



In situ observation of Cu segregation and phase nucleation at a solid–liquid interface in an Al alloy

Prakash Palanisamy, James M. Howe*

Department of Materials Science and Engineering, University of Virginia, 395 McCormick Rd., Charlottesville, VA 22904, USA

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Abstract

This paper presents a systematic study comparing experimental in situ transmission electron microscopy observation of microstructural and compositional evolution with complementary thermodynamic calculations, to better understand the redistribution of solute elements and the nucleation behavior of different phases in a commercial Al-alloy powder (AA390). The results show that Cu segregation to the solid Si–liquid Al interface, as well as the significant undercooling achieved in the liquid under non-equilibrium conditions because the Al phase cannot nucleate homogeneously, play an important role in nucleating Al_2Cu at the interface prior to the Mg_2Si phase in the alloy. Although Cu segregation can occur at various locations along the interface, the Al_2Cu phase appears to preferentially nucleate at a high-index Si–liquid interface as opposed to a low-index one. The Cu concentration during segregation remains essentially constant with time, indicating that the observed segregation behavior is a thermodynamic and not a kinetic phenomenon. These in situ observations and complementary thermodynamic calculations substantially enhance our understanding of potential crystal nucleation and growth processes.

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1. Introduction

Understanding and controlling microstructure is central to a wide range of applied materials applications, as it directly influences the optical, electronic, electrochemical and mechanical properties of materials [1]. In this regard, significant effort has been devoted to understanding crystal growth from the melt [2], as this technique offers good control over microstructure under equilibrium and non-equilibrium conditions. Unfortunately, only a few experiments have been performed to directly study the interface between a growing crystal and its melt, due to the difficulty of observing the buried interface at high temperatures and because the phases are opaque and one is a liquid [3–9]. Overcoming the experimental difficulties encountered in studying technologically important materials such as

metals and semiconductors could provide better control over the phase morphologies, defect densities, nucleation and growth behavior, and resulting materials properties [10]. In the recent years, progress has been made in instrumentation that enables study of the dynamic solid–liquid interface in organic and inorganic materials [3–14].

Aluminum alloys have high strength-to-weight ratios with good corrosion resistance and are important structural materials. Substantial amounts of alloying elements are added to achieve the required properties; for example, Cu and Mg are added to Al to strengthen it through precipitation hardening, and Si is added to increase the wear resistance [15,16]. As the number of alloying elements added to Al increases, so does the possibility of forming different phases [15,17], which poses a major challenge in understanding the developing microstructure. However, if one can understand and quantify microstructural development, one can use this processing knowledge to design materials with better or potentially novel properties.

* Corresponding author. Tel.: +1 4349825646; fax: +1 4349825660.

E-mail address: jh9s@virginia.edu (J.M. Howe).

This paper presents a systematic study comparing experimental in situ transmission electron microscopy (TEM) results with complementary thermodynamic calculations, to better understand the redistribution (partitioning) of solute elements and the nucleation behavior of different phases in a commercially available, rapidly solidified Al-alloy powder (AA390) containing 17.8 Si, 1.8 Cu and 0.6 Mg (at.%) supplied by Valimet, Inc. [18]. These studies of nucleation and segregation in Al alloys are possible because of the naturally formed thin-oxide layer on the particle that prevents the liquid from evaporating at high temperatures in the transmission electron microscope. With advances made in the design of new TEM holders such as the liquid cell [4], similar studies should be possible in a variety of material systems including metals and ceramics.

2. Experimental methods

Atomized Al-alloy particles of 0.5 g were dispersed in 25 ml of ethanol and ultrasonicated for 1 h. The solution was left undisturbed for 24 h to allow the larger-sized particles to settle. The remaining particles were collected near the top of the suspension using a pipette and deposited on an ultra-thin type A-carbon film supported on a 400-mesh Cu grid.

