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An FP-CVM calculation of pre-precipitation clustering in Al—Cu—Mg—Ag alloys

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Abstract

Trace element additions can efficiently control nucleation and, hence, affect final precipitate structures of metastable coherent second phases. As an improved and self-consistent treatment with respect to the quasi-chemical model [Aiwu Zhu et al. Acta Mater 2004;52:3671], a tetrahedron cluster-variation-method (CVM) based on first principles total energy calculation (FP-CVM) is employed to assess cluster formation prior to the second phase precipitation in Al—Cu—Mg—Ag alloys. The overall lattice elastic relaxation (accommodation of atomic unit cells of different volumes) is taken into account.

Keywords: Aluminum alloys; Nucleation; Trace element addition; First principles total energy calculation; Cluster variation method

1. Introduction

The addition of small amounts of additional elements to an alloy is an effective means of confining grain sizes and enhancing creep and fracture resistance of various aluminum alloys [2]. Moreover, trace elements and/or impurities can have an impact on production of coherent or semi-coherent strengthening second phases and their precipitate structures in heat-treatable alloys. To obtain the desired and balanced mechanical properties, one of the major tasks for intelligent design and development is to establish effective computational tools for identifying whether an element is helpful or deleterious for the desired second phases in a multi-component and multi-phase system. In a previous paper [1], an extended quasi-chemical model was employed for the prediction of the cluster formation tendency in Al—Cu—Mg—Si and Al—Cu—Mg—Ag solid solutions. Although efficient for short-range order (SRO) analysis for each pair of elements in the systems, the model is somewhat oversimplified; only pairing probability can be roughly calculated. Since the composition of the clusters is the controlling factor for orientation selection of the clusters and subsequent plate-like precipitates, as shown in both the strain energy analysis [1] and numerous experimental observations (*cf.*, Ref. [3] for Al—Cu—Mg alloys), it is relevant to evaluate more details concerning the formation of clusters or aggregates and particularly their composition dependence.

In this paper, a tetrahedron cluster-variation-method (CVM) based on first principles total energy calculation (FP-CVM) is explored. Since only the first neighbor atomic interaction is considered, a cluster configuration is defined by $\{ijkl\}$ where i, j, k and l represent the atomic species at each one of the four tetrahedron positions. The cluster energetics are obtained using CASTEP [4], a first principle calculation package, that is based on the density functional theory with the plane-wave pseudopotential method. The ultra-soft pseudopotentials are set globally while GGA-PBE [5]—a non-local

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gradient-corrected exchange-correlation functional—is chosen for each individual atom (GGA denotes "generalized gradient approximation"). The calculation quality is set as "fine" while the highest values for *K*-point meshing and energy cut-offs among the elements present in the structures is accepted. A few tests showed no significant differences were yielded when an "ultra-soft" calculation quality was chosen and/or the number of *K*-points was doubled as the preset values. The configuration entropy of a face-centered cubic (fcc) solid solution is formulated based on the cluster variation method under the tetrahedron approximation (T-CVM) as detailed below. Minimization of the total free energy yields the equilibrium probabilities of various fcc-like structures, as well as the overall lattice parameters for the alloy systems with various compositions at different temperatures. The information about the free energy and the cluster formation tendency, in terms of the cluster composition based on the nearest neighbor tetrahedron Ising-model, can thus be retrieved for alloy solid solutions with various overall compositions at aging temperatures. For comparison, the free energies of mixing of the solid solutions are also calculated by two independent methods: one uses CASTEP and allows each individual cluster to relax to their optimum lattice parameters and the second approach employs the corresponding CALPHAD databases.

2. Computational method

2.1. Cluster energetics

The formation energy $\Delta E_{ijkl} = \Delta E_{ijkl}(V)$ for a cluster configuration $\{ijkl\}$ (i, j, k, l =, e.g., Al, Cu, Mg and Ag) per lattice point, with the lattice parameter V, can be calculated employing the first principles total energy. For the simplest consideration,

