SAND2022-3881C

Self-organizing gradient nanostructures via chemical heterogeneities

PRESENTED BY

Brad L. Boyce, Khalid Hattar, Remi Dingreville, Doug Medlin, Joseph Monti, Alejandro Barrios, James Nathaniel, Zachary Milne, David Adams

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A growing recognition of the benefits of gradient nanomaterials

ELSEVIER

Scripta Materialia

Volume 187, October 2020, Pages 307-308

Viewpoint set

Preface to the viewpoint set on: Heterogeneous gradient and laminated materials

Lei Lu [a], Xiaolei Wu [b], Irene J. Beyerlein [c]

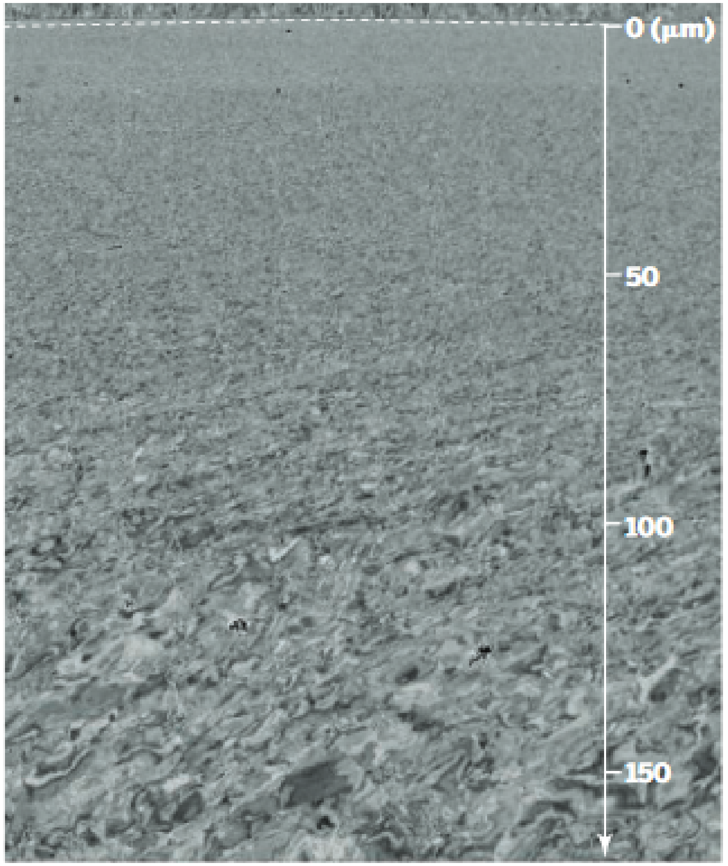
[1] T.H. Fang, W.L. Li, N.R. Tao, K. Lu
Revealing extraordinary intrinsic tensile plasticity in gradient nano-grained copper
Science, 331 (2011), pp. 1587-1590
View PDF CrossRef View Record in Scopus Google Scholar

[2] Z. Cheng, H.F. Zhou, Q.H. Lu, H.J. Gao, L. Lu
Extra strengthening and work hardening in gradient nanotwinned metals
Science, 362 (2018), pp. 559-566
View Record in Scopus Google Scholar

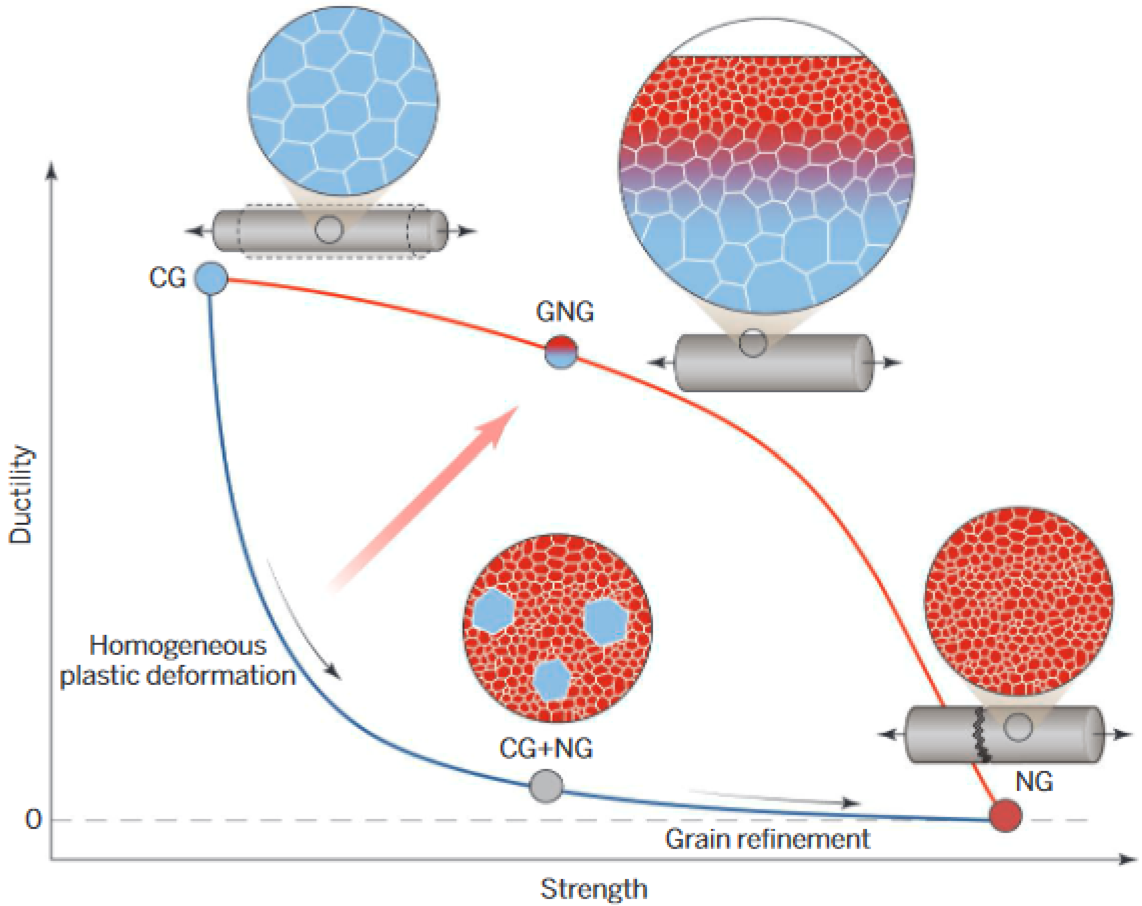
[3] X.L. Wu, P. Jiang, L. Chen, F.P. Yuan, Y.T.T. Zhu
Extraordinary strain hardening by gradient structure
Proc. Natl. Acad. Sci. U S A,, 111 (2014), pp. 7197-7201
View PDF CrossRef View Record in Scopus Google Scholar

[4] R.Q. Cao, Q. Yu, J. Pan, Y. Lin, A. Sweet, Y. Li, R.O. Ritchie
On the exceptional damage-tolerance of gradient metallic materials
Mater. Today, 32 (2020), pp. 94-107
Article Download PDF View Record in Scopus Google Scholar

Gradients offer strength/ductility payoff

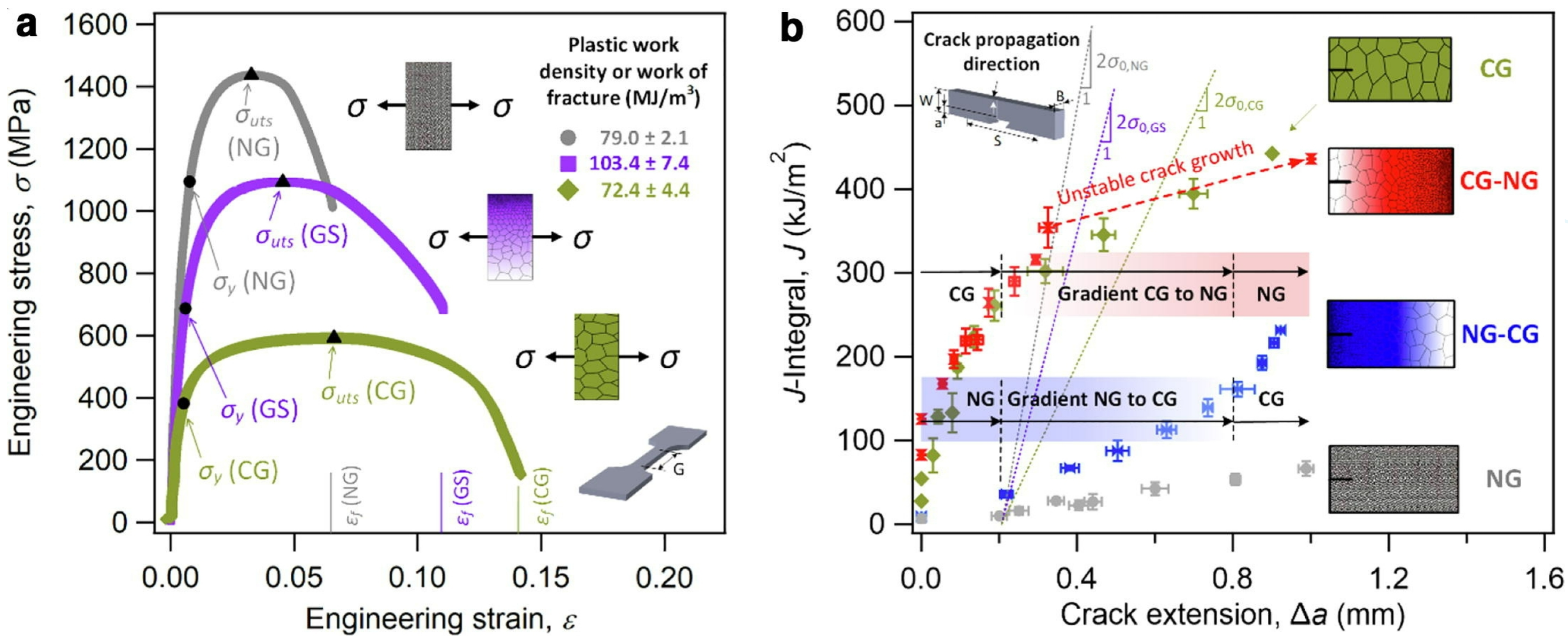


Gradient nanograined structure. After a surface mechanical grinding treatment to copper, grain sizes are about 20 nm in the topmost treated surface (outlined by dashed line) and increase gradually to the microscale with depth.



