INVESTIGATION OF THE BINODAL POINT OF BINARY AND TERNARY ALLOYS

YU. V. SHERSTENNIKOV

Dnipropetrovsk State Financial-Economic Institute
(12, Arzhanova Str., Dnipropetrovsk 49083, Ukraine)

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Interrelation between a location of the binodal point on a phase diagram and the energy parameters of the theory is established. The decomposition dome for the Cu—Rh system is calculated near the critical point.

The statistical theory of alloy decomposition (see [1]) is developed now insufficiently. For example, the theory results in the conclusion that a dome of decomposition on the diagram $T - c$ is symmetric. On the real phase diagrams, the dome of decomposition is, as a rule, asymmetric. A point on the binodal is moved to high-melting component, which has smaller compressibility and higher modulus of elasticity. In the given paper, the following model is used for the research of a binodal point. The free energy is calculated within the framework of the Bragg-Williams approximations; the potentials of the interatomic interaction in a vicinity of the critical point are considered as linear functions of concentration. The purpose of the paper is to establish the interrelation between a location of the binodal point on the phase diagram and the energy parameters of the theory.

1. Ternary Alloy. Conditions at the Critical Point

Let's consider a ternary substitution A—B—D alloy. The alloy has a fcc or bcc lattice and can be in a biphase state. The numbers of atoms of the first and second phases are equal to N_1 and N_2, respectively. The complete number of atoms is equal to $N = N_1 + N_2$. The concentrations of a component a $(a = A, B, D)$ in the first and second phases are designated, respectively, as p_a and q_a. The average concentration of the a component in the alloy is c_a. The parts of atoms of the first and second phases are

$$\nu_1 = \frac{N_1}{N}, \quad \nu_2 = \frac{N_2}{N}. \tag{1}$$

Eight parameters p_a, q_a, ν_1, ν_2 are connected by five equations:

$$\nu_1 + \nu_2 = 1, \quad \nu_1 p_A + \nu_2 q_A = c_A,$$

$$\nu_1 p_D + \nu_2 q_D = c_D, \quad p_A + p_B + p_D = 1,$$

$$q_A + q_B + q_D = 1. \tag{2}$$

As independent concentrations, we consider p_A, p_D, and q_A. The concentration q_D can be derived from (2) as

$$q_D = \frac{c_D - p_D}{c_A - p_A}(q_A - p_A) + p_D. \tag{3}$$

The concentrations c_a $(a = A, B, D)$ are considered given. The free energy of a homogeneous phase with the concentrations c_A, c_B, c_D will be a function of two concentrations: $F = F(c_A, c_D)$. Further, we designate the variable set (c_A, c_D) by one index $c = (c_A, c_D)$. Then we have $c = p = (p_A, p_D)$ for the first phase and $c = q = (q_A, q_D)$ for the second one. The free energy of a homogeneous phase per atom is

$$F(c) = \frac{z}{2}[w_{AB}c_A c_B + w_{AD}c_A c_D + w_{BD}c_B c_D] +$$

$$+\frac{z}{2}[v_{AA}c_A + v_{BB}c_B + v_{DD}c_D] - TS, \tag{4}$$

$$S = -k_{\rm B}\Big[c_A \ln c_A + c_D \ln c_D +$$

$$+(1 - c_A - c_D)\ln(1 - c_A - c_D)\Big],$$

where z is the number of the nearest neighbours in a lattice;

$$w_{ab} = v_{ab} - \frac{1}{2}(v_{aa} + v_{bb}). \tag{5}$$

Further, we take $k_{\rm B} = 1$. The concentration of atoms at the critical point is designated as $r = (r_A, r_D)$.

