HREM and Analytical TEM of the Rapidly Solidified Microstructure Evolved at the Extremes of the Coupled Crystal Growth Regime in Hypo-Eutectic Al-Cu Alloys

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Supported by the National Science Foundation, NSF-DMR 1607922.
Rapid solidification of metals and alloys is common in materials processing and laser based technologies.

Unique microstructures by Solidification under far from equilibrium conditions

Tayloring processing conditions for desirable microstructures

Solidification Conditions and Alloy System

Resultant Microstructures

In situ & post mortem Micro-Characterization

Accurate mechanistic understanding of Microstructure Formation
Rapid solidification of metals and alloys is common in materials processing and laser based technologies.

Use unique TEM instrumentation and techniques
Provide information desirable for improved experiment based understanding!

(A) In-situ TEM measurements
...mechanistic details of transformation processes, interface velocity & morphology, crystal growth modes...directly correlate with microstructure development

→ Major challenge: Transformation Interfaces migrate at \( v \geq 0.1 \text{ m/s} \! \)

(B) Post-mortem Quantitative analytical (S)TEM of transformation products
...Structure, composition, crystallography and fractions of phases present with nm-scale spatial resolution
Procedures and Materials

**Thin Film Preparation:**
- E-Beam Evaporation/Magnetron Sputtering under UHV conditions using elemental targets
- Pulsed Laser Deposition using alloy targets
- Windowed TEM grids as substrates, amorphous Si₃N₄ membranes (~50nm thin)
- **Al-Cu alloy film layers ~80-160nm thick**

**Micro-Characterization:**
- In-Situ TEM with DTEM, modified Jeol JEM2000FX, via collaboration with Lawrence Livermore National Laboratory
- STEM/TEM post-mortem & pre-PL melting studies with FEI Tecnai F20, FEI Titan 80-300, Jeol JEM2100F operated at 300 & 200kV.
- NanoMegas ASTAR/Digistar/Topspin, Ametek/EDAX TSL OIM software.
- Oxford Inca EDS (JEM2100), Bruker EDS (FEI Titan), EDAX-EDS (FEI Tecnai).
Eutectic system with terminal phases of $\alpha$-Al and $\theta$-$\text{Al}_2\text{Cu}$

Large body of thermo-physical, optical, and solidification data exists & Numerous studies on rapid solidification of bulk Al-Cu alloys

Solidification-Microstructure-Selection Maps constructed for Al-Cu based on thermodynamic calculations and post-mortem studies of RS microstructures

http://www.doitpoms.ac.uk
D.A. Porter and K. Easterling, 2nd ed, 1992
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As-deposited Al-11Cu: STEM-EDXS & PED-ACOM/TEM-OIM

![STEM-EDXS & PED-ACOM/TEM-OIM images of Al-11Cu alloy](image)

**Figure 1.** Microstructure, composition, phase constitution and texture of the as-deposited Al-11Cu at.% alloy film prior to in-situ laser melting and solidification:

- **(a)** HAADF image showing the presence of nanocrystalline grains in the film.
- **(b)** EDXS map of the same region of HAADF image display with color coding scale from 0 at.% Cu to 33.7 at.% Cu indicating the presence of $\alpha$-Al and $\theta$-Al$_2$Cu phases in the film.
- **(c)** Typical SADP pattern of the as-deposited film indexed the diffraction rings with Al and $\theta$-Al$_2$Cu phases.
- **(d)** PED maps of the as-deposited film: (i) phase map and (ii) Orientation map showing the presence of two phases $\alpha$-Al and $\theta$-Al$_2$Cu in the film with slight preference for <110> texture for $\alpha$-Al grains.

- **Nanocrystalline ($\alpha/\theta$)-Aggregates:**
  - FOV average composition 11.5at%Cu
  - FOV average grain size (30±5)nm
  - $\alpha$-Al : $2.3\pm0.7$at%Cu
  - $\theta$-Al$2$Cu : $29.90\pm2.5$ at%Cu
  - 69 vol% $\alpha$-Al in phase map
  - $\alpha$-Al has minor $<011>$-fiber thin film texture ($\approx3\times$ random)
Rapid Solidification in Hypo-eutectic Aluminum-Copper Alloys

i) In-Situ Movie-mode DTEM*

* DTEM via long-standing collaboration with LLNL

ii) Post-mortem STEM/TEM/HREM Analyses
- Focus on transition to unpartitioned single-phase solidification, Banded Region
A user-defined UV pulse train for electron pulse based study of structural evolution during irreversible transients of single trigger transitions.

