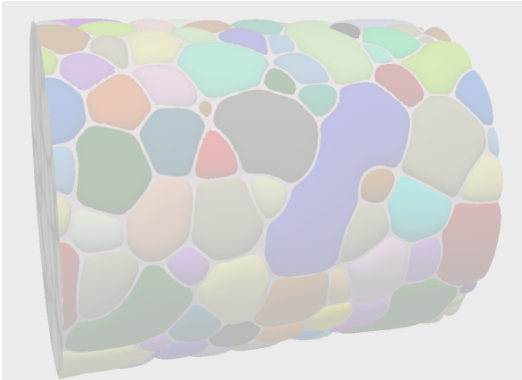
SAND2022-4968C

$$v_n = M\gamma H \qquad \gamma = \Delta F - \Gamma \frac{\partial f_{mix}}{\partial c}\bigg|_{eq}$$

$$\frac{\partial \mathbf{c}}{\partial \mathbf{t}} = \nabla \cdot \left[\mathbf{M_c} \nabla \left(\frac{\delta \mathcal{F}_{\mathbf{tot}}}{\delta \mathbf{c}} \right) \right]$$



Mesoscale Modeling of Grain Boundaries: From Interdiffusion Processes to Alloy Segregation

Fadi Abdeljawad, Paul Kotula, S. Parasad and Stephen M. Foiles

Sandia National Laboratories, Albuquerque, NM USA

Sandia National Laboratories

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Outline

- **Nanocrystalline Materials**
  - Thermal instability
  - Grain boundary (GB) segregation as route to mitigate grain growth processes
  - GB segregation isotherms and GB phase transitions
  - Simulations results

- **Kirkendall processes: Accounting for GBs**
  - Diffusion in substitutional binary alloys: Kirkendall effect
  - A model to account for GBs as sources/sinks for vacancies
  - Preliminary results

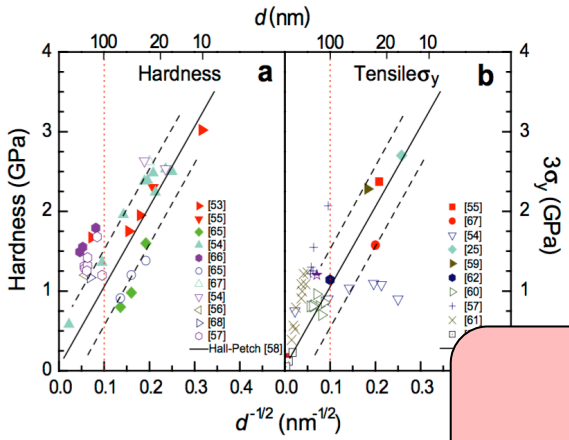
- **Concluding remarks**

Grain Boundary Segregation in Nanocrystalline Alloys

Nanocrystalline (NC) Metals

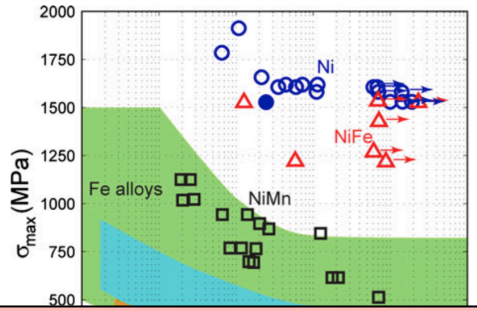
Sandia National Laboratories

Hardness and Yield

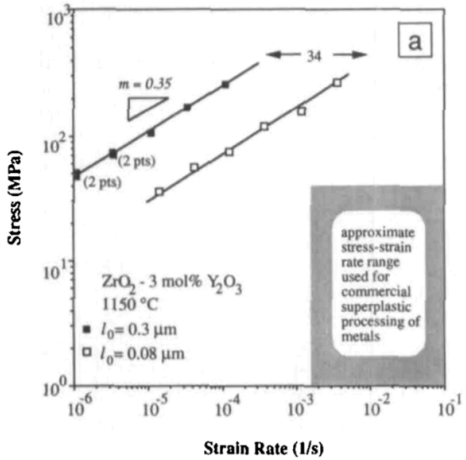


Dao *et al.*, Acta Mater. (2007)

Fatigue



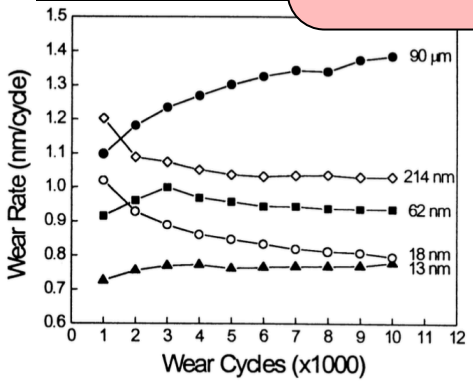
Strain Rate



Weertman *et al.*, MRS Bull. (1999)

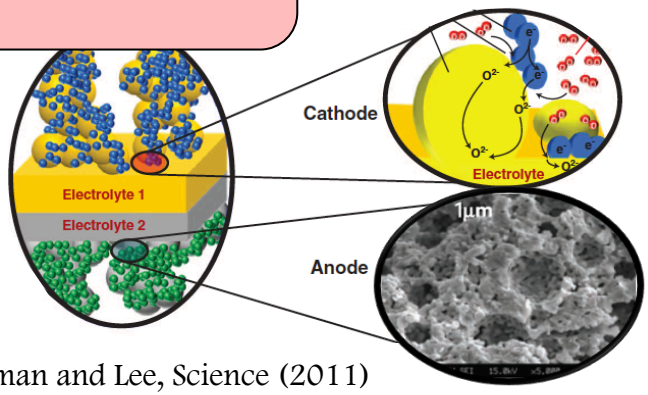
But …

Wear (electrica



Jeong *et al.*, Scripta Mat.(2001)

olid oxide fuel cells)



Wachsman and Lee, Science (2011)

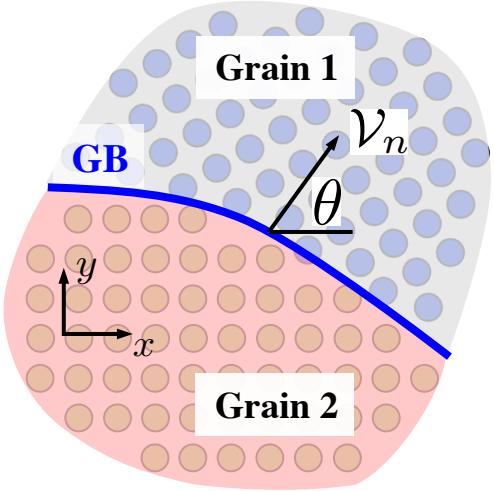
Suzuki *et al.*, Science (2009)

The Case for NC Metals

- **Problem:** High density of grain boundaries (GBs)
  - Excess free energy: $\Delta\mathcal{F} = \Delta\left(\gamma A\right)$
  - Grain-growth and homogenization processes

$$\mathcal{V}_n = M_{gb}\gamma_{gb}\mathcal{K}$$

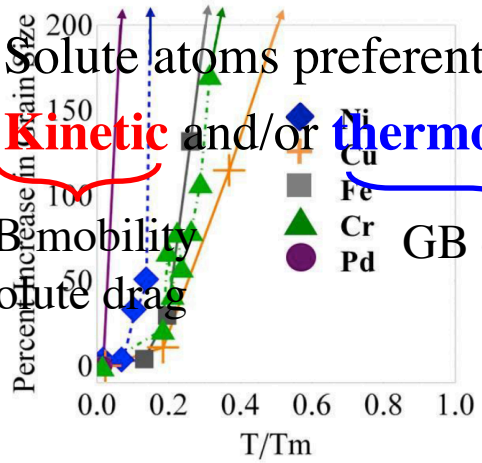
Herring, Phys. Powd. Metall. (1951)
Burke and Turnbull, Prog. Metal. Phys. (1952)
Mullins, J. App. Phys. (1956)



- **Possible solution:** Solute segregation to GBs
  - Solute atoms preferentially occupy GB sites
  - **Kinetic** and/or **thermodynamic** stabilization

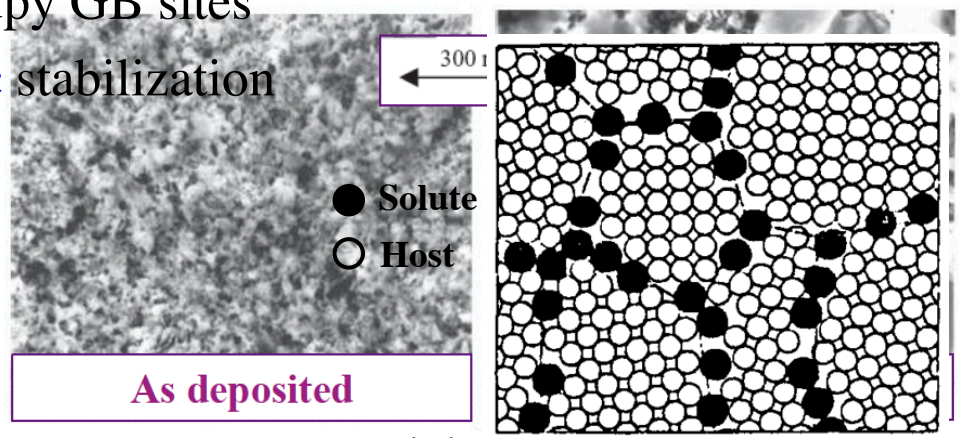
GB mobility
Solute drag

GB energy



Mat. Sci. and Eng. A 539 (2012), Nanostruct. Mat. 6 (1995)
J. Phys. Chem. C 111 (2007)

Rampant grain growth in pure NC Ni
Structure no longer NC after 20 min.

