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Rapid solidification growth mode transitions in Al-Si alloys by dynamic transmission electron microscopy

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ABSTRACT

In situ dynamic transmission electron microscope (DTEM) imaging of Al-Si thin-film alloys was performed to investigate rapid solidification behavior. Solidification of alloys with compositions from 1 to 15 atomic percent Si was imaged during pulsed laser melting and subsequent solidification. Solely α-Al solidification was observed in Al-1Si and Al-3Si alloys, and solely kinetically modified eutectic growth was observed in Al-6Si and Al-9Si alloys. A transition in the solidification mode in eutectic and hypereutectic alloys (Al-12Si and Al-15Si) from nucleated α-Al dendrites at lower solidification velocities to planar eutectic growth at higher solidification velocities was observed, departing from trends previously seen in laser-track melting experiments. Comparisons of the growth modes and corresponding velocities are compared with previous solidification models, and implications regarding the models are discussed.

1. Introduction

Aluminum silicon (Al-Si) alloys are known for their favorable castability, good wear and corrosion resistance, strength and weldability [1–3]. The microstructure of Al-Si alloys strongly depends on the overall composition and solidification history [4]. Primary aluminum/silicon, irregular eutectic, or dendritic structures can form depending on the composition, solidification velocity and thermal history [2,5–7]. Additionally, rapid solidification can result in kinetically modified structures that do not form under conditions closer to equilibrium. For example, the composition range that eutectic structures form is expanded under large thermal gradients and solidification velocities. The solidification velocity also controls the eutectic spacing, which can have an effect on the physical properties [8–10]. Moreover, under very large solidification velocities and thermal gradients partitionless growth, where no solute diffusion can occur, is possible [11].

Direct prediction of the structures that form under particular conditions has been a continuing challenge for solidification studies. A number of different models have been developed to predict the dendrite tip size, dendrite spacing, eutectic spacing, or transitions between growth modes, such as dendritic to eutectic or eutectic to partitionless growth [4,10–15]. These models are typically steady-state by design and often include adjustable parameters to fit experimental observations; as such, they can cease to be predictive outside a particular range of parameters. And while they have proven to be useful for a number of applications, extensions of these models to a broader range of processing parameters and emerging processes (*e.g.,* additive manufacturing) are needed to continue to develop and expand the field to allow predictive capabilities. A major limitation to the development of these extended models is the lack of experimental observations available for the solidification conditions of interest. Often, *ex situ* methods that infer solidification velocities are used for model development. Direct observation of the solidification front is possible in some cases using fast camera imaging and X-ray projection, but these are typically limited in spatial resolution to tens of micrometers, which once again limits the range of processing parameters that can be observed [16,17].

The dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory (LLNL) has the capability to monitor irreversible events down to tens of nanoseconds and tens of nanometers in time and space, respectively; including solidification [18–27]. This unique ability to directly observe

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microstructure formation while monitoring the solidification front in real time enables measurements of these solidification processes that are not possible with other techniques [25,27,28]. DTEM studies have shown that the solidification of metal thin films is very similar to that of bulk materials [25,28]. With the ability to monitor solidification in real time, at high spatial and temporal resolution, a more precise understanding of the conditions dictating microstructure formation can be realized, leading to more advanced solidification models. An additional advantage is that because of the simplified geometry of the experiments, two-dimensional models with reduced complexity can be used to refine the model's physics or physical parameters. A simple finite-element enthalpy model has been shown to closely agree to experiment in pure aluminum solidification [29]. This work demonstrates some of the capabilities of the DTEM method and the ability to monitor the fine details of solidification.

Here, thin films of Al-Si alloys of various compositions were melted *in situ* inside the DTEM and imaged during solidification. Compositions ranging from 1 to 15 at.% Si (Al-1Si–Al-15Si) were investigated. Studies were performed using a field-of-view (FOV) of approximately 11 μm to ensure sufficient resolution to monitor the solidification of single grains. In the hypoeutectic alloys, no growth mode transitions were observed, and solidification proceeded directly with columnar growth of either α-Al (Al-1Si and Al-3Si) or columnar growth of eutectic grains[1] (Al-6Si and Al-9Si) after the initial solidification of the "mushy" zone (two phase, solid + liquid). At the eutectic and hypereutectic compositions (Al-12Si and Al-15Si, respectively), a transition between the solidification of nucleated equiaxed-dendritic α-Al grains to planar/columnar[2] eutectic grains was observed, accompanied by a transition in the solidification velocity. The reasons for this transition of growth mode are discussed in the framework of previous solidification models, and the need for improved predictive capabilities is outlined.

