Theoretical determination of pair interaction energies for a Mg-Al alloy

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Abstract

Theoretical study of phase stability based on the Cluster Variation Method is extended to a hexagonal lattice. The validity of the developed code is examined in the limits of isotropic interaction and vanishing out-plane interaction.

The present results satisfactorily reproduces the ones for an fcc lattice and two dimensional triangle lattice. Then, the phenomenological calculations within the mold of Lennard-Jones type pair interaction energies are attempted for Mg-Al alloy system. The pair interaction energies for Mg-Mg and Al-Al are determined by cohesive energies for pure elements, while the one for Al-Mg is determined based on the experimental free energy of formation of solid solutions at 700K.

Riassunto

Lo studio teorico della stabilità di fase basato sul metodo della variazione del grappolo viene esteso ad un reticolo esagonale. La validità del codice sviluppato viene analizzata entro i limiti dell'interazione isotropica e quella del fuori piano annullantesi.

I presenti risultati riproducono in modo soddisfacente quelli descritti per un reticolo fcc e per il reticolo triangolare a due dimensioni. Vengono poi applicati al sistema di leghe Mg-Al i calcoli fenomenologici ipotizzando le energie di interazione tra coppie del tipo Lennard-Jones. Dette energie vengono determinate per Mg-Mg e per Al-Al dalle energie coesive per gli elementi puri, mentre l'energia per Al-Mg viene basata sull'energia libera sperimentale di formazione delle soluzioni solide a 700K.

INTRODUCTION

The Cluster Variation Method (hereafter CVM)[1] of statistical mechanics has been recognized as one of the most reliable tools in analyzing the phase stability and in predicting thermodynamic properties and quantities. The key to the method is the ability to incorporate wide range of atomic correlations which play an important role in the phase stability. By combining with electronic structure calculations to incorporate atomic interaction energies, we are even at the stage of carrying out first-principles thermodynamic studies[2]. Much to regret, however, most calculations performed so far have been overwhelmingly centred around fcc- and bcc-based alloy systems and not much studies on hexagonal alloy systems[3,4,5] have been attempted yet.

There are various demands for extending CVM calculations

to hcp alloys. Among them are the designing of Mg-based light metal alloys which is the main concern of the present symposium[6] and that of GaN type semiconductor alloys[3] which are characterized as wurtzite structure, a derivative of hcp symmetry. In view of these requirements, we developed CVM code for a hcp structure and attempted preliminary calculations.

The validity of the CVM code for hexagonal alloy is critically examined by comparing the calculated concentration dependency of the entropy in the two limiting cases of an anisotropy parameter which is, as will be more clearly described in the following section, defined as the ratio of outplane to in-plane pair interactions. One is the limit of isotropic interaction for which the distinction of hexagonal and face centered cubic lattices should be diminished and the derived quantities are expected to coincide with the one independently obtained for the fcc alloy. The second one is the case of vanishing out-plane interaction, for which the result should reproduce the one for two dimensional triangle lattice.

Among realistic alloy system to which the present CVM calculation is extended, Mg-Al alloy is adopted for the preliminary study. In the common practice of the theoretical analysis of the phase stability, one starts with the knowledge of the set of effective atomic interaction energies. Then, the free energy functional is minimized with respect to configurational variables to obtain the equilibrium state which

PROTOTYPE CVM CALCULATIONS FOR AN HCP ALLOY

In the analysis of energetics of hexagonal alloys, the anisotropy ratio, η , which is defined as the ratio of the outplane pair interaction (across the basal plane), v_0 , to the inplane pair interaction (in the basal plane), v_1 , plays a key role. It is emphasized that, even if the c/a ratio of the lattice constants are ideal, the two types of pair interaction energies, v_0 and v_1 should be clearly distinguished, which is the essential requirement originated from the crystal symmetry of the hexagonal structure.

The most common practice of the CVM calculation for fccbased structures is the employment of Tetrahedron approximation in which the entropy is written as

$$S / N = k_B \left[6 \sum_{ij} L(y_{ij}) - 2 \sum_i L(\chi_i) - 5 \sum_{ijkl} L(w_{ijkl}) + 1 \right]$$
(1)

where $L(\chi) = \chi \ln \chi - \chi$, *N* the total number of lattice point, χ_i , γ_{ij} , and ω_{ijkl} are, respectively, the probability of finding atomic arrangement specified by suffixes on the point, nearest neighbor pair and tetrahedron clusters.

The tetrahedron approximation is the simplest possible approximation for an fcc-based system and has been employed for various advanced calculations including the first-principles calculation.

