

Studying rapid solidification microstructure evolution in hypoeutectic ternary Al(Cu-Ag) alloys by fast in-situ and post-mortem TEM experiments

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The microstructures of materials processed by electron- and laser-beam based additive manufacturing, welding, and thermal spray deposition form by rapid solidification (RS) [1]. Detailed scientific understanding of RS related non-equilibrium phenomena, e.g. solute trapping, segregation patterns and metastable phase formation, and often extreme scale refinements, is required for improved process control and associated alloy development. Hence, determining the mechanism responsible for RS microstructures formation is technologically important and scientifically interesting.

Using electron-transparent thin film samples and combinations of unique *in-situ* transmission electron microscopy (TEM) via Movie-Mode Dynamic TEM (MMDTEM) and *post-mortem* scanning TEM (STEM) analyses enabled quantitative studies of RS microstructure development in Al, and binary Al-alloys [2],[3],[4],[5],[6],[7],[8]. Prior studies delivered quantitative measurements of the solidification interface velocity, permitted correlation with crystal growth modes and supported validation of computer models for RS alloy microstructure evolution [6],[7],[8],[9]. The current work investigates RS microstructure formation in hypoeutectic ternary Al(Cu,Ag) alloys, focusing on the interplay and respective roles of Ag and Cu solute. MMDTEM experiments have been used for in-situ observations and transformation interface velocity measurements during RS after pulsed laser melting. STEM imaging and energy dispersive X-ray spectroscopy (EDS) have been used to determine structure and elemental composition of the RS microstructures. Samples of Al-rich alloys with up to $\approx 30\text{at}\%$ of combined Ag and Cu solute have been prepared by magnetron sputtering [4]. Close to equilibrium these ternary alloys develop a multi-phase microstructure comprised of $\alpha\text{-Al}$, $\theta\text{-Al}_2\text{Cu}$ and $\zeta\text{-Ag}_2\text{Al}$. During RS diffusion becomes increasingly localized as the solidification interface accelerates, resulting in alloy specific non-equilibrium behaviors [6],[7],[8]. For the Al(Cu,Ag) ternaries anticipated effects related to the large differences in solid solubility of Ag ($\approx 22\text{at}\%$) and Cu ($\approx 2.5\text{at}\%$) in the primary $\alpha\text{-Al}$ phase, and could include solute species dependent solute trapping and segregation behavior, which would affect the formation of the Ag- and Cu-based secondary phases.

Fig. 1a shows four $20\mu\text{s}$ duration MMDTEM image series acquired in separate experiments from the same Al-11.5Cu-16Ag (at%) sample for $0\mu\text{s}$, $20\mu\text{s}$, $40\mu\text{s}$ and $60\mu\text{s}$ delays after laser pulse initiated melting. The $0\mu\text{s}$ image frame shows the initiation of melting (Fig. 1a i)). The elliptically shape melted pool exhibits dark grey contrast and is delineated from the medium grey unaffected solid alloy film (labels L, S, $5\mu\text{s}$ image, Fig. 1a i)) by a partially melted region in light grey contrast prior to onset of directional RS crystal growth. Using measurements of the minor and major axis dimensions of the melt pools for each image series permits determination of the melt pool area change and provides upper and lower limits for the solidification interface velocity (Fig. 1b) [5],[6],[8]. The melt pool expanded for about $10\mu\text{s}$ during the initial stage of incubation (Fig. 1b). For times longer than $12.5\mu\text{s}$ melt pool dimensions decreased monotonically with different rates in two separate interface velocity evolution regimes (Stage I and II, Fig. 1b). Fig. 2 shows composition sensitive STEM images and composition maps of the RS microstructure of the Al(Cu,Ag) alloy. The RS microstructure in hypoeutectic Al(Cu,Ag) develops four morphologically distinct zones: Zone 1. heat affected zone (HAZ); Zone 2. transition zone; Zone 3. columnar growth zone; 4. banded region (Fig. 1a, 2a). The multiphase microstructure comprises Ag-rich phase (brightest contrast) and Cu-rich phase (medium light grey) and Al solid solution (darkest).