X-rays data and the results of the approximation of coherent potentials show the expressed concentration dependence of the parameters of interatomic interactions in Fe—Al alloys [2]. The account of the parameters of interatomic interactions for the Cu—Fe system is done in [3]. The concentration dependence of interaction potentials in [3] was chosen linear. We consider that the energy v_{ab} depends on the concentration of atoms A and D in the given phase as

$$v_{ab} = V_{ab} + A_{ab}\,(c_A - r_A) + D_{ab}\,(c_D - r_D) \tag{6}$$

or

$$v_{ab} = U_{ab} + A_{ab}c_A + D_{ab}c_D,$$

where

$$U_{ab} = V_{ab} - A_{ab}r_A - D_{ab}r_D.$$

Equation (5) is now of the form

$$w_{ab} = u_{ab} + a_{ab}c_A + d_{ab}c_D, \tag{7}$$

where

$$u_{ab} = U_{ab} - \frac{1}{2}(U_{aa} + U_{bb}),$$

$$a_{ab} = A_{ab} - \frac{1}{2}(A_{aa} + A_{bb}),$$

$$d_{ab} = D_{ab} - \frac{1}{2}(D_{aa} + D_{bb}).$$

With regard for (7), expressions (4) read (keeping only the non-linear contribution in the concentration in F, as the linear contribution is insignificant further):

$$F(c) = a_1c_A^3 + a_2c_A^2c_D + a_3c_Ac_D^2 + a_4c_D^3 +$$

$$+b_1c_A^2 + b_2c_Ac_D + b_3c_D^2 - TS. \tag{8}$$

Here,

$$a_1 = -\frac{z}{2}a_{AB},$$

$$a_2 = \frac{z}{2}(-d_{AB} - a_{AB} + a_{AD} - a_{BD}),$$

$$a_3 = \frac{z}{2}(-d_{AB} + d_{AD} - d_{BD} - a_{BD}),$$

$$a_4 = -\frac{z}{2}d_{BD},$$

$$b_1 = \frac{z}{2}(a_{AB} - u_{AB}),$$

$$b_2 = \frac{z}{2}(d_{AB} + a_{BD} - u_{BD}),$$

$$b_3 = \frac{z}{2}(d_{BD} - u_{BD}). \tag{9}$$

The chemical potentials of components of a ternary alloy are defined by

$$\mu_A(c) = F(c) + (1 - c_A)\frac{\partial F(c)}{\partial c_A} - c_D\frac{\partial F(c)}{\partial c_D},$$

$$\mu_B(c) = F(c) - c_A\frac{\partial F(c)}{\partial c_A} - c_D\frac{\partial F(c)}{\partial c_D},$$

$$\mu_D(c) = F(c) - c_A\frac{\partial F(c)}{\partial c_A} + (1 - c_D)\frac{\partial F(c)}{\partial c_D}.$$

When $T < T_0$, the condition of balance of two phases with the concentrations p and q has the form

$$\mu_a(p) - \mu_a(q) = 0. \tag{10}$$

Designating the left part of relation (10) through f_a, we get the system of three equations

$$f_a(p, q, T) = 0. \tag{11}$$

Differentiating (11) with respect to p_A, we obtain the system of equations

$$\frac{\partial f_a}{\partial q_A}\frac{\partial q_A}{\partial p_A} + \frac{\partial f_a}{\partial p_D}\frac{\partial p_D}{\partial p_A} + \frac{\partial f_a}{\partial T}\frac{\partial T}{\partial p_A} = -\frac{\partial f_a}{\partial p_A} - \frac{\partial f_a}{\partial q_D}\lambda. \tag{12}$$

As we will be further interested in the limit $T \to T_0$ ($p \to r$, $q \to r$), we use relation (A5) (see Appendix) in (12). At the critical point, we have

$$\frac{\partial T}{\partial r_A} = 0. \tag{13}$$

Relation (12) yields

$$\frac{\partial T}{\partial p_A} = -\frac{\Delta_1}{\Delta}, \tag{14}$$

where

$$\Delta = \begin{vmatrix} \frac{\partial f_A}{\partial q_A} & \frac{\partial f_A}{\partial p_D} & \frac{\partial f_A}{\partial T} \\ \frac{\partial f_B}{\partial q_A} & \frac{\partial f_B}{\partial p_D} & \frac{\partial f_B}{\partial T} \\ \frac{\partial f_D}{\partial q_A} & \frac{\partial f_D}{\partial p_D} & \frac{\partial f_D}{\partial T} \end{vmatrix},$$

$$\Delta_1 = \begin{vmatrix} \frac{\partial f_A}{\partial q_A} & \frac{\partial f_A}{\partial p_D} & \frac{\partial f_A}{\partial p_A} + \frac{\partial f_A}{\partial q_D}\lambda \\ \frac{\partial f_B}{\partial q_A} & \frac{\partial f_B}{\partial p_D} & \frac{\partial f_B}{\partial p_A} + \frac{\partial f_B}{\partial q_D}\lambda \\ \frac{\partial f_D}{\partial q_A} & \frac{\partial f_D}{\partial p_D} & \frac{\partial f_D}{\partial p_A} + \frac{\partial f_D}{\partial q_D}\lambda \end{vmatrix}.$$