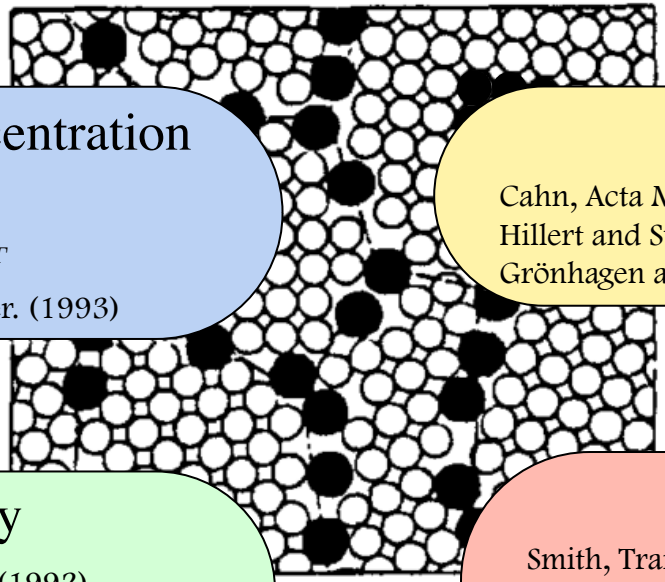


H. Murdoch, PhD thesis (2013)
Weissmüller, Nanostruct. Mater. (1993)

Key Questions

- Predict role of GB solute segregation on **microstructural evolution**
- Leverage information from lower length scales
- **Detangle** thermodynamic aspects from kinetic ones
- Use the framework in the **design** of NC metallic alloys

Phase field framework



GB energy vs. concentration

$$\Gamma = -\left(\frac{\partial \gamma_{gb}}{\partial \mu}\right)_{P,T}$$

Weissmüller, Nanostruct. Mater. (1993)

Solute drag

Cahn, Acta Metall. (1962)
Hillert and Sundman, Acta Metall. (1976)
Grönhagen and Ågren, Acta Mater. (2007)

GB anisotropy

Udler and D. Seidman, Phys. Stat. Sol. (1992)
Seki *et al.*, Acta Metall. Mater. (1991)
Hashimoto *et al.*, Acta Metall. (1984)

Zener pinning

Smith, Trans. AIME **175** (1948)
Hellman and M. Hillert, Scand. J. Met. (1975)
Chen *et al.*, J. Am. Ceram. Soc. (1998)
Moelens *et al.*, Acta Mater. (2005)

Phase Field Formalism

- Free energy
  - c(**r**,t): alloy concentration
  - $\boldsymbol{\phi}_i(\mathbf{r},t)$, $\{i = 1, \ldots, n_{\boldsymbol{\phi}}\}$: grain order parameters

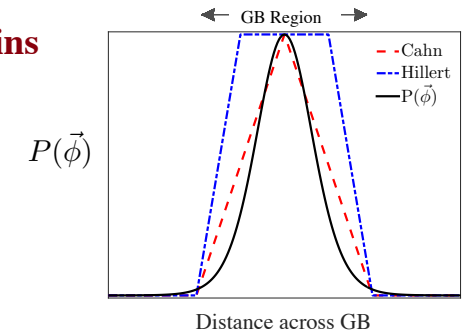
$$\mathcal{F}_{tot}[c,T] = \int d\mathbf{r}\left[f_{loc}(c,T) + \sum_i^{n_\phi} \frac{\epsilon^2}{2}|\nabla\phi_i|^2 + \frac{\kappa^2}{2}|\nabla c|^2\right]$$

Local energy density

Gradient terms for GBs and compositional damins

$$f_{loc}(c,T) = P(\vec{\phi})f_{gb}(c,T) + \left[1 - P(\vec{\phi})\right] f_b(c,T)$$

$P(\vec{\phi})$: interpolates free energy between bulk and GB



- Dynamics

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[M_c \nabla \left(\frac{\delta \mathcal{F}_{tot}}{\delta c}\right)\right]$$

Mass conservation

Cahn-Hilliard Eq.

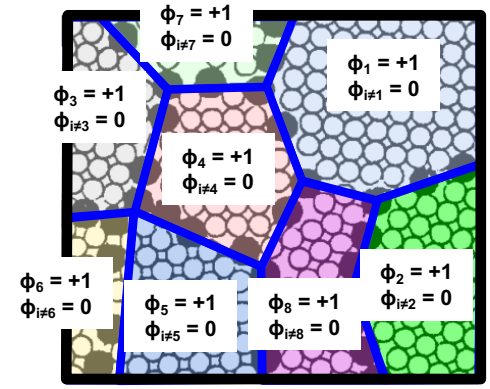
$$\frac{\partial \phi_i}{\partial t} = -L_i \left(\frac{\delta \mathcal{F}_{tot}}{\delta \phi_i}\right)$$

Gradient flow

Allen-Cahn Eq.

● **Solute**

○ **Host**



Abdeljawad and Foiles, Acta Mater. (2015)

GB Segregation Isotherm

$$f_i^{mix}(c,T) = \mathbf{G_i^B} c + \mathbf{G_i^A}(1-c) + \frac{RT}{V_m}\Big[c\ln c + (1-c)\ln(1-c)\Big] + \mathbf{\Omega_i} c(1-c), \quad i = gb, bulk$$

Free energy of pure states

Heat of mixing

A : Solvent
B : Solute atoms
c_∞ : Alloy concentration

Bulk: G_b^A, G_b^B, Ω_b

GB: $G_{gb}^A, G_{gb}^B, \Omega_{gb}$

$$\frac{c_{gb}}{1-c_{gb}} = \frac{c_\infty}{1-c_\infty}\exp\left[\frac{\Big\{(G_{gb}^A - G_b^A) - (G_{gb}^B - G_b^B) - (\Omega_{gb} - \Omega_b)\Big\} + 2c_{gb}\Omega_{gb} - 2c_\infty\Omega_b}{(RT/V_m)}\right]$$

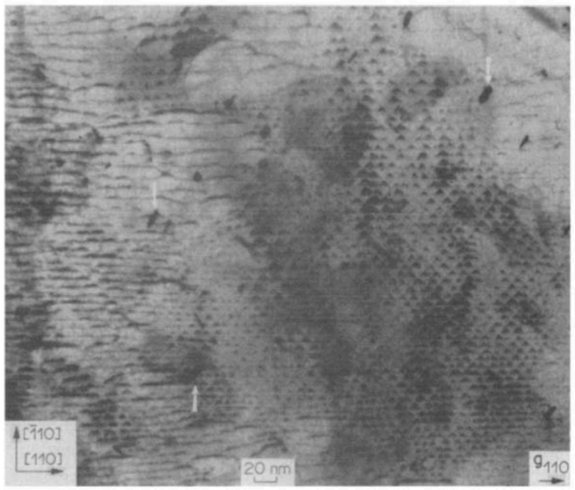
Langmuir-McLean isotherm*

Fowler-Guggenheim isotherm**

* McLean (1957)
** Fowler and Guggenheim(1939)

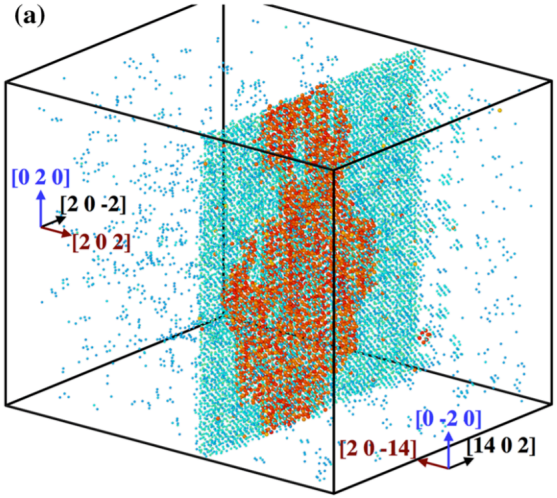
GB Segregation Isotherm

1.5° about [001], Fe-1.03 at.% Au



Sickafus and Sass, Acta Metall. (1987)

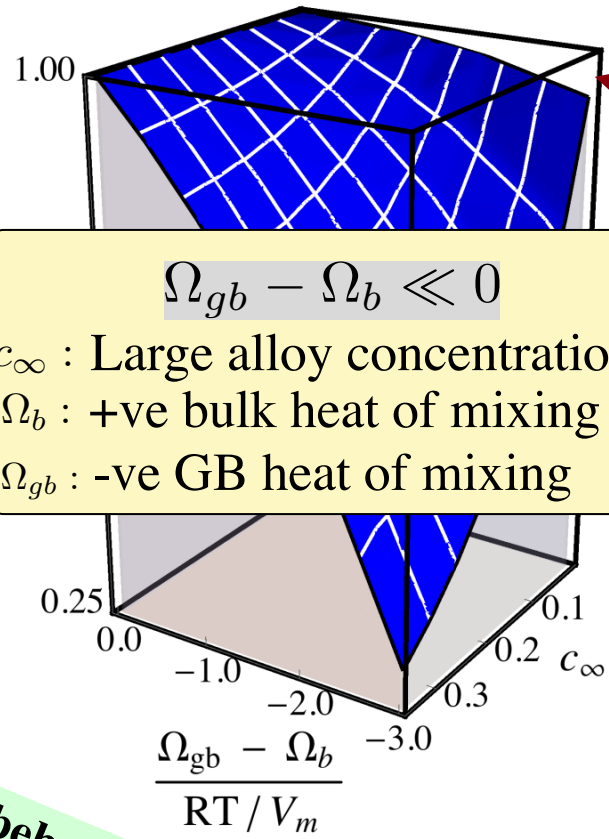
Σ5, Pt-15 at.% Au



O'brien et al. J. Mater. Sci. (2017)

GB energy $\gamma_{gb} = \gamma_{gb}(c, \Omega_{gb})$

- Gibbs adsorption eq.: $$\gamma = \Delta F - \Gamma \frac{\partial f_{mix}}{\partial c}\bigg|_{eq}$$



