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Atomic-scale pathway of early-stage precipitation in Al–Mg–Si alloys

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Abstract—Strengthening in age-hardenable alloys is mainly achieved through nano-scale precipitates whose formation paths from the atomic-scale, solute-enriched entities are rarely analyzed and understood in a directly verifiable way. Here, we discover a pathway for the earliest-stage precipitation in Al–Mg–Si alloys: solute clustering leading to three successive variants of face-centered cubic (fcc) clusters, followed by the formation of non-fcc *GP-zones*. The clusters, which originally assume a spherical morphology (*C*1), evolve into elongated clusters and orient themselves on $\{111\}_{Al}$ (*C*2) and subsequently on $\{100\}_{Al}$ planes and $\langle 100\rangle_{Al}$ directions (*C*3). We also analyze the association of quenched-in dislocations with clustering phenomena. The results of this work can open a new frontier in advancing alloy-process-property design for commercially important age-hardenable Al alloys.

Keywords: Phase transformation; Phase field crystal modeling; Precipitation; Al–Mg–Si alloys

1. Introduction

Al–Mg–Si alloys, i.e. the AA6000 series, are lightweight medium-strength heat-treatable Al alloys with a desirable combination of cost-effective engineering properties that has made them suitable for a wide range of applications, from various transportation [1] and building industry applications [2] to high-voltage power transmission [3]. The ever increasing interest in these alloys, particularly for automotive panel applications, has urged intense investigations on the formation kinetics and evolution of precipitates in such systems [4–12]. Automotive paint bake cycling processes involve early- to medium-stage underaging conditions [6,12–14]. Recent results on such early- and medium-stage precipitation hardening in Al–Mg–Si alloys have revealed that structure–hardening relationships are strongly dependent on the alloy composition and details of the aging process [9–12]. These factors have been reported to control the nucleation and growth conditions of the hardening phase, β'', which mainly forms during medium stage of aging [9,10,12,15] and is responsible for the highest hardening achieved in the peak-aged condition, while also contributing to hardening in underaged conditions [14,16–22].

Dedicated studies have attempted to analyze the early-stage precipitation in 6000 series Al alloys in terms of the sequential nature and compositional evolution of the so-called solute clusters and *GP-zones*. However, analyses of such phenomena have been mainly conducted through indirect measurements such as differential scanning calorimetry [18,23–26] and positron annihilation spectroscopy [25,27]. Semi-direct analyses by atom probe methodologies have also been used for several investigations [9,10,14,18,24,28,29]. These investigations have led to the identification of multiple clustering processes, which start to form immediately after quenching [14,18,23–25]. Although variations in the compositional characteristics of these clusters have been reported in the past, most recent studies indicate that the first group of clusters are Si-rich aggregates [9,25]. The second group of clusters, speculated to be descendants of the first Si-rich clusters, is shown to exhibit Mg-enrichment while growing [9,24,25,30]. It has been reported that a larger Si content in the alloy composition promotes cluster nucleation and leads to a finer

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distribution of β'' precipitates at later stages of aging [9,31,32]. The morphology of early-stage precipitates is generally reported from atom probe investigations to be spherical [9,24,28,29]. A few studies have also reported *GP-zones* with spherical morphology and unknown crystal structure [10,14,33]. Dedicated studies have been conducted to analyze the role of quenched-in vacancies in early stage precipitation phenomena in these alloys and a number of related hypotheses have been proposed [4,7,25–28].

