1 of 1

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PHASE STABILITY IN THE Cd-Mg SYSTEM

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Abstract

In this contribution we report on the results of a theoretical study of solid-state phase equilibria and short-range order in Cd-Mg alloys. The results of first-principles linear muffin-tin orbital method total-energy calculations for seven hcp-based superstructures have been combined with cluster-variation-method calculations of thermodynamic properties in order to compute the Cd-Mg phase diagram. The effect on the calculated phase diagram of contributions to the alloy free energy arising from atomic vibrations and structural relaxations are assessed using available experimental information for ordered and disordered alloys in the Cd-Mg system.

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Introduction

A variety of first-principles techniques for studying alloy phase stability have become available in the past twenty years. These techniques have been widely applied with great success to the calculation of short- and long-range-order, thermodynamic properties and phase diagrams of substitutional alloys. At present, however, such studies have largely been limited to alloys with crystal structures based on underlying fcc- and bcc-based lattices. Furthermore, the effects on alloy phase stability of contributions to the free energy arising from structural relaxations as well as static and dynamic atomic displacements have often been ignored. The purposes of the present investigation are: 1) to apply the formalism of the cluster variation method (CVM) [1,2] to the calculation of the phase diagram and short-range order for an alloy system with hcp-based crystal structures, and 2) to analyse how the relative stabilities of ordered and disordered phases are affected by the contributions to the free energy arising from structural relaxations and atomic vibrations.

The system which has been investigated in the present study is Cd-Mg. In Fig. 1 the solid-state portion of the assessed experimental Cd-Mg phase diagram [3] has been redrawn. At high temperatures (below the melt) continuous solid solution between hcp Cd and hcp Mg is found. As the temperature is lowered, three ordered phases with hcp-based structures are stabilized in composition ranges around the stoichiometries Cd_3Mg , CdMg_3 and CdMg . The Cd_3Mg and CdMg_3 phases form in the $D0_{19}$ structure, while CdMg has the $B19$ structure. The hcp-based $B19$ and $D0_{19}$ structures have the same atomic configurations on close-packed planes as do the fcc-based CuAu and Cu_3Au structures, respectively (see for example Ref. 4). Since the melting points of elemental Cd and Mg, and the transition temperatures of the ordered Cd-Mg phases are low, experimentally measured lattice parameters and thermodynamic properties are available for both disordered and ordered alloy phases [5,6]. This experimental information has been used in the present study to assess the effects on the

Fig. 1 - The experimentally determined solid-state portion of the composition-temperature Cd-Mg phase diagram, as assessed by Moser et al. [2]. Equilibrium phase boundaries are indicated by solid lines, and the temperatures of invariant reactions are indicated. (Cd, Mg) refers to the disordered, hcp-based solid solution. Regions of stability for ordered phases are indicated by the stoichiometries of the compounds: CdMg , Cd_3Mg and CdMg_3 .

calculated phase diagram of contributions to the free energy which arise from vibrational excitations and structural relaxations.

Computational Approach

The computational approach taken in this study was described in detail in Refs. 7 and 8, and it will only be very briefly summarized here. The total energies, equilibrium atomic volumes and bulk moduli of elemental hcp Cd and Mg and seven Cd-Mg superstructure compounds were calculated from first-principles by the method of linear muffin-tin orbitals using the atomic-sphere approximation (LMTO-ASA) [9]. In these total-energy calculations ideal close-packed hcp geometries were assumed for all crystal structures. The results of the LMTO-ASA calculations were used to extract a set of effective cluster interactions (ECI's) [2,10] from which the formation energy of any arbitrary Cd-Mg alloy phase could be computed. An elastic correction to the enthalpy of formation due to structural relaxations associated with the deviations of the axial (c/a) ratio from the ideal close-packed value was calculated from experimentally measured lattice parameters [6] and elemental elastic constants [11]. In deriving the elastic energy correction use was made of the following two assumptions: 1) that the elastic constants depend linearly on concentration, and 2) that structural relaxations are significant only for the disordered alloy phase. The second assumption was justified from an analysis of the experimentally measured lattice parameters of the ordered phases as described in Refs. 7 and 8. The contributions to the free energies of ordered and disordered alloy phases arising from atomic vibrations were calculated using a Debye model with parameters fit to experimentally measured entropies of formation [5]. The total free energies of the various experimentally observed Cd-Mg phases were calculated as functions of composition and temperature using the tetrahedron-octahedron approximation of the CVM [4]. From the results of these free energy computations, phase diagrams were then constructed. The contribution of the short-range order to the diffuse scattered intensity for the disordered alloy phase was also computed within the tetrahedron-octahedron approximation of the CVM in the manner described in Ref. 12.