$$\begin{aligned}\Delta E_{ijkl}(V) &= E_{ijkl}\left(V^{(0)}_{ijkl}\right) + \frac{B_{ijkl}V^{(0)}_{ijkl}}{2}\delta V^2_{ijkl} \\ &\quad - \sum_m f^{(m)}_{ijkl} E_{mmmm}\left(V^{(0)}_{mmmm}\right) \\ &= \Delta E_{ijkl}\left(V^{(0)}_{ijkl}\right) + \frac{B_{ijkl}}{2}V^{(0)}_{ijkl}\delta V^2_{ijkl},\end{aligned} \tag{1}$$

where $f^{(m)}_{ijkl}$ is the number of m-components in the cluster being considered divided by four (for the tetrahedron), e.g., $f^{(\mathrm{Mg})}_{\mathrm{AlCuMgMg}}$ for Mg would be 2/4, $\delta V = (V - V^{(0)})/V^{(0)}$ denotes the deviation of the lattice parameter V from the optimized or equilibrium volume $V^{(0)}$ for the configuration, E_{ijkl} is the energy of the configuration per lattice point. Essentially Eq. (1) is the energy difference for the *ijkl* cluster minus the pure component tetrahedron cluster energies *mmmm*. Only overall volume relaxation is considered when the components are mixed to form the solid solution. The electronic energies for each tetrahedron configuration can be described well with the linear volume-dependent bulk modulus B_{ijkl}

$$B_{ijkl} = V_0 \left.\frac{\partial^2 E}{\partial V^2}\right|_{V=V_0} = B^{(0)}_{ijkl} + B^{(1)}_{ijkl}\frac{\Delta V}{V_0}, \tag{2}$$

where the values of V^0_{ijkl}, $E_{ijkl}(V^0_{ijkl})$, B_{ijkl} for each configuration $\{ijkl\}$ are obtained by curve-fitting, as shown in Fig. 1 where the tetrahedral cluster {AlAlMgCu} is taken as an example. For application to the trace element additions to an aluminum matrix, only the data with volumes that are close to the Al—Al—Al—Al configuration are considered. Table 1 lists energies and curve fitting parameters for all 32 combinations.

2.2. Entropy S

An fcc lattice can be constructed using tetrahedrons of various configurations $\{ijkl\}$ ($ijkl$ = A, B, C, ...) to form the solid solution with composition $\{x_\mathrm{A}, x_\mathrm{B}, x_\mathrm{C}, \ldots\}$. Along the $\langle 0\,0\,1\rangle$ direction, using superposition of the sub-clusters: triangle, pairs and points, construction operations lead to the configuration entropy S for each lattice point [6,7]

$$\begin{aligned}\frac{S}{k_\mathrm{B}} &= -2\sum_{ijkl} U_{ijkl}\ln U_{ijkl} + 6\sum_{ij} Y_{ij}\ln Y_{ij} \\ &\quad - 5\sum_i X_i \ln X_i - 1,\end{aligned} \tag{3}$$

where U_{ijkl}, Y_{ij}, X_i denotes the forming probabilities of tetrahedron $\{ijkl\}$, pairs $\{ij\}$ and the point (elemental atom) $\{i\}$.

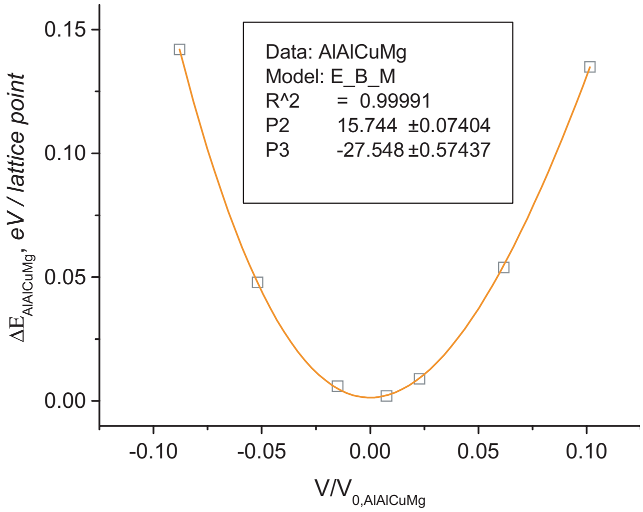

Fig. 1. The calculated first principle total energy of the Al—Al—Cu—Mg configuration per FCC lattice point versus the reduced atomic volume, V. The solid line represents the curve fitting by the model as detailed in the text and the data in the box give statistical fitting parameters.