K Lu, *Science*, 2014

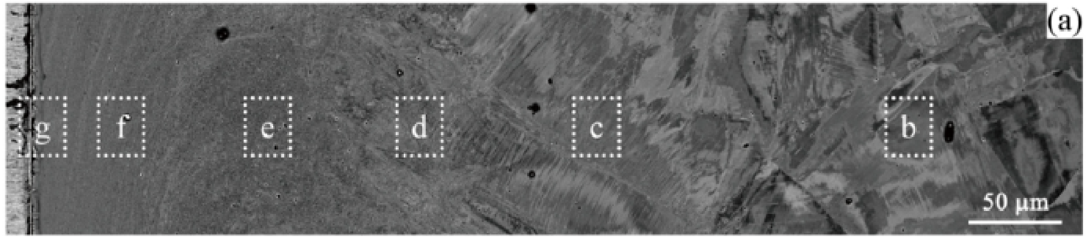
Gradients offer toughening

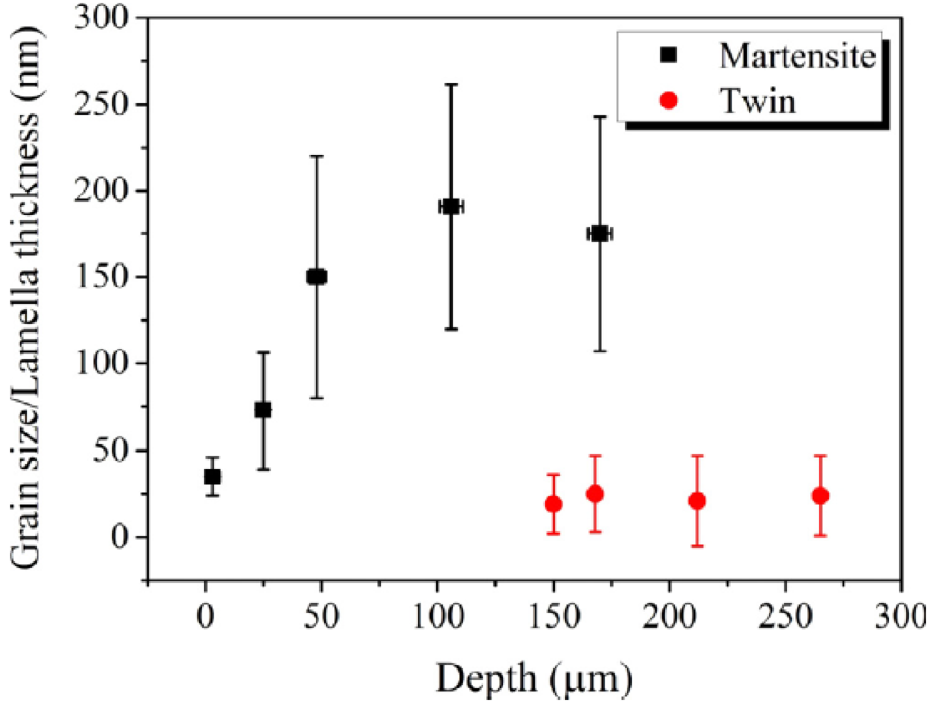


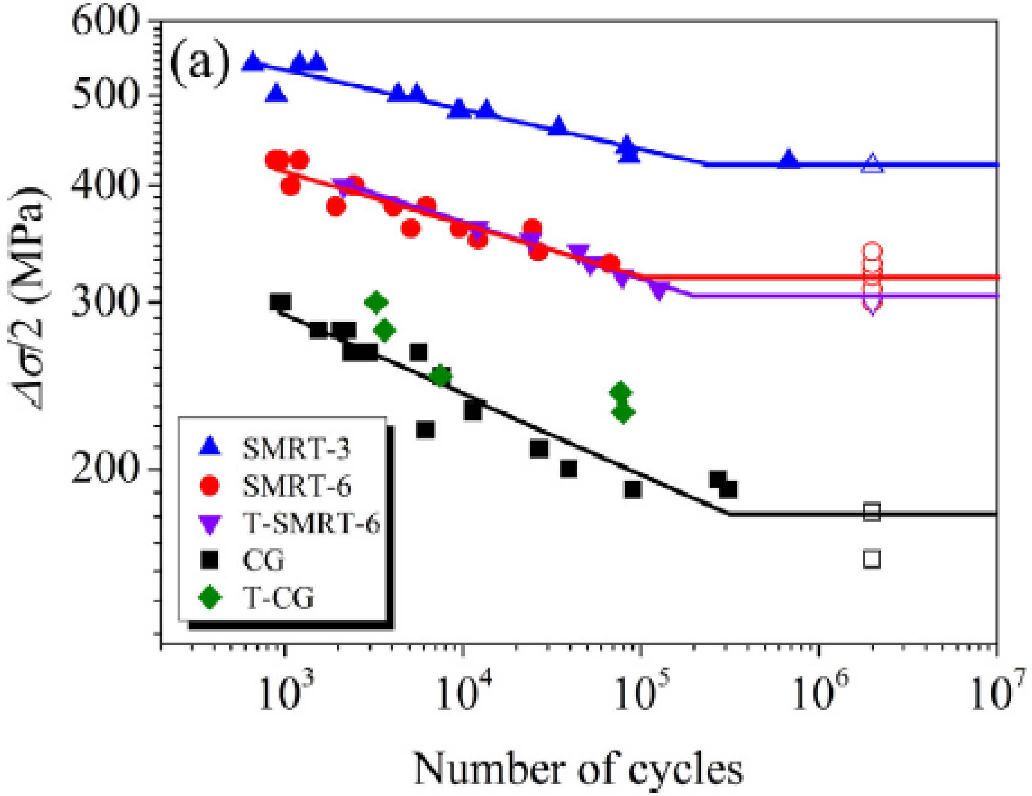
Cao…Ritchie, *Materials Today*, 2020

Gradients offer fatigue resistance

Gradient 316L by SMRT





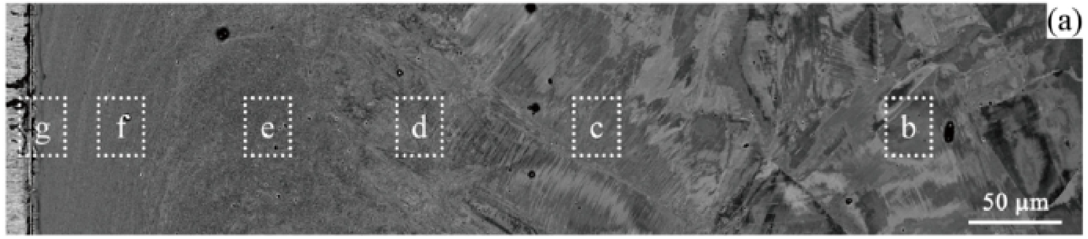


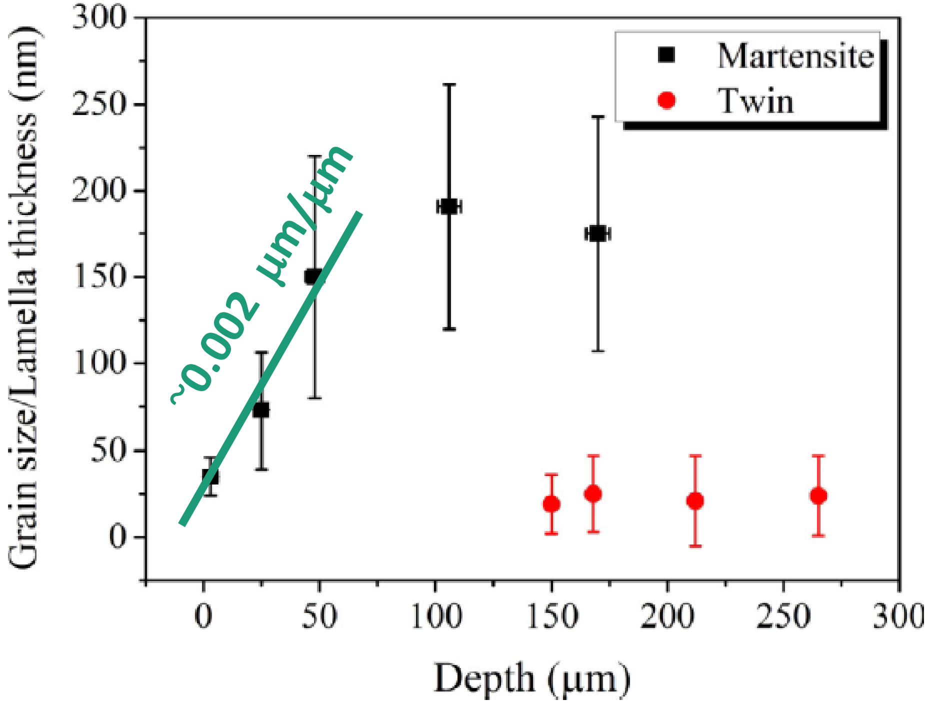
- Strain-induced martensite
- Compressive residual stresses of -1200 to -1500 MPa

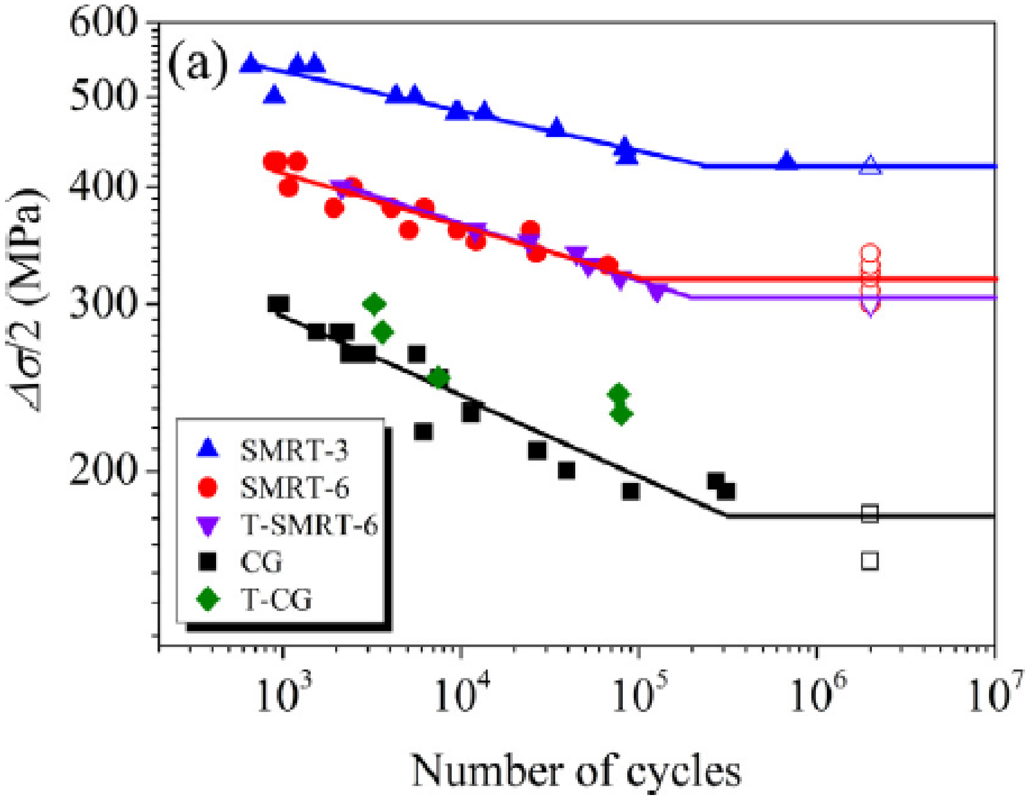
HW Huang, ZB Wang, J Lu, K Lu, *Acta Mater*, 2015

Gradients offer fatigue resistance

Gradient 316L by SMRT



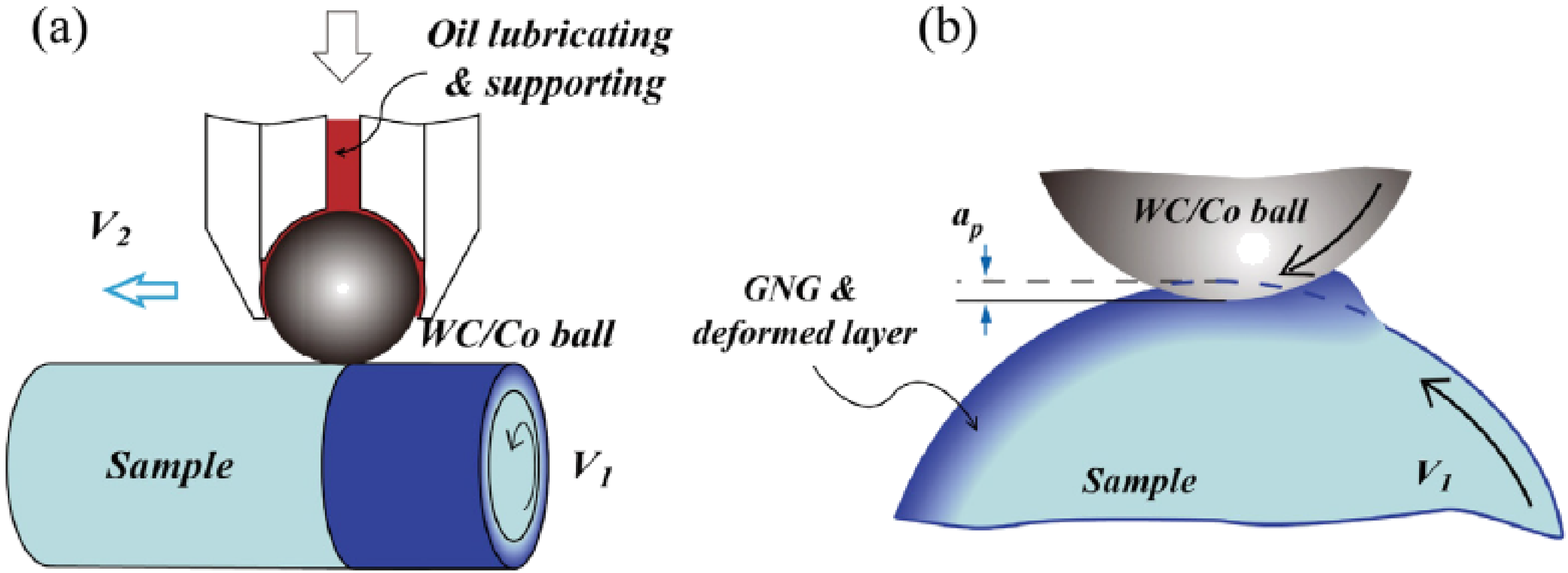




- Strain-induced martensite
- Compressive residual stresses of -1200 to -1500 MPa

HW Huang, ZB Wang, J Lu, K Lu, *Acta Mater*, 2015

SMRT, SMGT, SMAT

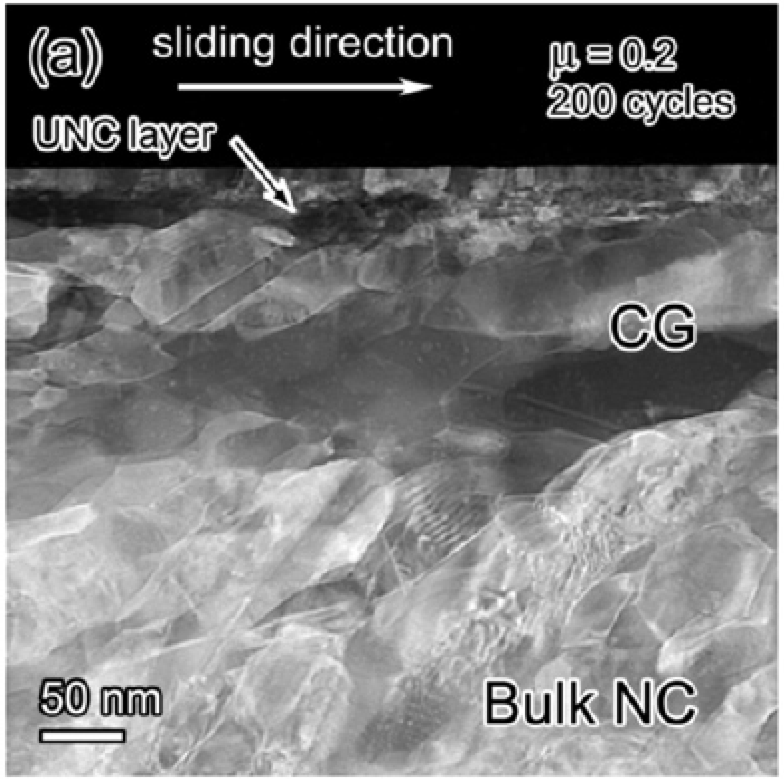


HW Huang, ZB Wang, J Lu, K Lu, *Acta Mater*, 2015

Severely deformed surface have complex microstructures…

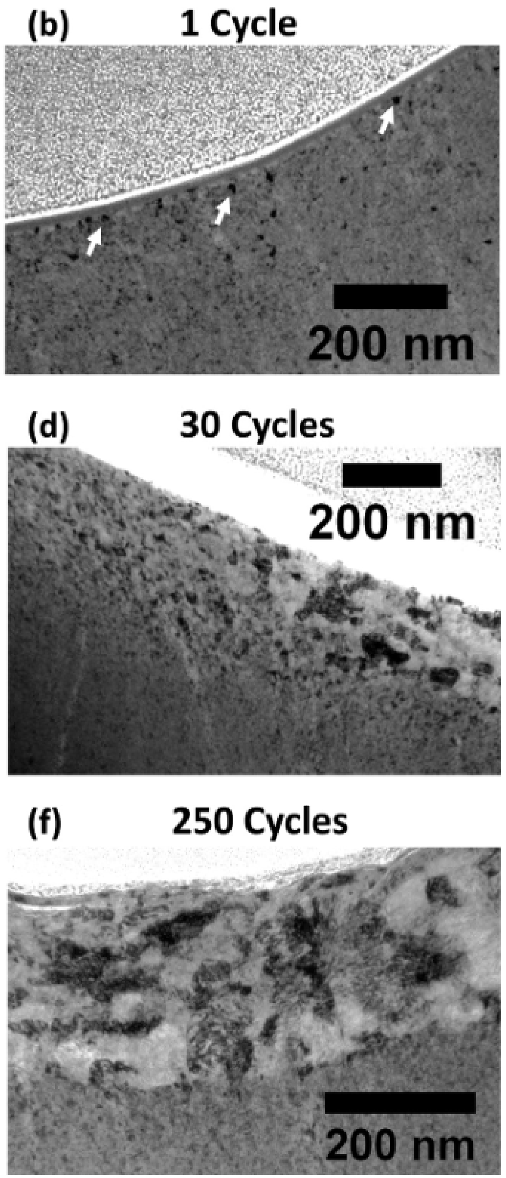
Cyclic sliding contact can surface grain refinement…

Ni



Padilla, Boyce, Battaile, Prasad, *Wear*, 2013

Ni-W



…or grain coarsening

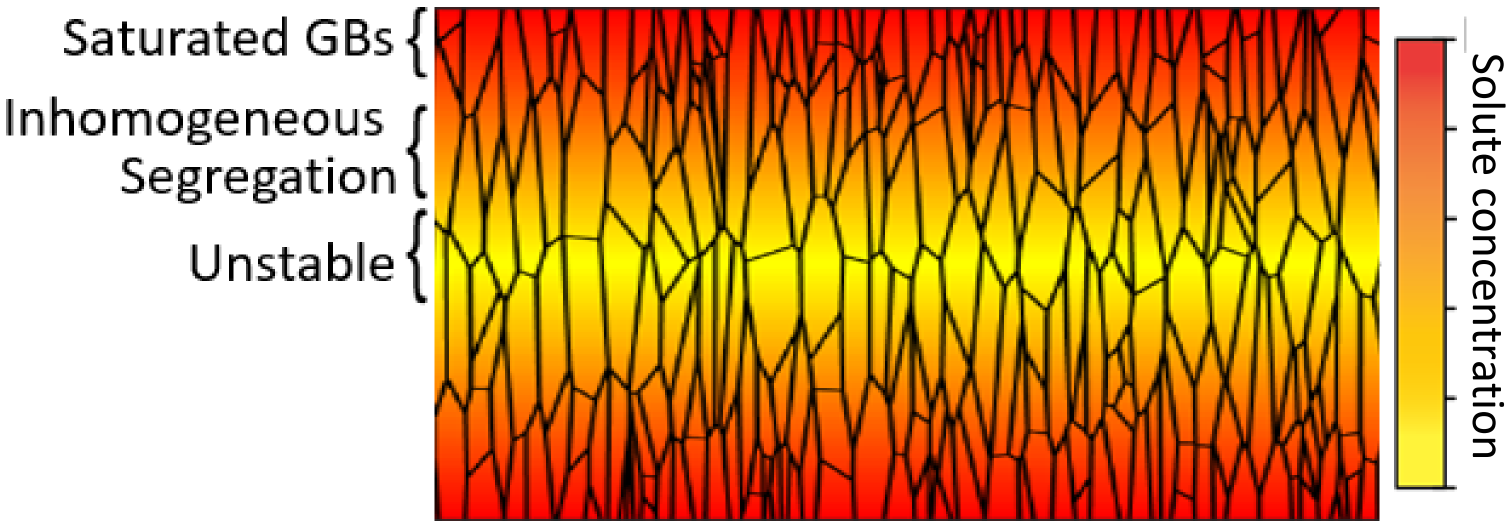
Panzarino & Rupert, *Materialia*, 2018

All these examples of heterostructures were achieved by gradients in “severe plastic deformation”

Can we achieve gradient nanostructures by chemical means?