- Temporal resolution per frame 20 ns to ~1 µs
- Variable number of pulses (typically 9)
- Variable inter-pulse time-steps, pulse spacing from ~50ns to ~20µs
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Graphical representation of velocity over time with stages I, II, and III, showing low and high magnification views with associated information.
Post-mortem: Al-11Cu – RS Microstructure Zones

1. Heat-affected zone

2. Transition zone

\[ V_{SL} \leq \sim 0.6 \text{ m/s} \]

3. Columnar Growth, ‘\( \alpha \)-cells’

\[ \sim 0.6 \text{ m/s} \leq V_{SL} \leq \sim 0.75 \text{ m/s} \]

4. Banded region

Single-Phase Growth for \( V_{SL} = V_a \approx 0.8 \text{ m/s} \)

Start of Banded Region marks transition from coupled-phase to single-phase growth in RS
Post-mortem: Al-11Cu – RS Microstructure Zones

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Start of Banded Region marks transition from coupled-phase to single-phase growth in RS
Solidification Products in Banded Region
– “At the Extremes of Coupled Growth to Complete Solute Trapping”

- **COUPLED Two-Phase Growth Regime (‘T’):**
  - Coupled Growth of $\alpha$-Al and $\theta$-$\mathrm{Al_2Cu}$ in Zones 1, 2 & parts of 3 (Zone 3, only at beginning)...
  - Coupled Growth of $\alpha$-Al and $\theta'$-$\mathrm{Al_2Cu}$ in most of Zone 3
  - Coupled growth of Al and $\mathrm{Al_2Cu}$ for $V_{SL} < V_a \approx 0.8$ m/s

- **Single-Phase Growth Regime (‘S’):**
  - Cu solute partitioning rate insufficient to support coupled growth for $V_{SL} \geq V_a \approx 0.8$ m/s
  - Zone 3 to Zone 4 Transition from Coupled Growth Regime to Single-Phase (unpartitioned) $\alpha$-Al growth
Banded Region Al-11Cu: Phase OR’s in Two-Phase bands

Phase map

Orientation map

Index map

θ'-variants & α-Al exhibit cube OR

\{001\} \(\theta'\) || \{100\} \(\alpha\) & \<100>\(\theta'\) || \<100>\(\alpha\)

⇒ The OR enables coherent nucleation interfaces which impart a kinetic advantage to metastable θ'-phase over stable θ-phase!
Al-11Cu, Banded Region: [001]-ZA HREM $\theta'$-Al$_2$Cu and $\alpha$-Al in coupled two-phase growth bands

$\theta'$-Al$_2$Cu and $\alpha$-Al (001) lattice planes Fully Coherent

{110} and {100} family planes in $\theta'$-Al$_2$Cu and $\alpha$-Al Lattice perfectly match for cube OR

Atom arrangements for cube OR in <001>-Al-projection
Al-11Cu, Banded Region: STEM-EDS composition measurements in Two-phase and in Single-phase Bands

a) HAADF STEM, banded region; red rectangle and circles indicating location for EDS measurements in Table. b) Heat-map of Cu.

<table>
<thead>
<tr>
<th>Location</th>
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<tr>
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Regions T: Cu partitioning sufficient to permit coupled growth of $\alpha$- and $\theta'$-phase
Regions S: Partitionless single-phase growth of maximally super-saturated $\alpha$-Al
Al-11Cu, Banded region: Composition variation developed during partitionless single-phase crystal growth

Spatial scale of Cu% fluctuations in SINGLE PHASE α-Al GROWTH RS PRODUCT on average ~10-20nm

Propose: Spatial Cu% variation in single-phase RS product represent ‘frozen-in’ Cu%-modulations of liquid boundary layer

Line Scan in single-phase band
Average 11.3at% Cu (stdev ±1.7at%Cu)
Min 7.4at%Cu    Max 16.4at%Cu
Evidence for $\theta'$-phase ‘embryos’ in liquid boundary layer
θ’-like regions in Single-Phase Growth Bands at or below Critical Size for Nucleation

- Size of θ’-regions on average ~2.2nm (range 1.5nm ≤ D ≤ 5.4nm)
- At v_{sl}=0.8m/s the Solidification Interface is undercooled by ΔT_i ≈ 110K (mostly due to solute trapping within cellular/dendritic growth model)

⇒ Classical Nucleation Theory, T_i = min:
- r^*(Al_2Cu) ≈ 1.2nm – 2.8nm
- Critical nucleus size exceeds size of most θ’-regions in Single-Phase Bands

⇒ Partitionless solidification if D/δ = v_a
- At T=755K, Cu diffusivity in liquid is D=2.32x10^{-9} m^2s^{-1}
- Liquid Boundary Layer width, δ=D/v_a is δ=2.32/0.8 [nm]= 2.9nm

⇒ Evidence for θ’-phase ‘embryos’ in liquid boundary layer
Summary and some Conclusions:

- Thin film alloy platform S/TEM/ & DTEM suitable for basic research of RS microstructure evolution in multi-component alloys.
- Quantitative experimental measurements from in situ TEM and post-mortem structural and composition analyses by HREM and STEM enabled determination of
  - solid-liquid interface temperature,
  - solid-liquid interface velocity evolution,
  - limiting estimate of width of the diffusional boundary layer ahead of RS interface during single-phase (partitionless) growth.

- Discontinuous $\text{Al}_2\text{Cu}$-phase implies repeated Nucleation in coupled growth regime.
- Ability to form coherent interface sections with the $\alpha$-$\text{Al}$ crystal imbues kinetic advantage and $\theta'$-phase replaces the thermodynamically stable $\theta$-$\text{Al}_2\text{Cu}$-phase.
- During single-phase growth composition modulations in the boundary layer of liquid adjacent to crystal growth interface are ‘frozen-in’ and persist as embryos.
The authors gratefully acknowledge financial support from the National Science Foundation and the Department of Energy for the effort associated with the DTEM and the collaborators at LLNL, as detailed below.

Work at the University of Pittsburgh supported by the National Science Foundation, Grant No. DMR 1105757 & 1607922. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.