Dilute limit

$$\Omega_{gb} - \Omega_b \ll 0$$

c_∞ : Large alloy concentration

Ω_b : +ve bulk heat of mixing

Ω_{gb} : -ve GB heat of mixing

c_∞ : Alloy concentration

Ω_b : Bulk heat of mixing

Ω_{gb} : GB heat of mixing

Non-ideal behavior

Concentration away from dilute limit

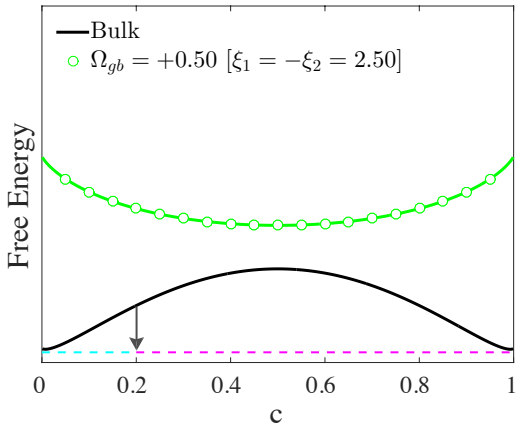
Considerable reduction in GB energy

Abdeljawad *et al.*, Acta Mater. (2017)

Murdoch *et al.*, Acta Mater. (2013)

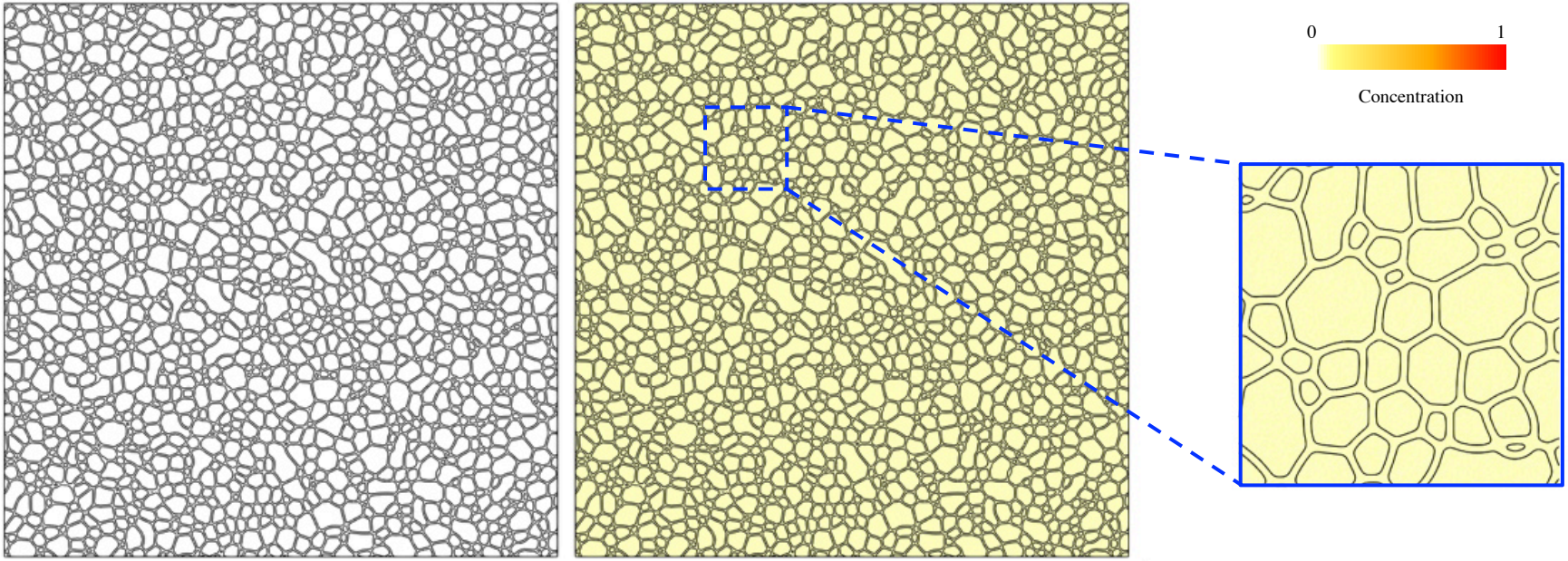
Competing Processes

- Polycrystalline systems
  - Initially (t=0): **1560** grains
  - $c(\mathbf{r}, t = 0) = \langle c \rangle = 0.2$



Normal grain growth
No segregation

With GB segregation and
phase separation



Abdeljawad *et al.*, Acta Mater. (2017)

Role of GB Free Energy

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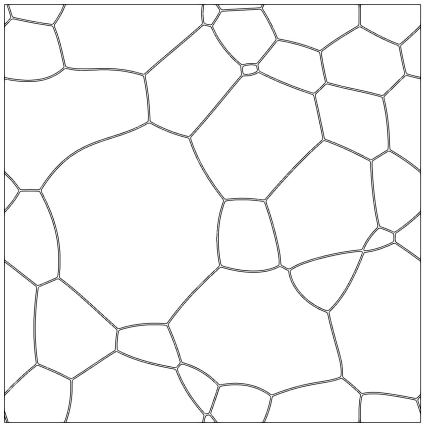
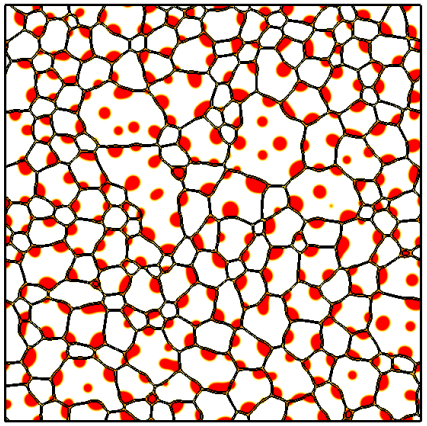
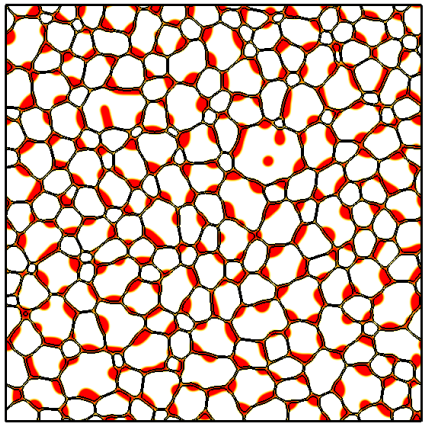
Normal grain growth (No segregation)



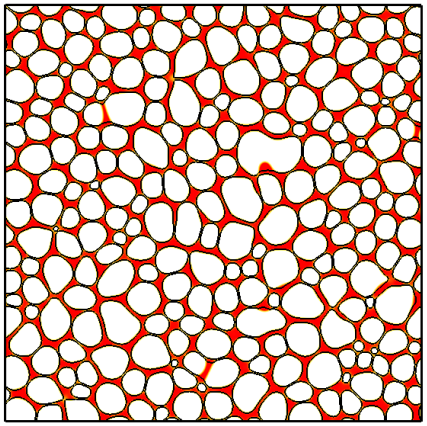
$G^B_{gb} - G^B_b = 0.60$



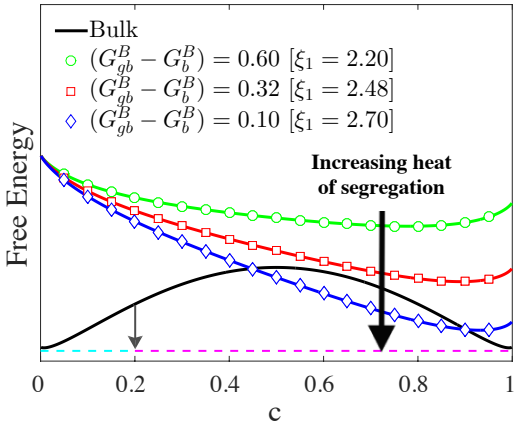
$G^B_{gb} - G^B_b = 0.32$

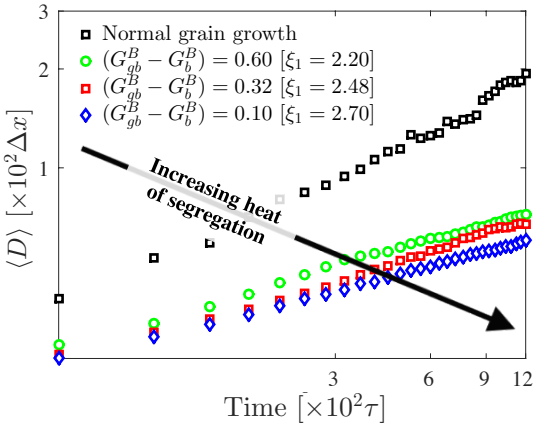


$G^B_{gb} - G^B_b = 0.10$

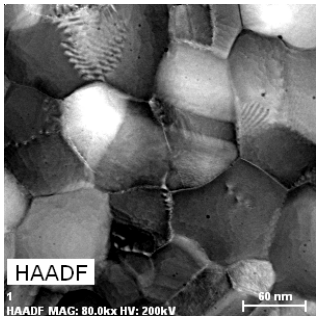


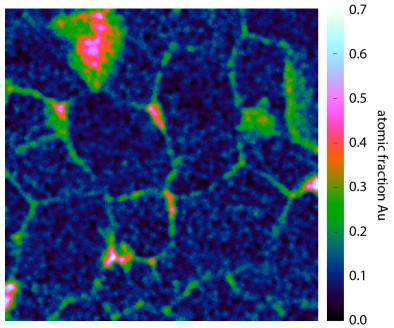
Increasing heat of segregation





Experimental: Pt-Au

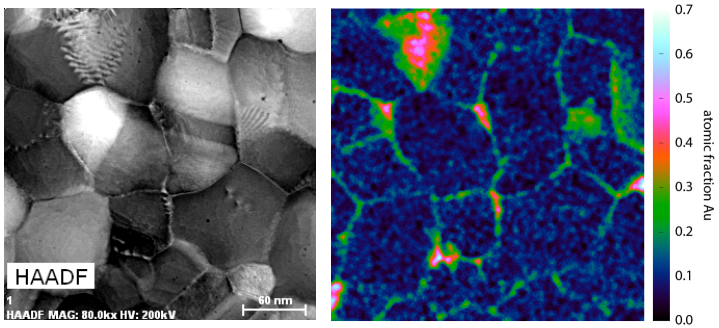




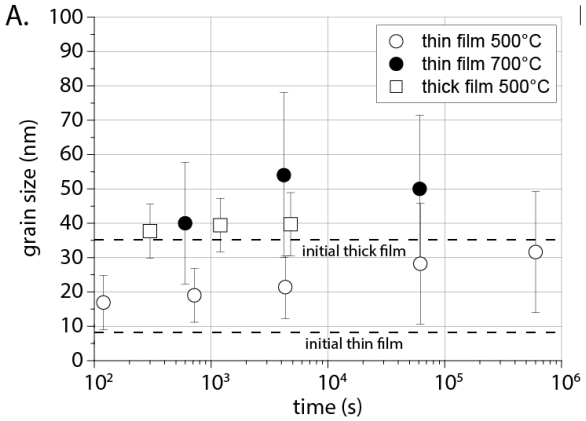
Abdeljawad *et al.*, Acta Mater. (2017)