A JEOL 2000FX-II transmission electron microscope with a LaB₆ filament operating at an accelerating voltage of 200 kV was used for the present study. A Gatan double-tilt heating holder (Model 652-Ta) was used to heat the sample to high temperatures and a thermocouple in contact with the furnace was used to measure the temperatures to within ± 15 K.

Concentrations in the particle and at the solid–liquid interface were measured by energy-dispersive X-ray spectrometry (EDS) using a high-angle (70° take-off angle) spectrometer from Gresham (Sirius 30/SUTW/AR). The probe size used for the compositional analyses was approximately 25 nm, and hence this is the spatial resolution of the analyses. Although this probe size is larger than the thickness of the solid–liquid interface, it permits measurements of an average concentration for the interface region. Concentrations measurements performed by EDS at high temperature is challenging because of thermal noise, i.e. infrared (IR) radiation, emitted from the holder furnace. A Cu shield was used to conduct heat away from the furnace and to reduce the IR radiation reaching the detector to reasonable levels [19]. Cu fluorescence occurred from the Cu shield and support grid and this was temperature dependent, generally increasing with temperature. In order to quantify the small-probe EDS spectra, we acquired an additional EDS spectrum over the entire particle at the end of the analysis at each temperature (e.g. 585, 565 and 470 °C). These spectra were then used to determine the temperature- and absorption-corrected k-factors for each particle at temperature, knowing the nominal composition of the alloy (for more details see Ref. [31]).

Thermodynamic calculations employing the CALPHAD method [20] were performed using Thermo-Calc version S with the COST 507 database [21]. The calculations were performed for the Al, Si, Cu and Mg concentrations in liquid Al, with and without allowing Al to nucleate in the liquid, to obtain results for metastable equilibrium. The formation of different phases during cooling was also studied to compare directly with the experiments.

X-ray diffraction (XRD) was performed using an XDS2000 powder diffractometer containing a Cu target and at a step size of $0.04^\circ \text{ min}^{-1}$. Thermal analysis was performed on the alloy powders by differential scanning calorimetry (DSC) with a heating rate of $5^\circ \text{ C min}^{-1}$ under N₂ flow to prevent oxidation of the particles. These techniques were used to compare the high-temperature in situ TEM experimental results with thermodynamic calculations to understand the phases formed during cooling.

3. Results and discussion

3.1. Preliminary characterization of the Al-alloy powder

The XRD pattern in Fig. 1a shows that the major phases in this alloy are α -Al, β -Si, and Al₂Cu(θ) at room temperature. The DSC data in Fig. 1b revealed that Mg₂Si phase is also present in the alloy particles, but this was not detected using XRD, because its volume fraction is low and/or due to overlapping of its peaks with those of the other phases. The DSC results indicate that above 560 °C, the alloy particles only have two phases: solid Si and liquid Al alloy. Therefore, the alloy particles can be heated above this temperature inside a transmission electron microscope using a heating holder, and cooled to directly observe the developing microstructure as well as measure the concentrations of elements in the solid and liquid phases and in the interface region.

3.2. Partitioning across a singular Si{111}–liquid Al interface

Fig. 2a shows a bright-field TEM image of an Al–Si–Cu–Mg alloy particle taken at 585 °C. The particle contains a faceted Si{111} interface in contact with liquid Al alloy containing Cu, Mg and Si in solution. Compositional analyses were performed at three different temperatures during cooling, namely 585, 565 and 470 °C, and a schematic of the particle (Fig. 2b) shows where the EDS spectra were acquired at locations 1–8. Three X-ray spectra were acquired at each location and the error bars were plotted (Fig. 2c) to give the average concentration of the elements and their deviations. At 470 °C metastable liquid Al was observed in contact with solid Si (the undercooling required for homogeneous nucleation of Al is around 100 °C [22]). At location 7, the Si concentration in the liquid Al is 8 at.% at 585 °C and this decreases to 0.7 at.% at 470 °C. This shows that with decreasing temperature, Si moves from the liquid Al to enable growth of the

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