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Calculation of Co-Cu Phase Diagrams Using The Cluster Site Approximation

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Calculations using the cluster-site approximation have been applied to fcc phases in the Co-Cu system, where the pair exchange energies are determined by fitting to the critical temperature. The topology of the calculated coherent phase diagram is similar to the one obtained using the cluster variation method. By using different values of the adjustable parameter γ, we have been able to obtain an improved phenomenological description of this system. It is suggested that the modified cluster site approximation should replace the use of large clusters in the cluster variation method for first principles phase diagram calculations for binary systems.

Key Words: Coherent phase diagram, Order disorder transition, Cluster site approximation.

INTRODUCTION

Calculations of the thermodynamic properties are usually carried out to determine phase diagrams. These estimations are based on the statistical thermodynamics with the cluster variation method[1-4], which has been widely used for calculations of binary and ternary phase diagrams[5,6] and classified as one of the most successful methods. However it has a great computational cost in multicomponent systems[7].

It has been demonstrated that the cluster site approximation (CSA) progresses accuracy to the cluster variation method (CVM) in phase diagram calculations[8-12]. This method is applied to estimate different fcc-binary phase diagrams: Cd-Mg[13], Al-Ni[14] and also ternary systems like Al-Ni-Cr[15]. In this work, the possibility of applying the cluster site approximation to the coherent phase diagram is explored and determined some thermodynamic properties.

The main purpose of this paper is to show, with the system Co-Cu as an example, that the cluster site approximation can not only keep the accuracy of the CVM method but also decrease the computational cost.

EXPERIMENTAL

Cluster site approximation: The free energy in the cluster site approximation method is taken equal to the sum of the internal energy and the configurational entropy which defined in the substitutional solutions as:

$$E = \gamma N \sum_{J} p_J . e_J \quad (1)$$

$$S = S_n + (1 - 4\gamma)S_1 \quad (2)$$

where p_J = probability of finding the cluster in the configuration J, e_J = energy of this cluster in the same configuration, S_n = cluster entropy and S_1 = site entropy given by:

$$\frac{S_n}{R} = -\gamma \sum_{ijkl} W_{ijKl} \ln W_{ijkl} \text{ and } \frac{S_1}{R} = (4\gamma - 1) \sum_{m=1}^{4} \sum_{i=A,B} f_m y_i^m \ln y_i^m$$

in this formula, y_A^1, y_A^2, y_a^3 and y_A^4 are the occupation site probabilities of the four sites of the cluster and f_m is the fraction of sublattice i.

Using the Fowler-Yang-Li transformation this expression can be given as a function of the partition function φ by:

$$F = \gamma RT \left(\sum_{q=I,II,...} \lambda_i y_A^i - \ln \varphi \right) - \left(\frac{4\gamma - 1}{4} \right) RT \sum_{q=I,II,...} \sum_{i=A,B} y_i^q \ln y_i^q \quad (3)$$

In this formula, the independent variables are the Lagrangian multipliers λ_i or equivalently the point probabilities. The equilibrium is defined by the minimization of the free energy function with respect to the site occupation probabilities.

RESULTS AND DISCUSSION

For the present investigation the values of the formation energies were assessed in the previous work form the transition temperature in the experimental Co-Cu phase diagram. The energies are listed in Table-1 and the ground state line in the E_f -x % diagram is presented in Fig. 1. From this figure it is observed that all the phases are unstable therefore there is equilibrium only between the fcc Cu-rich solid solution and the fcc Co-rich solid solution.

TABLE-1
FORMATION ENERGIES OF DIFFERENT fcc COMPOUND IN THE Co-Cu SYSTEM

Phases	A1 (A)	L12 (A3B)	L10 (AB)	L12 (A3B)	A1 (B)
E_f (J/mol)	0	6986.1	9314.8	6986.1	0

The Co-Cu phase diagram calculated using the cluster site approximation method is shown in Fig. 2. In this system two phases are identified: the fcc Cu-rich solid solution (γ Cu), the fcc Fe-rich solid solution (γ Fe). At 2000 K and for $\gamma = 1.4$ the Co-Cu phase diagram presents a demixing phenomena. In the previous calculation in the literature the parameter γ is taken as an adjustable parameter. For this reason we calculate the Co-Cu system with $\gamma = 1$ where the transition temperature found is T = 1450 K. It is clearly observed that the transition temperature increases with increasing of the adjustable parameter γ. However up to the value $\gamma = 1.8$ the equilibrium is lost.

