A Coherency Strain Model for Hexagonal-Close-Packed Alloys

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Abstract

Encouraged by the success of first-principles cluster expansion methods for large-scale modeling of cubic alloys, we are developing a mixed-space cluster expansion approach for hexagonal-close-packed alloys. Here we discuss an explicit strain model, an essential component of cluster expansion models for modeling precipitate formation. We illustrate the method for magnesium alloys containing calcium and yttrium, two common additives in magnesium alloys.

The automobile industry is interested in using materials substitution to achieve weight reduction. In many applications, magnesium alloys are being considered for substitution of aluminum alloys. Developing improved alloys will be facilitated by a better understanding of the relatively immature field of the basic science of magnesium alloys. First-principles calculations, combined with cluster expansion techniques have been extremely successful in modeling cubic alloys. Encouraged by this success, we are developing a mixed-space cluster expansion for hexagonal alloys.

The Ising-like cluster expansion approach cannot fully account for the energetic effects of atomic relaxations without a separate and explicit treatment of the coherency strain [1]. Therefore, it is necessary to provide an explicit strain model to complete the cluster expansion. Here we illustrate the method in determining and modeling the coherency strain energy for magnesium alloys containing yttrium and calcium, two common additives in magnesium alloys. Yttrium and hcp calcium both exhibit a significant lattice mismatch with respect to magnesium, 12.7% and 19.7% respectively. As such, the strain energy in these systems is a significant component of the formation enthalpy of alloys and must be taken into account in cluster expansion models.

To describe the strain properties, two types of quantities are needed, the hydrostatic deformation energy and the epitaxial strain energy. The hydrostatic deformation energy, $\Delta E_A^{\text{bulk}}(a)$, is the energy required to hydrostatically deform the solid element A to the lattice constant a of the alloy [2]. The epitaxial strain energy, $\Delta E_A^{\text{epi}}(a, \hat{G})$, is the energy needed to deform the elemental solid A *epi-*
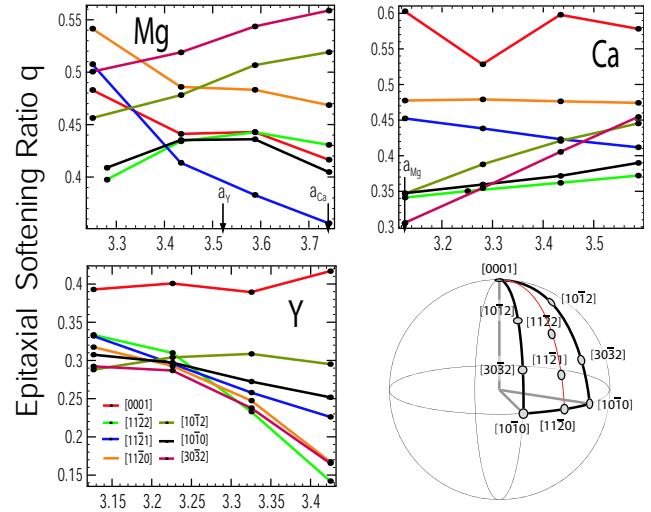

Figure 1: Epitaxial softening function $q(a, \hat{G})$ for Mg, Ca, and Y. The sphere on the right illustrates the symmetrically distinct directions for a hexagonal lattice.

taxially to the substrate lattice constant in the two directions orthogonal to $\hat{G}$, allowing it to relax along $\hat{G}$. [2] As a hexagonal lattice has 24 symmetry operations, one can define all of the symmetrically distinct points by 1/24 of the unit sphere, corresponding to the ranges $0 < \theta < \pi/2$ and $0 < \phi < \pi/6$. For seven directions in this symmetrically distinct region (see Fig. 1), the epitaxial strain energies were calculated using the Vienna Ab-Initio Simulation Package (VASP) [3]. The ratio between these energies, the epitaxial softening function $q(a, \hat{G})$, was also determined for each direction and is shown in Fig. 1, as well. A detailed description of these quantities and the method with which to calculate them can be found in References [1, 2]. Overall, yttrium shows the smallest q values, thus, relative to the hydrostatic deformation, epitaxially deformed Y is softer than Mg or Ca.

The coherency strain energy, $\Delta E_{\text{CS}}^{\text{eq}}(x, \hat{G})$, is defined as the equilibrium value of the composition weighted sum of the epitaxial strain energies of A and B. Discussion of the coherency strain can be found in References [1, 2]. The coherency strains for both $Mg_x Ca_{1-x}$ and $Mg_x Y_{1-x}$ are shown in Fig. 2.