Formation of Zone 1 microstructure is accomplished towards the end of the incubation stage (Fig. 1b), while Zone 2 and 3 developed by directional RS behind solidification interface segments migrating at rates of on average about 0.07m/s in Stage I and 0.23m/s in Stage II (Fig. 1b), respectively. The STEM image contrast features for the α -Al grains (labels 1-5, Fig. 2b) indicate composition modulations on the nanoscale and Cu- and Ag-solute based phase formation at intercellular and interdendritic regions. EDS mapping showed that α -Al grains in Zone 1 contained \approx 6-7at% Cu and 13-14.5at% Ag. This represents non-equilibrium solute trapping, especially regarding Cu. In Zone 2 the initially stagnant solidification interface accelerated rapidly to about 0.1m/s (Fig. 1b) over a short distance of about 0.7-1.0 μ m. This resulted in additional solute trapping with concentrations increasing from about 14at% to 16at% for Ag and about 6at% to 10.5at% for Cu in α -Al phase at the transition to Zone 3 (Fig. 2c,d). The Al phase incorporated Ag more readily than Cu, which partitioned significantly to intercellular regions in Zone 1 and Zone 2. The α -Al cells of Zone 3 are nearly maximally supersaturated with Cu and Ag solute. The modulations of the concentrations of \pm 5at% Cu and \pm 6at% Ag about the local averages on the scale about 20nm (Fig. 2c, d) correlate with the STEM image contrast of the α -Al cells in Zone 2 (Fig. 2b). Peaks of Ag concentration are typically displaced by about 10nm relative Cu concentration to peaks (Fig. 2d). These features are attributed to kinetically arrested solute clustering and partitioning, indicate localization of diffusion to the 20nm length scale, and manifest spatially correlated solute fluxes.

The presentation will use quantitative metrics uniquely accessible with MMDTEM to nano-scale resolved imaging and analytical STEM data to elaborate the reactions and transformation mechanisms responsible for the non-equilibrium RS microstructures in Al-Cu-Ag alloys. Furthermore, advantages, limitations, and needs and opportunities for future developments of the promising MMDTEM platform will be discussed.