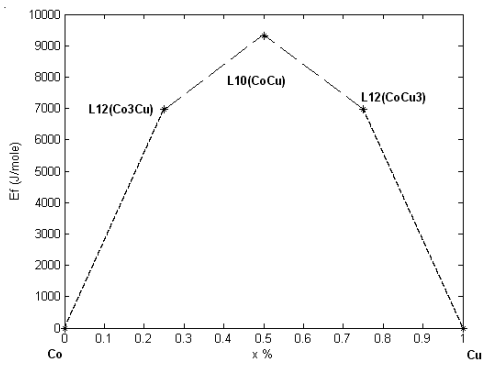

Fig. 1. Formation energies (J/mol) as a function of composition for the different Fcc superstructures

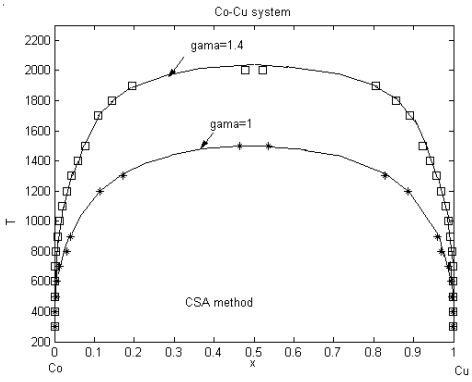

Fig. 2. Co-Cu phase diagram computed with $\gamma = 1$ and 1.4

For the comparison we estimate the Co-Cu phase boundaries using the CVM method (Fig. 3), where we found that the T_c temperature is 1450 K (Fig. 1). Thus if we increase γ it is find that the value $\gamma = 1.04$ gives a very good agreement between the results of the two methods, CVM and the cluster site approximation one.

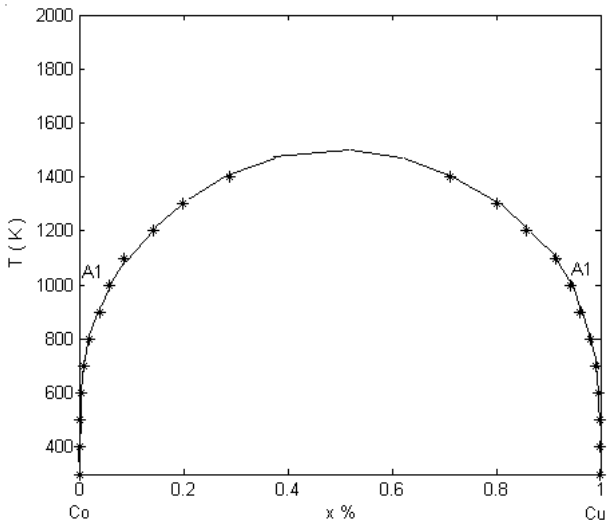

Fig. 3. Co-Cu phase diagram calculated with CVM method

Conclusion

In this study, it is shown that the cluster site approximation method can be applied for determining the equilibrium between the fcc coherent phases successfully. This model was applied to estimate the equilibrium in the Co-Cu system, where the energetic term was obtained from fitting results published previously. The Co-Cu

phase diagram calculated with different values of γ indicates that the transition temperature increase with increasing this parameter. Consequently it is possible to obtain an excellent description for the T_c temperature by using an exact value of the adjustable parameter γ. The phase diagram calculated of this system is in good agreement with the CVM one. This gives a starting point for generalizing the cluster site approximation method to all alloy structures and thus applying to a real alloy with a large number of elements.

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