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Calculations of Phase Diagrams in Associated Solution Model

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The development of an ideal associated solution model concerned with complexes of various compositions, sizes, and shapes is described. Such models were used earlier to calculate thermodynamic characteristics and the position of the liquidus line for binary eutectic systems as well as those having a stable compound in the solid phase. In all the cases, the model parameters were not adjusted but were estimated from melting temperatures of the components. The latest studies deal with the influence of arbitrary stoichiometry associates on the equilibrium thermodynamic properties of liquid alloys. The application of the model to eutectic systems and systems having an unlimited miscibility in solid and liquid states close to the liquidus has been considered. It was shown that if the difference in melting temperatures of the components was small, different types of fusibility diagrams were possible: eutectic diagrams, cigar-shaped diagrams, or diagrams with upper or lower azeotropic points. Peritectic transformations could take place if the difference in melting temperatures of the components were large.

1. Introduction

Many papers are dedicated to calculation of thermodynamic mixing characteristics of binary alloys in terms of associated models [1954Pri, 1982Was, 1982Som, 1982Ber, 1985Sch]. Usually these models are applied to systems having a stable compound in the solid state. The theory of ideal associated solutions was developed for associates of different compositions, sizes, and shapes [1954Pri]. As a rule, practical calculations take into account only minimum-size associates and disregard the possibility of self-association. Several researchers [1954Pri, 1964Keh, 1989Mor] analyzed in theoretical terms how self-association influences thermodynamic mixing functions. However, this influence was rarely subject to practical calculations [1992Sin, 1991Iva].

A variant of the associated solutions model, which takes into account the presence of associates having different sizes and shapes in the liquid phase, has already been presented [1986Tka1, 1988Shu1]. The calculation of the associated energy was reduced to pair interaction of the nearest neighbors. This consideration was limited by taking into account only configurational contributions to the entropy. It was found that for an infinite-size associate (e.g., a crystal) it was possible to obtain the energy parameter of the model from the melting temperature of the stable compound. Moreover, the number of properties (e.g., melting characteristics, including melting diagrams), which are usually calculated in associated models [1986Tka1, 1988Shu1, 1988Tka2, 1989Tka3, 1989Tka4, 1990Tka5, 1993Shu2, 1993Shu3, 1998Shu4], could be increased. It was also shown that the model could be applied to any system including a eutectic one due to the fact that it took into account self-association.

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A successful use of self-associates for calculation of pure metals and simple eutectic properties suggested that arbitrary-stoichiometry associates could also exist in multicomponent melts. If the presence of such associates is postulated, they mostly affect systems with unlimited solubility in solid and liquid states. It was shown for simple eutectic systems and systems having a stable compound in the solid phase that arbitrary-stoichiometry associates affect the calculated properties and the qualitative pattern of their behavior.

2. Theory

Let us consider a binary system A_cB_{1-c}, whose components form a solution with complete mutual dissolution in the liquid phase. It may be viewed as an ideal solution of the associates A_n (i), B_n (j), and A_nB_m (i, j, q), (n and m being the number of appropriate atoms in the complex; i, j, and q the number of pairs of nearest neighbors, such as AA, BB, and AB in the complex, respectively). The energy of the complex is the sum of energies of nearest neighbor pairs. The entropy contains only configurational contributions. Therefore, the mole fractions of complexes are given by the following equations [2002Shu5, 2004Shu6]:

$$x_{A_{n,i}} = K_{A_{n,i}} x_{A_1}^n = \exp\left(\frac{\alpha_A i}{kT}\right) x_{A_1}^n$$

$$x_{B_{n,j}} = K_{B_{n,j}} x_{B_1}^n = \exp\left(\frac{\alpha_B j}{kT}\right) x_{B_1}^n$$