2. Experimental methods

Al-Si thin films were deposited simultaneously onto square, 0.25 × 0.25 mm wide, 50 nm thick SiN_x windows and lacey carbon TEM grids using DC magnetron sputtering in a chamber with a base pressure of <6.7 × 10^{-6} Pa (5 × 10^{-8} Torr). The process pressure was 0.44 Pa (3.3 × 10^{-3} Torr). The main sputter target was Al-1at.% Si, run using a power of 300 W, with a secondary Si target to increase the Si content, run using a power of 25–75 W. The alloy films spanned a composition range from Al-1at.%Si (Al-1Si) to Al-15 at.% Si (Al-15Si), with six nominal compositions investigated: Al-1Si, Al-3Si, Al-6Si, Al-9Si, Al-12Si, and Al-15Si. The films on SiN_x were used for the *in situ* melting experiments. The lacey carbon TEM grids were used for measurement of the film compositions via energy dispersive x-ray spectroscopy (EDS) in the TEM. The compositions were measured by collecting spectra from five random areas of the metal alloy that were over holes in the carbon film and taking the average. The target and measured compositions are given in Table 1. Deposited alloy film thicknesses were approximately 80–100 nm. Initial grain sizes were on the order of 50 nm with no preferred crystallographic orientation.

The films were melted *in situ* using a 1064 nm Nd:YAG laser with a 15 ns full-width half maximum (FWHM) and a Gaussian beam profile with a 135 μm 1/e^2 diameter. The shot-to-shot variation in the melting laser energy was ~10%. As each alloy composition required a different energy to achieve melting due to differences in thermal and optical properties, the melt pool size was held approximately constant for all alloy compositions. The DTEM was operated using an accelerating voltage of 200 kV. DTEM imaging was carried out using 50 ns electron pulses with either 1 or 2.5 μs interframe time-spans between the end of one electron pulse to the beginning of the next. Nine-frame movies of a single melting/solidification event were collected with a user-defined delay between the initial melting laser pulse and the first electron pulse. In the DTEM figures shown, specific frames were selected from nine-frame acquisitions to highlight particular features of the solidification process. The full nine-frame Movie Mode data can be found in the Supplementary Material. A schematic of the experimental setup is shown in Fig. 1. For further details of the DTEM technique, see Refs. [18–27].

Post-mortem energy filtered TEM (EFTEM) mapping was carried out using the jump-ratio method with a FEI Titan transmission electron microscope (TEM) operating at an accelerating voltage of 300 kV and equipped with a Gatan image filter (GIF). Bright-field TEM images were acquired in the DTEM (a modified JEOL 2000FX TEM) operating at 200 kV in conventional thermionic emission mode.

Table 1
Nominal (Target) and measured compositions of the Al-Si thin films.

Target composition (atomic %)	Measured composition[a]
Al-1Si	1.1 ± 0.2 at %
Al-3Si	2.6 ± 0.1 at %
Al-6Si	5.7 ± 0.3 at %
Al-9Si	8.4 ± 0.5 at %
Al-12Si	10.8 ± 0.9 at %
Al-15Si	14.0 ± 0.2 at %

[a] Errors are 1 standard deviation from the mean of 5 measurements from random areas on the film.

3. Results

3.1. Hypoeutectic Al-Si

The sample melting laser used a Gaussian profile with a 1/e^2 diameter of approximately 135 μm, with a 45° angle of incidence on the sample. This resulted in an elliptical melt pool with a minor axis radius of about 25 μm. The spatial profile led to a "mushy" zone several microns wide at the perimeter of the initial melt pool. This occurred because the deposited energy at the Gaussian edges was not enough to fully melt the metal. Due to the thin nature of the film, the lateral melted state of film, solid or mushy, was identical through the thickness of the metal down to the SiN_x substrate (at the timescales of interest, *i.e.* after melting, during solidification). Quick calculations showed that any energy deposited at the film's surface diffused to the other side within ~1 ns. The heat flow after melting was radially outward in the plane of the film into the surrounding solid, preferentially through the metallic film due to the low thermal conductivity of the amorphous silicon nitride (<10 W/mK) [30,31] relative to that of the alloy films (~100–200 W/mK) [32,33]. A low magnification solidification movie (field-of-view ~80μm) of an Al-1Si alloy film is included in the Supplementary Material for the reader's reference (Fig. S1).

Fig. 2 shows the solidification of an Al-1Si thin-film starting at 0.00 μs (the first imaging pulse was coincident with the laser melting pulse). The initial solidification of the mushy region can be seen by the small grains rapidly appearing at 2.10 μs. If any solid

[1] Al-Si alloys display an irregular, branched eutectic structure, and in rapidly solidified alloys the eutectic structure can be "fibrous" [3–7].

[2] Columnar growth simply refers to directional growth of a grain, whether it is dendritic, cellular, or planar.