Observations

Experimental: Pt-Au



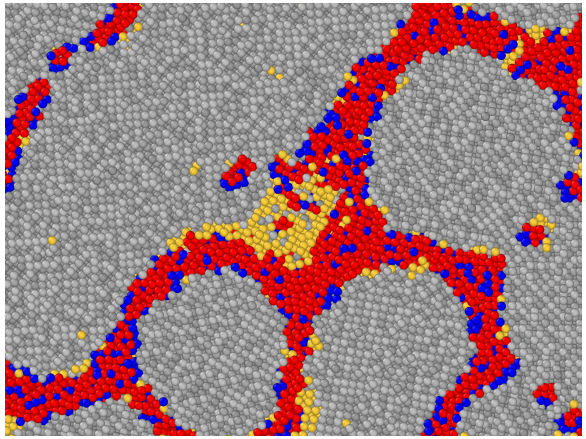
Abdeljawad *et al.*, Acta Mater. (2017)



Lu *et al.* (Under review in Scripta Mater.)

Atomistics: Pt-Au

Hybrid MC/MD, T = 775K, 15 at.% Au



FCC Pt

Non FCC Pt

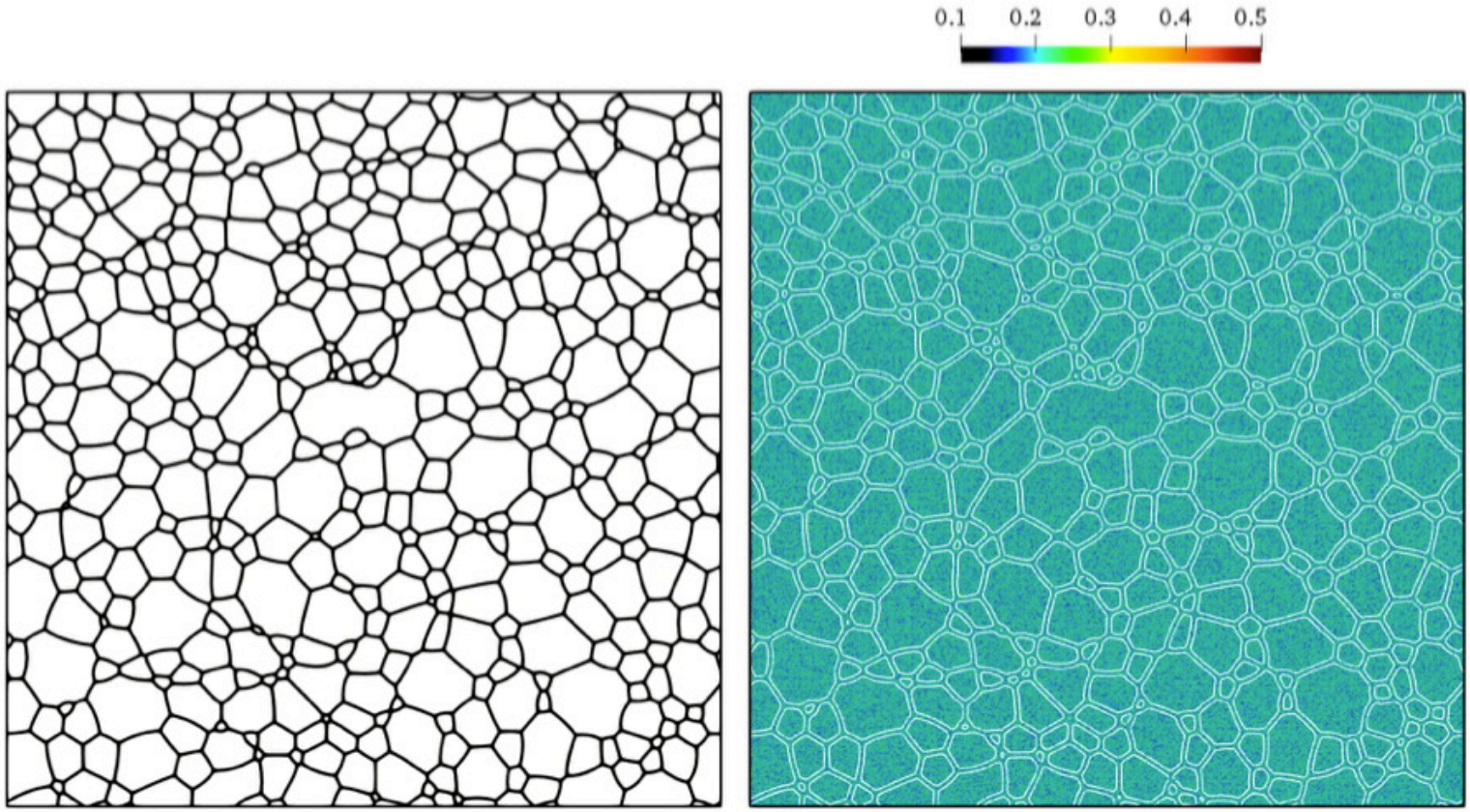
FCC Au

Non FCC Au

Foiles *et al.*, In preparation (2017)