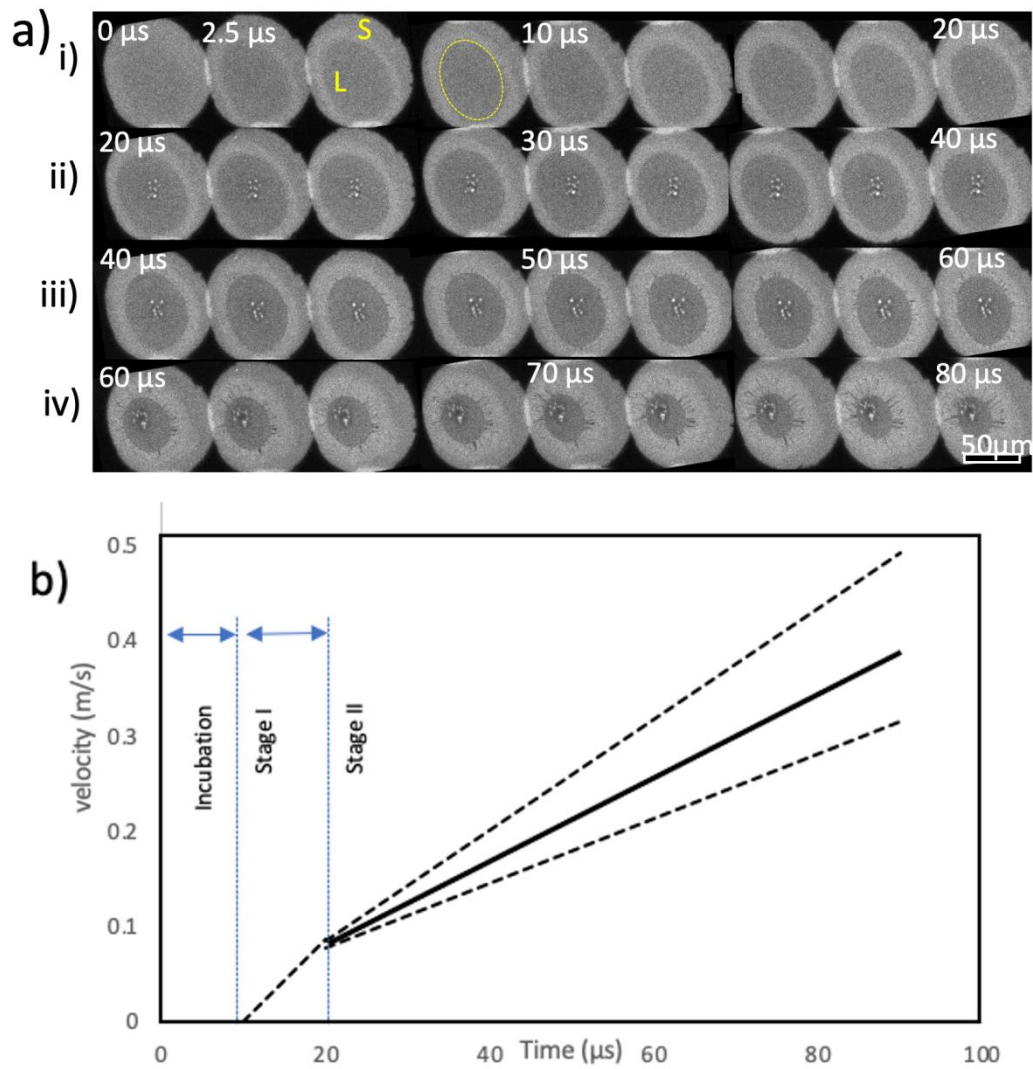


Figure 1. a) Examples of four MM-DTEM image series of RS in Al-(Cu, Ag), 50ns exposure/frame, $2.5 \mu\text{s}$ interframe step, acquired a different delay times Δt post melting, i) $\Delta t = 0 \mu\text{s}$, ii) $20 \mu\text{s}$, iii) $40 \mu\text{s}$, iv) $60 \mu\text{s}$; b) evolution in solidification interface velocity with time.

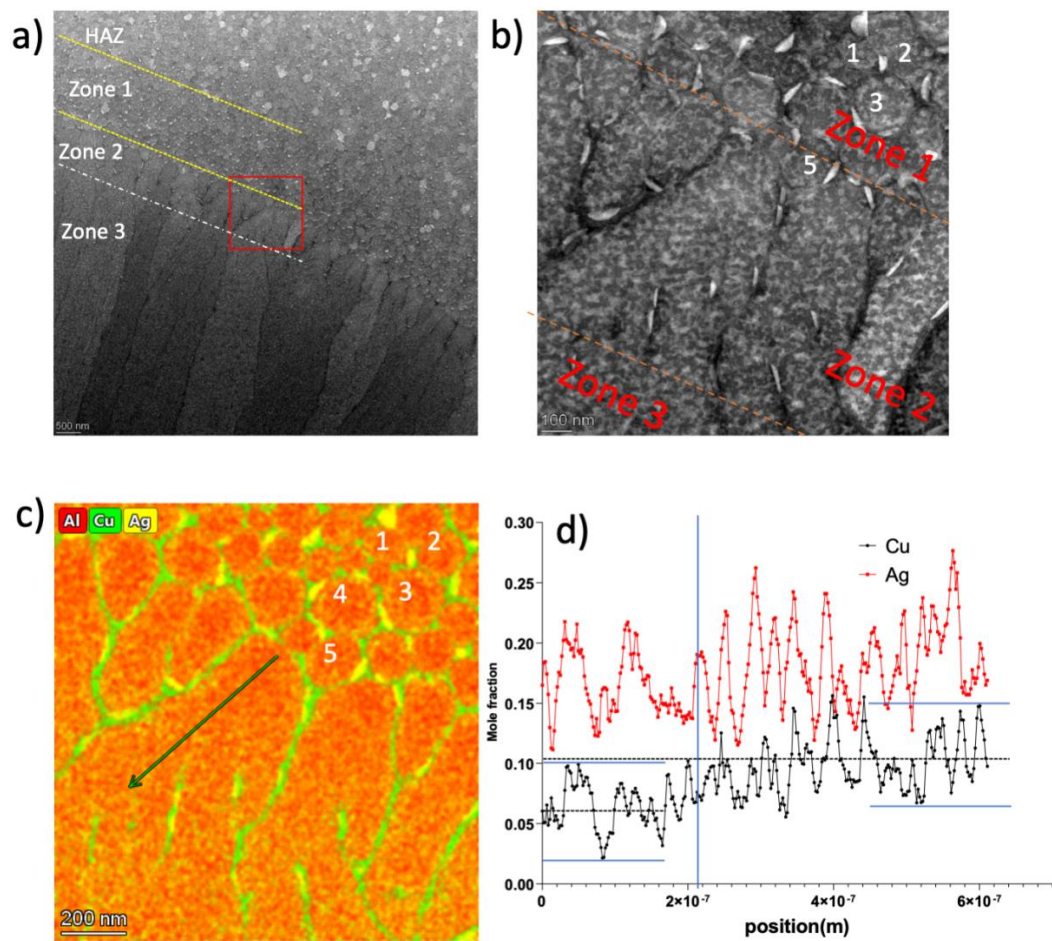


Figure 2. RS microstructure examples - (a), (b) STEM ADF images; (c) EDS composition map for Al, Cu, Ag, (d) Cu, Ag concentration profiles along arrow in (c).

References

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