- Create a structure with no/few existing dislocations & twins
- Tailor features that are not “accessible” to surface mechanical treatments
- Create microstructure that is also **stable against evolution**

Chemical gradient concept

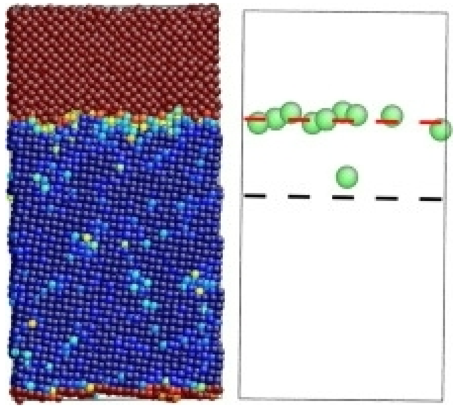


What is the role of solute in creating the microstructural gradient?

Solute effects on grain size stability

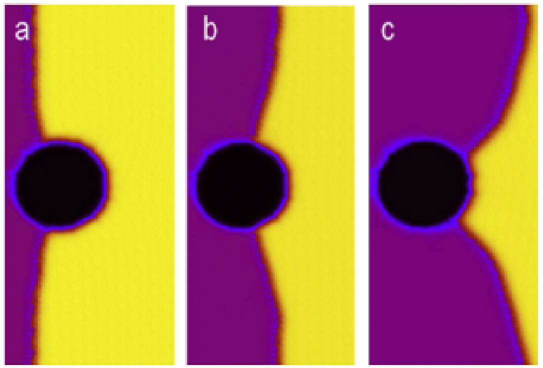
Kinetic

Solute drag



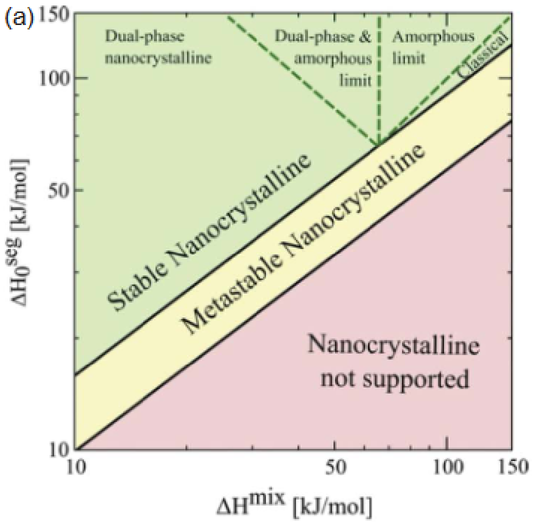
H Sun & C Deng, *Comp. Mater. Sci.*, 2014

Zener pinning



Wang, Ji, Wang, Wen, Chen, *Acta Mater*, 2017

Thermodynamic



See works by Weissmuller; Schuh; Koch; Darling; others

Phase field model development…

Segregation-enhanced thermal stability via a phase-field model

Free energy functional

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

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

Local energy density

Gradient terms for GBs and phase boundaries

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

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.

GB energy vs. concentration

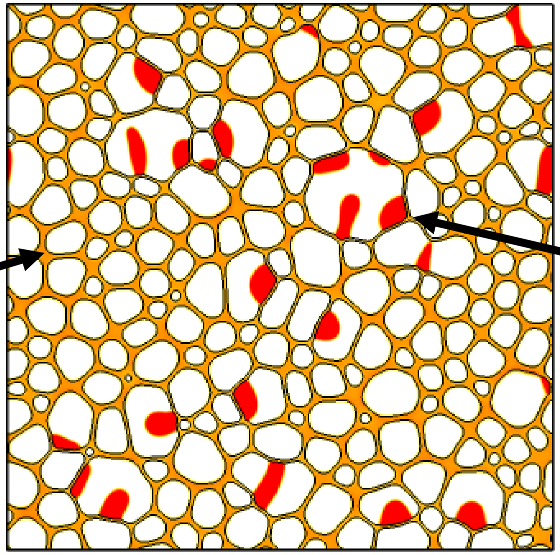
$$\Gamma = -\left(\frac{\partial \gamma_{gb}}{\partial \mu} \right)_{P,T}$$

Weissmüller, Nanostruct. Mater. (1993)

GB anisotropy

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

Segregation



Precipitation

Solute drag

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

Zener pinning

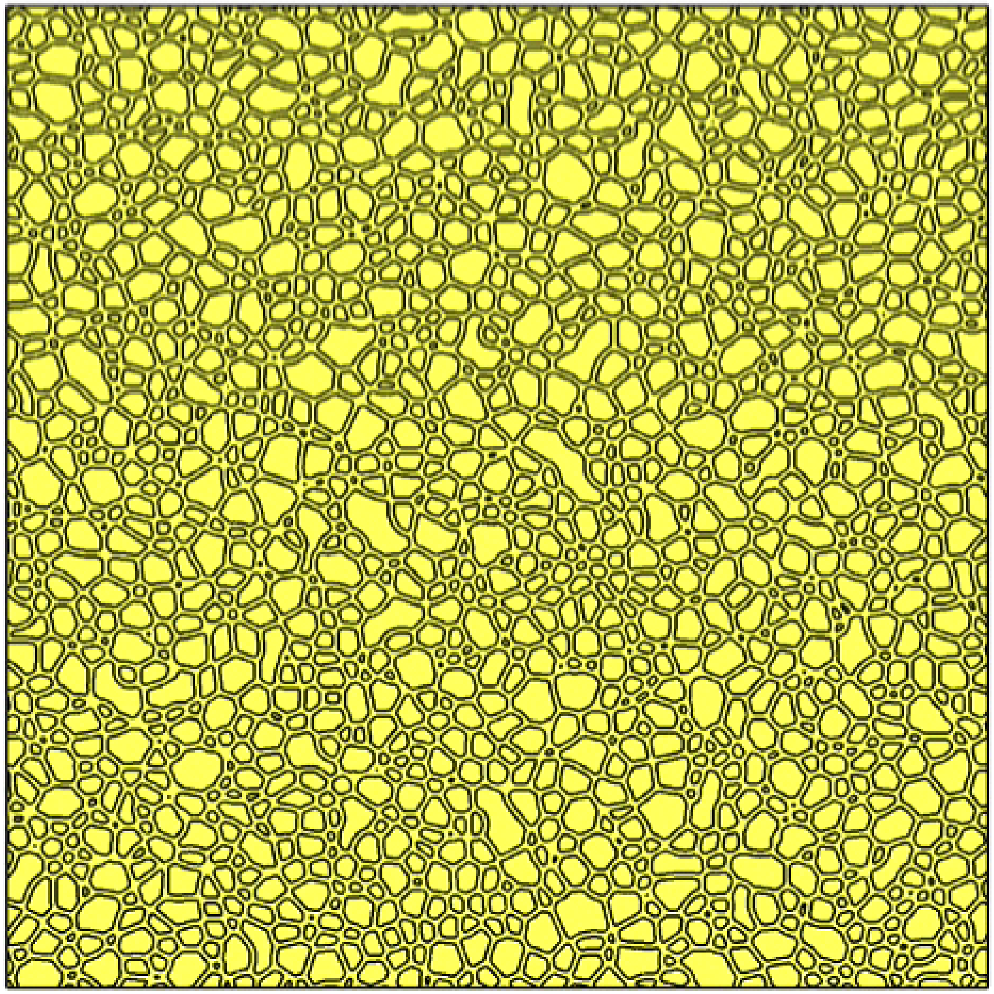
Smith, Trans. AIME **175** (1948)
Hellman and M. Hillert, Scand. J. Met. (1975)
Chen *et al.*, J. Am. Ceram. Soc. (1998)
Moelens *et al.*, Acta Mater. (2005)

Abdeljawad and Foiles, *Acta Mater*, 2015

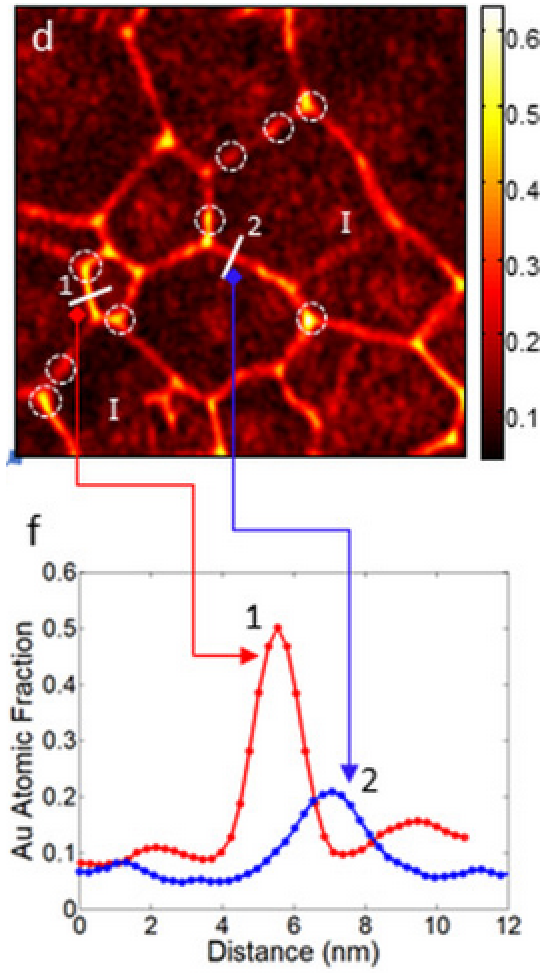
Abdeljawad, Lu, Argibay, Clark, Boyce, Foiles, *Acta Mater*, 2017

Segregation and stabilization

Phase-field model of segregation and stabilization



Pt-Au experiments



Improvements:

Anisotropic Mobility

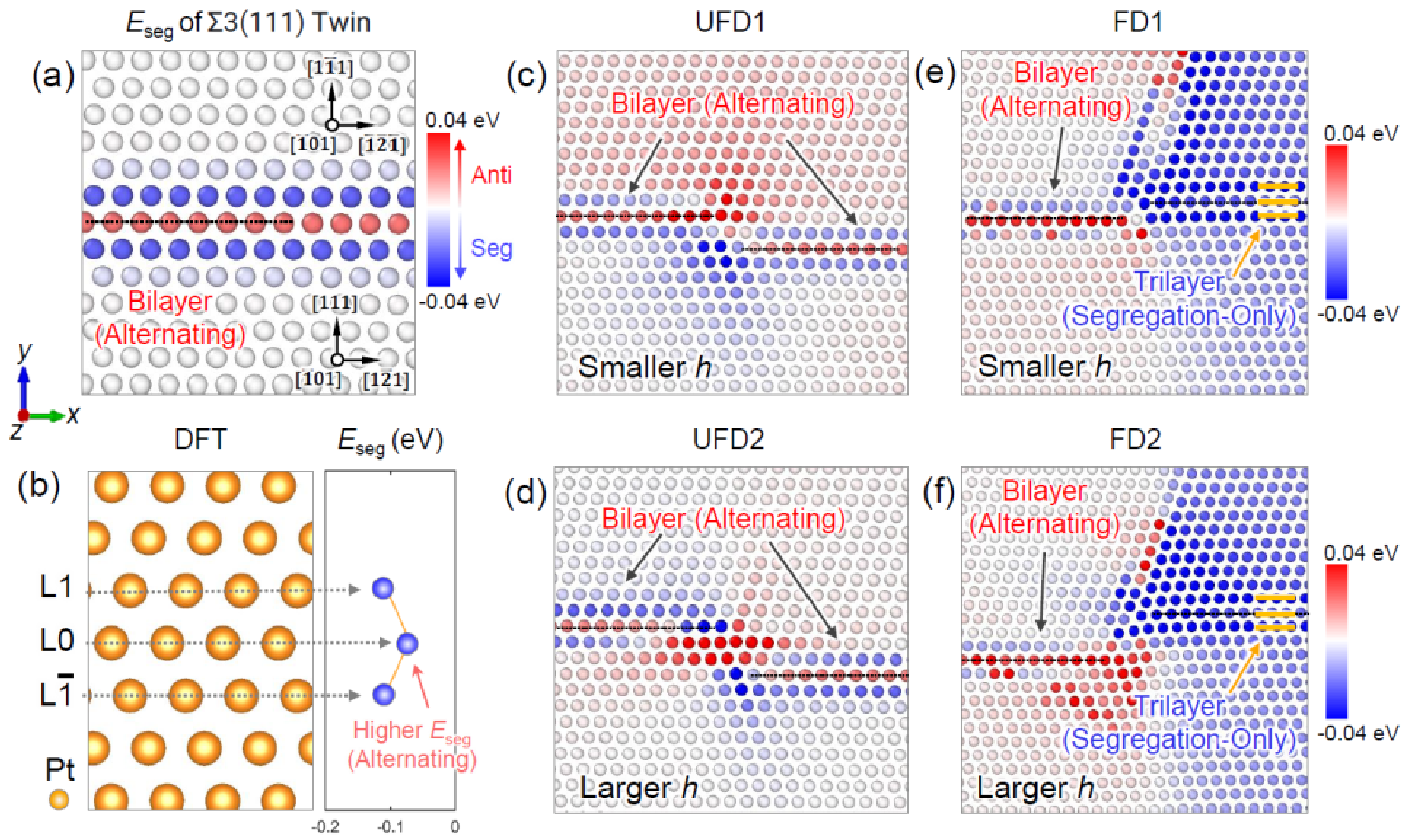
Anisotropic Energy

Heterogeneous solute segregating behavior

Adaptive grain tracking algorithm

Segregation at GBs is not so simple…

Segregation energy $E_{seg} = E_{GB} - E_{bulk}$



Chongze Hu's talk
Wednesday, 9:50am, 304C

Hu, et al, J. Phys. Chem. Lett. 2021

Grain growth with segregation

$$f_{loc}(c,T,\{\vec{\phi}\}) = f_b(c,T) + [W - \xi_1 c - \xi_2 c^2]g(\vec{\phi})$$

bulk grain boundary

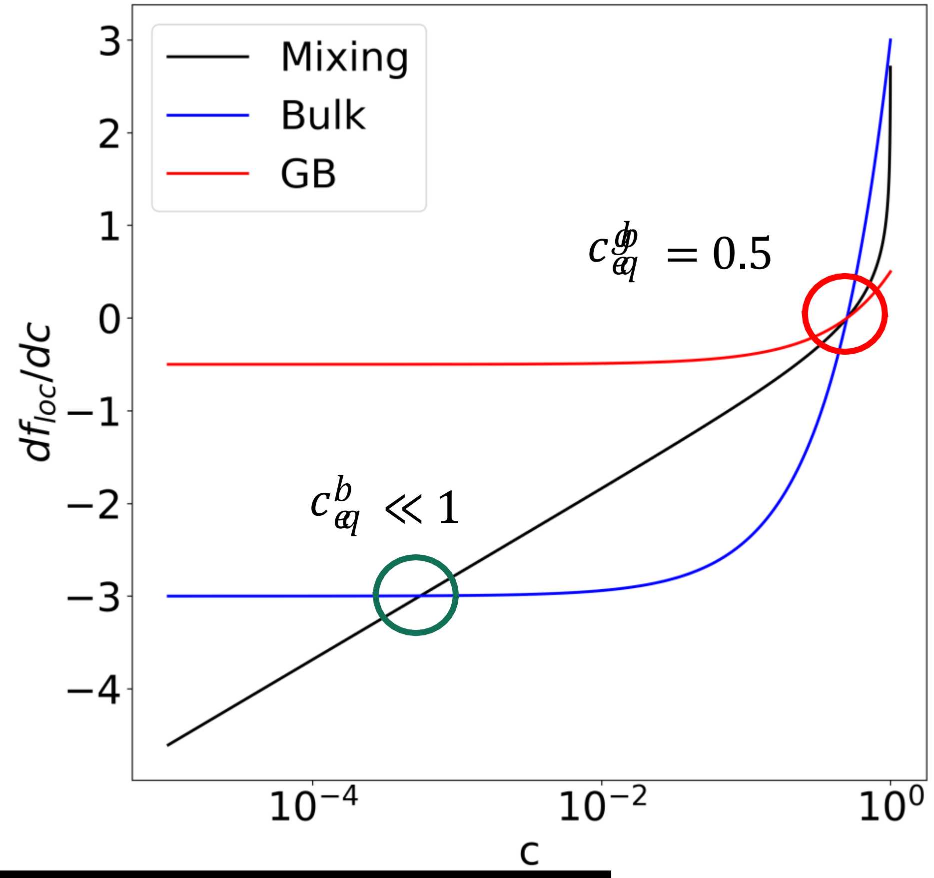
$$f_b = G_b^B c + (1-c)G_b^A + \Omega_b c(1-c) + \frac{RT}{V_m}[c \ln c + (1-c)\ln(1-c)]$$