Corresponding to the Tetrahedron approximation of the fccbased system is the Tetrahedron-Triangle approximation for the hexagonal based system in which the basic cluster is the combination of Tetrahedron and Triangle clusters involving seven kinds of independent cluster correlations. The difference of these basic clusters between two systems originates from the different nature of the out-plane pair interaction, v_0 , and the in-plane pair interaction energy, v_1 . The final exis characterized as the optimized configurational variables and corresponding minimum of the free energy. Then, the relevant thermodynamic quantities are calculated based on these quantities.

In this preliminary study, however, a complete set of effective interaction energy is not available. Hence, we take rather a reverse procedure, and the main focus is placed on the determination of the atomic pair interaction energies, ie. CVM calculations are repeated until assumed pair potentials reproduce thermodynamic data of Mg-Al system. The next section is devoted to the entropy calculations for a general hexagonal lattice. The main results for a Mg-Al alloy are presented in the third section.

pression of the entropy term for the hexagonal-based system is given by

$$S / N = k_B \left[6 \sum_{ijk} L(v_{ijk}) + 3 \sum_{ij} L(p_{ij}) + 3 \sum_{il} L(q_{il}) - 2 \sum_{ijkl} L(z_{ijkl}) - \sum_{ijkl} L(w_{ijk}) - 5 \sum_{i} L(x_i) \right]$$
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where x_i , p_{ij} , q_{il} , v_{ijk} , w_{ijk} and z_{ijkl} are, respectively, point, in-plane pair, out-plane pair, basal triangle, pyramidal triangle and tetrahedron cluster probabilities. The distinction of in-plane and out-plane pair probabilities and the addition of basal triangle probability should be noticed.

Among various calculations attempted, two main results for the entropy are presented. Shown in Fig. 1 by open squares are the concentration dependencies of entropy for four temperatures at $\eta = 1$. Note that the temperature scale throughout this study is normalized with respect to in-plane pair interaction energy, v_i . Since isotropic interaction ($\eta = 1$) does not distinguish hcp from fcc structures, the present results exactly coincide with the ones independently obtained for an fcc disordered phase by tetrahedron approximation indicated by solid lines. Also one recognizes that the two minima appear near 1:3 and 1:1 stoichiometries with decreasing the temperature. These imply the existence of underlying ordered phases. In fact, the ground state analysis[4,5] suggests the stabilization of D019 (1:3) and B19 (1:1) ordered phases below transition temperatures.

The concentration dependencies of the entropy in the other extreme regime at $\eta = 0.0$ are demonstrated in Fig. 2 for four temperatures. The solid lines are present results and open squares are the ones independently obtained for the



Figure 1: Concentration dependencies of the entropy at four temperatures 2.5, 1.5, 1.0 and 0.75 calculated for a hcp disordered solid solution by the Tetrahedron-Triangle approximation of the CVM (open squares). The anisotropy ratio, η , is 1.0. The solid lines indicate the results of Tetrahedron approximation for a fcc lattice



Figure 2: Concentration dependencies of the entropy at four different temperatures (2.5, 1.5, 1.0 and 0.75) calculated for a hcp disordered solid solution based on the Tetrahedron-Triangle approximation of the CVM. The anisotropy ratio, η , is 0.0. The open squares indicate the results obtained by Triangle approximation of the CVM for the twodimensional lattice

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two dimensional triangle lattice. One can see that the two results coincide exactly, confirming that the three dimensional hexagonal lattice split into the two dimensional triangle lattice at the vanishing of out-plane pair interaction. These results, thereby, prove the accuracy of extended CVM code.

PHENOMENOLOGICAL CALCULATIONS FOR A MG-AL BINARY SOLID SOLUTION

Among various Mg alloys, Mg-Al alloy system is adopted for the present study. This is because, despite the fact that Mg-Al has been recognized as one of typical light metal alloys, no CVM-based investigations have been reported to the best of authors' knowledge. In the conventional calculation of the phase stability, a common practice is to start with the construction of free energy functional with an assigned set of atomic interaction energies. Then, the free energy functional is minimized with respect to configurational variables to obtain the equilibrium state. The derived thermodynamic quantities as well as optimized configurational variables are compared with experimental results to examine the validity of calculation procedures as well as assumptions adopted in the study. In the present study, however, we take rather a reverse procedure, ie the CVM calculations are repeated until assumed pair interaction reproduces experimental data. Hence, the main objective is placed on the determination of the atomic interaction energies within the mold of Lennard-Jones type pair potential [7].