$$x_{A_nB_m}(i,j,q) = K_{A_nB_m} x_{A_1}^n x_{B_1}^m = \exp\left(\frac{\alpha_A i + \alpha_B j + \alpha_{AB} q}{kT}\right) x_{A_1}^n x_{B_1}^m \quad \text{(Eq 1)}$$

where $x_{A_{n,i}}$, $x_{B_{n,j}}$, $x_{A_nB_m}$, x_{A_1}, x_{B_1} denote the mole fractions of complexes $A_{n,i}$, $B_{n,j}$, A_nB_m, and single atoms A_1 and B_1,

respectively; α_A, α_B, and α_{AB} are bond energies of nearest neighbors pairs AA, BB, and AB taken with opposite sign and $K_{A_{n,i}}$, $K_{B_{n,i}}$, and $K_{A_nB_m}$ denote constants of appropriate equilibria.

Consequently, the concentrations of A_1 and B_1 in the solution are:

$$\sum_n \sum_i x_{A_{n,i}} + \sum_n \sum_j x_{B_{n,j}} + \sum_{n,m} \sum_{i,j,q} x_{A_nB_m} = 1$$

$$c = \frac{\sum_n \sum_i n x_{A_{n,i}} + \sum_{n,m} \sum_{i,j,q} n x_{A_nB_m}}{\sum_n \sum_i x_{A_{n,i}} + \sum_n \sum_j x_{B_{n,j}} + \sum_{n,m} \sum_{i,j,q} (n+m) x_{A_nB_m}} \quad \text{(Eq 2)}$$

where first summation is performed by the number of atomic pairs AA, BB, and AB, and the second summation by the number of atoms A and B.

From Eq 1 and 2, it is possible to find the mole fraction of single atoms in the solution and calculate thermodynamic characteristics of the system and the melting diagram; see, for example, [1954Pri, 1982Was, 1982Som, 1986Tka1, 1988Shu1, 1998Shu4, 2004Shu6, 2004Shu7].

To complete the calculations, it is necessary to know the energy parameters α_A, α_B, and α_{AB}, and the number of nearest neighbor pairs for all the associates. The energy parameters α_A and α_B can be estimated from melting temperatures of pure components [1988Tka2]. Then α_{AB} remains the only unknown parameter. It is possible to calculate the total number of pairs in an associate on the assumption that the local crystal structure is invariable in the liquid phase. The model assumes a linear chain approximation for the associate structure as has been done [1988Tka2] for a simple eutectic. This simplification allows making up the summation in Eq 2. The properties are calculated to within 10% [1993Shu3].

3. Results

The parameters α_A and α_B were determined from melting temperatures of the components, and the parameter $W = [\alpha_{AB} - 0.5(\alpha_A + \alpha_B)]$ was chosen as a variable. The model allows both positive and negative deviations from ideality to be described [2002Shu5, 2004Shu7]. The negative deviation can be arbitrarily large. If W acquires large positive values, thermodynamic characteristics of the mixture are similar to those of systems with a strong interaction of components. A different situation is observed when W is negative, i.e., when the formation of pairs like AB is unfavorable in energy terms. The enthalpy of mixing grows at small W as long as the configuration entropy compensates the energy loss. The mixture enthalpy begins decreasing as W increases further. The mixture entropy passes through the maximum at smaller W values, while activity of components and the Gibbs energy of the mixture changes monotonically. Moreover, the model proved to be capable of describing the situation when the mixture enthalpy is negative and components activities deviate from the Raoult law to the positive side. Thus, the proposed model explains various properties of solutions. For example, in the regular solution model, the sign of the deviation of all properties from ideality depends on the sign of the energy parameter. This unequivocal dependence is not required in the advanced model. The property value is determined from the correlation between the direct pair and indirect configuration contributions to the internal energy. Thus, the result depends on the energy and melting temperatures of the components.