Results and Discussion

In Fig. 2 (a) the result of a first-principles LMTO/CVM calculation of the Cd-Mg phase diagram is shown. In calculating the phase diagram shown in Fig. 2 (a), the elastic contributions to the alloy free energy due to structural-relaxations, as well as the vibrational enthalpy and entropy were neglected. The Cd_3Mg and CdMg phases are predicted to disorder congruently at roughly 420°C , while CdMg_3 is found to undergo a peritectoid reaction to $\text{CdMg} + (\text{Cd}, \text{Mg})$ at roughly 380°C . Therefore, the shape of the calculated phase diagram shown in Fig. 2 (a) is in agreement with the experimentally determined one (Fig. 1) for Mg-rich alloys only.

In Fig. 2 (b) is plotted the result of a phase diagram calculation in which all contributions to the alloy free energy, including those arising from vibrations and structural relaxations, were included. The agreement between the experimental phase diagram (Fig. 1) and the calculated one shown in Fig. 2 (b) is excellent. The calculated temperatures of the invariant reactions in Fig. 2 (b) are roughly 30°C too high for $\text{Cd}_3\text{Mg} \rightarrow \text{CdMg} + (\text{Cd}, \text{Mg})$, 150°C too high for $\text{CdMg}_3 \rightarrow \text{CdMg} + (\text{Cd}, \text{Mg})$, and 170°C too high for the congruent order-disorder transition of the CdMg phase, when compared to the experimental phase diagram. The relatively small differences between the calculated and experimentally measured reaction temperatures shown in Figs. 1 and 2 (b), respectively, can be largely attributed to discrepancies between the LMTO-ASA-calculated heats of formation for the ordered Cd-Mg compounds and the values which have been measured experimentally, as discussed in detail in Ref. 7.

From a comparison of Figs. 2(a) and 2(b) it can be seen that the elastic (relaxation) and vibrational contributions to the alloy free energy are significant for the purposes of accurately

Fig. 2 - (a) First-principles LMTO-ASA/CVM calculated phase diagram for solid-state phases in the Cd-Mg system. In the calculation of this phase diagram, elastic contributions to the alloy free energy arising from structural relaxations as well as the contributions due to vibrations were neglected. (b) Cd-Mg phase diagram calculated by the CVM including the relaxation energy and the contributions to the free energy arising from atomic vibrations. The dashed line indicates the locus of the calculated spinodal temperature versus concentration for $\langle 1/2 \ 0 \ 0 \rangle$ ordering.

describing the detailed features of the Cd-Mg phase diagram. In particular, the large difference between the calculated transition temperatures for the Cd_3Mg phase shown in Figs. 2 (a) and (b) is almost entirely due to the elastic contributions to the free energy of Cd-rich disordered alloys [7]. In other words, it was found that the elastic energy due to structural relaxations had the effect of stabilizing the solid solution with respect to the ordered Cd_3Mg phase in our calculations. It was also found that the vibrational entropy gave rise to a significant contribution to the difference in entropy between ordered and disordered alloy phases with equivalent compositions. The vibrational entropy was found to be larger in magnitude for the disordered solid solution than it was for the ordered phases. Therefore, when vibrational contributions to the entropy were included in our calculations, computed transition temperatures were lowered by as much as 200°C .

In Fig. 3 the results of a CVM calculation of the short-range-order (SRO) contribution to the diffuse intensity in the (001) plane of reciprocal space for a disordered CdMg alloy at $T=750$ K is plotted. The SRO diffuse intensity is shown in Fig. 3 to have maxima located at the following positions: $[1/2 \ -1 \ 0]$, $[1/2 \ 1/2 \ 0]$, $[1 \ -1/2 \ 0]$, $[-1/2 \ 1 \ 0]$, $[-1/2 \ -1/2 \ 0]$ and $[-1 \ 1/2 \ 0]$. By the translational symmetry of reciprocal space for the hcp structure, the positions $[1/2 \ 0 \ 0]$, $[-1/2 \ 0 \ 0]$, $[0 \ 1/2 \ 0]$, $[0 \ -1/2 \ 0]$, $[-1/2 \ 1/2 \ 0]$ and $[1/2 \ -1/2 \ 0]$ are equivalent to those where the diffuse intensity maxima are located. Weak intensity peaks are also calculated at these latter positions, and the difference in the magnitude of the diffuse intensities at $[1/2 \ 0 \ 0]$ and $[1/2 \ -1 \ 0]$ is due to the phase factor introduced by the two atoms in the unit cell of the hcp structure. The fact that the SRO diffuse intensity is observed to peak at $\langle 1/2 \ 0 \ 0 \rangle$ positions for disordered Cd-Mg alloys is consistent with the fact that the $D0_{19}$ and $B19$ structures can be constructed from concentration waves of type $\langle 1/2 \ 0 \ 0 \rangle$ as discussed by Ducastelle [13].