Future Work

- Anisotropy in GB segregation
  - Dependency on GB geometric degrees of freedom

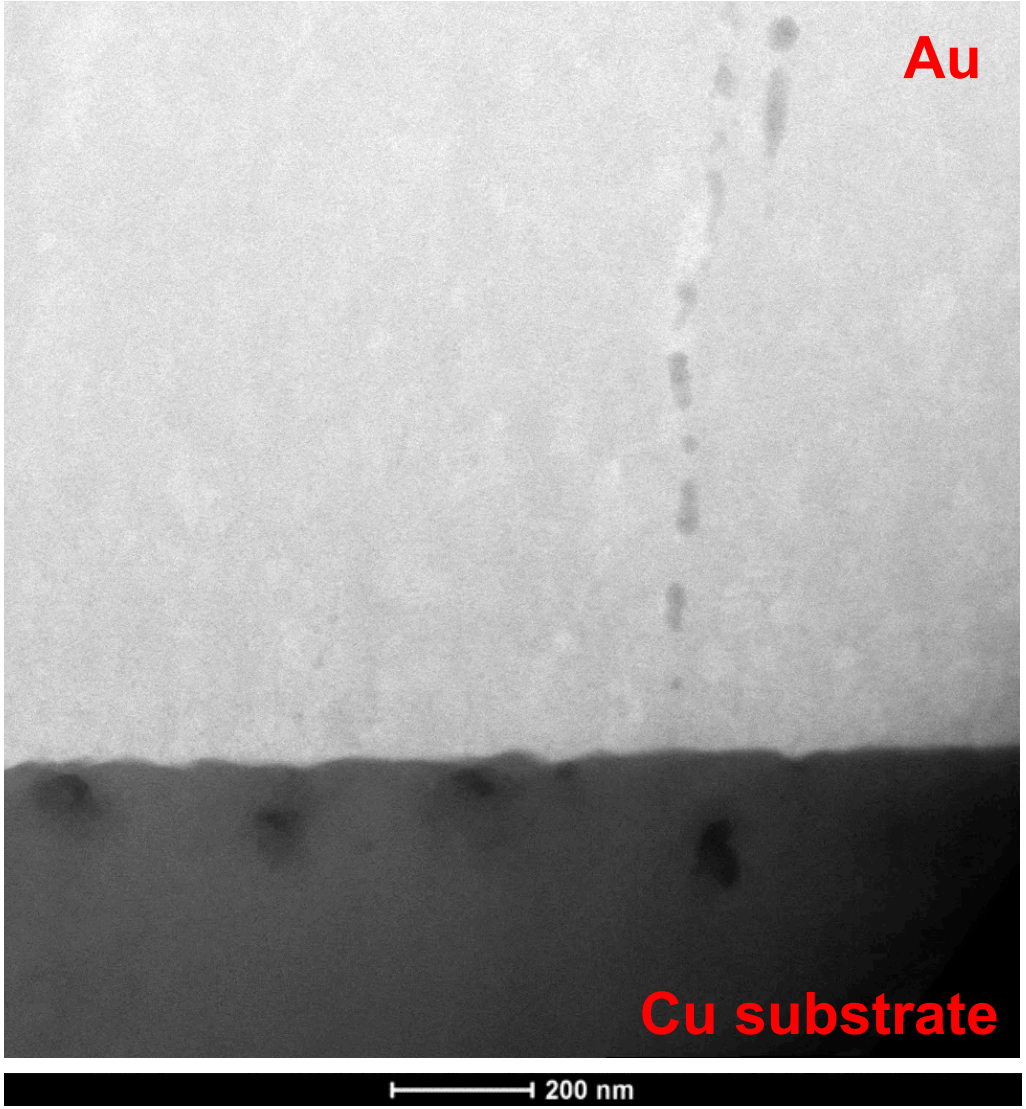


Substitutional Diffusion in Polycrystals

Observations: Seeing is Believing

Sandia National Laboratories

heating to 250°C for 40 minutes



Each frame represents 2 minutes at 250C for a total heating of about 40 minutes

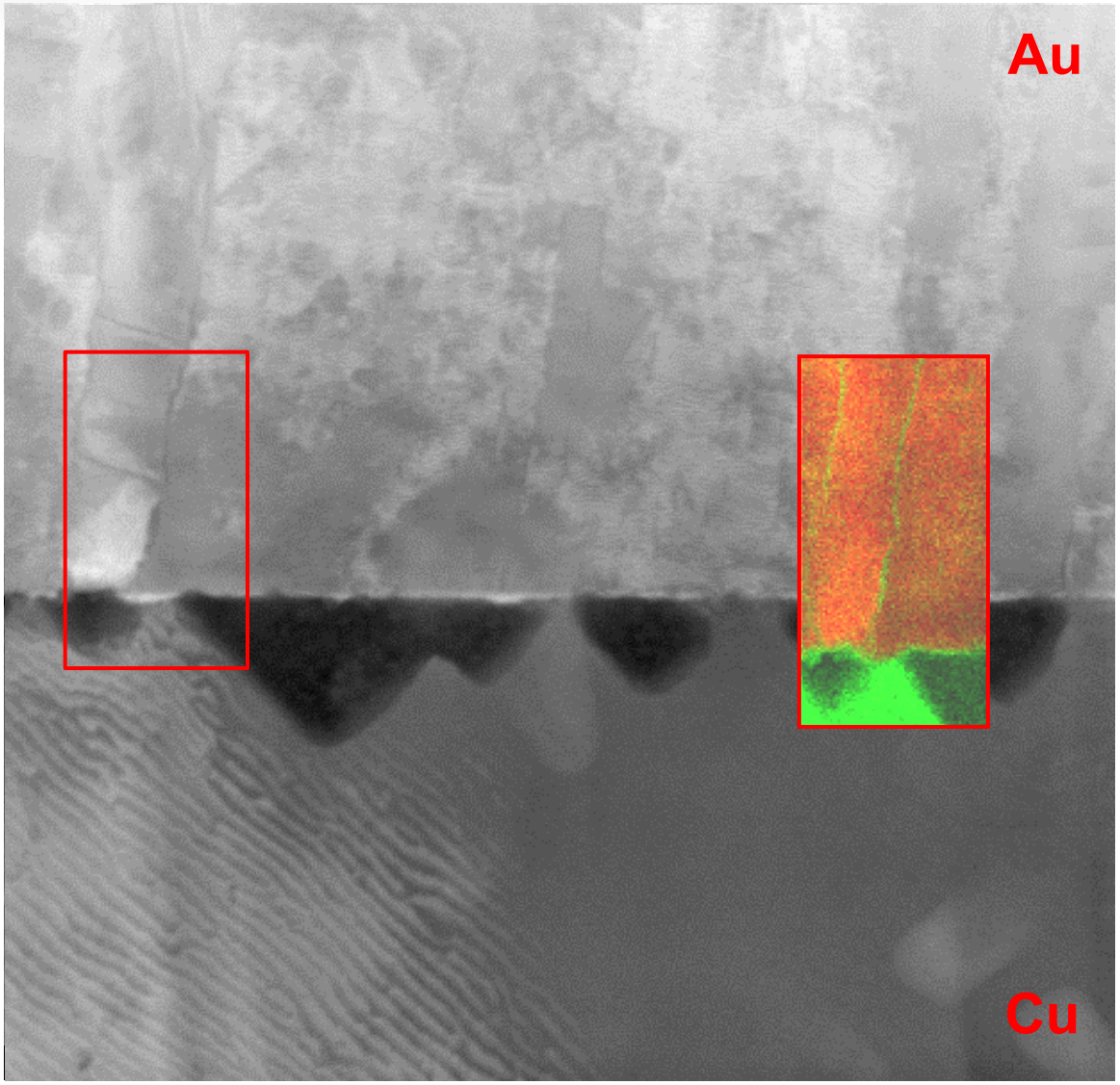
Paul Kotula (SNL, 2018)

Nano-grained electroplated Au

Observations: Seeing is Believing

Sandia National Laboratories

heating to 200°C for 10 minutes
Kirkendall voids

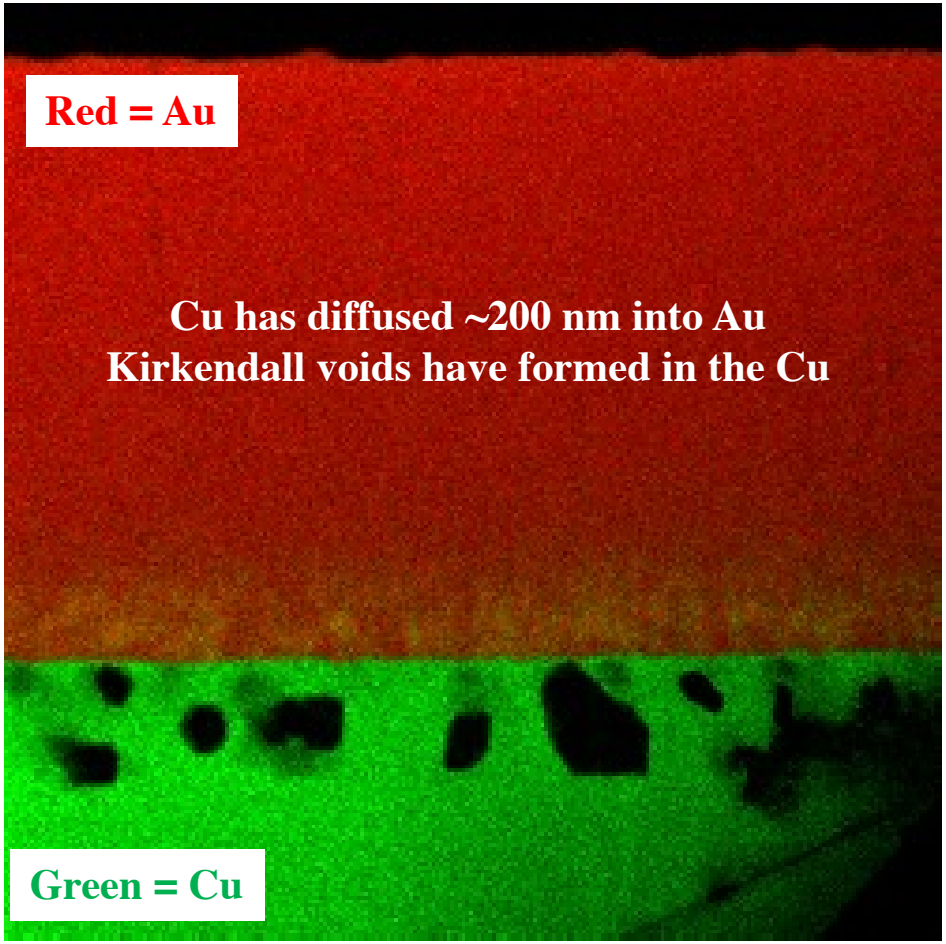


Paul Kotula (SNL, 2018)

Questions to Address

2) Kirkendall effect in cases when $\mu_V \neq$ const ➔ GB/surface/dislocations: sources/sinks

Vacancy mediated transport, kirkendall voids



Paul Kotula (SNL, 2018)

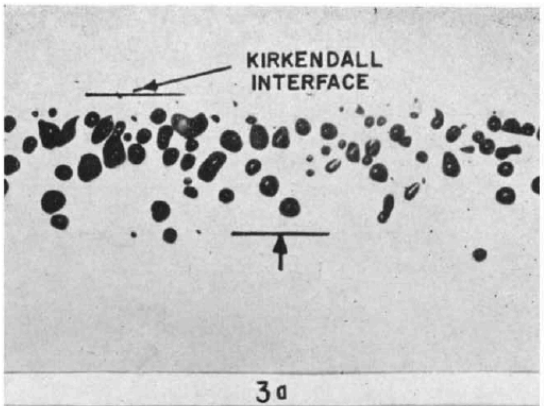
Kirkendall Effect

Kirkendall, Thomassen and Uethegrove, Trans. AIME 133 (1939)

Kirkendall, Trans AIME **147** (1942)

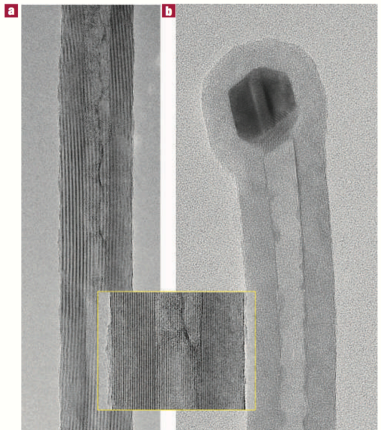
Darken, Trans. AIME 175 (1948)

Bardeen and Herring, Atom Movements (1951)



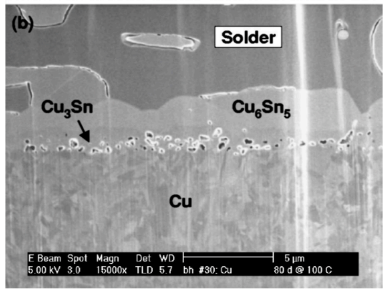
Balluffi, Acta Metall. **2** (1954)

Nanotube fabrication



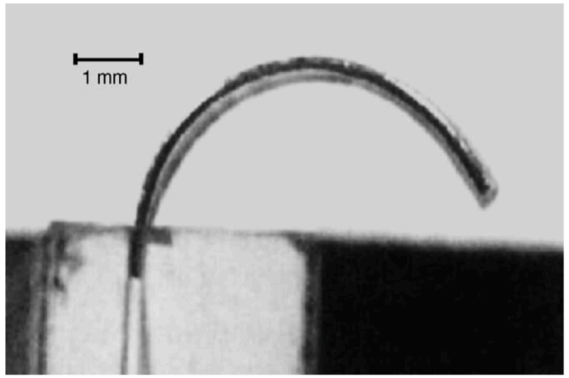
Fan et al., Nature Mater. 5 (2006)

Solder joints
After 80 days at 100C



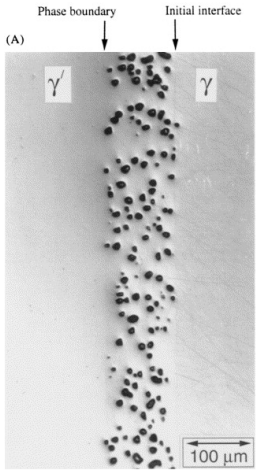
Zeng et al., J. App. Phys. 97(2005)

Bending of Ti/Zr at 1223 K after 150 min.