The Lennard-Jones type pair interaction energy, $e_{ij}(r)$, for atomic species *i* and *j* at the distance r is given by

$$e_{ij}(r) = e^0_{\ ij} \left\{ \left(\frac{r_{ij}}{r}\right)^n - \frac{m}{n} \cdot \left(\frac{r_{ij}}{r}\right)^n \right\} \quad (3)$$

where e_{ij}^{0} and r_{ij} are Lennard-Jones parameters to be determined for three kinds of atomic pairs, Al-Al, Mg-Mg and Al-Mg. For the exponent terms *m* and *n*, 8 and 4, respectively, are assigned since this combination has been recognized to describe the metallic alloy system quite well. Among six unknown parameters for the binary system, the parameters for like pairs, e_{ij}^{0} and r_{ij} are directly determined through the experimental data of cohesive energy and equilibrium lattice constant, respectively. The derived Lennard-Jones parameters are tabulated in Table 1 together with the experimental data cited [8,9]. Shown in Fig. 3 are the resultant Lennard-Jones pair potentials. A deeper Aluminum pair potential reflects the high cohesive energy, and a longer atomic distance for Magnesium is due to the bigger unit cell. It is noted that the c/a ratio of Magnesium is close to the ideal value, hence the Lennard-Jones potential for Magnesium is extracted for a hypothetical fcc unit cell.

Within the frameworks of phenomenological calculations, the atomic potential for an unlike-pair can be also determined with the knowledge of heats of formation and lattice constants of an ordered phase. From the practical point of view, it is desirable to employ data of an ordered phase with a high symmetric structure such as Ll_0 or Ll_2 . This requirement, however, is not fulfilled for the Mg-Al alloy system. Hence, in the present study, experimental data of free energy of formation of a disordered solid solution are referred to determine the unlike-pair potential. Because of the entropy effects of a disordered solution at a finite temperature, however, the calculation is not straightforward and demands brute force type trial and error procedure as described below.

The free energy of formation of a solid solution per a lattice point, ΔF , is given by

$$\Delta F = \frac{1}{2} \omega \sum_{ij=l}^{2} e_{ij}(r^*) (y^*_{ij} - \delta_{ij}) T S^*$$
(4)

where ω is the coordination number, r^* and y_{ij}^* indicate the atomic distance and pair probability at an equilibrium state, respectively, δ_{ij} the Kronecker's delta, suffixes 1 and 2 correspond to Al(Mg) and Mg(Al) and S^{*} is the entropy evaluated at the equilibrium state. Hence, once the combination of the Lennard-Jones parameters, e^0_{Mg-Al} and r^0_{Mg-Al} , is assigned, together with the potentials for like-pairs, free energy functional of a disordered solid solution is constructed. The minimization of the free energy with respect to cluster variables as well as the volume (lattice parameter) determines the equilibrium values of r^* and y_{ij}^* . The repetition of the procedure for different composition yields concentration dependency of free energy of formation ΔF which is to be compared with experimental results.

The experimental free energy of formation are cited from Hultgren [8] for Al-rich α solid solution and for Mg-rich δ solid solution at 700K. The comparison with the calculated values are demonstrated in Fig. 4. The employed values of e^0_{Mg-Al} and r^0_{Mg-Al} are tabulated in Table 1 together with the ones for like-pairs. The resultant potential curve is also demonstrated in Fig. 3. The agreement between the experimental data and present calculation in Fig. 4 is quite appreciable for α -solid solution.



Figure 3: Lennard-Jones potentials for three types of pairs, Mg-Mg, Al-Al and Al-Mg. The horizontal axis is the nearest neighbor pair distance in Å and the vertical axis is the energy in kcal/mole. It should be noted that the origin of the horizontal axis is not 0 but 2.3. For Al-Mg potential, the experimental data of α-solid solution is employed

TABLE 1 - The Lennard-Jones parameters of
three kinds of pairs for a Mg-Al
alloy. The employed experimental
data of cohesive energy and lattice
constants are also tabulated

	e ^o _{Mg-Al} [kcal/mol]	r _{Mg-AI} [A]
Al-Al	12.90	2.863
Mg-Mg	5.884	3.203
Mg-Al	9.708	2.896
	Cohesive energy [kcal/mol]	Lattice constant [A]
Al	77.40	4.050
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Mg	35.30	a=3.209

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For Mg-rich d phase, since e^{0}_{Mg-Al} and r_{Mg-Al} determined for α -solid solution were by no means able to reproduce the heats of formation data, a different Lennard-Jones potential function is sought. Despite numerous attempts, a severe numerical problem encountered did not enable us to calculate the free energy of formation value except at only one concentration as is indicated in Fig. 4. Although the agreement is satisfactory, a further calculation for entire concentration range is necessary. For such a calculation for δ -solid solution, one may require an explicit introduction of the additional optimization procedure for c/a ratio. Together with the first-principles calculation, this is the subject remained for the future investigation.



Figure 4: Free energy of formation for a disordered solid solution at 700K. Solid lines are experimental data from the literature [8] while the solid circles are the results of present calculations. The employed Lennard-Jones parameters are tabulated in Table 1. It is noted that only one point is calculated for the δ solid solution

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