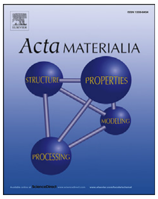
Acta Materialia 140 (2017) 240–249

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat



Full length article

Ab initio modelling of the early stages of precipitation in Al-6000 alloys

Daniele Giofré [a], [*], Till Junge [b], W.A. Curtin [b], Michele Ceriotti [a]

[a] Laboratory of Computational Science and Modeling, Institute of Materials, École Polytechnique Fédérale de Lausanne, 1015, Lausanne, Switzerland
[b] Laboratory for Multiscale Mechanics Modeling, Institute of Mechanical Engineering, EPFL, 1015, Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 27 April 2017
Received in revised form
21 July 2017
Accepted 8 August 2017
Available online 10 August 2017

Keywords:
Ab initio simulations
Aluminum alloys
Precipitation
Nucleation

ABSTRACT

Age hardening induced by the formation of (semi)-coherent precipitate phases is crucial for the processing and final properties of the widely used Al-6000 alloys. Early stages of precipitation are particularly important from the fundamental and technological side, but are still far from being fully understood. Here, an analysis of the energetics of nanometric precipitates of the meta-stable β'' phases is performed, identifying the bulk, elastic strain and interface energies that contribute to the stability of a nucleating cluster. Results show that needle-shape precipitates are unstable to growth even at the smallest size β'' formula unit, i.e. there is no energy barrier to growth. The small differences between different compositions points toward the need for the study of possible precipitate/matrix interface reconstruction. A classical semi-quantitative nucleation theory approach including elastic strain energy captures the trends in precipitate energy versus size and composition. This validates the use of mesoscale models to assess stability and interactions of precipitates. Studies of smaller 3D clusters also show stability relative to the solid solution state, indicating that the early stages of precipitation may be diffusion-limited. Overall, these results demonstrate the important interplay among composition-dependent bulk, interface, and elastic strain energies in determining nanoscale precipitate stability and growth.

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1. Introduction

Pure aluminum is lightweight metal that has little strength or resistance to plastic deformation. Alloying aluminum introduces either solutes or the formation of nanometric precipitates that hinder the motion of dislocations, thereby dramatically improving the mechanical properties [1–3]. A major alloy class used in the automotive industry is the Al-6000 series that contains silicon and magnesium in the range of 0.4–1 wt% with a Si/Mg ratio larger than one. In the initial stages of processing at elevated temperatures, the alloy is a supersaturated solid solution (SSSS), with the solutes randomly dispersed in the Al matrix. After quenching to lower temperatures, the solutes aggregate to form nanometer-sized precipitates (e.g Guinier-Preston (GP) zones, metastable phases, or stable phases, depending on the thermal history). The time evolution of precipitate nucleation and growth is accompanied by a concomitant mechanical strengthening, referred to as age-hardening. Furthermore, precipitation proceeds through a sequence of competing phases that differ in composition, morphology, thermodynamic stability, and kinetics of growth and dissolution, as well as in the contributions to the mechanical properties [4,5]. Control of the kinetics of age-hardening is crucial for the optimization of the final mechanical properties.

In commercial 6000-series Al alloys, precipitation commences at room temperature shortly after quenching, and this "natural aging" is undesirable. Subsequent "artificial aging" at elevated temperature is then used to achieve the desired precipitate type(s) and sizes. The most effective hardening conditions are obtained in the early stages of precipitation, where fully-coherent GP zones coexist with the semi-coherent β'' phase [6], which forms needle-shaped precipitates 200–1000 Å in length and ≈ 60 Å in diameter [7,8]. High-resolution electron microscopy and quantitative electron diffraction [7,9] studies have revealed that the β'' phase is characterized by a Mg/Si ratio close to 1 but with different possible stoichiometries that include Mg_5Si_6, $Mg_4Al_3Si_4$, $Mg_5Al_2Si_4$. Recent first-principles calculations have predicted that the latter composition is the most stable [10]. While considerable progress has been made in understanding the structure of the β'' phase, and the behavior of the SSSS [11], little is known on the early stages of the

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[*] Corresponding author.
E-mail address: daniele.giofre@epfl.ch (D. Giofré).

http://dx.doi.org/10.1016/j.actamat.2017.08.017
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aging mechanism, and in particular on the thermodynamics of the initial clustering of solutes to form the precipitate [1,2,9,12]. Such knowledge is crucial to gain better control over the balance between natural and artificial aging.

In the present work we study the energetics of nanoscale precipitates using *ab initio* electronic structure methods so as to identify the different contributions to the thermodynamic in-situ precipitation energetics. We compute the energy contributions due to the precipitate formation energy, the precipitate/matrix interface energies, and the elastic energy due to lattice and elastic mismatch between precipitate and matrix. We show that these contributions semi-quantitatively capture the total energy of in-situ precipitates as a function of precipitate size. Our results demonstrate that – down to the size of a single formula unit of the β'' phase, fully encapsulated in the Al matrix – the precipitate growth process can proceed without energetic barriers. Since the nucleation process of the β'' phase has nearly zero barrier, control of precipitation kinetics should focus on aggregates of atoms of even smaller size.

The remainder of this paper is organized as follows. In Section 2 we describe the details of our *ab initio* simulations. In Section 3 we report a few benchmarks on the bulk properties of the different stoichiometries proposed for the β'' phases. In Section 4 we discuss a classical-nucleation-theory (CNT) model of precipitate stability, including surface energies and the continuum elasticity model of lattice mismatch relaxation, and compare with DFT results for needle-like precipitates. In Section 5 we present *ab initio* simulations of fully-encapsulated clusters. We finally draw conclusions.

