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Abstract

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ON THE THERMODYNAMICS OF PHASE TRANSFORMATIONS IN BINARY ALLOYS

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A phase transformation in a binary alloy, in contrast to phase transformations in a one-component system, is the result of the superposition of two processes: an increase in the volume of the new phase (as in the case of one-component substances) and a redistribution of the components between the phases in contact. In this case the magnitude of the change in free energy is composed of the change in free energy df_c, associated with the transfer of a certain amount of substance from the initial phase with specific free energy f_1 into the new phase with specific free energy f_2 (at constant concentration C), and of the change associated with the redistribution of the components of the alloy with initial concentration C_0 (at constant mass of each phase) df_a. As a result of the redistribution, the phase concentrations are C_1 and C_2, which in the general case are not equal to the equilibrium concentrations.

Each of the quantities df_a and df_c characterizes the change in free energy in two limiting processes: df_a in the process of redistribution of components (a diffusion process—the process of exchange), df_c in the transition from one phase to another without a change in concentration (the process of a phase transformation with capture of atoms of the second component).

Let the total number of atoms in the alloy be N, the number of all atoms in phase I be N_1, and in phase II N_2. The fraction of substance in phase I is $a_1 = N_1/N$, and in phase II $a_2 = N_2/N$. The concentration of atoms of type A in phase I is C_1, in phase II C_2, and in the initial solution C_0 (for substitutional solutions). The condition of conservation of matter gives the relations:

$$a_1 C_1 + a_2 C_2 = C_0, \qquad a_1 + a_2 = 1. \tag{1}$$

In the case of interstitial solutions, the same relations are obtained if a_1 and a_2 denote the fraction of solvent atoms in both phases, and C_1 and C_2 the ratio of the number of impurity atoms to solvent atoms in both phases. For a two-phase system

$$f = a_1 f_1(C_1) + a_2 f_2(C_2). \tag{2}$$

Of the four variables (C_1, C_2, a_1, and a_2), two are independent variables, for example a_2 and C_2 (the other two are determined by relations (1)). Expressing C_1 and a_1 in terms of C_2 and a_2, one may represent the quantity f as a function only of C_2 and a_2. The differential of the function f transformed in this way has the form

$$df = a_2 \left(\frac{\partial f_2}{\partial C_2} - \frac{\partial f_1}{\partial C_1} \right) dC_2 + \left[f_2(C_2) - f_1(C_1) + (C_1 - C_2) \frac{\partial f_1}{\partial C_1} \right] da_2. \quad (3)$$

Equation (3) makes it possible to analyze a number of possible cases of partial equilibrium and phase transitions.*

* In the present work the curvature of the phase-boundary surface is not taken into account. In addition, it is assumed that the concentration in each phase is homogeneous.

a) The amount of each phase remains unchanged (the phase boundary does not move). This case corresponds to:

$$a_2 = \text{const}, \qquad da_2 = 0. \quad (4)$$

The equilibrium condition for the system, $df = 0$, is satisfied if

$$\frac{\partial f_1}{\partial C_1} = \frac{\partial f_2}{\partial C_2}. \quad (5)$$

Consequently, condition (5) corresponds to the case in which redistribution of the components in the coexisting phases occurs without changing the ratio of their volumes.

Conditions (4) and (5) determine the concentrations at which the redistribution (exchange) process ceases. These concentrations depend on the ratio of the volumes of the coexisting phases (the quantity a_2).

b) The concentration of the second phase remains unchanged (the new phase grows without a change in composition). In this case

$$C_2 = \text{const}, \qquad dC_2 = 0. \quad (6)$$

The condition $df = 0$ is satisfied if

$$f_2(C_2) - f_1(C_1) + (C_1 - C_2) \frac{\partial f_1}{\partial C_1} = 0. \quad (7)$$

Equations (6) and (7) are the equilibrium equations for this case. When $C_2 = C_0$, it follows from (1) that $C_1 = C_0$ as well (the concentrations of the phases are identical), and condition (7) takes the form

$$f_1(C_0) = f_2(C_0). \tag{8}$$

Condition (8) determines the temperature T_0 at which both phases with the initial concentration are in equilibrium, and below which a transition without a change in concentration is thermodynamically favorable (see ([1],[2])).