Beke et al., Mater. Sci. Eng. A 387 (2004)

Superalloys
Ni/Ni–14.7Al–9.9Ti (at.%)



Matan et al., Acta Mater. 46 (1998)

A Model Accounting for GBs

- Treat the system as a ternary alloy
  - Metal **A** (slow diffusor), Metal **B** (fast diffusor), and Vacancies **V**
- Irreversible thermodynamics

$$J_i = -L_{iA}\nabla\mu_A - L_{iB}\nabla\mu_B - L_{iV}\nabla\mu_V \qquad i = \mathrm{A, B, V}$$

- Convert $\nabla\mu_i$ to ∇C_i using alloy free energy (ideal alloy)

$$\begin{bmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{bmatrix} = \begin{bmatrix} L_{AA} & L_{AB} \\ L_{BA} & L_{BB} \end{bmatrix} \begin{bmatrix} \partial\mu_A/\partial C_A & \partial\mu_A/\partial C_B \\ \partial\mu_B/\partial C_A & \partial\mu_B/\partial C_B \end{bmatrix}$$

- Far from vacancy sources/sinks

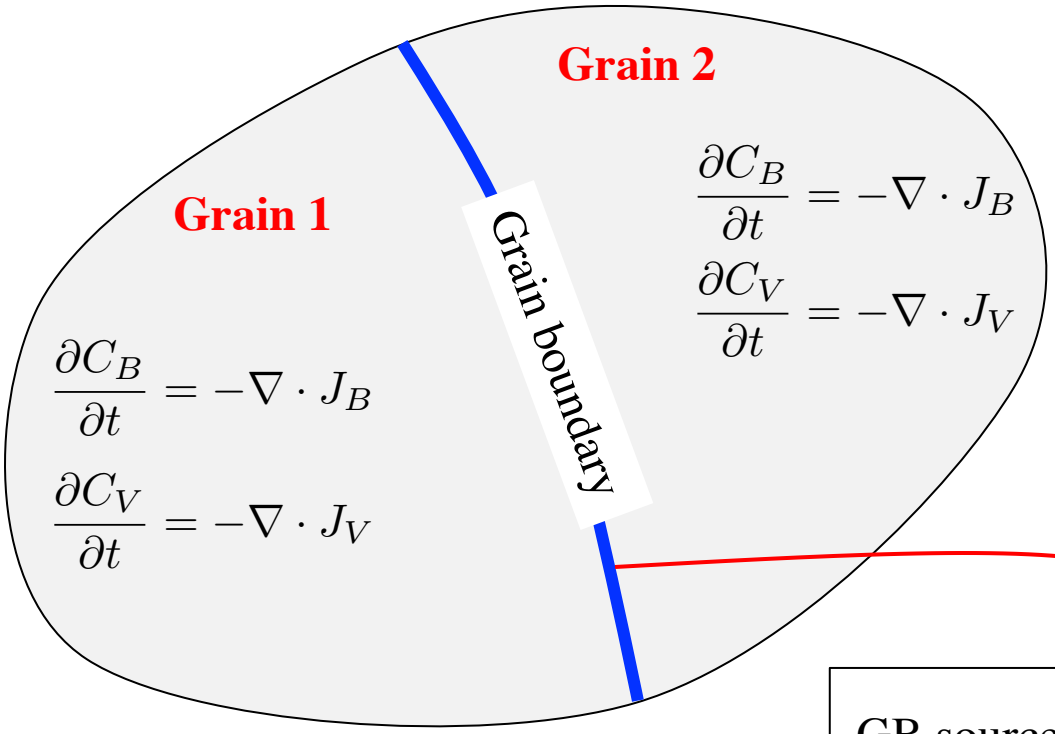
$$J_V = -D_{VV}\nabla C_V - D_{VB}\nabla C_B$$
$$J_B = -D_{BV}\nabla C_V - D^*\nabla C_B$$

$D_{VV} = D_{AA} + D_{BA}$
$D_{VB} = D_{AA} - D_{AB} + D_{BA} - D_{BB}$
$D_{BV} = -D_{BA}$
$D^* = D_{BB} - D_{BA}$

Yu et al., Acta Mater. **55** (2007)

Accounting for GBs

- GBs are assumed as efficient sources/sinks for vacancies
  - Vacancy concentration at GBs is maintained at its equilibrium value C_V^{eq}
  - This introduces fluxes of vacancies into the bulk grains



$$J_V = -D_{VV}\nabla C_V - D_{VB}\nabla C_B$$
$$J_B = -D_{BV}\nabla C_V - D^*\nabla C_B$$

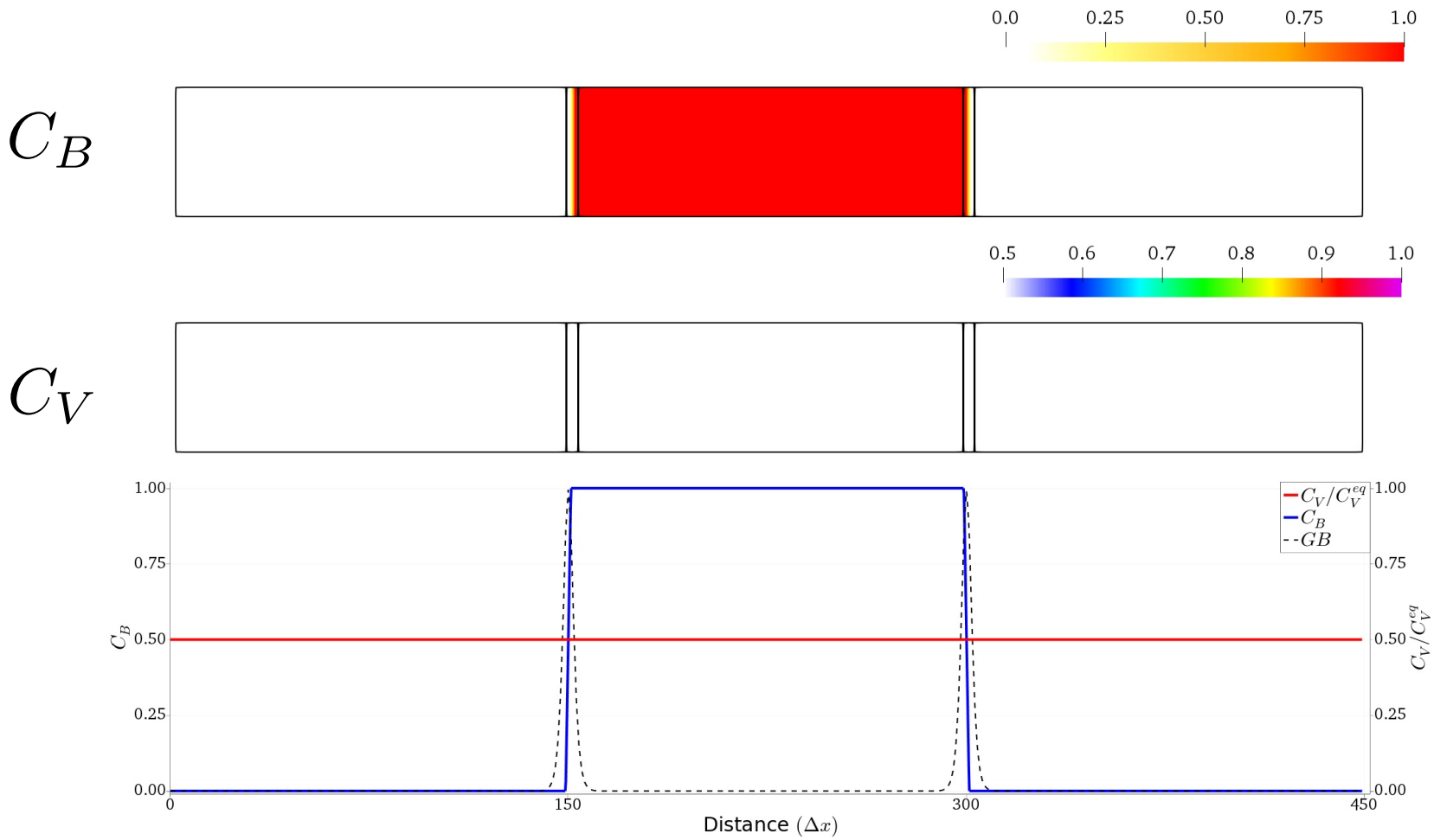
GB source/sink such that

$$C_V^{eq} = const. \rightarrow g = \frac{\nabla \cdot J_V}{1 - C_V^{eq}}$$

$$\frac{\partial C_B}{\partial t} = -\nabla \cdot J_B - \frac{C_B}{1 - C_V^{eq}}\nabla \cdot J_V$$