The following decomposition takes place near r:

$$\frac{\partial f_a}{\partial p_A} = \frac{\partial f_a}{\partial q_A} + \frac{\partial^2 f_a}{\partial q_A^2}(p_A - q_A),$$

$$\frac{\partial f_a}{\partial q_D} = \frac{\partial f_a}{\partial p_D} + \frac{\partial^2 f_a}{\partial p_D^2}(q_D - p_D). \tag{15}$$

In view of (15), it is possible to write down

$$\Delta = A_1\frac{\partial f_A}{\partial T} + A_2\frac{\partial f_B}{\partial T} + A_3\frac{\partial f_D}{\partial T}, \tag{16}$$

$$\Delta_1 = A_1\left[\lambda^2\frac{\partial^2 f_A}{\partial p_D^2} - \frac{\partial^2 f_A}{\partial q_A^2}\right]\delta +$$

$$+A_2\left[\lambda^2\frac{\partial^2 f_B}{\partial p_D^2} - \frac{\partial^2 f_B}{\partial q_A^2}\right]\delta + A_3\left[\lambda^2\frac{\partial^2 f_D}{\partial p_D^2} - \frac{\partial^2 f_D}{\partial q_A^2}\right]\delta, \tag{17}$$

where $\delta = q_A - p_A$. In (17), we use relation (A6). We note that the determinants A_1, A_2, A_3 have a finite value as $T \to T_0$. By (A7), the determinant Δ has the order δ. Thus, since the right part of equality (14) turns in zero as $T \to T_0$, the expression in square brackets in (17) should turns in zero in this limit as well. The analysis of these expressions shows that it is necessary that the conditions

$$\lim_{p\to r}\frac{\partial^2 f_a}{\partial p_D^2} = \lim_{q\to r}\frac{\partial^2 f_a}{\partial q_A^2} = 0. \tag{18}$$

be satisfied. Analyzing three first relations in (A8) in the same limit as in (18), we find

$$\frac{\partial^2 F}{\partial r_A^2} = 0, \quad \frac{\partial^3 F}{\partial r_A^3} = 0, \quad \frac{\partial^3 F}{\partial r_D \partial r_A^2} = 0. \tag{19}$$

Similarly, we obtain from three last relations (A8) that

$$\frac{\partial^2 F}{\partial r_D^2} = 0, \quad \frac{\partial^3 F}{\partial r_D^3} = 0, \quad \frac{\partial^3 F}{\partial r_A \partial r_D^2} = 0. \tag{20}$$

The equality of the mixed derivative of the free energy (8) in (19) and (20) to zero leads to $a_2 = a_3$. Let's designate $a = a_2 = a_3$. Then relations (8), (19), and (20) yield the system of five equations

$$6a_1 r_A + 2ar_D + 2b_1 + T_0\left(\frac{1}{r_A} + \frac{1}{1 - r_A - r_D}\right) = 0,$$

$$6a_4 r_D + 2ar_A + 2b_3 + T_0\left(\frac{1}{r_D} + \frac{1}{1 - r_A - r_D}\right) = 0,$$

$$6a_4 + T_0\left(-\frac{1}{r_D^2} + \frac{1}{(1 - r_A - r_D)^2}\right) = 0,$$

$$6a_1 + T_0\left(-\frac{1}{r_A^2} + \frac{1}{(1 - r_A - r_D)^2}\right) = 0 \quad ,$$

$$2a + T_0\frac{1}{(1 - r_A - r_D)^2} = 0. \tag{21}$$

2. Analysis of the Conditions at the Critical Point

If the coordinates of the critical point (r_A, r_D, T_0) are considered known, the energy parameters a, a_1, a_4, b_1, b_3 can be found from (21). Equations (19), (20) impose no restriction on the parameter b_2. We write three last equations in system (21) as

$$t_0 = (1 - r_A - r_D)^2,$$

$$\frac{t_0}{r_A^2} = 1 - 3a_1^*, \quad \frac{t_0}{r_D^2} = 1 - 3a_4^*, \tag{22}$$