It should be noted that, in this case, equality (5) does not apply.

c) The phase transition proceeds with a change both in the amount and in the composition of each phase. The equilibrium condition of the system, $df = 0$, in this general case is satisfied if both multipliers at dC_2 and da_2 are simultaneously equal to zero. The equations thus obtained can be written in the form:

$$\frac{\partial f_1}{\partial C_1} = \frac{\partial f_2}{\partial C_2}, \qquad f_1(C_1) - C_1\frac{\partial f_1}{\partial C_1} = f_2(C_2) - C_2\frac{\partial f_2}{\partial C_2}. \tag{9}$$

Equations (9) are the well-known conditions of complete phase equilibrium in a binary system.

Let us note that conditions (4) and (5) will correspond to a minimum of the free energy when $\partial^2 f/\partial C_2^2 > 0$, conditions (6) and (7) when $\partial^2 f/\partial a_2^2 > 0$, and, finally, condition (9) when

$$\frac{\partial^2 f}{\partial C_2^2} > 0, \qquad \frac{\partial^2 f}{\partial a_2^2} > 0, \qquad \frac{\partial^2 f}{\partial C_2^2}\frac{\partial^2 f}{\partial a_2^2} - \left(\frac{\partial^2 f}{\partial C_2 \partial a_2}\right)^2 > 0. \tag{10}$$

If the system is not in a state of equilibrium, then one of the three processes described above will occur. The rate of these processes depends on the degree to which the free energy of the system, Δf, deviates from its equilibrium value. The quantity Δf is the energetic driving force of the process.

In the general case, the rate of the process of transition to the equilibrium state will depend both on the quantity $\Delta f_a = (\partial f_2/\partial C_2 - \partial f_1/\partial C_1)a_2$, corresponding to the purely diffusional exchange process, and on the quantity $\Delta f_c = f_2(C_2) - f(C_1) + (C_1 - C_2)\partial f_1/\partial C_1$, which stimulates the growth process in which the concentration of the precipitating phase remains unchanged.

The rates of each of the processes can be estimated by considering, as is done in works ([3],[4]), the rate of overcoming the energy barrier q during the transition from phase I to phase II and the rate of overcoming the energy barrier $q + \Delta f$ during the reverse transition.

The rate of the process of redistribution of components (the exchange process) between the coexisting phases must be equal to the difference between the rates of transition from phase I to phase II and from phase II to I:

$$V_{\text{dif}} = A_{\text{dif}} e^{-q_{\text{dif}}/kT} \left[1 - e^{-\Delta f_a/kT}\right], \quad (11)$$

where A_{dif} is a coefficient including the diffusion coefficient; q_{dif} is the activation energy of the process; k is Boltzmann' s constant; T is the temperature (°K).

For the rate of the process without a change in the composition of the second phase, we similarly obtain

$$V_{\text{capt}} = A_{\text{capt}} e^{-q_{\text{capt}}/kT} \left[1 - e^{-\Delta f_c/kT}\right], \quad (12)$$

where A_{capt} is a coefficient including the mobility of atoms in the process with capture; q_{capt} is the activation energy of the process.

The question of the conditions under which a phase transformation of an alloy proceeds without a change in composition is of considerable interest. To establish these conditions it is necessary to compare the rates $V_{\text{dif}}(C_0)$ and $V_{\text{capt}}(C_0)$ for the case in which both phases have one and the same composition $C_1 = C_2 = C_0$. In this case the rate of the process of redistribution of components between coexisting phases of the same composition is determined from (11). The rate of the process of phase transition without a change in composition is determined from (12).

Whether the process will proceed without a change in concentration (with capture) or will be accompanied by a change in composition is determined by the ratio of the rates $V_{\text{dif}}(C_0)$ and $V_{\text{capt}}(C_0)$. Each of these rates varies with temperature, and the relation between them is different in different temperature intervals.

