ON BINARY SUBSTITUTIONAL SOLID SOLUTIONS BETWEEN NONISOMORPHOUS CRYSTALS

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ON BINARY SUBSTITUTIONAL SOLID SOLUTIONS BETWEEN NONISOMORPHOUS CRYSTALS

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Let us consider two crystalline substances A^* and B^*, really existing or fictitious modifications of which A and B are isomorphous to the substitutional solid solution $A_{1-x}B_x$. Naturally, the following cases are possible: $A^* = A$, $B^* = B$; $A^* = A$, $B^* \neq B$; $A^* \neq A$, $B^* = B$; $A^* \neq A$, $B^* \neq B$.

Let the atoms of the solid solution be arranged in n sublattices, in each of which there are m_i equivalent positions. In accordance with this, we shall represent the isomorphous components A and B in the form of a table

$$\mathrm{R} = \{\mathrm{R}_{ji}\} = \{r_{1i}, \dots, r_{ji}, \dots, r_{q_i i}\}. \tag{1}$$

$\mathrm{R} = A, B;\ r = a, b;\ i = 1, \dots, n$ is the number of the sublattice; q_i is the greatest number of kinds of atoms of component R; r_{ji} is the number of atoms of kind R_{ji}, with

$$\sum_{j=1}^{q_i} r_{ji} = m_i. \tag{2}$$

In the general case one may assume that the first k_i kinds of atoms A_i and B_i, respectively, are equivalent. Assuming further that the i-th sublattice of the solution is formed by atoms of the i-th sublattices of A and B, we obtain

$$A_{1-x}B_x = \{\Delta_{1i}x + a_{1i}, \dots, \Delta_{k_i i}x + a_{k_i i},\ (1-x)a_{k_i+1,i}, \dots, (1-x)a_{q_i i}, \\ xb_{k_i+1,i}, \dots, xb_{q_i i}\}, \tag{3}$$

where $\Delta_{ji} = b_{ji} - a_{ji}$.

The free energy of the solution is

$$\Phi(x) = \sum_{s=0} \alpha_s x^s - T\Delta S(x). \tag{4}$$

Here the first term corresponds to the change in internal energy, $\alpha_0 = \Phi(0) + T\Delta S(0)$; $\alpha_1 x$ and $\alpha_2 x^2$ account sufficiently well for the energies of mixing and of elastic deformations associated with substitution, so that usually one is limited to terms with $s \leq 2$ (^{1}).

$\Delta S(x)$ is the configurational entropy, equal in the case of disordered solid solutions to

$$\Delta S = k \ln \prod_{i=1}^{n} (Nm_i)! \Big/ \prod_{i=1}^{n} \left\{ \prod_{j=1}^{k_i} [N(\Delta_{ji} x + a_{ji})]! \prod_{j=k_i+1}^{q_i} [N a_{ji}(1-x)]! \, [N b_{ji} x]! \right\}. \tag{5}$$

The limiting solubilities x_1 and x_2 (see Fig. 1) are determined from the known equations (^{1})

$$\Phi_{A^*} - \Phi(x_1) = -x_1 \, \partial\Phi(x)/\partial x\big|_{x=x_1}; \tag{6}$$

$$\Phi_{B^*} - \Phi(x_2) = (1-x_2) \, \partial\Phi(x)/\partial x\big|_{x=x_2}. \tag{7}$$

Substituting (4) and (5) into (6) and (7) and expressing a_0 through $\Phi_A = \Phi(0)$, or $\Phi_B = \Phi(1)$, we obtain:

$$\varphi_A = \frac{\Phi_{A^*} - \Phi_A + \alpha_2 x_1^2}{RT} = \sum_{i=1}^{n} \left\{ \sum_{j=1}^{k_i} a_{ji} \ln(x_1 \Delta_{ji} + a_{ji}) + \sum_{j=k_i+1}^{q_i} a_{ji} \ln(1-x_1) a_{ji} - \sum_{j=1}^{q_i} a_{ji} \ln a_{ji} \right\}; \tag{8}$$

$$\varphi_B = \frac{\Phi_{B^*} - \Phi_B + \alpha_2 (1-x_2)^2}{RT} = \sum_{i=1}^{n} \left\{ \sum_{j=1}^{k_i} b_{ji} \ln(x_2 \Delta_{ji} + a_{ji}) + \sum_{j=k_i+1}^{q_i} b_{ji} \ln x_2 b_{ji} - \sum_{j=1}^{q_i} b_{ji} \ln b_{ji} \right\}. \tag{9}$$

The modifications A and B that are isomorphic to the solid solution can be selected easily if one knows the principal features of the structure of the solution, even in the case where these modifications do not actually exist or are unknown. In this case it may turn out that the number of positions in the i-th sublattice of the solution, m_i, is greater than the number of atoms in the i-th sublattice of A and B. Such a situation is characteristic of substitution-subtraction solutions.