In the past, coherency strain has only been stud-

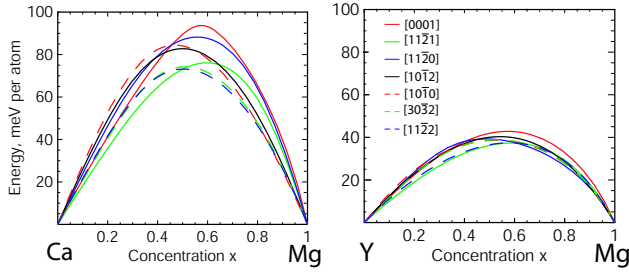Figure 2: Coherency strain energies $\Delta E_{\mathrm{CS}}^{\mathrm{eq}}$ for $\mathrm{Mg}_x\mathrm{Ca}_{1-x}$ and $\mathrm{Mg}_x\mathrm{Y}_{1-x}$ as a function of concentration. All calculated energy differences are with respect to the ideal undistorted hcp-crystal of Mg, Ca, and Y.

ied in the case of cubic alloys and, consequently, was parametrized in terms of a sum of cubic harmonics [2, 4]. Thus for hexagonal alloys, we have defined a set of "hexagonal harmonics," $H_{l,m}(\theta, \phi)$. The method for deriving the hexagonal harmonics can be found in Reference [5]. As the pure hcp lattice belongs to the 6MMM space group, the hexagonal harmonics that apply to this space group were used in fitting the coherency strain. Several hexagonal harmonics are shown in Fig. 3.

The coherency strain for the seven directions illustrated in Fig. 1 was fit with the first five hexagonal harmonics, with relative errors in the strain for Mg-Ca and Mg-Y less than 3% and 8%, respectively. Fig. 4 shows the parametrization of the coherency strain for $\mathrm{Mg}_{0.9}\mathrm{Ca}_{0.1}$ and $\mathrm{Mg}_{0.9}\mathrm{Y}_{0.1}$.

In both binary systems, low Mg concentrations result in similar strain models. In these cases, the strain energies are due almost entirely to Mg, as small Mg concentrations are not likely to adjust the lattice and will conform to the lattice spacing of the solute. Contrariwise, the strains in
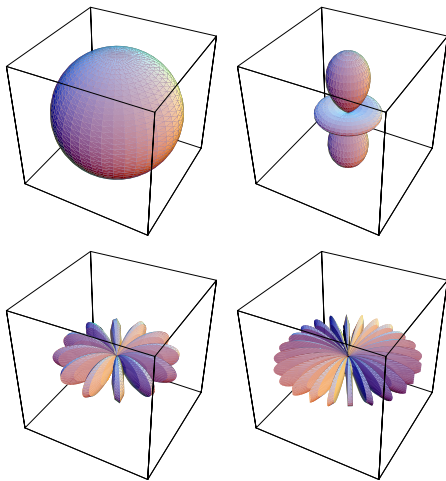

Figure 3: Parametric plots of the $H_{0,0}$(top left), $H_{2,0}$(top right), $H_{6,6}$(bottom left), and $H_{12,12}$(bottom right) hexagonal harmonics.
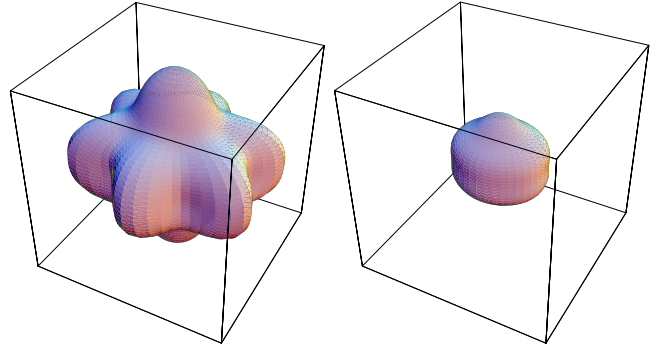

Figure 4: Parametric three dimensional presentation of the coherency strain $\Delta E_{\mathrm{CS}}^{\mathrm{eq}}(x, \hat{G})$ for $\mathrm{Mg}_{0.9}\mathrm{Ca}_{0.1}$(left) and $\mathrm{Mg}_{0.9}\mathrm{Y}_{0.1}$(right).

the high Mg-concentration plots are due mostly to Ca and Y, resulting in a different structure in the strain. Fig. 4 shows that strain energies along [0001] are greatest for Ca and Y but smallest along directions between $[10\bar{1}0]$ and $[30\bar{3}2]$ for Ca and azimuthally for Y.

In summary, the parametrization of the coherency strain with the hexagonal harmonics provides the explicit strain term for a cluster expansion. In addition, the first-principles calculation of the epitaxial energies yields interesting insight about the elastic properties of magnesium alloys. Combining the results here with a complete mixed space cluster expansion methodology for hcp alloys will enable a predictive model of coherent precipitate formation and phase stability in a wide variety of magnesium alloys.

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