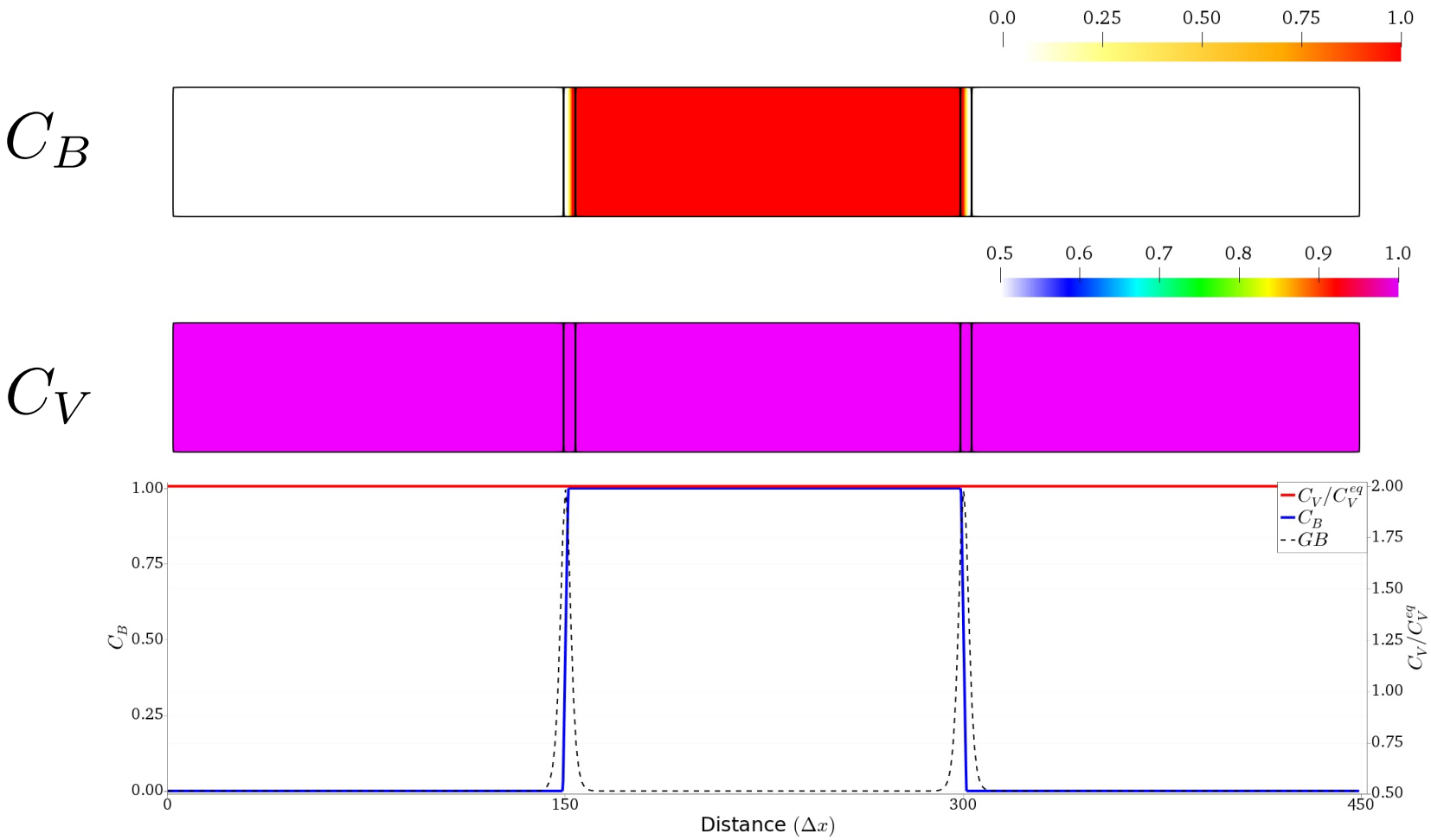
Results: Bi-crystals

- Initial condition: $C_V^{eq} > C_V(t=0)$

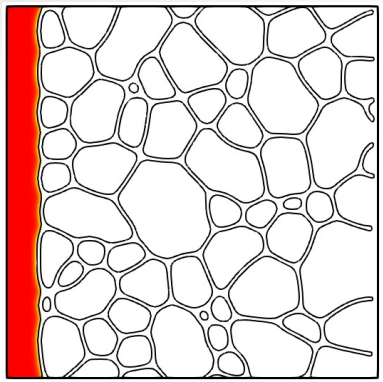


Results: Bi-crystals

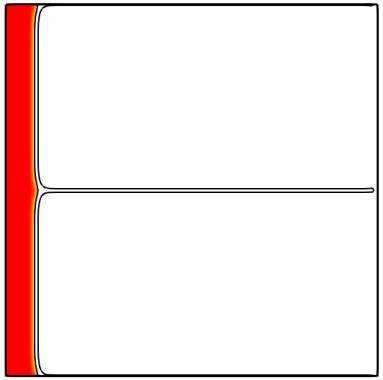
- Initial condition: $C_V^{eq} < C_V(t=0)$



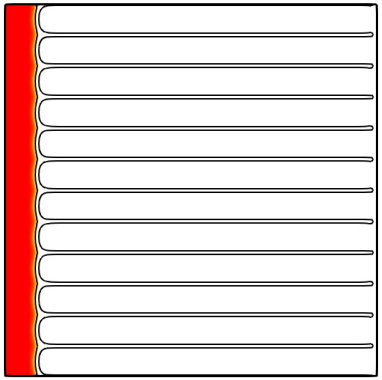
Results: Polycrystals



Equi-axed



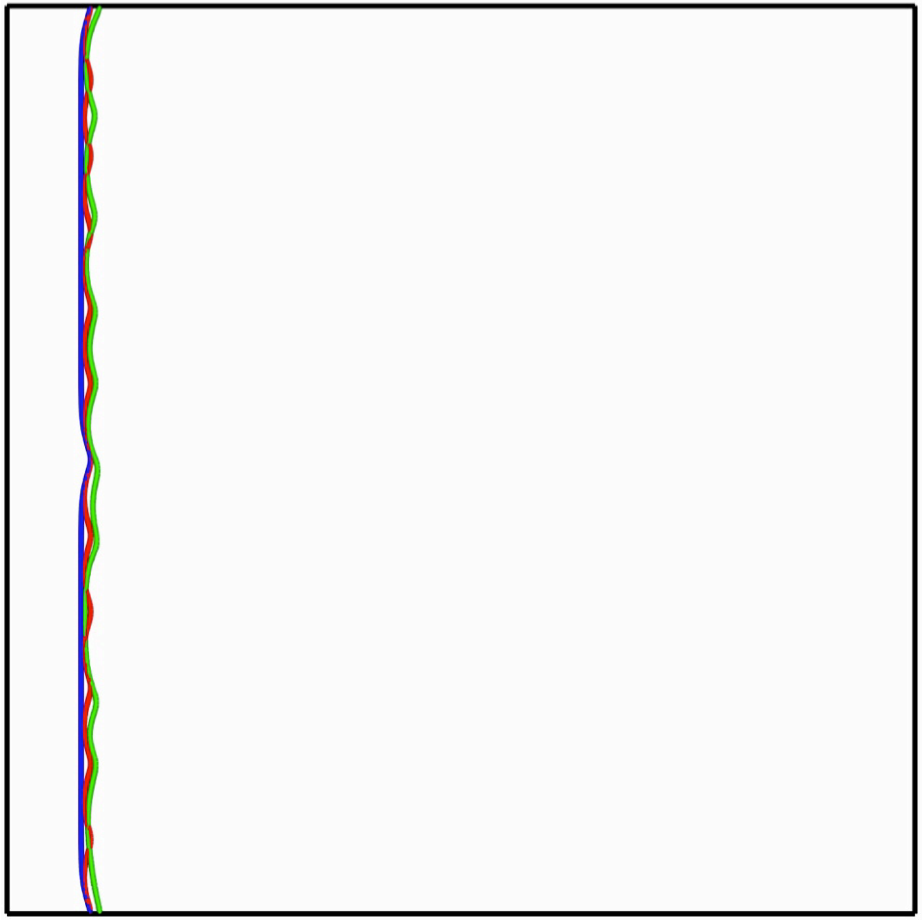
2-grain slab



12-grain slab

: Equi-axed
: 2-grain slab
: 12-grain slab

$c_B = 0.5$ iso-lines

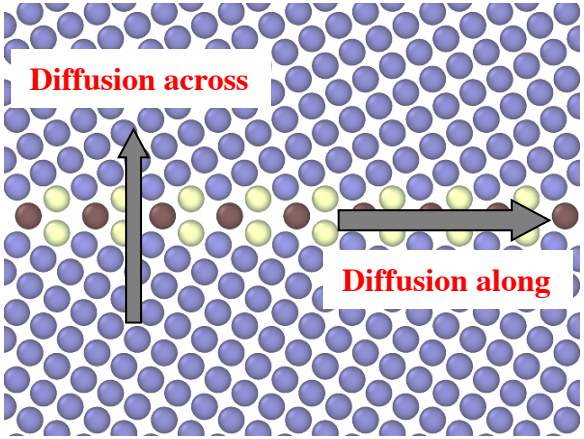


Future Work

- Atomistically informed description of D_{ij} through L_{ij}

$$L_{ij} = \frac{\langle \left(\Sigma_p \Delta \mathbf{R}_p^j(t)\right) \cdot \left(\Sigma_q \Delta \mathbf{R}_q^j(t)\right) \rangle}{2d\Omega t M k_B T}$$

- GB short circuit diffusion and anisotropy



Thank you

Publications relevant to this presentation

Kotula, Prasad, and Abdeljawad, Under preparation (2018)

Barr, Abdeljawad, Foiles, and Boyce, Under preparation (2018)

Abdeljawad, Lu, Argibay, Clark, Boyce and Foiles, Acta Mater. **127** (2017)

Abdeljawad, Medlin, Foiles, Hattar and Zimmerman, J. App. Phys. **119** (2016)

Abdeljawad and Foiles, Acta Mater. **101** (2015)