Figure 1. Diagram illustrating the possibility of forming solid substitution solutions between isomorphic modifications A and B

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This means that there are vacancies among R_i, the number of which satisfies relation (2), written in the form

$$\sum_{j=1}^{q_i-1} r_{ji} + r_{\text{vac},\,i} = m_i.$$

If the temperature interval under consideration is substantially lower than the temperature of the $R^* \to R$ transition, T_{0R}, then, as is known,

$$\Phi_R = \Phi_{R^*} = Q_R(T_{0R} - T)/T_{0R}, \tag{10}$$

where Q_R is the latent heat of the transition.

Fig. 1. Diagram illustrating the possibility of formation of solid substitution solutions between isomorphic modifications A and B

In the special case where the atoms of the i-th sublattices A_i and B_i have close radii ρ_i and are surrounded only by atoms of other sublattices (coordination crystals), the interaction may be limited to the first coordination sphere, and the term containing

$$\alpha_2 = -N \sum_{i=1}^{n} \left[U_{A_iB^i} - \frac{1}{2}(U_{A_iA^i} + U_{B_iB^i}) + \text{const} \left(\frac{\Delta\rho_i}{\rho_i} \right)^2 \right], \tag{11}$$

may be neglected, since $U_{R_iR^i}$ represent interactions with atoms of the second coordination sphere.

In this approximation

$$\varphi_R = -Q_R(T_{0R} - T)/RT_{0R}T \tag{12}$$

and, consequently, (8) and (9) contain only two parameters each: Q_R and T_{0R}, which may be considered known if the $R^* \to R$ transformation is actually feasible. These parameters can also be determined by substituting solubility data at two temperatures into formulas (8) and (9).

Let us use the expressions obtained to calculate the boundary of the one-phase region in the case of two specific examples.

Fig. 2 and Fig. 3: plotted phase-boundary comparisons

Figure 2: Fig. 2 and Fig. 3: plotted phase-boundary comparisons

As is known (2,3), in the system $MgAl_2O_4$ (spinel $Fd3m$)—α-Al_2O_3 (corundum $R\bar{3}c$), at high temperatures, substitutional solid solutions with cation vacancies occur over a wide range of concentrations (up to $\sim$ 70 mol.% Al_2O_3). These solutions have the spinel structure, the unit-cell parameter of which obeys Vegard' s rule. Extrapolation gives for the second component a value of the parameter practically coinciding with the lattice constant of γ-Al_2O_3. Thus, upon dissolution the situation is as if aluminum oxide were in the spinel γ-form. Recall that γ-Al_2O_3 is a metastable modification formed as a result of the decomposition of certain aluminum compounds. On heating, γ-Al_2O_3 transforms into the stable α-form.

Fig. 2. Comparison of the calculated boundary of the single-phase region in the $MgAl_2O_4$—Al_2O_3 system with experimental data: 1 —work (2), 2 —work (3)

Fig. 3. Comparison of the calculated boundary of the single-phase region with experimental data: 1 —system ZrO_2—CaO (6), 2 —system ZrO_2—MgO (7)

On the basis of the above, we have $A^* = A = MgAl_2O_4$; $B^* = \alpha\text{-}Al_2O_3$; $B = \gamma\text{-}Al_2O_3 = {}^3/_4Al(Al^{5/3}\square^{1/3})O_4$. The symbol $\square$ denotes vacancies, which in γ-Al_2O_3, according to (4), are located in octahedral positions.

$$(1-c)MgAl_2O_4 + cAl_2O_3 = (1-x)MgAl_2O_4 + xAl(Al^{5/3}\square^{1/3})O_4, \qquad (13)$$

where $c = 4x/(3+x)$.

