30.0 MICROSTRUCTURAL EVOLUTION OF METALLIC ALLOYS DURING RAPID SOLIDIFICATION (LEVERAGED)

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30.1 Project Overview and Industrial Relevance

Understanding the relationship between processing, microstructure, and final performance of a metallic alloy is a fundamental goal of materials science. This begins with understanding the as-solidified microstructure of a metal, as this can be largely determinant of subsequent solid-state phase transformations during processing. While conventional solidification techniques have been extensively studied, far from equilibrium processes that involve rapid solidification, such as additive manufacturing, are not entirely understood. These processes are especially interesting due to the metastable phases achieved that are not observed or behave differently in materials produced via conventional equilibrium solidification techniques. Understanding how these novel phases and microstructures determine the development of subsequent solid-state phase transformations is especially important for predicting behavior in a material during processes such as heat treatments or thermal cycling that occur following solidification. While some studies have investigated solid-liquid and solid-state phase transformations in rapidly solidified alloys, these are rare and generally evaluate post mortem microstructures (**Fig. 30.1**) [30.1, 30.2]. Using in situ techniques will allow for observations of the mechanisms that control microstructural development during and following rapid solidification. Imaging various length and time scales, considering both bulk and thin samples, will allow for a more complete understanding of the details of these mechanisms. To focus on specific phenomena, the model systems Al-Cu, Al-Ag, and Al-Cu-Ag will be used to consider microsegregation and precipitation, in addition to more complex reactions in ternary alloys. Investigating the complete solidification pathway of metallic alloys will not only improve fundamental knowledge of phase transformations during rapid solidification, but will allow for better prediction of solid-state microstructural evolution during far from equilibrium processes such as additive manufacturing.

30.2 Previous Work

In situ rapid solidification studies have been performed on Al-Cu and Al-Si alloys using the Dynamic Transmission Electron Microscope (DTEM) at Lawrence Livermore National Laboratory (LLNL) [30.3]. This technique allows for direct observations of the melt-pool during rapid solidification and imaging of microstructural evolution at microsecond time scales, which also allows for the velocity of the solidification front to be determined. Although not directly measurable, the thermal gradient experienced during solidification can be estimated by modeling. Previous studies were performed at solidification velocities higher than those experienced in processes such as additive manufacturing. However, the more recent addition of a hot stage (also with tailoring of the laser beam characteristics) allows for experiments with controlled, reduced cooling rates that are directly applicable to processes such as additive manufacturing. Importantly, these types of conditions have historically been experimentally challenging to access, especially during in-situ experiments. Images showing the novel microstructures observed during this process can be seen in **Fig. 30.2**. Rapid solidification often results in kinetically trapped solute. This can greatly affect subsequent solid-state precipitation behavior; and, possibly alter the maximum volume fraction of precipitates that can be achieved in an alloy during complex thermal cycling. Also seen in this study is the development of bands due to morphological instability in the solidification front experienced at high solidification velocities. This can be seen in the center of the microstructure displayed in the bottom right photo in **Fig. 30.2b**. This could also lead to interesting precipitation behavior, as the bands alternate between microsegregation free zones and eutectic growth regions. More recently, rapid solidification studies have been done using an additive manufacturing set up at the Advanced Photon Source (APS) at Argonne National Lab (**Fig. 30.3**) [30.4]. This set up more accurately represents the solidification velocities experienced during additive manufacturing, and is also used to track solidification front velocities.

Additional state-of-the-art imaging techniques will be pursued to monitor the evolution of solid-state phase transformations in this project. One such example is the use of Transmission X-ray Microscopy (TXM) to image precipitates in 4-D in an Al-Cu alloy [30.5]. Imaging in 4-D allowed for direct observation of precipitate nucleation and growth that lead to the discovery that θ precipitates nucleate and grow from θ’/θ’ or θ’/θ intersections, rather than at the expense of θ’ by diffusion through the matrix (**Fig. 30.4**). This was not able to be seen in 2D imaging due to the complex morphology of the precipitates, but new 3-D and 4-D imaging allows for direct observations of these solid-state transformations.

Precipitation studies have been performed in ternary Al-Cu-Ag alloys that have focused on the effects of more complex systems on precipitation behavior [30.6]. Previously, our group has studied microsegregation during solidification in Al-Ag alloys and the impact on solid-state phase transformations. In situ directional solidification was performed, and the resulting microstructure was studied using multiple characterization techniques (**Fig. 30.5**), which showed how the solidification conditions directly affected the observed microstructure.