Fig. 3 - Calculated short-range order diffuse intensity in the (001) plane for the disordered CdMg phase at $c=50\%$ Mg and $T=750$ K. The step in the contours is 0.2 and the intensity is normalized to have a maximum value of 1.0. The hexagon drawn by the solid thick line is the portion of the first Brillouin zone cut by an (001) plane. The thick solid circles indicate reciprocal lattice points. The diffuse intensity maxima in this figure are located at the points: $[1/2 -1 0]$, $[1/2 1/2 0]$, $[1 -1/2 0]$, $[-1/2 1 0]$, $[-1/2 -1/2 0]$ and $[-1 1/2 0]$. Weaker peaks in the diffuse intensity are also located at the points $[1/2 0 0]$, $[-1/2 0 0]$, $[0 1/2 0]$, $[0 -1/2 0]$, $[-1/2 1/2 0]$ and $[1/2 -1/2 0]$, although they are somewhat difficult to see in this plot.

Summary and Conclusions

The main results of this study can be summarized as follows: 1) Structural relaxation of the hcp c/a ratio away from its ideal value gives rise to an important contribution to the enthalpy of formation for Cd-rich disordered alloys; the relatively low experimentally measured temperature of the peritectoid reaction for the Cd_3Mg phase shown in Fig. 1 can only be reproduced in our calculations if the elastic contribution to the free energy associated with structural relaxations is taken into account. 2) Vibrational excitations primarily affect thermodynamic properties through their contribution to the entropy; the vibrational entropy is larger at a given composition and temperature for disordered than it is for ordered phases in the Cd-Mg system.

The results of the present study clearly demonstrate that computed phase diagrams are sensitive to small changes in the values of calculated free energies used in their construction. It can therefore be concluded that in order to accurately describe detailed features of alloy phase diagrams from first principles, techniques are needed for efficiently calculating elastic and vibrational contributions to the free energies of ordered and disordered alloy phases.

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References

1. R. Kikuchi, Phys. Rev. **81**, 988 (1951).
2. J. M. Sanchez, F. Ducastelle, and D. Gratias, Physica **128A**, 334 (1984).
3. Z. Moser et al., Bulletin of Alloy Phase Diagrams **5**, 23 (1984).
4. R. McCormack et al., Phys. Rev. B **48**, 6767 (1993).
5. R. R. Hultgren, P. D. Anderson, and K. K. Kelley, eds., Selected Values of Thermodynamic Properties of Metals and Alloys (J. Wiley and Sons, Inc., New York, 1963), 604.
6. W. Hume-Rothery, and G. V. Raynor, Proc. Roy. Soc. **A174**, 471 (1940).
7. M. Asta, R. McCormack and D. de Fontaine, Phys. Rev. B **48**, 748 (1993).
8. M. Asta, "First-Principles Calculations of Thermodynamic Properties and Phase Diagrams of Binary Substitutional Alloys" (Ph. D. thesis, University of California at Berkeley, 1993), Chapter 4.
9. O. K. Andersen, O. Jepsen, and D. Glötzel, in Highlights of Condensed-Matter Theory, edited by F. Bassani, F. Fumi, and M. P. Tosi (North Holland, New York, 1985); O. K. Andersen, O. Jepsen, and M. Sob, in Electronic Band Structure and its Applications, edited by M. Yussouff (Springer Lecture Notes, 1987).
10. M. Asta et al., Phys. Rev. B **44**, 4914 (1991).
11. E. A. Brandes, ed., Smithell's Metals Reference Book, Sixth Edition (Butterworth and Co. Ltd., Boston, 1983), 15-5.
12. J. M. Sanchez, Physica **111A**, 200 (1982).
13. F. Ducastelle, "Order and Phase Stability in Alloys," Vol. 3 of Cohesion and Structure, edited by F. R. de Foer and D. G. Pettifor (North-Holland, New York, 1991).

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