2. Computational details

Density functional theory (DFT) has been shown to provide reliable energetics for aluminum and its alloys [10,11,13,14]. We have used self-consistent DFT as implemented in the Quantum ESPRESSO (QE) package [15]. We used a gradient corrected exchange and correlation energy functional (PBE) [16], together with a plane-waves expansion of Kohn-Sham orbitals and electronic density, using ultra-soft pseudopotentials for all the elements involved [17–19]. All calculations were performed with a *k*-point sampling of the Brillouin zone using a grid density of $\approx 5 \cdot 10^{-6}$ Å^{-3} and a Mokhorst-Pack mesh [20]. The plane-wave cut-off energy was chosen to be 35 (280) Ry for the wavefunction (the charge density) when evaluating the energetics of defects (i.e. for computing formation, surface, and precipitation energies). Test calculations performed at larger cutoffs showed that these parameters are sufficient to converge the atomization energy of Al at a level of 0.3 meV/atom. Cutoffs were increased to 50 (400) Ry so as to converge the value of the elastic constants to an error below 1 GPa. Comparison with previous literature results, where available, will be presented below.

3. Bulk properties of matrix and precipitate phases

Bulk properties (lattice structures, lattice constants, elastic constants) of Al and the various β''-precipitates studied here have been previously computed in the literature. Here, we present our results as a means of benchmarking our methods, verifying literature results, and most importantly obtaining reference values that are fully consistent with our computational details – which is crucial to evaluate the energy differences that determine surface and defect energies.

For bulk *fcc* Al, we computed the lattice parameter to be 4.057 Å, in excellent agreement with the experimental value and with previous modelling using the same functional [21,22]. These lattice parameters are used throughout our study to build supercells representing the Al matrix. All of the β'' phases we considered can be described by a monoclinic cell containing two formula units (f.u.). We considered three compositions, Mg_5Si_6, $Mg_5Al_2Si_4$ and $Mg_4Al_3Si_4$, as shown in Fig. 1. We computed the crystal structures of these β''-precipitates starting from the geometries proposed in previous works [7]. The equilibrium lattice parameters and monoclinic angles are shown in Table 1, and agree well with existing literature [4]. Inside the Al matrix, the main crystallographic directions (lattice vectors) of the precipitate are aligned with those in the *fcc* lattice of aluminum as follows:

$$[100]_{\beta''} \parallel [203]_{\text{Al}} \quad [010]_{\beta''} \parallel [010]_{\text{Al}} \quad [001]_{\beta''} \parallel \left[\bar{3}01\right]_{\text{Al}}. \tag{1}$$

The ideal monoclinic unit cell can be deformed, relative to the fully relaxed structures, to substitute for 22 Al atoms. The corresponding lattice vectors and lattice constants of the 22-atom Al are shown Table 1. The difference between the ideal monoclinic unit cell and the 22-atom Al unit cell uniquely determines the misfit strain tensor of the precipitate in the Al lattice, which will be used below to determine the corresponding elastic energy of precipitates in the matrix.

We computed the elastic constants of all bulk phases by evaluating the stresses generated by small displacements of the unit cell around the equilibrium structure. A suitable set of displacements was used, and the stresses were then modeled as a linear function of the displacements to obtain the elastic constants [23]. The elastic constants for bulk Al and for the three β'' phases studied here are shown in Table 2, and were computed according to a reference system consistent with the Al matrix, as shown in Fig. 2. Our values are in good agreement with available experimental values [24] and previous computations [10,25,26].

In order to define a reference state for the thermodynamics of the precipitates we define the solid solution energies as

$$E^{ss}_{\text{Al}} = E^{tot}_{\text{Al}_M} \Big/ M \tag{2}$$

$$E^{ss}_{\text{x}} = E^{tot}_{\text{Al}_{M-1}(x)} - (M-1)E^{ss}_{\text{Al}}, \tag{3}$$

for $x = \text{Si}, \text{Mg}$. Here, $E^{tot}_{\text{Al}_M}$ and $E^{tot}_{\text{Al}_{M-1}(x)}$ are the total energies of a bulk-Al supercell containing M Al atoms and $(M-1)$ Al atoms and 1 atom of $x = \text{Si}$, Mg, respectively. The energy $E^{tot}_{\text{Al}_{M-1}(x)}$ is computed using a single solute in a $4 \times 4 \times 4$ unit periodic cell with the cell volume held fixed. The cell develops a small pressure due to the misfit volume of the solute, but this contribution to the energy is negligible for the large cell size used.

The formation energy for a precipitate can then be defined as the total energy of a precipitate formula unit relative to that of the total energies of the precipitate atoms in the solid solution state. Thus, the formation energy is

$$E_{form} = \frac{1}{2}E^{tot}_{\beta''} - \sum_{x=\text{Al},\text{Si},\text{Mg}} n_x \cdot E^{ss}_x, \tag{4}$$

where $E^{tot}_{\beta''}$ is the (DFT) total energy of a fully-relaxed unit cell of the β'' phase containing 22 atoms (2 formula units), n_x is the number of atoms of element x in one formula unit, and E^{ss}_x is the energy of solute x in the (dilute) solid solution state. Knowing all the terms in Eq. (4), we can compute the formation energies of the three proposed β''-phase compositions as shown in Table 3. The precipitates are strongly favorable, with negative formation energies in excess of -2eV/f.u., or greater than −0.2 eV/atom on average. Precipitate formation is thus thermodynamically highly preferable relative to the solid solution state.

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