The above examples focused either on solidification and precipitation separately, or considered equilibrium conditions of solidification and solid-state phase transformations. Another study considered the complete solidification pathway during rapid solidification (**Fig. 30.1**). Using transmission electron microscopy (TEM) and x-ray diffraction (XRD), this study was able to see the effect of the microstructural features, such as a supersaturated solid solution and metastable phases, on the solid-state transformations for different compositions of Al-Mn. However, this study focused on post-mortem samples, missing many details that could have been observed in an in-situ study that could confirm the behavior of certain metastable or not well understood precipitates, such as a typically metastable G-phase that showed stable behavior under these conditions and an elusive T-phase.

30.3 Recent Progress

To begin solidification studies, a proposal was submitted for beam time at APS to use the additive manufacturing experimental apparatus for in-situ rapid solidification of Al-Cu, Al-Ag, and Al-Cu-Ag foils. Foils are currently being acquired for the compositions listed in **Table 30.1**. An application is also being prepared for a training program offered this summer on x-ray and neutron techniques at national user facilities. Solidification studies with DTEM will also be at LLNL. Discussions to make samples for these experiments are currently in progress with collaborators at LLNL.

30.4 Plans for Next Reporting Period

Depending on the results of the APS proposal submitted, beam time could be granted as early as this summer (2018). If this is the case, rapid solidification studies will be performed on the additive manufacturing set up and evaluated for use in the solid-state phase transformation studies. Discussions are also underway with collaborators at LLNL to perform DTEM rapid solidification studies. In preparation for these studies, some initial laser passes on aluminum sheets will be done at CSM to get a better understanding of what parameters will work best for these experiments, as well as to do some initial post-mortem microstructural evaluation after rapid solidification conditions. This may also be a viable pathway for preparing rapidly solidified conditions for follow-on solid-state phase transformation studies.

30.5 References

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30.6 Figures and Tables

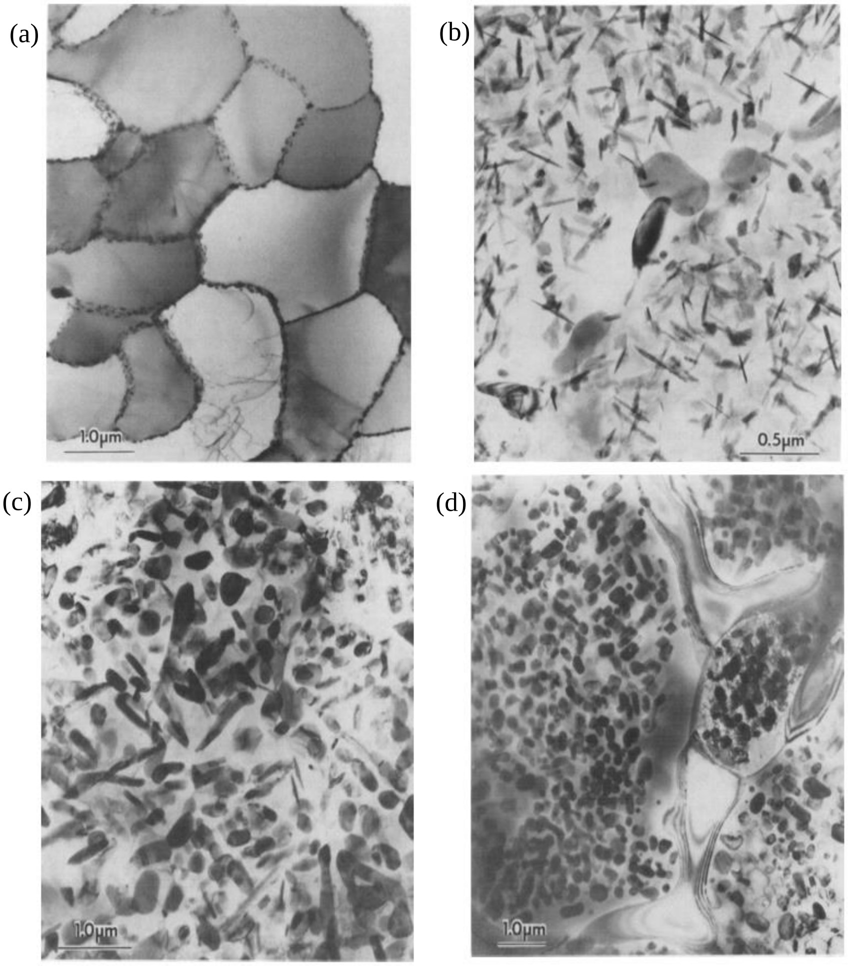
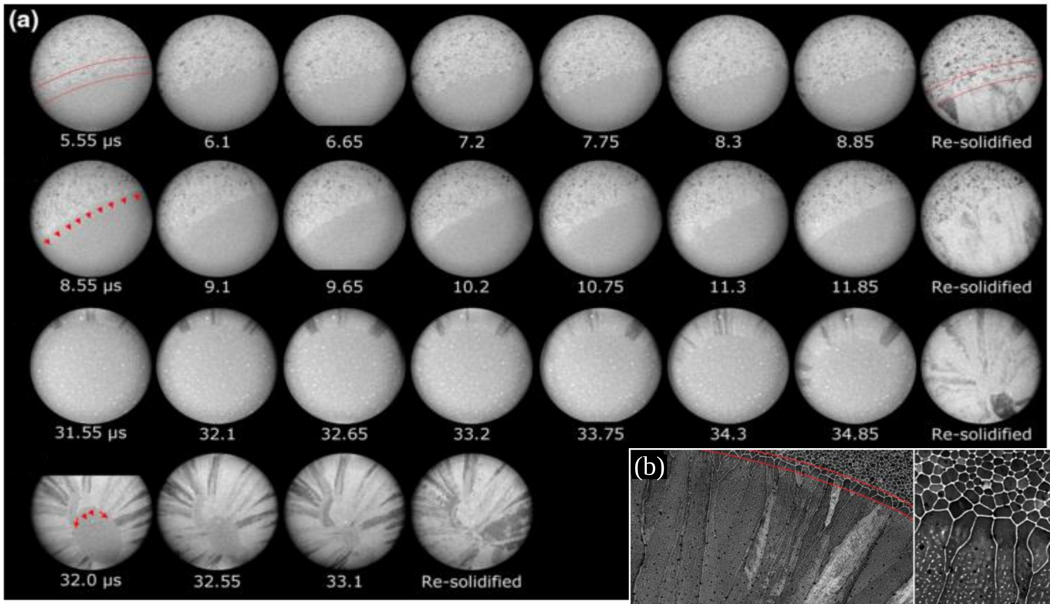


