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Precipitates in Al–Cu alloys revisited: Atom-probe tomographic experiments and first-principles calculations of compositional evolution and interfacial segregation

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Abstract

Atom-probe tomography, transmission electron microscopy, X-ray diffraction and first-principles calculations are employed to study: (i) compositional evolution of GPII zones and θ' precipitates; and (ii) solute segregation at α-Al/θ' interfaces in Al–1.7 at.% Cu (Al–4 wt.% Cu) alloys. GPII zones are observed after aging at 438 K for 8 h, whereas higher aging temperatures, 463 K for 8 h and 533 K for 4 h, reveal only θ' precipitates. Most GPII zones and θ' precipitates are demonstrated to be Cu-deficient at the lower two aging temperatures; only the 533 K treatment resulted in θ' stoichiometries consistent with the expected Al_2Cu equilibrium composition. For alloys containing ~200 at. ppm Si we find evidence of Si partitioning to GPII zones and θ' precipitates. Significant Si segregation is observed at the coherent α-Al/θ' interface for aging at 533 K, resulting in an interfacial Si concentration more than 11 times greater than in the α-Al matrix. Importantly, the Si interfacial concentration undergoes a transition from a non-equilibrium delocalized profile to an equilibrium localized profile as the aging temperature is increased from 463 to 533 K. Consistent with these measurements, first-principles calculations predict a strong thermodynamic driving force favoring Si partitioning to Cu sites in θ'. Silicon segregation at, and partitioning to, θ' precipitates results in a decrease in interfacial free energy, and concomitantly an increase in the nucleation current. Our results suggest that Si catalyzes the early stages of precipitation in these alloys, consistent with the higher precipitate number densities observed in commercial Al–Cu–Si alloys.

Keywords: Three-dimensional atom probe; First-principles electron theory; Interface segregation; Precipitation; Aluminum alloys

1. Introduction

The binary Al–Cu system is a well-studied precipitation strengthening system because it forms the basis for a wide range of age-hardening alloys that are technologically important. The precipitation sequence observed on aging these alloys, GPI → GPII(θ'') → θ' → θ, is often used as a model system for describing the fundamentals of precipitation hardening [1]. This sequence commences with the formation of coherent GPI and GPII zones. GPI zones are described as consisting of single layers of pure Cu atoms on $\{0\,0\,1\}_{\alpha\text{-Al}}$ planes. An accepted structural model of GPII consists of two Cu {0 0 2} layers separated by three Al planes [2,3], with the stoichiometry Al_3Cu. First-principles calculations [4] also strongly support these structural models. Metastable θ', the main strengthening phase, has a body-centered tetragonal crystal structure with the stoichiometry Al_2Cu [5,6]. The precipitation sequence ends

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with the transformation of the θ' phase to the incoherent equilibrium θ phase, Al_2Cu, that possesses a tetragonal C16 crystal structure.

Given its importance for strengthening Al, a large number of studies of the Al–Cu precipitation sequence have focused on the properties of metastable θ' precipitates [7–11]. These precipitates exhibit a high-aspect-ratio plate-like morphology with coherent $(0\,0\,1)\ \theta' \| \{0\,0\,1\}_{\alpha\text{-Al}}$ interfaces parallel to their broad faces and semi-coherent interfaces at their peripheries [7]. This morphology is often rationalized by a large anisotropy in the interfacial free energy (γ) and elastic strain energies between the coherent and semi-coherent interfaces, with the broad coherent interfaces possessing a smaller γ value than the semi-coherent interfaces. Aaronson et al. [8,9] estimated the interfacial energy anisotropy factor to be ~12. Recent first-principles calculations, which decoupled the contributions of interfacial and elastic-strain energies, reported an anisotropy factor of ~3 [10,11].