$$W = W_\phi + (G_{gb}^A - G_b^A)$$

$$\xi_1 = (G_{gb}^A - G_b^A) - (G_{gb}^B - G_b^B) - (\Omega_{gb} - \Omega_b)$$

$$\xi_2 = (\Omega_{gb} - \Omega_b)$$

Anti-segregating parameters



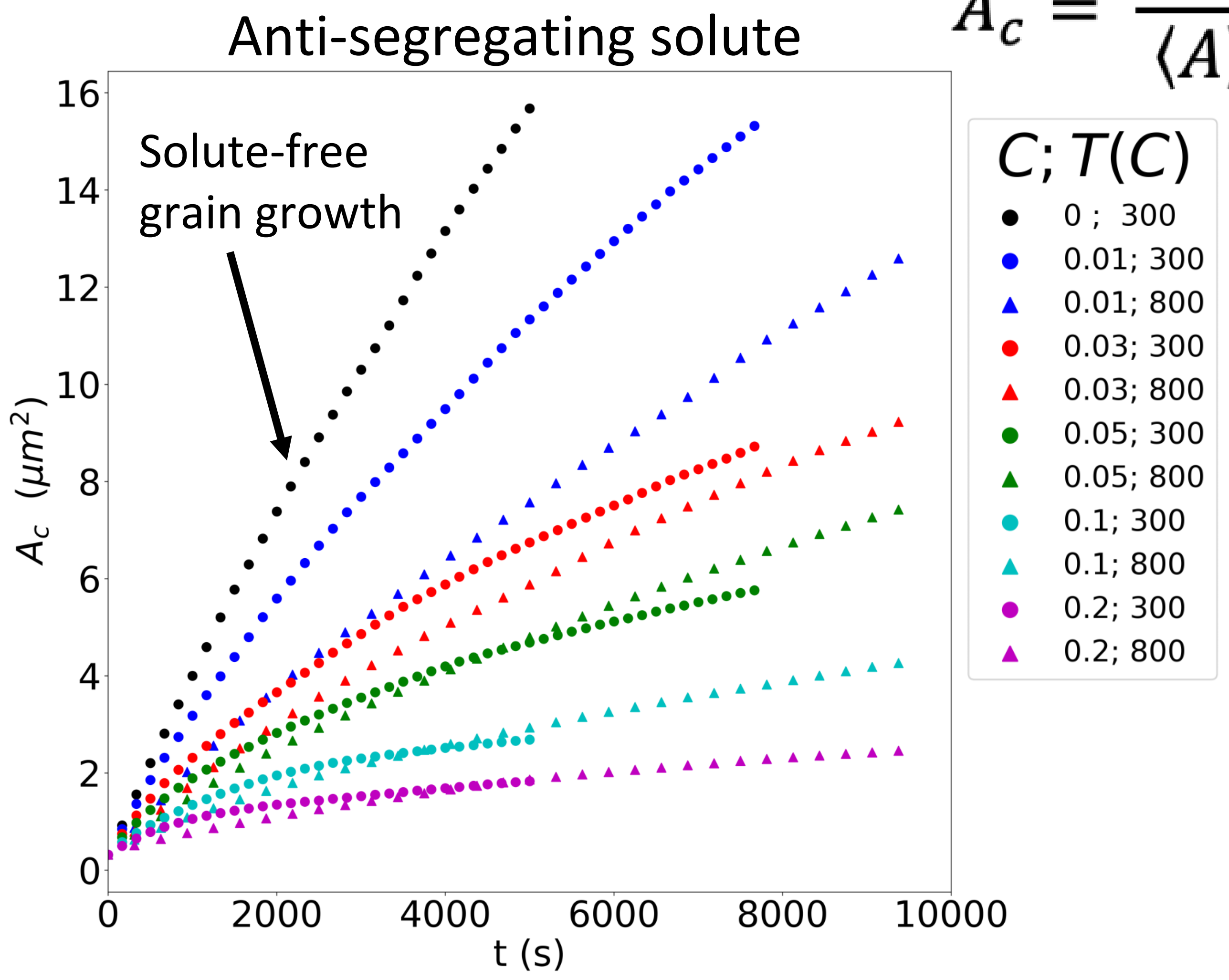
Anti-segregation: $\Omega_{gb} - \Omega_b > 0$

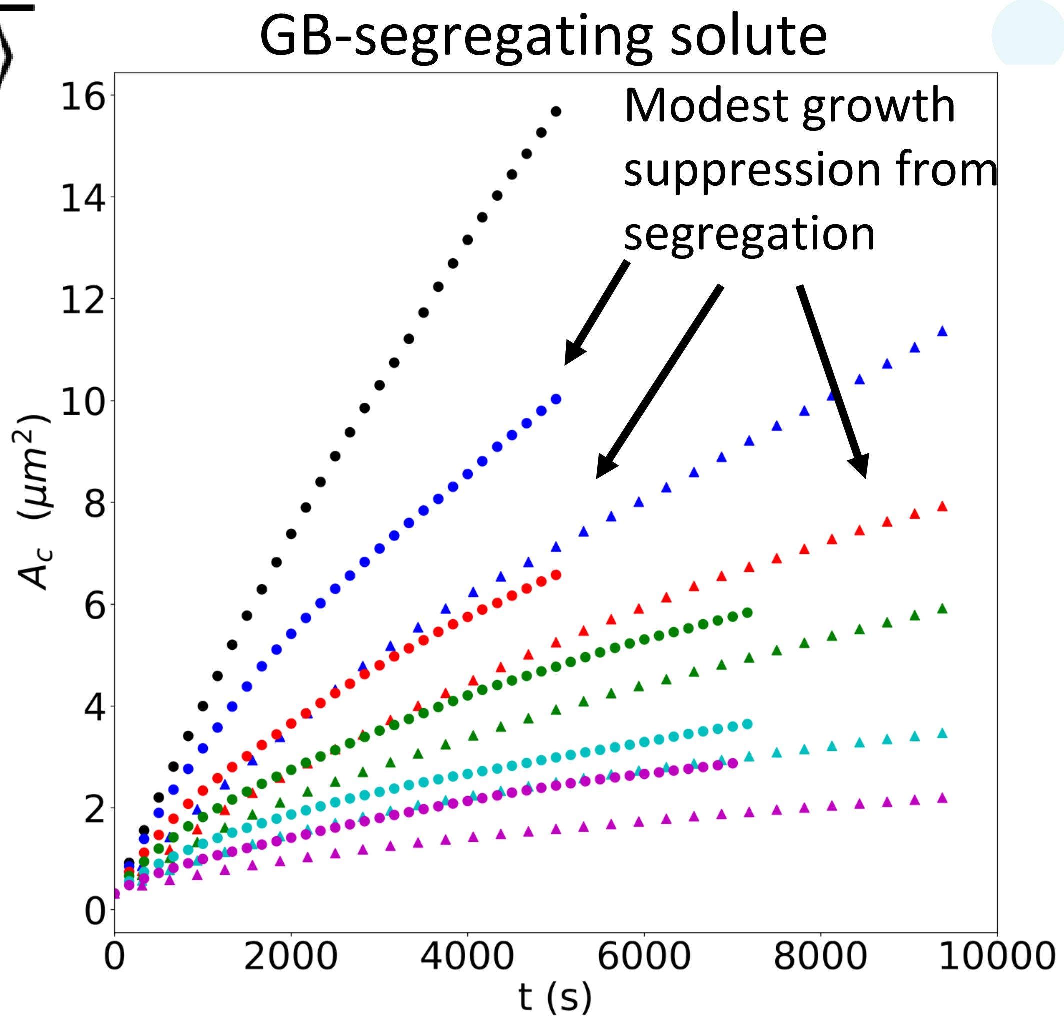
GB segregation: $\Omega_{gb} - \Omega_b < 0$

Abdeljawad and Foiles, *Acta Mat.* 101, 2015
Abdeljawad et al., *Acta Mat. 126* 2017

Solute impedes grain growth even without segregation

$$A_c = \frac{\langle A^2 \rangle}{\langle A \rangle}$$





Five generic classes of GBs

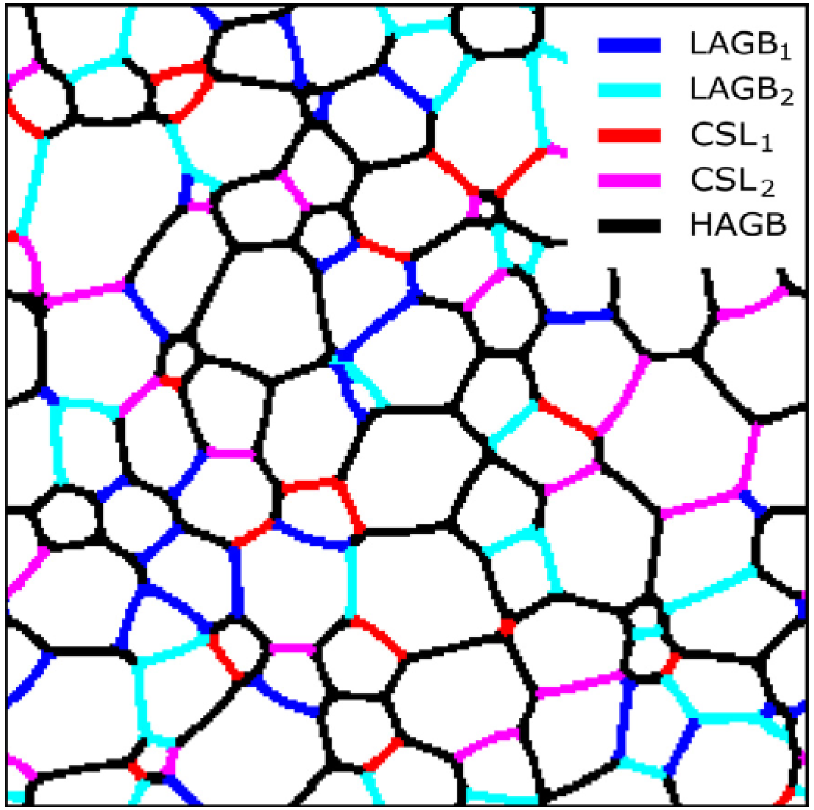


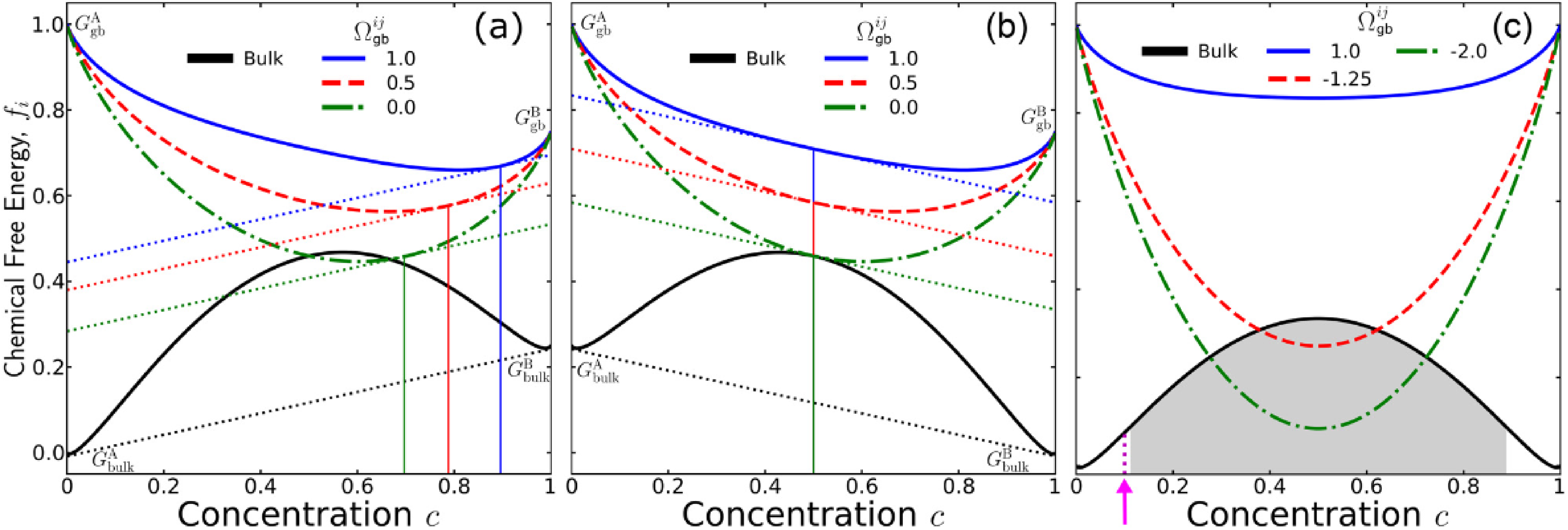
Table 1
Anisotropic grain-boundary parameters.

Grain-Boundary Type	GB energy σ^{ij}_{gb} (J/m^2)	GB mobility μ^{ij}_{gb} ($\times 10^{-19}$ m^4/sJ)	Cahn-Hilliard Kinetic Coefficient L^{ij} (reduced unit)	Thermal Coupling Coefficient γ^{ij}	Misorientation Range θ^{ij} Range
General Low Angle	0.50	1.0	0.006	0.56	$0^\circ < \theta^{ij} \leq 20^\circ$
Special CSL	0.70	1.0	0.009	0.63	$45^\circ < \theta^{ij} \leq 55^\circ$
General High Angle	0.85	1.0	0.011	0.73	$20^\circ < \theta^{ij} \leq 45^\circ$, $\theta^{ij} > 55^\circ$

J.M. Monti et al., *Acta Mater*, 2022

See Joe Monti's talk at TMS 2022…

Free energy diagrams for different scenarios



	Parameter	S1	S2
Free Energies	G_{bulk}^{A}	0	0
	G_{gb}^{A}	1.0	1.0
	G_{bulk}^{B}	0.25	0.25
	G_{gb}^{B}	0.75	0.75
GB heat of mixing	$LAGB_1/CSL_1\ \Omega_{gb}$	1.0	0.5
	$LAGB_2/CSL_2\ \Omega_{gb}$	0.5	0
	HAGB Ω_{gb}	0.5	0