Figure 30.1: TEM images of a melt-spun (rapidly solidified) Al-12 wt % Mn alloy (a) as solidified and following a heat treatment at 450°C for (b) 5 min, (c) 1 h, and (d) 16 h. From [30.1].



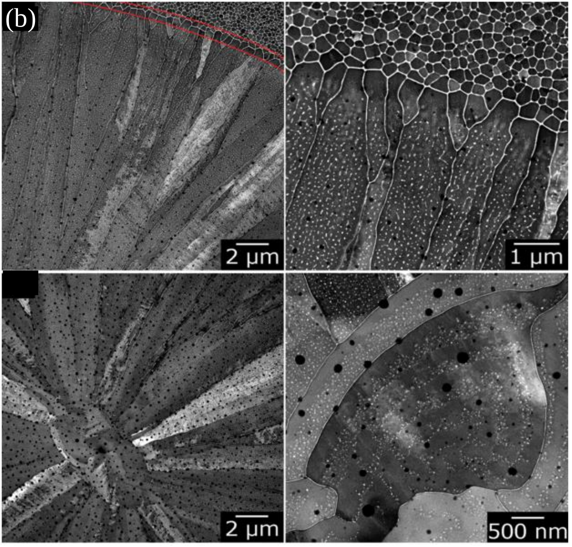


Figure 30.2: (a) Images taken of a rapidly solidified Al-Cu alloy using the DTEM at various stages of solidification. (b) A detailed image of the microstructural features following rapid solidification. From [30.3].