Acknowledgments

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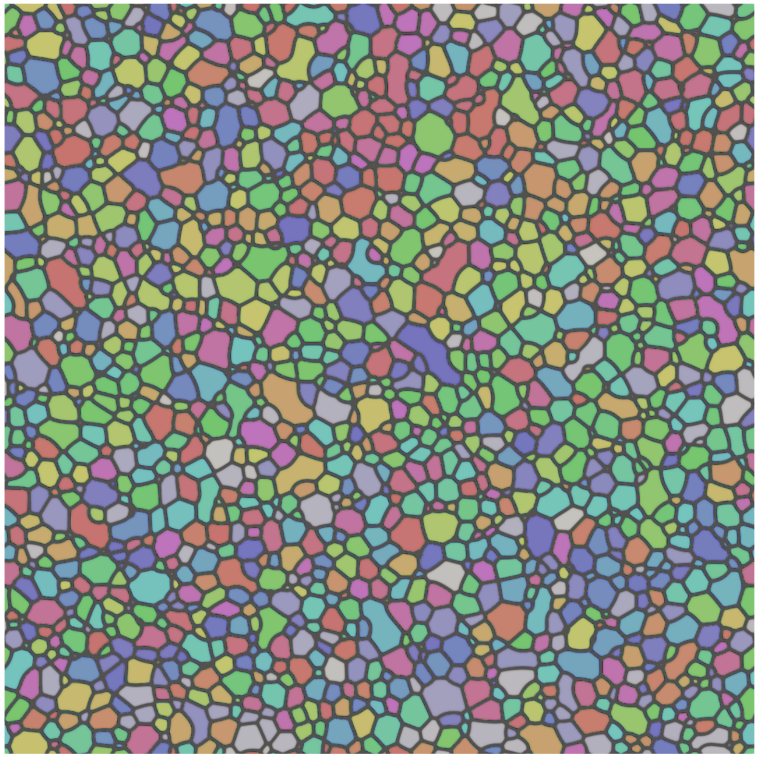
Department of Energy (DOE) Basic Energy Sciences (BES)

Backup Slides

Competing Processes

- Grain growth, GB segregation and phase separation
  - Initially (t=0): **1560** grains
  - $c(\mathbf{r}, t = 0) = \langle c \rangle = 0.2$ (unstable alloy)
  - Vary GB free energies

Initial (t = 0): Colors are for grain IDs



- Metrics
  - Average grain dimeter $\langle D \rangle$
  - Define solute partitioning factor

$$\Upsilon(t) = \frac{\int d\mathbf{r}\ c(\mathbf{r}, t) P(\vec{\phi})}{\int d\mathbf{r}\ c(\mathbf{r}, t)}$$

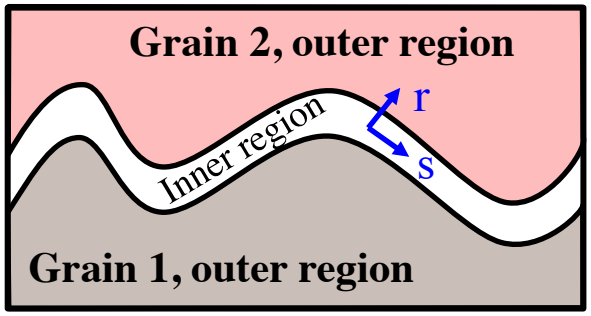
$$\Upsilon = \begin{cases} 0, & \text{No solute at GBs} \\ 1, & \text{GBs saturated with solute} \end{cases}$$

Relation to Solute Drag

- Sharp interface asymptotics (underway)

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[W f_{loc}(c, \phi, T) + \frac{\epsilon^2}{2} |\nabla \phi|^2 \right]$$

$$\frac{\partial \phi}{\partial t} = -L \left(\frac{\delta \mathcal{F}_{tot}}{\partial \phi} \right)$$



$$\phi = \phi_0 + \omega \phi_1 + \omega^2 \phi_2 + \cdots$$

$$c = c_0 + \omega c_1 + \omega^2 c_2 + \cdots$$

Provatas and Elder (2009)

Karma and Rappel, Phys. Rev. E **57** (1998)

Normal grain growth

$$\mathcal{V}_n = M_{gb} \gamma_{gb} \mathcal{K} = L \epsilon^2 \mathcal{K}$$

With GB solute segregation

$$\mathcal{V}_n = \frac{L\epsilon^2}{1 + \left(\frac{LW}{D}\right) \frac{K_I}{K_{II}}} \mathcal{K} \simeq L\epsilon^2 \left(1 - \frac{LW}{D} \frac{K_I}{K_{II}} \right) \mathcal{K}$$

$$K_I = \int_{-\infty}^{+\infty} \frac{\partial c_o}{\partial x} \int_0^x (c_o - c_\infty)\, dx' dx$$

$$K_{II} = \int_{-\infty}^{+\infty} \left(\frac{d\phi_0}{d\xi} \right)^2 d\xi$$

D: solute diffusivity

Young Man, in mathematics you don't understand things. You just get used to them

J. Von Neumann

Abdeljawad *et al.*, In preparation (2018)

Relation to Solute Drag

- Phase field sharp interface asymptotics (underway)

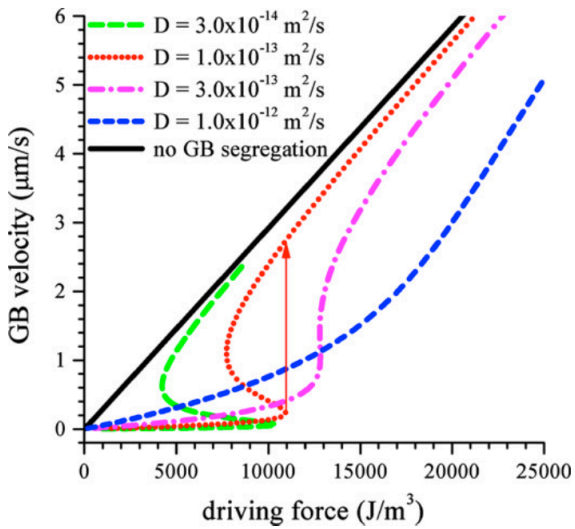
$$\mathcal{V}_n = \frac{L\epsilon^2}{1 + \left(\frac{LW}{D}\right)\frac{K_I}{K_{II}}}\mathcal{K} \simeq L\epsilon^2\left(1 - \frac{LW}{D}\frac{K_I}{K_{II}}\right)\mathcal{K}$$

- Solute drag model [ideal, dilute alloys]

$$\mathcal{V}_n = M_{gb}\Big(P - P^*(\mathcal{V}_n)\Big)$$

$P = \gamma_{gb}\mathcal{K}$: Curvature driven flow

$P^*(\mathcal{V}_n)$: Drag pressure



Kim and Park, Acta Mater. (2008)

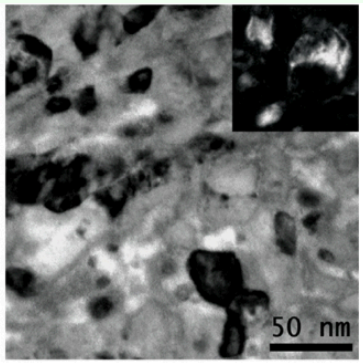
Cahn, Acta Metall. (1962)
Hillert and Sundman, Acta Metall. (1976)
Gottstein and Shvindlerman (1999)

An Active Area of Research

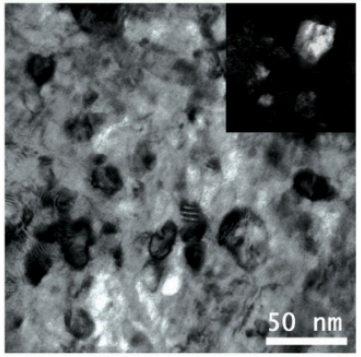
Sandia National Laboratories

Sluggish growth dynamics
W-20 at.% Ti

As milled



Annealed 1 week at 1100°C



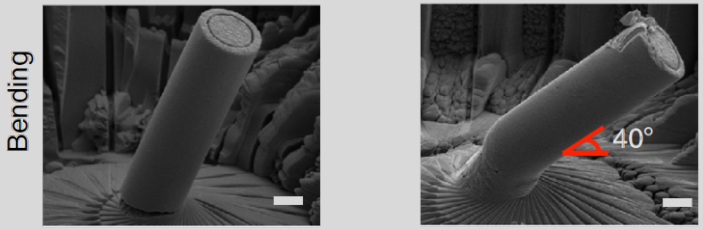
Chookajorn *et al.*, Science. (2012)
Chookajorn *et al.*, Acta Mater. (2014)

Pure Cu

$\varepsilon_{failure} = 4.4 \pm 0.5\%$

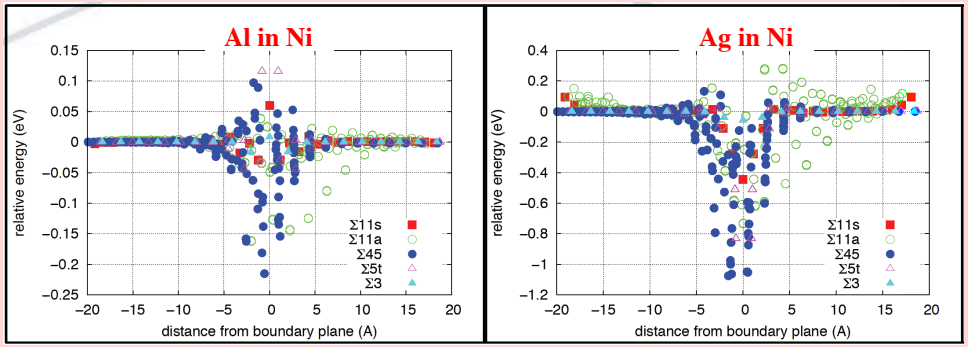
Cu-Zr (d = 45nm)

$\varepsilon_{failure} = 56 \pm 2.5\%$



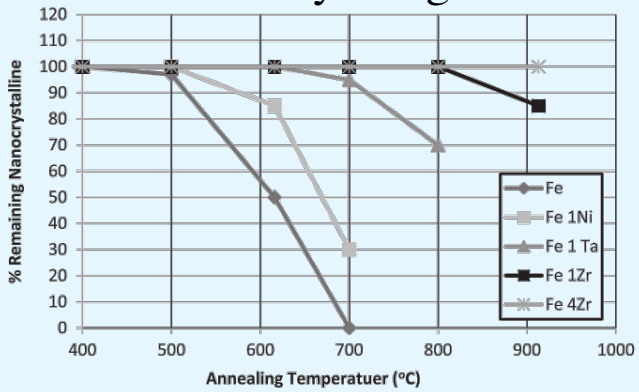
Khalajhedayati *et al.*, Nature Comm. (2016)

Dependency on solute and GB types



B. Uberuaga, E. Martinez *et al.*, LANL (2016)

NC alloy design



Darling *et al.*, Mat. Sci. Eng. A (2011)