In the temperature region above T_0 (in the interval $T_0 - T_l$, where T_l is the temperature of the upper boundary of the two-phase region), the quantity $\Delta f_c(C_0)$ is negative (the free energy of phase II is higher than that of phase I) and $V_{\text{capt}}(C_0) < 0$. If phase I is the initial phase, this means that in the temperature interval under consideration a transition without a change in concentration cannot occur, and only a phase transition accompanied by redistribution of components is possible. At the temperature T_0, $\Delta f_c(C_0) = 0$ and $V_{\text{capt}}(C_0) = 0$ (see (12)).

At temperatures below T_0 both processes may proceed; both lead to a decrease in the free energy of the entire system. However, the rates of these processes are different, and the leading one will be that whose rate at the given temperature is greater. At some temperature below T_0 the two rates prove to be equal. Let us denote this temperature by T_D. In the temperature interval $T_0 - T_D$, the process of redistribution of components proceeds faster, and it is the leading one.

At temperatures below T_D, the process of phase transition without a change in composition proceeds faster, and it is the leading one.

At equilibrium of both phases, $\Delta f_a = 0$ and $\Delta f_c = 0$, and the rates of both processes are equal to zero (see (11) and (12)).

Since the mobility of atoms in a phase transition (rearrangement of the lattice) is greater than the mobility in redistribution of components, the temperature T_D corresponds to the condition $\Delta f_a > \Delta f_c$, and this inequality is the stronger, the more the factors before the brackets in (11) and (12) differ.

Thus, from thermodynamic consideration it follows that the temperature region below the upper boundary of phase equilibrium T_l (when considering the process of transition from the high-temperature phase to the low-temperature one) can be divided into three intervals: 1) $T_l - T_0$, where the process of phase transition with redistribution of components is energetically favorable; 2) $T_0 - T_D$, where two processes are possible, but the process of phase transition with redistribution of components is the faster; and 3) below T_D,

where the more rapid process is the phase transformation without a change in composition.

The position of the point T_D relative to the equilibrium curves depends on the ratio of the quantities q_{diff}, q_{capt} to a_2, and on the character of the dependence of the free energy of both phases on temperature and concentration for the given binary system, as well as on the ratio of the coefficients A_{diff} and A_{capt}. The curve of the dependence of T_D on concentration lies below T_0. At $a_2 = 0$ the curve T_D merges with the curve T_0.

Depending on the nature of the alloy and the magnitude of a_2, the point T_D may be above or below the temperature T_S (T_S is the temperature of the lower boundary of the two-phase region). In the case where $T_D < T_S$, there is a temperature interval $T_S - T_D$ in which the homogeneous second phase is stable, but the transformation process proceeds in two stages: the first stage is a phase transformation with redistribution of the components; the second stage is equalization of the composition.

In work ([5]) it was shown experimentally that the crystallization process of an alloy of Cu with 50% Ni proceeds differently in the temperature intervals $T_l - T_0$, $T_0 - T_S$, and below T_S. This effect agrees with the conclusions of the present work.

For a certain character of the dependence of the free energy on composition and temperature, the point T_D may lie at very low temperatures. In such cases observation of the transformation process without a change in concentration will be difficult. This may possibly explain the results of work ([6]).

When $T_0 > T_D > T_S$, then in the interval $T_D - T_S$, where the two-phase state will be stable, the process proceeds in two stages: the first stage is a phase transformation without a change in concentration; the second stage is decomposition of the metastable II phase into two phases. When the transformation process proceeds at temperatures below T_D, but close to it, the "capture" process may be accompanied by a process of exchange through the moving boundary. In this case the concentration of the matrix changes, and the ratio of the rates of the processes of "capture" and "exchange" also changes. For some volume of the new phase the exchange process may become the leading one. As a result of such a mixed process, inhomogeneity of the composition and of the metallographic structure of the alloy should be expected.

It is necessary to note that when the transformation process is accompanied by an appreciable redistribution of the components, for a complete description of the process it is necessary to take into account the removal of matter from the boundary of the growing phase, which may limit the rate of the transformation process ([4]).

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Note: Figure translations are in progress. See original paper for figures.