From (13) we have $n = 3$, $a_{11} = 1$, $a_{12} = 2$, $a_{13} = 4$, $b_{11} = 1$, $b_{12} = 5/3$, $b_{22} = 1/3$, $b_{13} = 4$ (the remaining $r_{ji} = 0$), $k_1 = 0$, $k_2 = 1$, $k_3 = 1$, $q_1 = 1$, $q_2 = 2$, $q_3 = 1$, $m_1 = 1$, $m_2 = 2$, $m_3 = 4$. Substituting these values into (9) and using (12), we obtain the equation of the solubility curve

$$x_2^4\left(\frac{6-x_2}{5}\right)^5 = \exp\left[-\frac{3Q(T_0-T)}{RT_0T}\right]. \qquad (14)$$

From the experimental values of x_2 at two temperatures taken from the region where the data of (2,3) practically coincide, we obtain from (14) for the transition α-$Al_2O_3 \to \gamma$-Al_2O_3: $Q \simeq 12.5$ kcal/mol, $T_0 \simeq 2350$°K. These values make it possible, from (14), to calculate the boundary of the single-phase region and to compare it with the experimental data (2,3).

It is seen in Fig. 2 that at $T \leqslant 1600$°K the experimental points (3) lie to the left of the points obtained in (2) and of the theoretical curve. This discrepancy is apparently due to the fact that, at these temperatures, the time during which the components were heated together in (³) was insufficient for equilibrium to be reached. In work (²), a more equilibrium state at the indicated temperatures was attained owing to hydrothermal treatment.

The melting temperature of Al_2O_3 is $\sim 2320^\circ$ K, so that the $\alpha \to \gamma$ transition does not occur under equilibrium conditions or, if the possible error in determining T_0 is taken into account, occurs immediately before melting. Incidentally, we note that γ-Al_2O_3 is formed during very rapid crystallization of the finest particles, which takes place in the process of applying a protective coating to a metal surface by spraying aluminum oxide in a plasma jet (⁵).

As a second example, let us take the system ZrO_2–CaO or ZrO_2–MgO (the individual features of the second component are reflected by the quantity a_2, which, for the reasons indicated above, may be neglected).

At room temperatures ZrO_2 has a monoclinic lattice; at the temperatures of formation of solid solutions ($T \geq 1500^\circ$ K), a tetragonal one. The crystal structure of CaO(MgO) belongs to the NaCl type. Solid solutions in these systems have a cubic lattice of the fluorite type with anion vacancies. Thus $A^* \neq A$, $B^* \neq B$, where A is the fluorite-like cubic modification of ZrO_2, $B \equiv$ CaO (MgO) is the fluorite-like modification of calcium (magnesium) oxide with anion vacancies, the necessity of which is due to the fact that the number of positions in identical sublattices of the isomorphous components must be the same.

To calculate the boundary of the single-phase region on the ZrO_2 side, in (8) one should substitute the values $n = 2$, $a_{11} = 1$, $a_{12} = 2$, $b_{11} = 1$, $b_{12} = 1$, $b_{22} = 1$ (the remaining $r_{ji} = 0$), $k_1 = 0$, $k_2 = 1$, $q_1 = 1$, $q_2 = 2$, $m_1 = 1$, $m_2 = 2$. As a result we obtain the equation

$$(1 - x_1)(1 - x_1/2)^2 = \exp[-Q(T_0 - T)/RT_0T], \tag{15}$$

which, for $Q \simeq 3.12$ kcal/mole and $T_0 \simeq 2550^\circ$ K, agrees rather well with the experimental data for the systems ZrO_2–CaO (⁶) and ZrO_2–MgO (⁷) (Fig. 3).

The polymorphic transformation from the tetragonal to the cubic CaF_2-type modification of zirconium dioxide was recently discovered by several researchers (⁸,⁹). The temperature of this transformation ($2558 \pm 15^\circ$ K) is very close to the calculated value T_0.

The author is not aware of studies devoted to experimental determination of the heat of transition to the cubic modification of ZrO_2. However, comparison with the heat of transition from the monoclinic to the tetragonal form of ZrO_2 (~ 1.42 kcal/mole (¹⁰)) indicates the reasonableness of the estimate obtained in the present work.

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