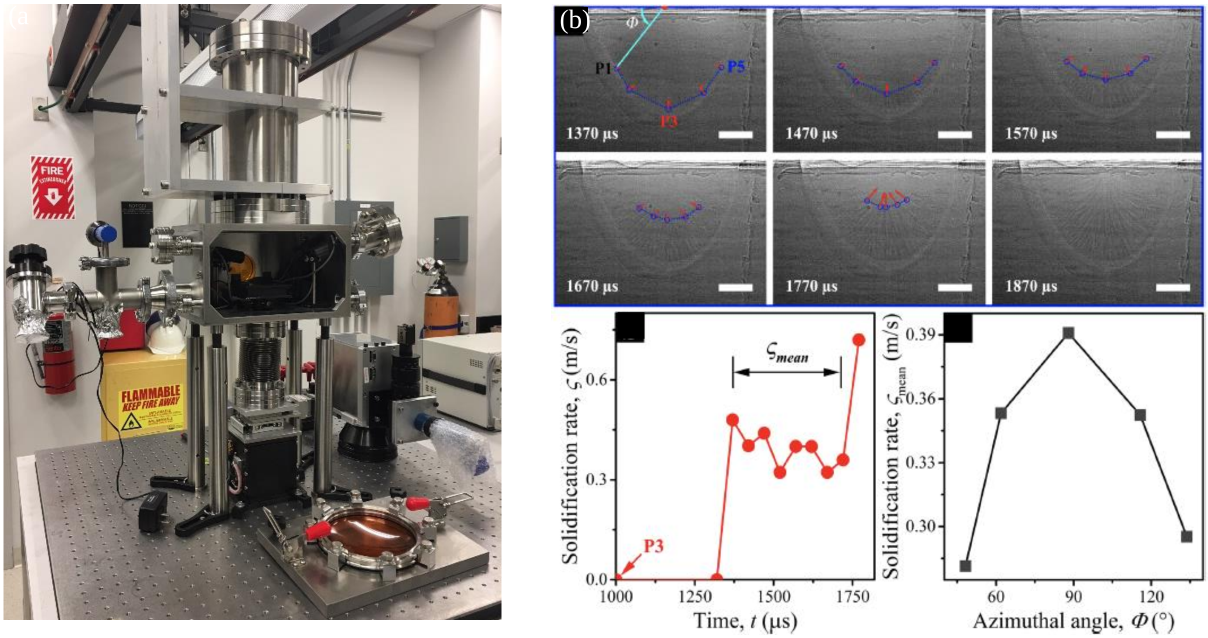


Figure 30.3: (a) Additive manufacturing set up at APS. (b) Imaging and solidification rate data taken from in-situ experiments. From [30.4].

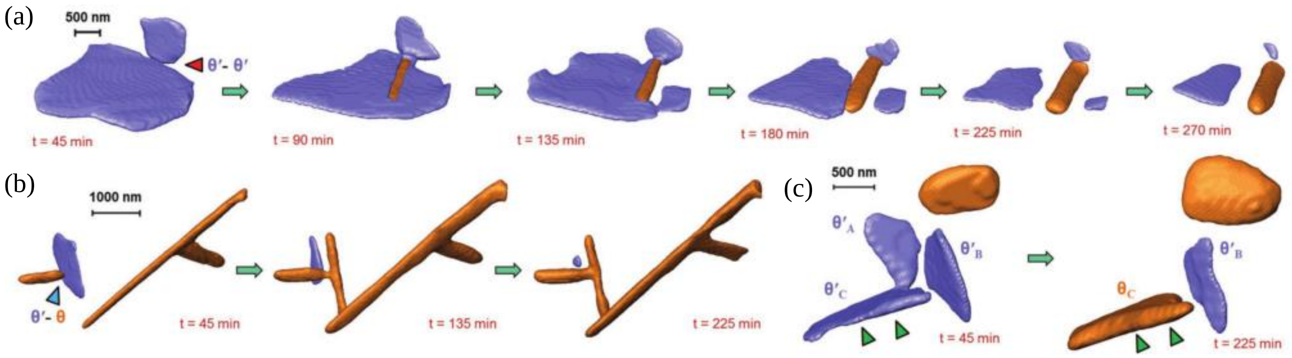


Figure 30.4: (a) 4D nondestructive microstructural characterization using TXM. (b) Nucleation and growth of θ from θ′/θ ′ intersection. (c) Varying transformation of different θ′ precipitates. From [30.5].

Table 30.1: Aluminum Alloy Sample Compositions

Alloy System	Sample 1 (wt. %/at. % Solute)	Sample 2 (wt. %/at. % Solute)	Sample 3 (wt. %/at. % Solute)
Al-Cu	1.9/0.8	10/4.5	20/9.6
Al-Ag	3/0.8	14.3/4.5	30/9.6
Al-Cu-Ag	1.9 Cu, 3 Ag /0.8 Cu, 0.8 Ag	10 Cu, 14.3 Ag /4.5 Cu, 4.5 Ag	20 Cu, 30 Ag /9.6 Cu, 9.6 Ag