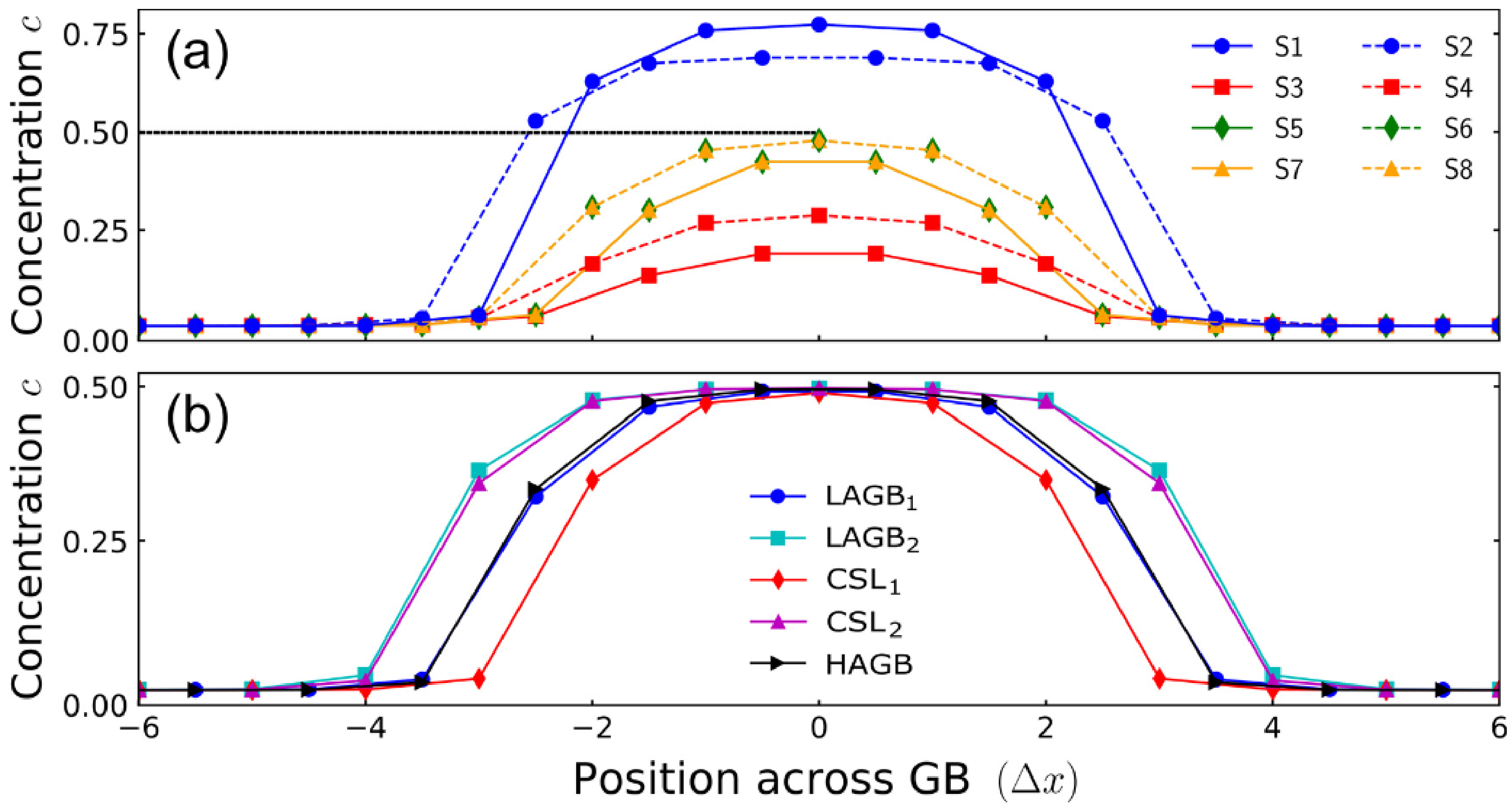
Parameter	S7	S8
G_{bulk}^{A}	0.25	0.25
G_{gb}^{A}	1.0	1.0
G_{bulk}^{B}	0	0
G_{gb}^{B}	0.75	0.75
$LAGB_1/CSL_1\ \Omega_{gb}$	1.0	0.5
$LAGB_2/CSL_2\ \Omega_{gb}$	0.5	0
HAGB Ω_{gb}	0.5	0

Additional grain-boundary segregation parameters.

Grain-Boundary Type	GB ID	$\{\Omega_{gb}^{ij}\}_{(1)}$	$\{\Omega_{gb}^{ij}\}_{(2)}$
General Low Angle	$LAGB_1$	1.00	-1.25
	$LAGB_2$	-2.00	-2.00
Special CSL	CSL_1	1.00	-1.25
	CSL_2	-2.00	-2.00
General High Angle	HAGB	-2.50	-2.50

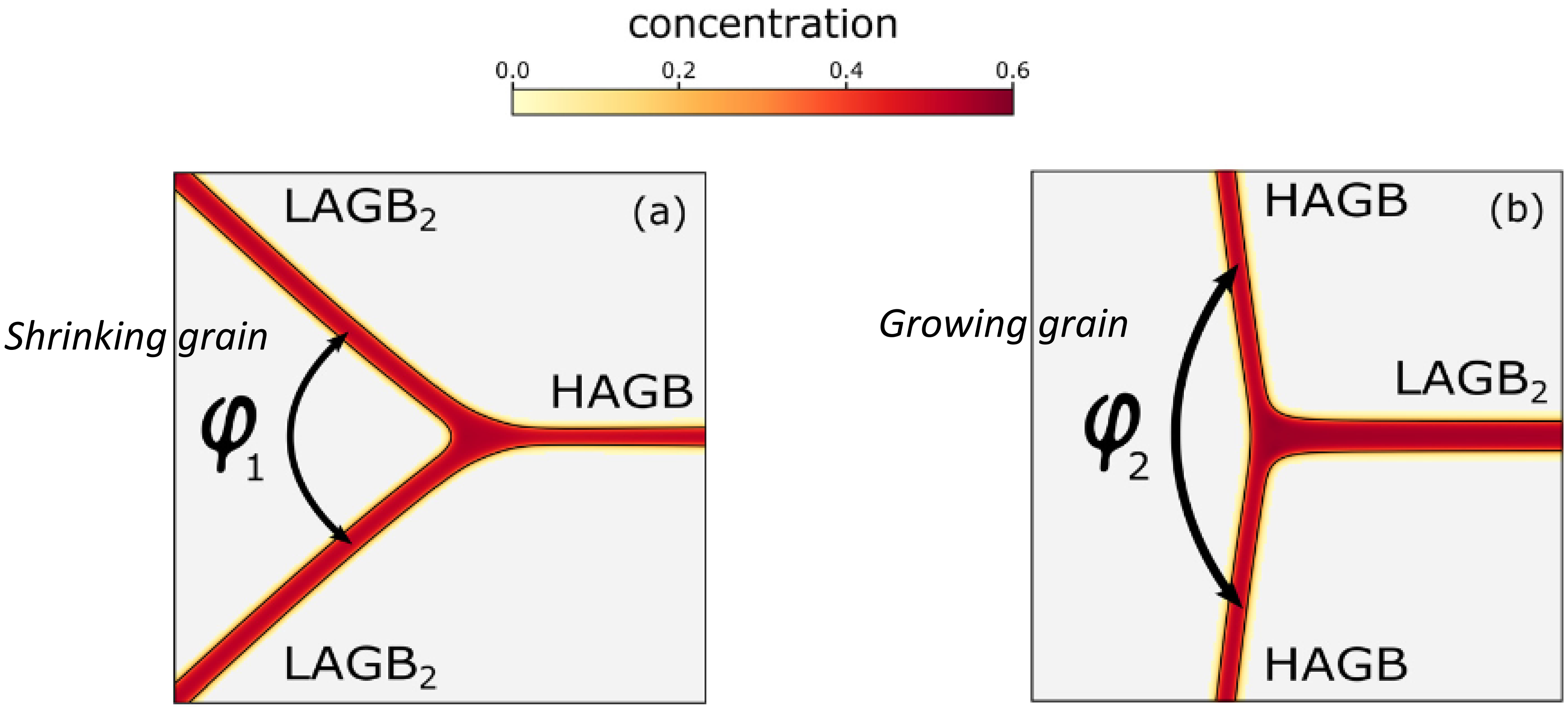
J.M. Monti et al., *Acta Mater*, 2022

Composition profiles



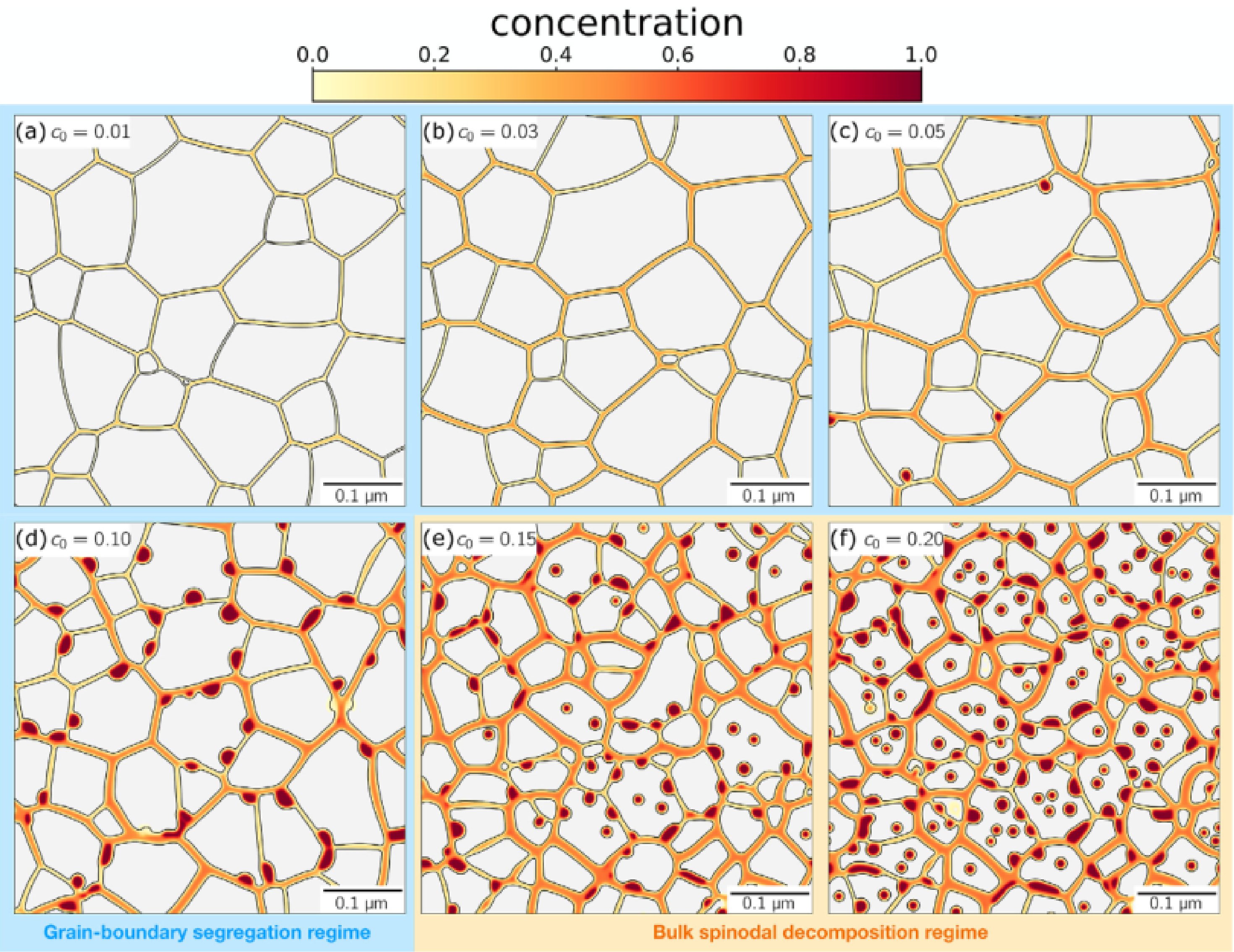
J.M. Monti et al., *Acta Mater*, 2022

Triple junction evolution



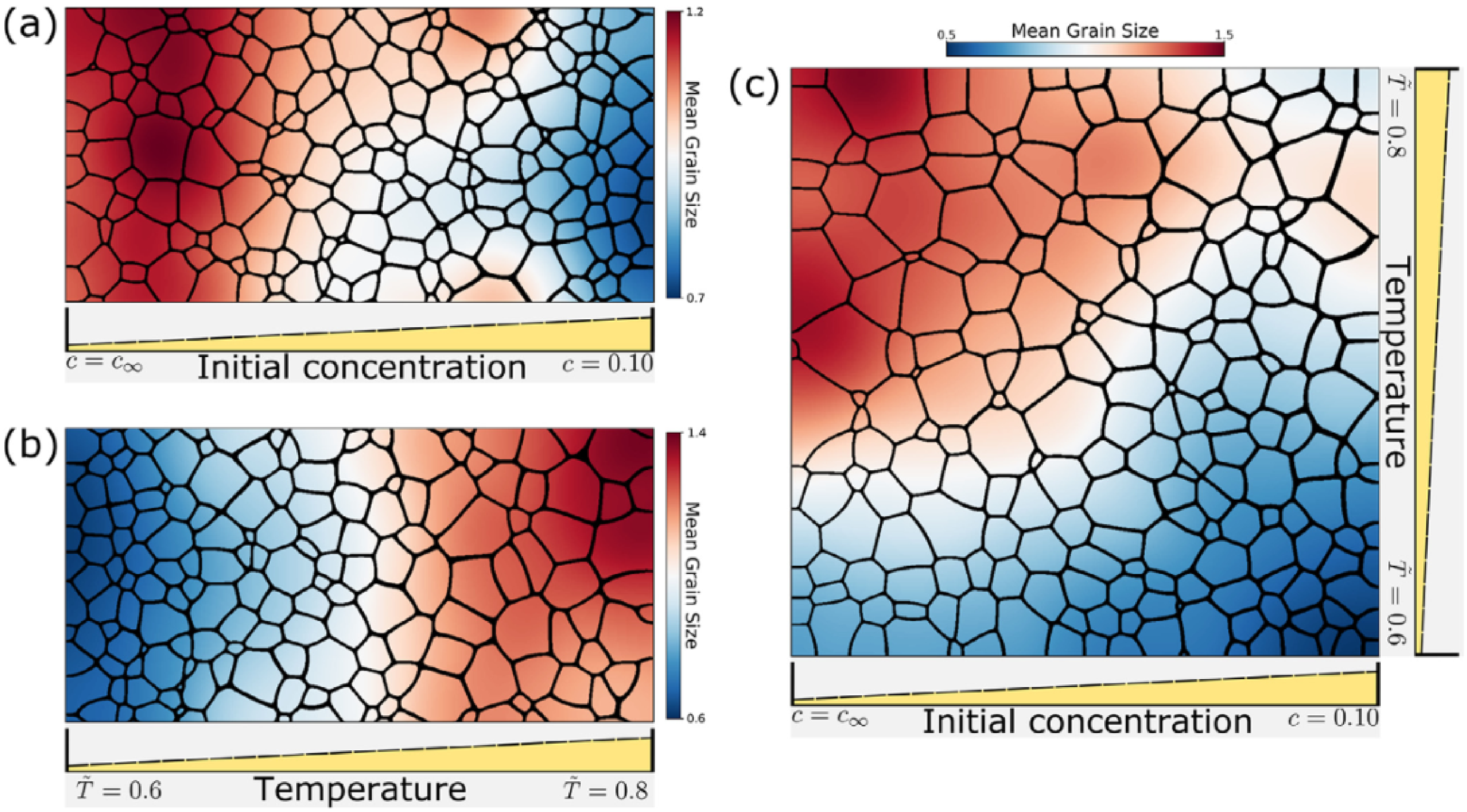
J.M. Monti et al., *Acta Mater*, 2022

Concentration Dependence.