The associated solution melting process was analyzed in [2004Shu6]. The solid phase was viewed as a regular solution of two components with melting points at 700 and 1000 K. The liquid in this system was an ideal associated solution composed of associates of various dimensions and arbitrary stoichiometry values. It was assumed that the energy parameter did not change during melting. Therefore, only one

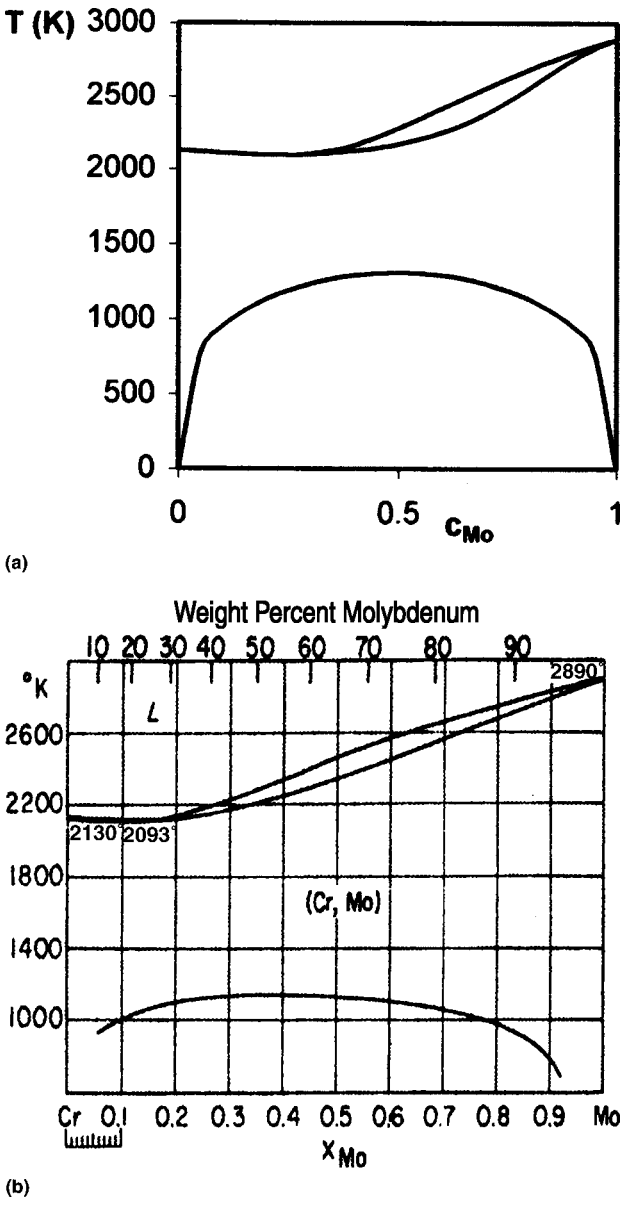

Fig. 1 (a) Calculated and (b) experimental [Hultgren,E] Cr-Mo phase diagram

parameter was a variable. It was shown that the type of the equilibrium diagram depended on the value and the sign of this parameter. In this case, four types of equilibrium diagrams are possible, namely eutectic, "cigar-type," and azeotropic diagrams with both upper and lower azeotropic points.

If the difference between melting temperatures of the components is large, the shape of the phase diagram changes (for example, the "cigar" becomes much thicker), and a qualitatively new type of diagram with peritectic equilibrium appears [2004Shu7]. In this case, the diagram with the eutectic transformation and the diagram with the lower azeotropic point are absent. It is possible to show that the peritectic equilibrium can be achieved only when melting temperatures of the components are largely different ($T_B/T_A > 2.25$).

The calculated phase diagram of the Cr-Mo system with the parameter $W = -1300$ J/mol is shown in Fig. 1. It looks very much like the experimental diagram [Hultgren,E] in the region of the melting temperatures. The calculated values of the azeotropic point are $c_{az} = 0.236$ and $T_{az} = 2097$ K, and the experimental values are $c_{az} = 0.125$ and $T_{az} = 2093$ K.

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