Despite the vast amount of published information, there continues to remain important unanswered questions about the structural/morphological evolution of early clusters as well as the fundamental mechanisms and characteristics of diffusional transformations that occur at the earliest stages of precipitation in Al–Mg–Si alloys. Although indirect methods such as electrical resistivity and semi-direct atom probe studies have shown evidence for cluster formation, these clusters have not been directly imaged in a systematic way and no sequence of evolution in clustering itself has been reported. All previous works have suggested that, up until the formation of needle-like pre-β'' *GP-zones* [34], there exist only spherical clusters with a face-centered cubic (fcc) structure similar to the matrix, followed by spherical *GP-zones* [10,14,33] which have been poorly shown and never been structurally or chemically analyzed. Furthermore, there exists a significant gap of knowledge in theoretical analysis of solute clustering phenomena, and the roles that quenched-in dislocations may play during early-stage transformations in these alloys. The gap also includes directly verifiable (i.e. large-scale) atomistic simulation strategies that are essential for the development of future breakthrough strategies in alloy and process designs. The aim of this work is to move a major step forward in filling an important gap in this knowledge through both atomic-scale observations and computational modeling. The computational approach is based on the recently developed modeling paradigm, known as the phase field crystal (PFC) methodology [35–39], which has shown a remarkable capacity in capturing the salient physics of diffusional phase transitions involving atomic scale elastic and plastic interactions [40–43]. Using the PFC approach, Fallah et al. [41,43] analyzed, for the first time, atomistic transformations and the full free-energy-based path leading to the earliest stage precipitation in the presence of quenched-in and mobile dislocations in the Al–Cu–(Mg) alloy system. They also used high-resolution transmission electron microscopy (HRTEM) and high-resolution and scanning transmission electron microscopy methods to assess the 3-D atomic-scale simulation results through direct observation of clustering that occurs during natural aging in the Al–Cu system [40]. That study demonstrated well the validity of the simulated dislocation-induced early-stage clustering phenomena and the preferred orientation of the early clusters on the fcc close-packed (i.e. $\{111\}_{Al}$) planes. However, the possibility for other orientations was not analyzed. This work reports a pioneering systematic study based on atomic-scale direct observations and the PFC approach to analyze clustering phenomena in Al–Mg–Si alloy system.

In this study, the early-stage precipitation phenomenon is studied for solutionized/aged Al–Mg–Si alloys using HRTEM and scanning transmission electron microscopy (STEM), along with atomic-scale 3-D PFC simulations conducted on a continuous isothermal aging basis. We not only report direct imaging of the earliest clusters, but also identify, for the first time, that clusters themselves undergo a morphology and orientation evolution prior to evolving to non-fcc *GP-zones*. In other words, we introduce the missing links of clustering in the evolutionary path of early-stage precipitation, connecting the early spherical clusters with an fcc structure to non-fcc *GP-zones*, which may then act as precursors to the previously reported pre-β'' *GP-zones* with a well-defined C-centered monoclinic structure [34]. The experimental and numerical analysis of early-stage precipitation in this study, however, is focused only on the evolution of clusters with an fcc structure similar to the matrix. In reporting the analysis, our convention is to name all early precipitates with a lattice structure similar to the matrix lattice (i.e. fcc) as "*clusters*" and those which deviate from the fcc structure as "*GP-zones*".

2. Experimental

High-purity Al–0.8Mg–0.8Si and Al–0.94Mg–0.47Si (at.%) alloys (hereinafter called *A*1 and *A*2 alloys, respectively), representing two widely different atomic Mg/Si ratios (1 and 2), were supplied by Novelis Inc. as 1 mm thick cold-rolled sheets. They were solution treated in an air furnace at 560 °C for 20 min, quenched in water and immediately aged at 180 °C for various times (5, 15 and 20 min). Immediately after the heat treatment, the samples were mechanically ground, electropolished and kept in liquid nitrogen (LN2) prior to electron microscopy. Electropolished TEM samples were imaged at high resolution using an FEI Titan low base microscope, operated at 300 kV and equipped with a CEOS image corrector.

3. Model structure

A 3-D ternary PFC model was adopted from the multi-component formalism of structural PFC (XPFC) methodology developed by Ofori-Opoku et al. [42]. As also documented in Refs. [41,40,43], the mean-field approximations of PFC free energy was carried out following the procedure detailed in Ref. [39]. The resultant free energy of the alloy was used to construct the relevant phase diagram and also to estimate the work of formation of clusters through calculation of individual contributing terms (i.e. the driving force, strain energy and surface energy). The descriptions of such methodologies can be found in detail in Refs. [41,40,43]. Below, we present the details of the above PFC calculations and simulation methodologies for clustering in a ternary alloy system in three dimensions.

3.1. XPFC formalism for a ternary system

In a three-component system, the free energy functional can be described by the sum of two terms: ideal and excess free energy, each as a function of three individual density fields (i.e. ρ_A, ρ_B and ρ_C). The ideal term, which represents the local free energy, drives the density fields to a uniform state. On the contrary, the excess term favors periodic density fields, which arise due to species interactions (i.e. between various density fields). The following free energy functional can be written from classical density functional theory as [42]:

$$\frac{\Delta\mathcal{F}}{k_B T \rho^o} \equiv \int d\mathbf{r} f = \int d\mathbf{r}\{\Delta F_{id} + \Delta F_{ex}\} \quad (1)$$

where ΔF_{id} and ΔF_{ex} are the dimensionless ideal energy and excess energy, respectively, k_B is the Boltzmann constant, T