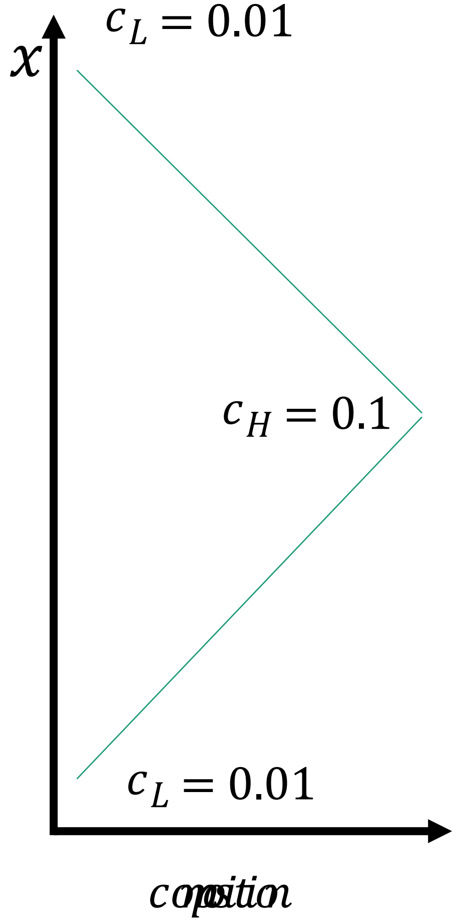
J.M. Monti et al., *Acta Mater*, 2022

Gradient predicitons…

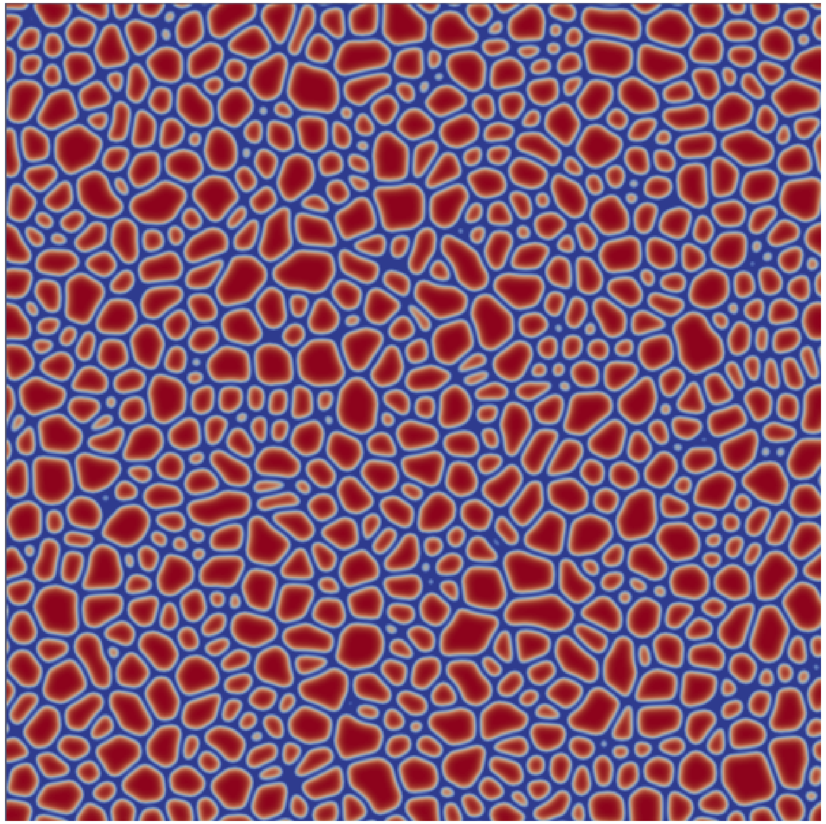


J.M. Monti et al., *Acta Mater*, 2022

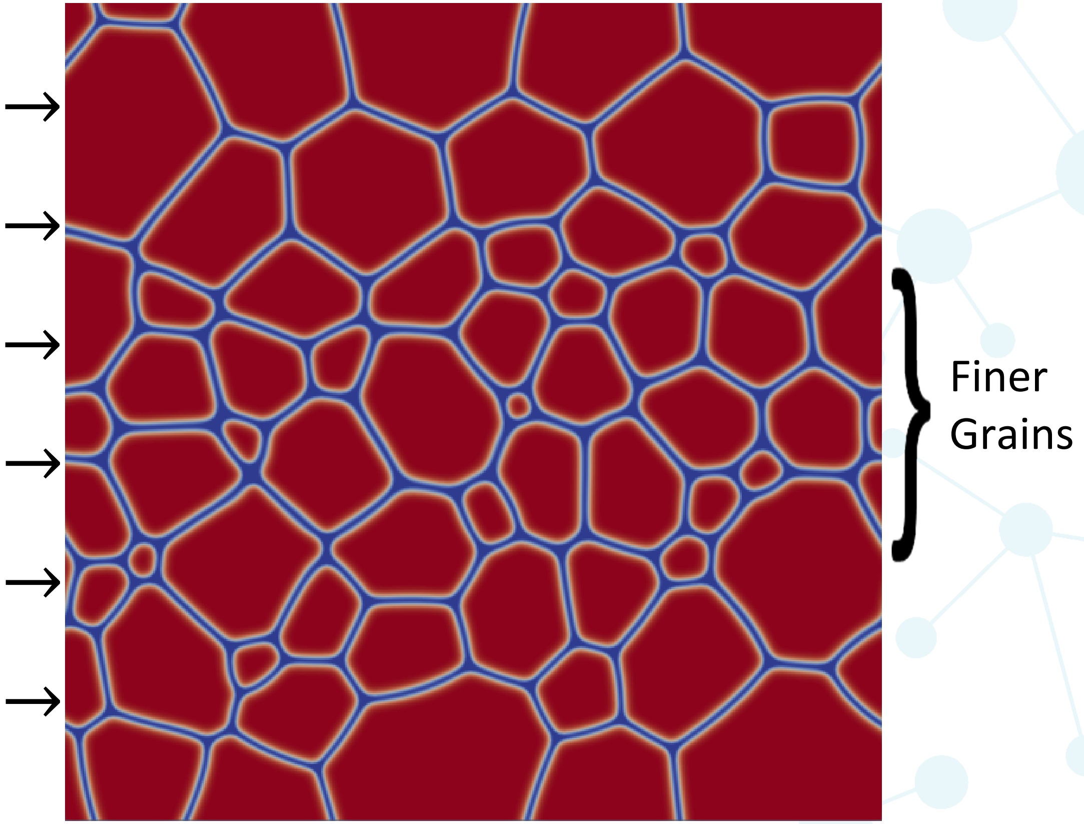
Using concentration gradient to trigger grain size gradient