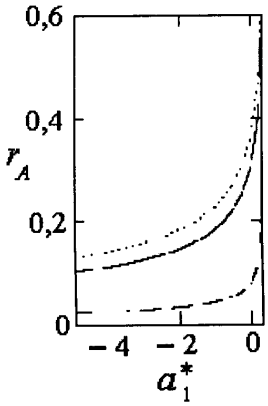

Fig. 1. Plots of r_A vs a_1^*. Solid line — $a_4^* = 0.1$, dashed — $a_4^* = 0.33$, dotted — $a_4^* = -0.4$

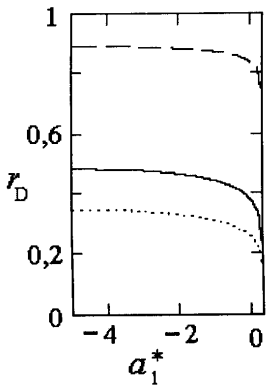

Fig. 2. Plots of r_D vs a_1^*. Solid line — $a_4^* = 0.1$, dashed — $a_4^* = 0.33$, dot — $a_4^* = -0.4$

where $t_0 = -\frac{T_0}{2a}$, $a_1^* = \frac{a_1}{a}$, $a_4^* = \frac{a_4}{a}$. It is seen from (22) that $t_0 > 0$ and $a_1^* < \frac{1}{3}$, $a_4^* < \frac{1}{3}$. Relations (22) yield

$$r_A = \frac{1}{1 + y + \sqrt{1 - 3a_1^*}}$$

$$r_D = y r_A,$$

$$t_0 = [1 - (1 + y) r_A]^2, \tag{23}$$

where $y = \sqrt{\frac{1-3a_1^*}{1-3a_4^*}}$. The dependences r_A, r_D, t_0 on a_1^* are shown in Figs. 1, 2, 3 at various values of a_4^*. It is seen from Fig. 1 that r_A increases up to 1 as a_1^* approaches $1/3$. When a_4^* grows, r_A decreases. It follows from Fig. 2 that r_D decreases to zero, when a_1^* approaches $1/3$. When a_4^* grows, r_D increases. From Fig. 3, we see that t_0 decreases to zero as $a_1^* \to 0$. Thus, the value a_1^*=1/3 is the special point for parameter a_1^*. Similarly from system of the equations (23), one can make a conclusion that the value a_4^*=1/3 is the special point for the parameter a_4^*.

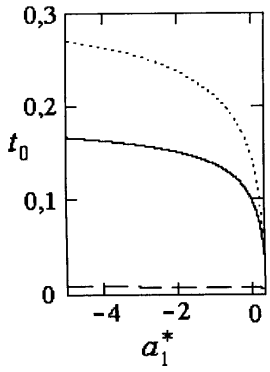

Fig. 3. Plots of r_0 vs a_1^*. Solid line — $a_4^* = 0.1$, dashed — $a_4^* = 0.33$, dotted — $a_4^* = -0.4$

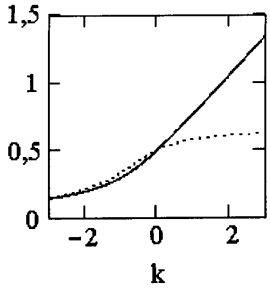

Fig. 4. Plots of $T_0/\mid a_2 \mid$ and c_0 vs k. Solid line — $T_0/\mid a_2 \mid$, dotted — c_0

3. Binary Alloy

One of the widespread methods of construction of the phase diagrams of ternary alloys is a method based on the use of the phase diagrams of boundary binary alloys. We execute the comparison of the above-stated theory to the experimental data on binary alloys.

