Delta F(n)]/dn$, which describes the change in $\Delta F(n)$ depending on n. If for an increase in n the value of $\Delta F(n)$ also increases, i.e. the free energy of the system increases, there is no thermodynamic stimulus for extension of the region occupied by the new phase. We will look into this in greater detail [19, p. 294].

In accordance with the basic laws of the thermodynamics of non-equilibrium states, for a deviation from the equilibrium condition in the system with unchanged external conditions there take place natural processes connected with the increase in entropy. The rate at which the change in entropy occurs may be written down as the sum of the products of conjugate forces X_k and currents I_k [20]:

$$\left(\frac{dS^*}{dt}\right)_{irrev} = \sum_k I_k X_k. \tag{3}$$

Further, we will take

$$I_i = \sum_k L_{ik} X_k, \tag{4}$$

$$\left(\frac{dS^*}{dt}\right)_{irrev} = \sum_{i,k} L_{ik} X_i X_k. \tag{5}$$

The coefficients L_{ik}, which depend on the choice of conjugate forces and currents, are connected with parameters that determine the mechanism of the processes in question. For an appropriate choice of the forces and currents L_{ik} are scalar quantities characterizing in themselves the mobility of atoms in the system and not changing in time. If we confine ourselves to processes taking place at constant temperature and pressure L_{ik} are to be considered as constant quantities.

The irreversible change in entropy dS^*_{irrev} is equal to the change of this quantity in the system and in the surrounding medium:

$$dS^*_{\text{irrev}} = dS^* + dS^*_{\text{s.m}}. \tag{6}$$

Let us assume that the process takes place entirely within the system and the surrounding medium only absorbs heat, maintaining its own temperature; then

$$dS^*_{\text{s.m}} = -\frac{dq}{T}, \tag{7}$$

where dq is the heat liberated in the system:

$$dq = dU_0 + P\,dV. \tag{8}$$

In the present case dU_0 and dV are respectively the change in internal energy and volume of the reacting system (P and T are constant). Thus

$$dS^*_{\text{irrev}} = dS^* - \frac{dU_0 + P\,dV}{T} = \frac{T\,dS^* - dU_0 - P\,dV}{T}. \tag{9}$$

It is well known that the thermodynamic potential

$$G = U_0 + PV - TS^*, \tag{10}$$

and its differential

$$dG = dU_0 + P\,dV - T\,dS^*. \tag{11}$$

Hence

$$dS^*_{\text{irrev}} = -\frac{dG}{T}. \tag{12}$$

As a consequence of the small compressibility of condensed bodies and the relatively small pressures in which they are usually situated (unless otherwise stated):

$$dG \approx dF = dU_0 - T \cdot dS^*.$$

Consequently

$$\left(\frac{dS^*}{dt}\right)_{\text{irrev}} \approx -\frac{1}{T} \cdot \frac{dF}{dt}. \tag{13}$$

The growth of the center of new phase during a phase transformation of the diffusionless type leads to a shifting of the boundary which divides two regions with different free energies. If $d\Delta F(n)$ is the change in free energy of one atom on the phase interface and there are n^* such atoms, then [21]:

$$\left(\frac{dS^*}{dt}\right)_{\text{irrev}} = -\frac{n^*}{T}\frac{d\Delta F(n)}{dt} \,. \tag{14}$$

Under the condition that the process comprises only a change in n

$$\left(\frac{dS^*}{dt}\right)_{\text{irrev}} = -\frac{n^*}{T}\frac{d\Delta F(n)}{dn}\frac{dn}{dt} \,. \tag{15}$$

From formula (4), we have

$$\frac{dn}{dt} = -\frac{L}{T}n^*\frac{d\Delta F(n)}{dn} \,, \tag{16}$$

where $[d\Delta F(n)]/dn$ has the role of motive force of the process. It should be noted that in deriving the expression (16) no assumption regarding the mechanism of the process in question was made. In particular the temperature dependence of the kinetic coefficient L is not clear from the point of view of this theory. However, the thermodynamic account of a phenomenon is a limiting case of the kinetics. It is valid only under definite conditions which are characteristic of small departures of the state of the system from the equilibrium. It is possible to throw light on these conditions from the point of view of the more general theory of absolute rates of reactions [22] using a definite mechanism of the process close to one realized under conditions of normal growth of crystals.

According to the theory of absolute rates of reactions the connection of an atom with the center comprising n atoms takes place through an intermediate configuration corresponding to a larger change in free energy than during the formation of a center comprising n or $(n+1)$ atoms. This intermediate configuration may be realized in different ways, of which one corresponds to the lowest maximum value of the free energy of the system. Such a configuration is called an activated complex. The difference in the free energies of an activated complex and the quantity $\frac{\Delta F(n) + \Delta F(n+1)}{2}$ is denoted by U (Fig. 3) [23].

The entire process of diffusionless phase transformation reduces to a transition of atomic distribution corresponding to the initial state into one characteristic of the new phase. The kinetics of the change in the dimensions of the region occupied by the new phase is determined by the speed at which the atoms situated on the phase interface cross definite energy barriers. With normal kinetics of diffusionless phase transformation individual instances of atoms joining the center or separating from it are consi-