Initial microstructure

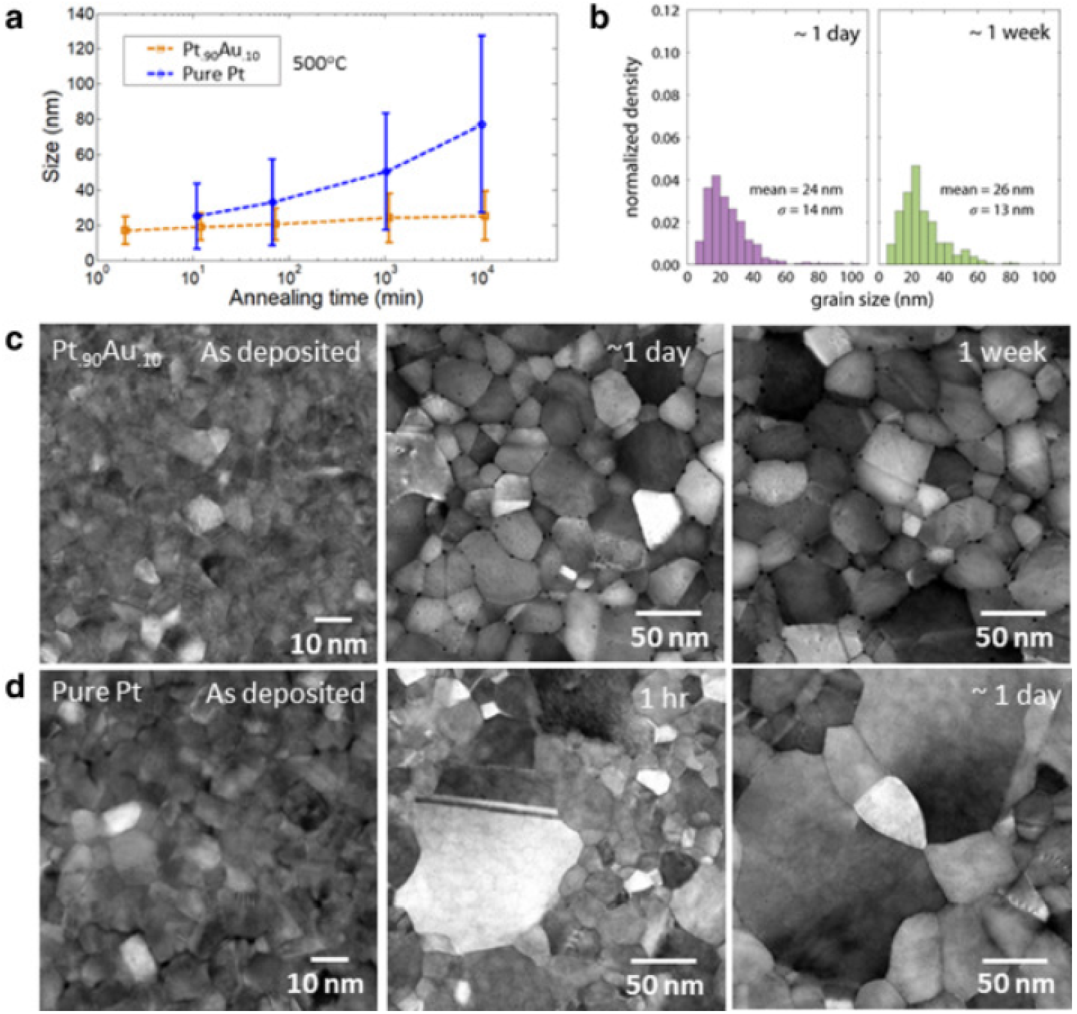


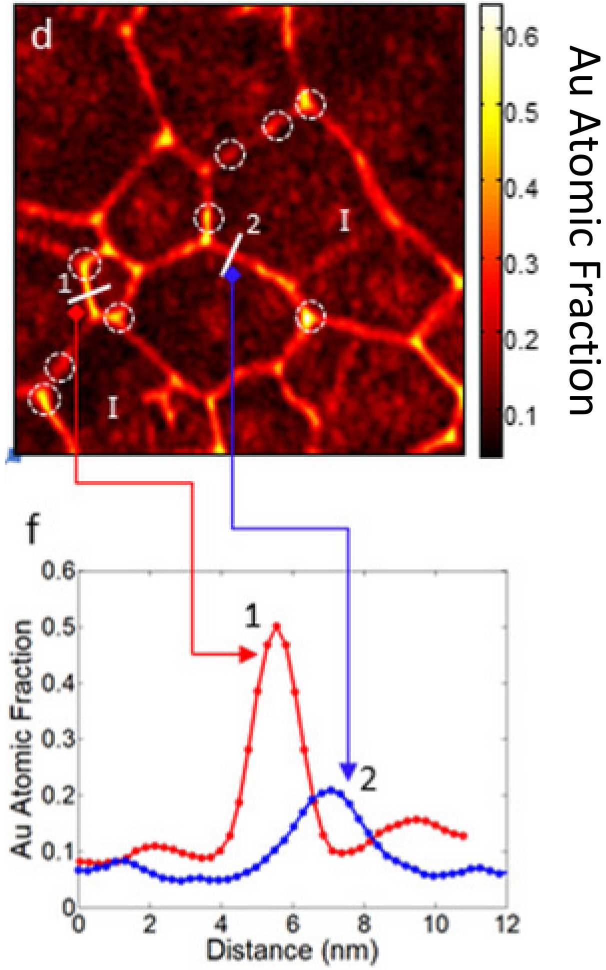
After annealing



Experimental Confirmation

The Pt-Au nc system

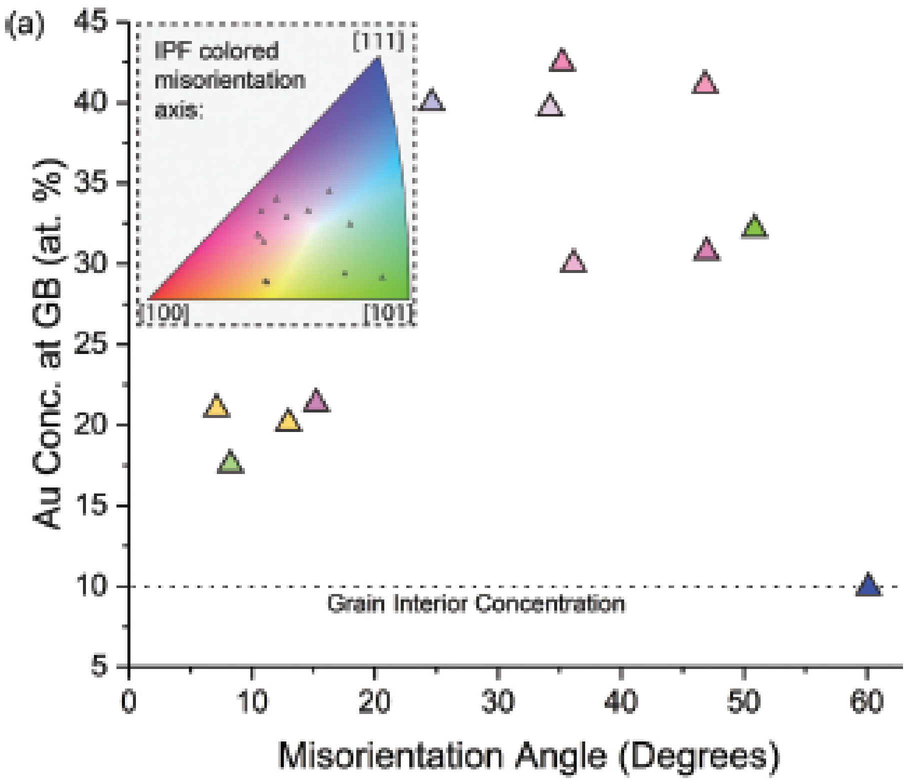




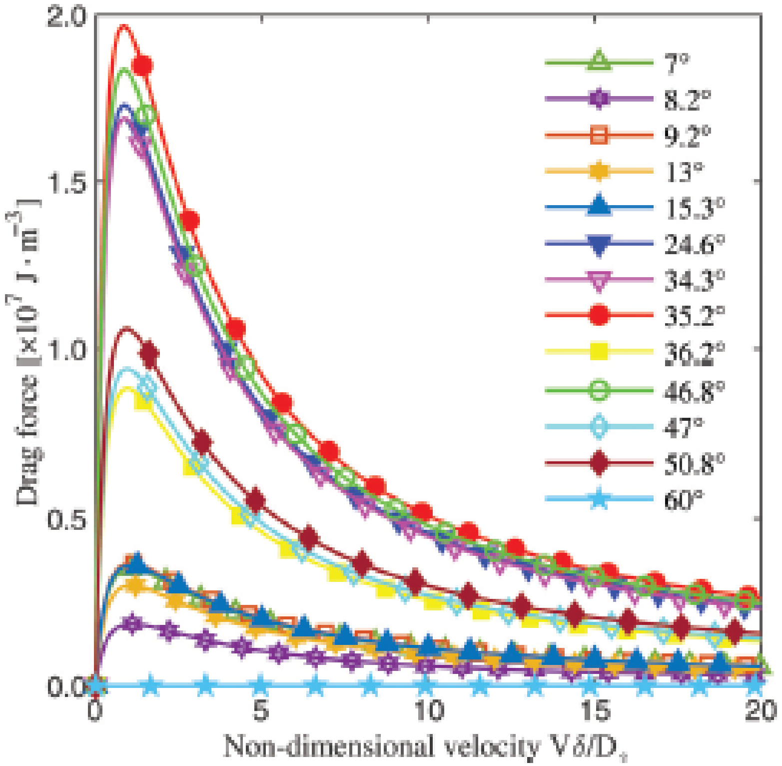
P. Lu, et al., *Materialia*, 2019

More details on Pt-Au

Au does not segregate uniformly…



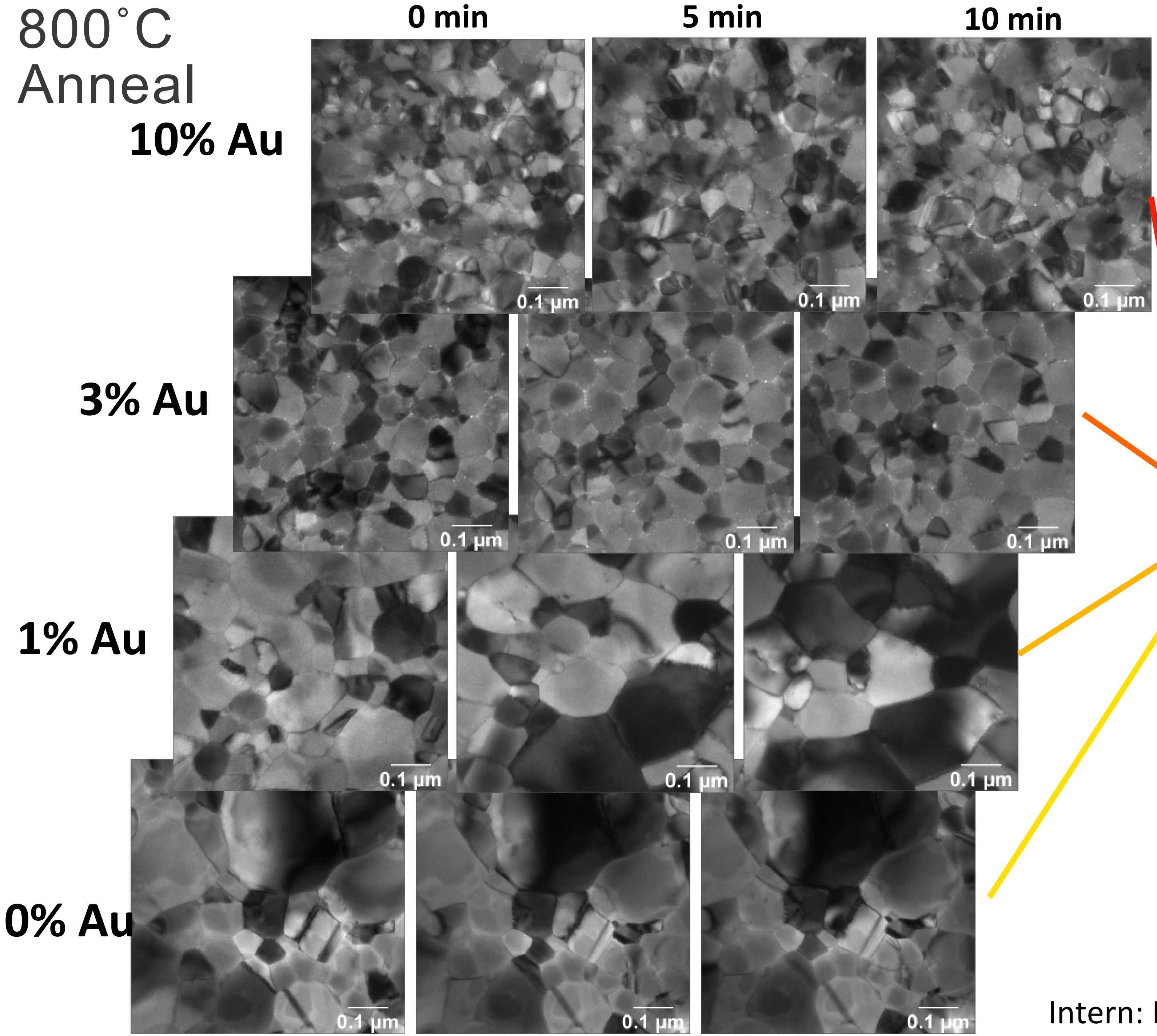
Au plays both a thermodynamic & kinetic role

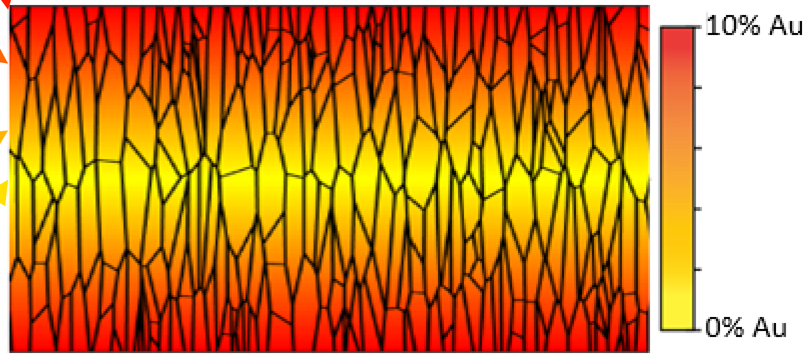


For more information…

GB character: C.M. Barr, et al., *Nanoscale,* 2021
Wear response: J.F. Curry, et al., *Adv. Mater.*, 2018
GB phase transformations: C.J. O'Brien et al., *J. Mater. Sci.*, 2018
Tensile behavior: N.M. Heckman et al., *Nanoscale*, 2018

800˚C Anneal

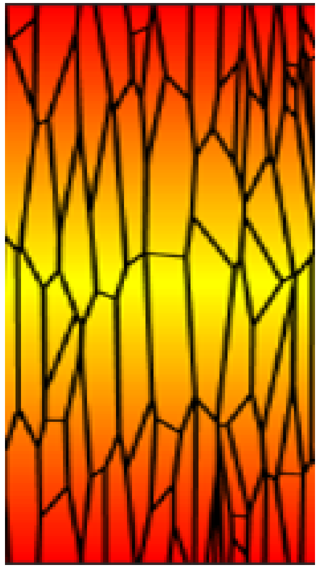




Intern: Emily Hopkins, JHU

Step-wise compositional gradient

PVD deposition



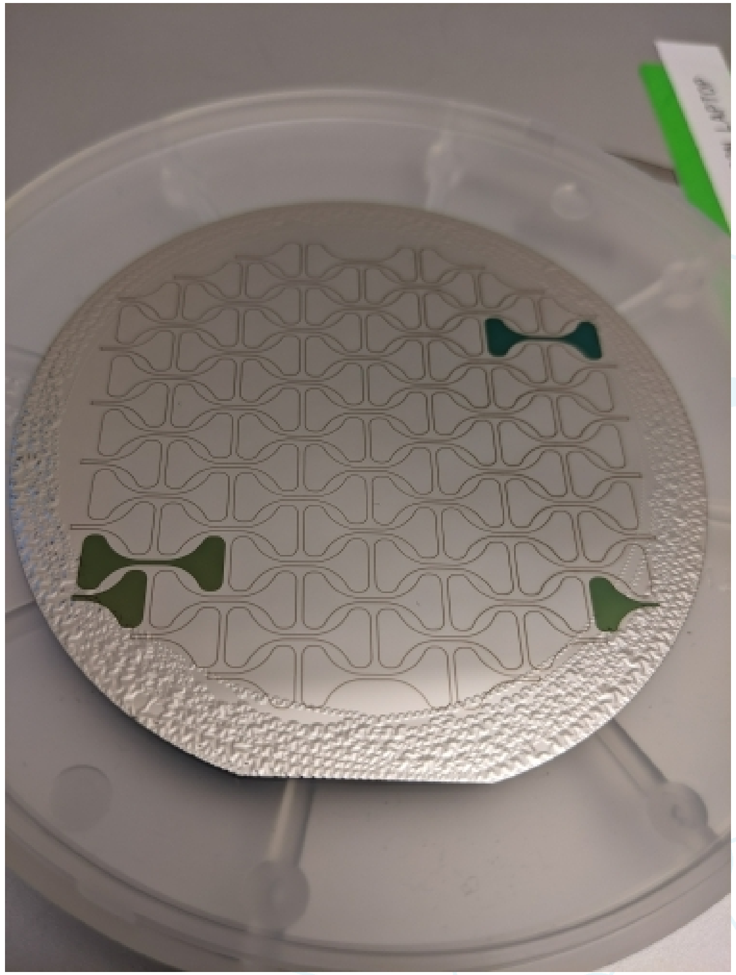
Pt-10Au	0.2 um
Pt-3Au	0.2 um
Pt-1Au	0.2 um
Pt	0.8 um
Pt-1Au	0.2 um
Pt-3Au	0.2 um
Pt-10Au	0.2 um

Across Thickness (2 um)

*only the 90/10 layers have been quantified for atomic %; Others are new targets

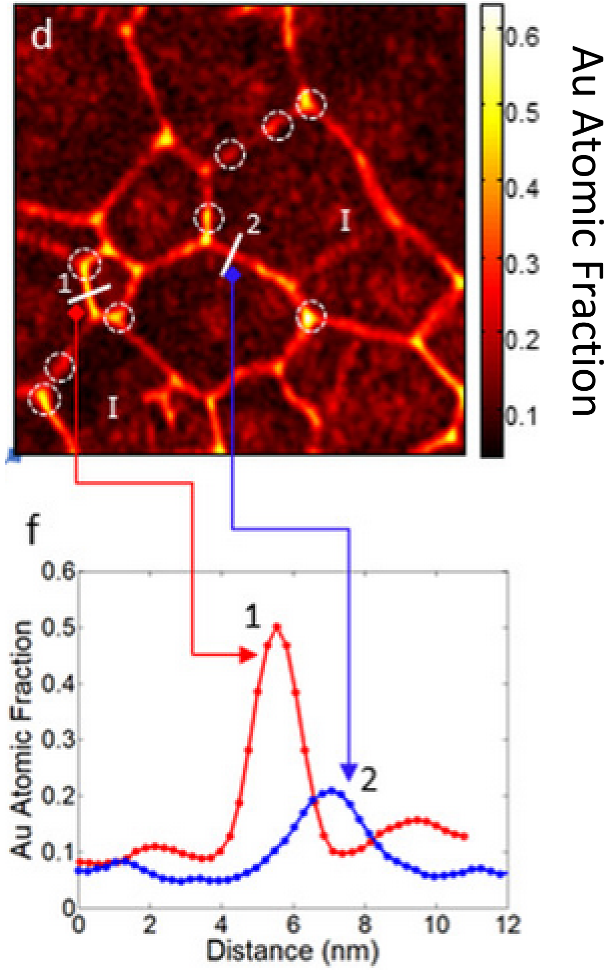
Deposited on Si/SiO wafer

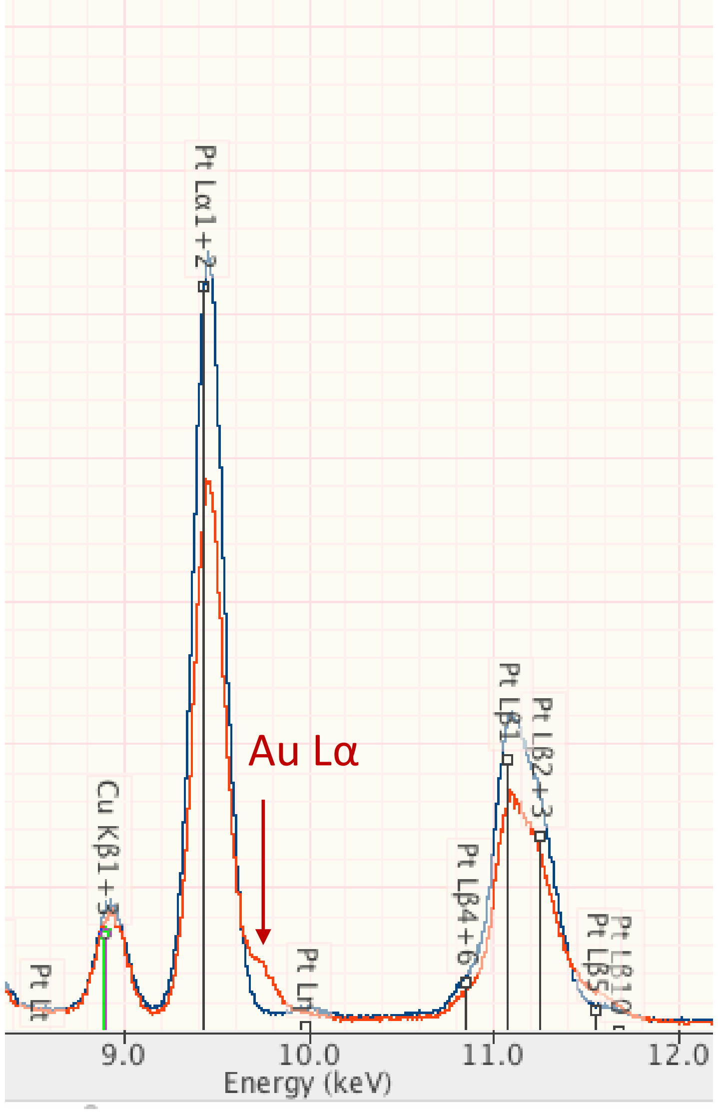
Films femtolaser cut into dogbones



A. Barrios et al., *in preparation*

A brief sidenote on the difficulty of using EDS to quantify small quantities of Au in Pt

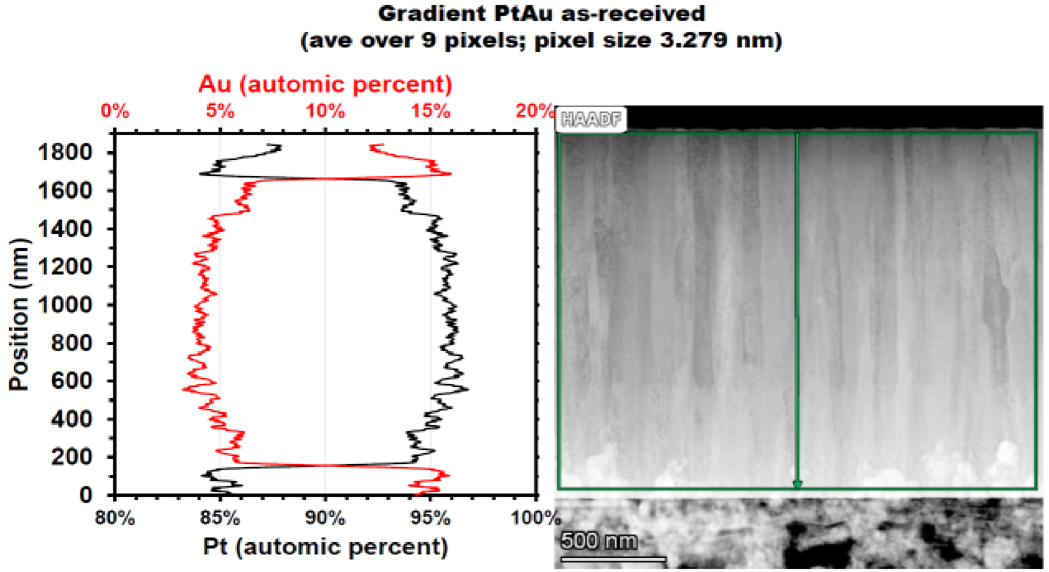




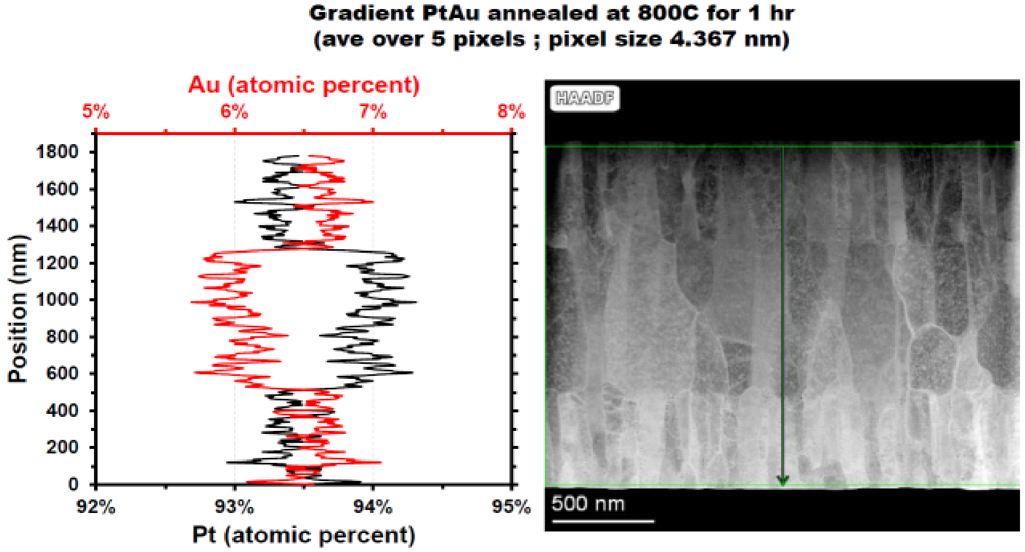
Quantifying low-levels of Au is difficult due to overlap of the Pt Lα and Au Lα x-ray lines