Let's consider a binary substitution A—B alloy. The alloy has a fcc or bcc lattice and can be in the biphase state. In this case according to (8), the free energy of the alloy per atom is

$$F(c) = a_2 c^2 + a_3 c^3 - TS,$$

$$S = -\{c \ln c + (1 - c) \ln(1 - c)\}, \tag{24}$$

where c is the concentration of the B component in the alloy;

$$a_2 = z\left[\frac{A_{BB} - A_{AA}}{2} - W + (1 + c_0)u\right], \quad a_3 = -zu,$$

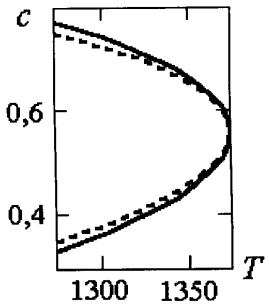

Fig. 5. Decomposition dome for the Cu—Rh system. Solid line — theory, dotted line — experiment

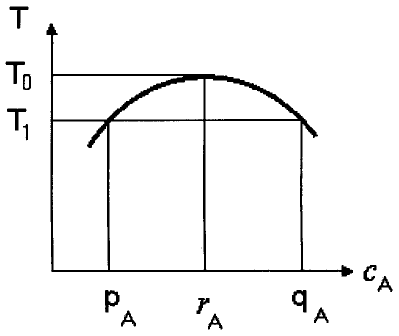

Fig. 6. Decomposition dome near the critical point

$$W = V_{AA} - \frac{1}{2}(V_{AA} - V_{BB}),$$

$$u = A_{AA} - \frac{1}{2}(A_{AA} - A_{BB}).$$

Taking $r_A = r_D = c_0$ in (22), we obtain

$$c_0 = \begin{cases} \frac{1}{3}\left[1 - \frac{1}{k} + \sqrt{\left(1 - \frac{1}{k}\right)^2 + \frac{3}{k}}\right], k > 0, \\ \frac{1}{3}\left[1 - \frac{1}{k} - \sqrt{\left(1 - \frac{1}{k}\right)^2 + \frac{3}{k}}\right], k < 0; \end{cases} \quad (25)$$

$$\frac{T_0}{a_2} = -2(1 + kc_0)c_0(1 - c_0),$$

where $k = \frac{3a_3}{a_2}$. The dependences of c_0 and $\frac{T_0}{|a_2|}$ $(a_2 < 0)$ on k are shown in Fig. 4. Let's notice that, at $k = 0$ (i.e., $a_3 = 0$), relation (25) yields that $c_0 = 0.5$, as it should be in the absence of the concentration dependence of interatomic potentials.

The equality of the chemical potentials of components in the first and second phases allows us to calculate a dome of phase decomposition. The result of calculations of a dome of phase decomposition for the Cu—Rh system is shown in Fig. 5. The a_2 and a_3 parameters in the free energy (24) were adjusted to the coordinates of the critical point (c_0, T_0). Thus, the values of these parameters in terms of k_B are $a_2 = -2.026 \cdot 10^3$, $a_3 = -456.3$ (for the Cu—Rh system). The agreement with experiment is satisfactory.

It is possible to make the following conclusions. The account of the concentration dependence of the potentials of interatomic interaction allows executing the adequate research of a decomposition dome near the critical point and to connect the coordinates of the critical point with the energy parameters of the theory.

APPENDIX

1. The equilibrium diagram of a separating ternary alloy represents a dome in space (c_A, c_D, T). Let's consider the section of a decomposition dome by a plane $c_D = r_D$ (see Fig. 6). The function $T = T(c_A)$ may be expanded in a serious in a vicinity of r_A:

$$T = T_0 + \frac{1}{2}T''(r_A)(c_A - r_A)^2 +$$

$$+\frac{1}{6}T'''(r_A)(c_A - r_A)^3 + ... \quad (A1)$$

As $T \to T_0$, it is possible to be limited in (A1) by the second degree with respect to $(c_A - r_A)$. Then, the curve $T(c_A)$ (see Fig. 6) will be a parabola. Hence, the following equalities will hold:

$$q_A - r_A = r_A - p_A,$$

or

$$q_A - p_A = 2(r_A - p_A). \quad (A2)$$

Similarly, we prove the following equality:

$$q_D - p_D = 2(r_D - p_D). \quad (A3)$$

From relation (3), which is written down for $c = r$, we find

$$\frac{\partial q_D}{\partial p_A} = \frac{r_D - p_D}{r_A - p_A}\left[\frac{q_A - p_A}{r_A - p_A} - 1\right],$$

which gives, with regard for (A2),

$$\frac{\partial q_D}{\partial p_A} = \frac{r_D - p_D}{r_A - p_A}. \quad (A4)$$

Let's assume that

$$\lambda = \lim_{T \to T_0 - 0} \frac{r_D - p_D}{r_A - p_A} \quad .$$

Then, as $T \to T_0$, we get

$$\frac{\partial q_D}{\partial p_A} = \lambda. \quad (A5)$$

The parameter λ is determined by the energy parameters of the theory, i.e., by a_i, b_k (9). Relations (A2) and (A3) yield

$$\lim_{T \to T_0 - 0} \frac{q_D - p_D}{q_A - p_A} = \lambda. \quad (A6)$$

2. Consider the derivative with respect to T.

$$\frac{\partial f_A}{\partial T} = \frac{\partial \mu_A(p)}{\partial T} - \frac{\partial \mu_A(q)}{\partial T} = T[S(q) - S(p)] +$$

$$+T(1-c_A)\left[S'_A(q) - S'_A(p)\right] - Tc_D\left[S'_D(q) - S'_D(p)\right],$$

where $S'_a(c) = \frac{\partial S(c)}{\partial c_a}$. The values in square brackets have the order δ. The similar estimate takes place for the derivatives f_B and f_D with respect to T.

Thus, we obtain

$$\frac{\partial f_a}{\partial T} \sim \delta. \tag{A7}$$

3. Consider the derivative with respect to the concentration:

$$\frac{\partial^2 f_A}{\partial q_A^2} = \frac{\partial^2 F(q)}{\partial q_A^2} - (1-q_A)\frac{\partial^3 F(q)}{\partial q_A^3} + q_D \frac{\partial^3 F(q)}{\partial q_D \partial q_A^2},$$

$$\frac{\partial^2 f_B}{\partial q_A^2} = \frac{\partial^2 F(q)}{\partial q_A^2} + q_A \frac{\partial^3 F(q)}{\partial q_A^3} + q_D \frac{\partial^3 F(q)}{\partial q_D \partial q_A^2},$$

$$\frac{\partial^2 f_D}{\partial q_A^2} = \frac{\partial^2 F(q)}{\partial q_A^2} + q_A \frac{\partial^3 F(q)}{\partial q_A^3} - (1-q_D)\frac{\partial^3 F(q)}{\partial q_D \partial q_A^2},$$

$$\frac{\partial^2 f_A}{\partial p_D^2} = (1-p_A)\frac{\partial^3 F(p)}{\partial p_A \partial p_D^2} - \frac{\partial^2 F(p)}{\partial p_D^2} - p_D \frac{\partial^3 F(p)}{\partial p_D^3},$$

$$\frac{\partial^2 f_B}{\partial p_D^2} = -p_A \frac{\partial^3 F(p)}{\partial p_A \partial p_D^2} - \frac{\partial^2 F(p)}{\partial p_D^2} - p_D \frac{\partial^3 F(p)}{\partial p_D^3},$$

$$\frac{\partial^2 f_D}{\partial p_D^2} = -p_A \frac{\partial^3 F(p)}{\partial p_A \partial p_D^2} - \frac{\partial^2 F(p)}{\partial p_D^2} + (1-p_D)\frac{\partial^3 F(p)}{\partial p_D^3}. \tag{A8}$$

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ДОСЛІДЖЕННЯ КРИТИЧНОЇ ТОЧКИ БІНОДАЛІ ДВО- І ТРИКОМПОНЕНТНИХ СПЛАВІВ

Ю.В. Шерстенников

Р е з ю м е

Встановлено взаємозв'язок між положенням критичної точки бінодалі на діаграмі станів з енергетичними параметрами теорії. Для системи Cu—Rh розраховано купол розшарування поблизу критичної точки.