Beyond solution growth – solidification under controlled heat flow

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Physics 509 Lecture
Outline

• Solution growth limitations
• Directional solidification basics
• Bulk crystal techniques
  – Czochralski method
  – Bridgman method
Solution growth

• Conditions favorable for solution growth
  – Exposed primary solidification surface
  – Sufficiently large temperature range
  – Stable faceted growth (i.e., no intergrowth and minimal branching)

Can the growth conditions be altered for stable, faceted growth?
Stable growth regimes

- Growth temperature not constant
- Growth rates and supersaturation are coupled
- Growth rate is a complicated function of cooling rate and liquidus slope

Liquidus slope \( m = \frac{dT}{dC_L} \)

Cooling rate = \( \frac{dT}{dt} = m \frac{dC_L}{dt} \)

Growth rate = \( \frac{d(C_L-C_0)}{(C_L-C_s)/dt} \)
Morphology of growth

Large intergrowths of small Pb$_3$Pr crystals

Small clusters of large Pb$_3$Pr crystals

Pb$_3$Pr single crystals

Isolated crystals
Morphological maps of stable growth regimes

Solution growth limitations

- Requires faceted growth regime
- Growth rates and supersaturation cannot be decoupled
- Overall volumes limited by
  - Diluted compositions for limited nucleation
  - Interface breakdown
Growth of bulk crystals

- Decouple growth rate from supersaturation
- Use directional heat flow
- Allows for control of growth fronts
- Stabilizes planar growth regimes

- Must control nucleation
- Must control growth conditions
Interface stability

- Flat (planar) S/L interface is formed at the melting $T_m$
- The temperature profile in solid and liquid is determined by the thermal conductivity
  - $K_S > K_L$
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- If heat is then extracted from one end the interface will begin to move forward
Interface stability

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- The temperature profile in solid and liquid is determined by the thermal conductivity:
  - $K_S > K_L$

- If heat is then extracted from one end, the interface will begin to move forward.

- If the solid is perturbed and grows forward into the liquid, it will see higher temperatures and will melt back.
Dendrites

- Primary arms grow in specific crystallographic directions and generally opposite to the heat flow.

- Secondary and tertiary arms develop in a self similar manner.
Exploiting directional heat flow

• Suppresses undesirable growth morphologies or undesirable phases

• Application of temperature gradient in direction of growth
  – Low gradients – applicable to congruent compounds and pure elements
  – High gradients – applicable to alloys with freezing range or non-congruent (peritectic) compounds
Pure elements - Silicon

- Congruent melting point
- Nucleation controlled through seeding
- Low undercooling
- Fairly fast growth velocities
Czochralski method (CZ)
Control of Growth

- Heat flow conditions change as solid/liquid proportions change
- Counter-rotation for better heat/mass transfer
- Heat flow balance between solid/liquid
  - Weight change
- Shape of growth front
  - Meniscus curvature
Thermal heat balance

- At the solid liquid interface, for the steady state movement of the interface (heat in = heat out)

  - \( \text{Latent heat released} = \text{heat conducted} \)
  - \( v \Delta H_{SL} = - k_L \Delta T_c \)

- Growth Velocity \( v = (K_L \Delta T_o) / (\Delta H_{SL} r) \)
Alloys and Compounds

- Nickel superalloy turbine blades
- Nucleation controlled through seeding or shaping
- High gradients
- Modest growth velocities
Alloy dendritic growth - Constitutional supercooling

- Planar breakdown occurs at
  - low gradient or low velocity
  - As composition increases
  - For systems with greater melting point depression
  - Large solidification ranges ($k<, >1$)
  - Low mixing in liquid

Constitutional supercooling criterion

$$G/v > [m X_0 (1-k_e)]/ k_e D$$
Bridgman Method - Typical Configuration

- $T_{\text{operating}} = T_m + 150\ K$
- Pull velocity – fixed (typically 1-15 mm/hr)
- Cone promotes single nucleation event
- Growth dynamics non steady state
  - Crystal is an active thermal transfer element
  - Variable temperature gradient and growth velocity
Bridgman Method Solidification Modeling

(a) \( \psi_{max} = 30 \, \text{cm}^2/\text{s} \)

(b) \( \psi_{max} = 70 \, \text{cm}^2/\text{s} \)

\( \psi_{max} = 187 \, \text{cm}^2/\text{s} \)

\( \psi_{max} = 23 \, \text{cm}^2/\text{s} \)

\( \psi_{max} = 88 \, \text{cm}^2/\text{s} \)

Courtesy J. Derby U. Minnesota
Toward optimization of crystal growth for materials discovery, synthesis, and processing: Two cases of interest

Jeffrey J. Derby
Complete mixing liquid - no diffusion in solid

- Solid/liquid interface temperature follows the liquidus
- Scheil equation
  - $X_S = k_e X_o (1-f_S)^{(ke-1)}$
  - $X_L = X_o f_L^{(ke-1)}$
- Non uniform compositional profile
Fe-Ga alloy crystals

Fe-20 wt% Ga
Fe-Ga alloy crystals

Fe-20 wt% Ga
Inverted temperature gradient freeze
Stationary Bridgman configuration

Liquid Sn-melt sealing technique

Inverted temperature gradient technique

Mirror like surface with in-plane size 2x1 cm²

THANK YOU!

QUESTIONS