The increasing use of Al–Cu alloys in commercial applications (e.g. cast 319 alloys for automobile engine blocks) continues to drive further studies of the properties of θ' precipitates [12–18]. Relatively little is known, however, concerning the compositional evolution of θ' precipitates since its nanometer-scale platelet-like morphology makes quantitative analytical electron microscopy analyses extremely difficult. This is reflected in the scant literature on solute-atom segregation at the platelets's cores and at the α-Al matrix/precipitate interfaces. This dearth of information is unfortunate since this data is essential for the development of accurate models of precipitation kinetics and strengthening. For example, segregation at interfaces is a result of a decrease in γ, which leads to a Gibbsian interfacial excess of solute (Γ) and retards precipitate coarsening. Moreover, deviations from the expected precipitate stoichiometry, in the form of excess concentrations of solute in the precipitate core, may indicate the existence of heterogeneous nucleation [19] and identify mechanisms that limit the coarsening rate. Since commercial process optimization tools rely upon accurate predictions of alloy microstructure as a function of processing conditions, it is desirable to understand and quantify the impact of nanoscale chemical composition on precipitation kinetics.

Three-dimensional (3-D) atom-probe tomography (APT) is capable of addressing these issues [20], and is currently the most suitable instrument at the subnano- to nano-scale for studying the compositions of nanoscale θ' platelets and their heterophase interfaces with the α-Al matrix. Prior evidence for magnesium segregation at coherent α-Al/$Al_3Sc(L1_2)$ heterophase interfaces, utilizing APT, demonstrates the power of this approach for measuring small values of Γ [19]. Nevertheless, prior APT studies of precipitation in Al–Cu-based alloys by different groups have reported differing results [21–25]. For instance, Karlik et al. [23] have summarized the conflicting results [21,22] pertaining to the compositions of GP zones. Additionally, Shollock et al. [24] and Sano et al. [25] performed APT analyses of θ' precipitates in Al–1.7Cu–0.34 Mg–0.1Ag at.% and Al–2.7Cu–0.5 Mg–0.1Ag–0.26Mn–0.04Zr at.% alloys, respectively, and reported different Cu concentrations for the θ' phase. Shollock et al. [24] obtained an Al_3Cu stoichiometry for the θ' phase, whereas Karlik et al. [23] found a stoichiometry of Al_2Cu. Furthermore, there have been relatively few APT studies of the temporal evolution of θ' platelets, with the majority of studies focusing on precipitate nucleation. Employing atom-probe field-ion microscopy and APT, respectively, Ringer et al. [26] and Honma et al. [27] investigated whether trace additions of tin could enhance θ' nucleation. Similarly, little is known regarding solute interfacial segregation in Al–Cu alloys: Cu segregation at a small-angle grain boundary has been studied in thin films [28], and Srivastava et al. [29] studied segregation at equilibrium θ precipitates.

In view of the above, the objective of this work is to study the nanoscale chemical composition in the Al–Cu precipitation sequence, and to elucidate whether these compositional differences correlate with variations in the observed precipitation kinetics. Specifically, using a combination of 3-D local-electrode atom-probe (LEAP) tomography, X-ray diffraction (XRD), transmission electron microscopy (TEM) and first-principles calculations, we examine: (i) the compositional evolution of GPII zones and θ' platelets; and (i) Si solute segregation at coherent α-Al/ θ' interfaces in Al–1.7 at.% Cu (Al–4 wt.% Cu), with ~200 at. ppm additions of Si. The ternary Al–Cu–Si system was studied to clarify the role of Si in the faster precipitation kinetics observed in commercial Si-containing 319 alloys [30]. For aging at 438 and 463 K, our analyses reveal clear evidence of significant partitioning of Si at the cores of the GPII zones and θ' precipitates, consistent with Si playing a catalytic role in nucleating these phases. At 533 K, the Si core concentration of θ' decreases in favor of forming a Si-rich, localized segregation profile at the coherent α-Al/θ' interface. We quantify this segregation with the relative Gibbsian interfacial Si excess, and use this data to estimate the segregation-induced reduction of interfacial free energy. Additionally, first-principles calculations of solute substitutional energies and partitioning behavior provide energetic explanations for the experimentally measured phenomena.

2. Methodologies

2.1. Experimental methods

Aluminum (ALCOA) of two different purities was used in conjunction with high-purity (99.99%) Cu (Alfa Aesar) to prepare Al–1.7 at.% Cu (Al–4 wt.% Cu) specimens. The first Al source was 99.99% pure, while the second source contained two main impurities, ~216 at. ppm Si and ~267 at. ppm Fe. These alloys were melted in an alumina crucible in a resistance-heated furnace and directionally solidified in a graphite mold. The high-purity Al alloy