EDS line-scan to observe chemical gradient

As-deposited



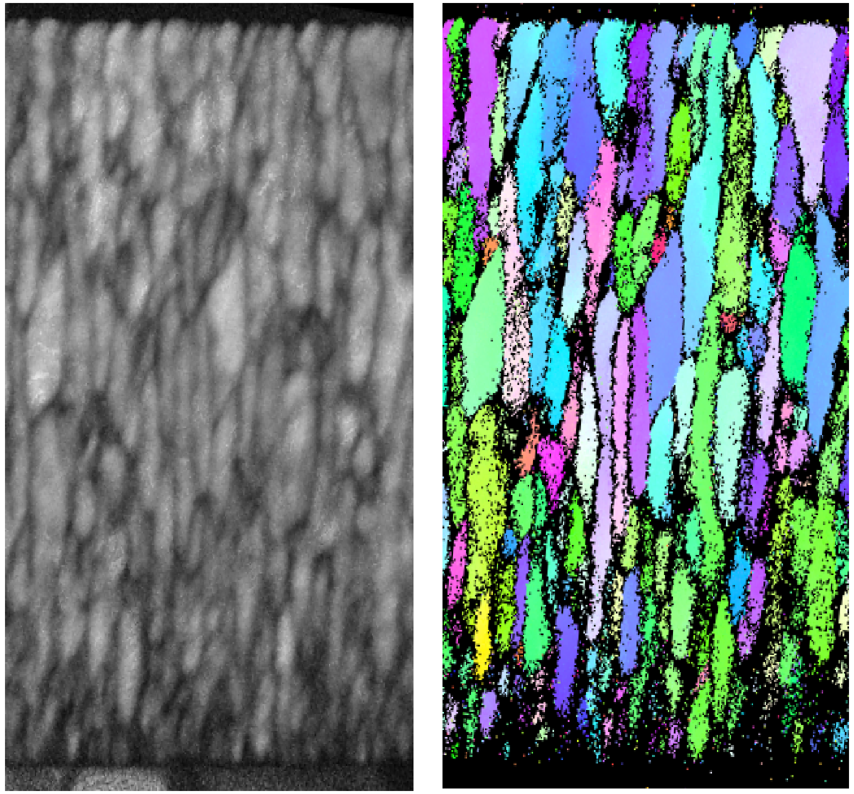
800C/1hr Anneal



A. Barrios et al., *in preparation*

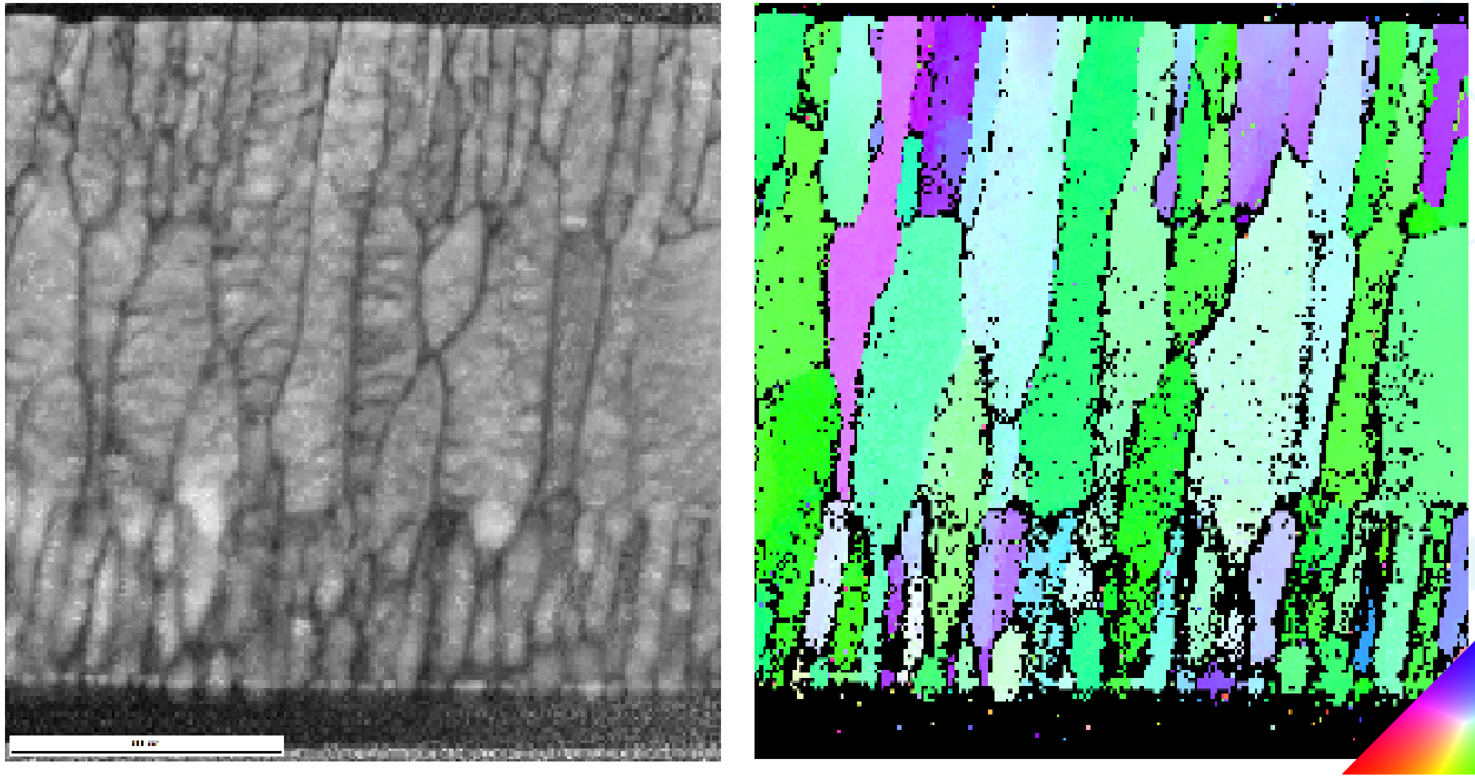
Transmission Kikuchi diffraction / Automated Crystal Orientation Maps for heterogeneous grain growth

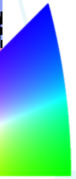
As-deposited



200 nm

800C/1hr Anneal



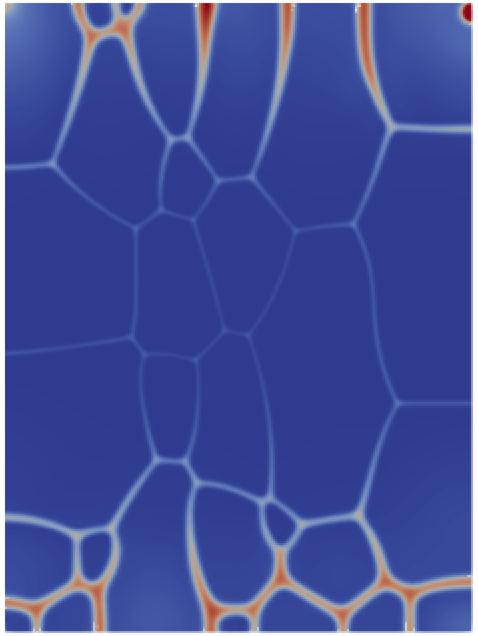


Orientation w.r.t. out-of-plane

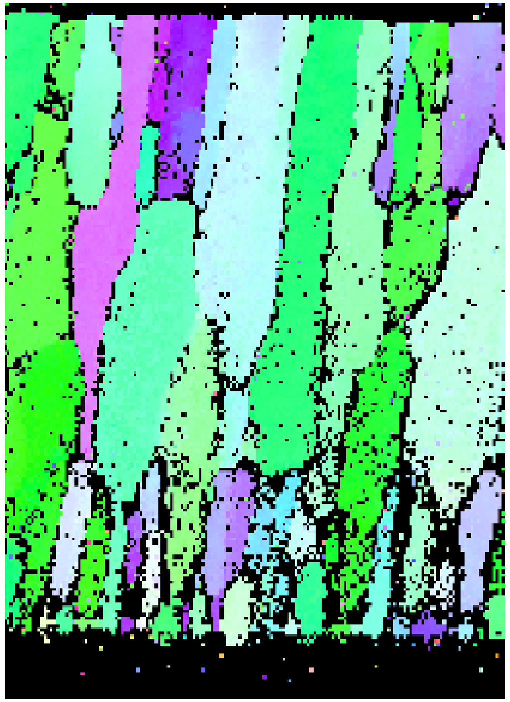
A. Barrios et al., *in preparation*

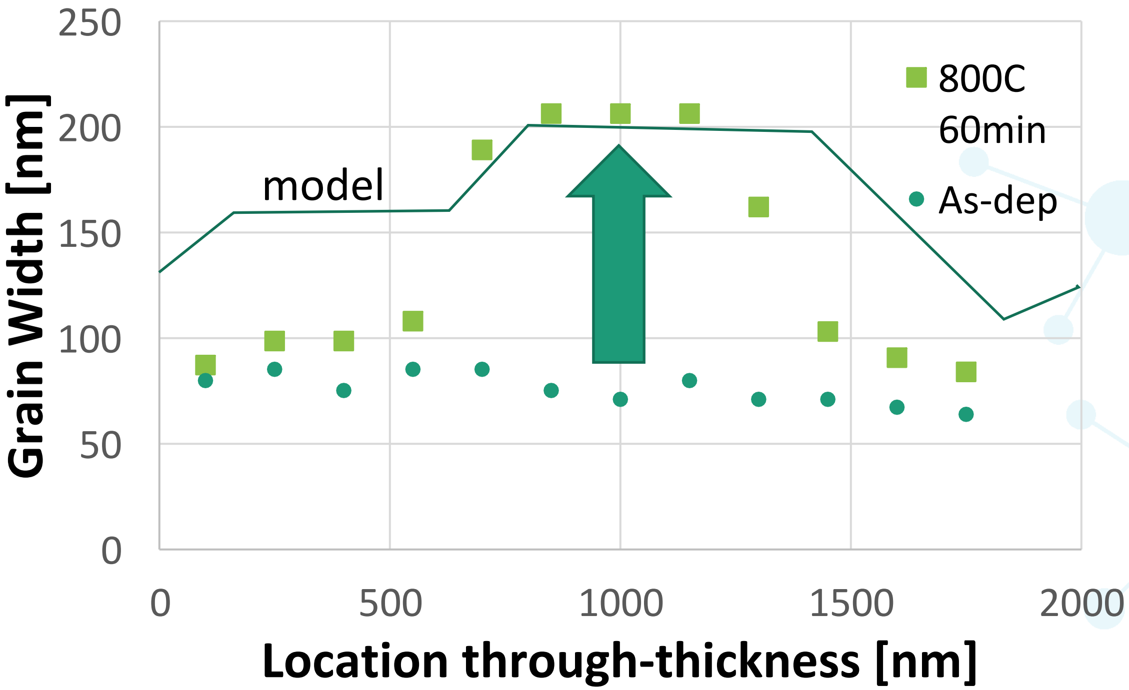
RESULT: Thermochemically-driven heterogeneous nanostructures

model



experiment





Grain size gradient ~ **0.1** μm/μm

A. Barrios et al., *in preparation*

Summary

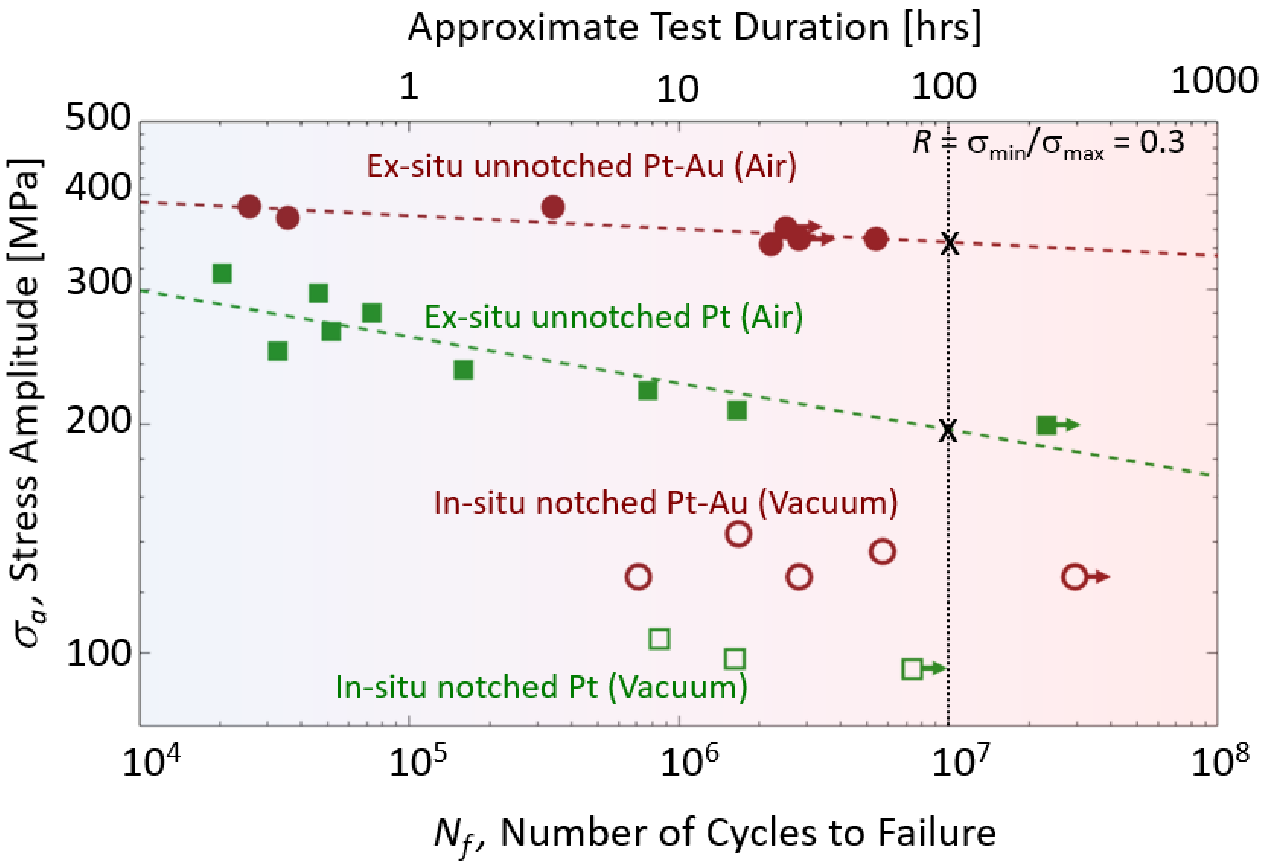
- Most gradient nanostructures are formed by severe plastic deformation, and are expected to be thermally unstable.

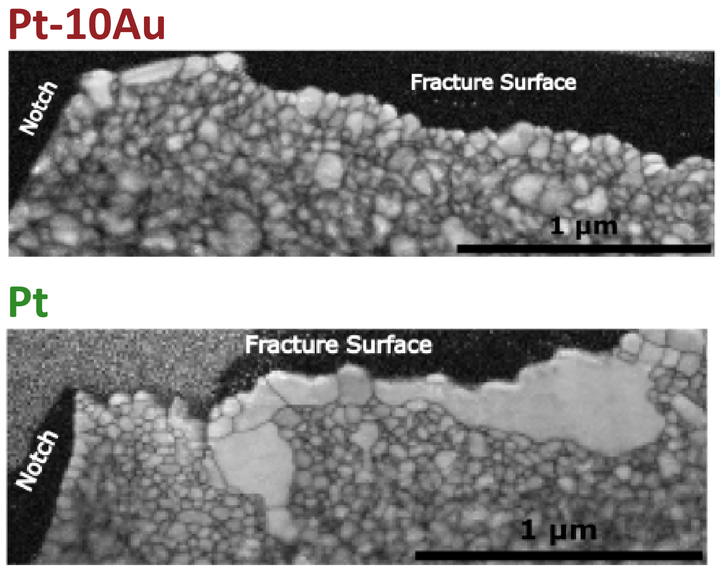
- Compositional gradients can create grain size gradients during annealing

- Such chemical gradients are naturally stable, unlike SPD gradients.

- **Outlook:** Can steep microstructural gradients be manipulated to control tensile, fracture, fatigue resistance, wear resistance, radiation tolerance?

Au solute dramatically enhances high-cycle **fatigue** resistance by inhibiting fatigue-induced grain growth





N. Heckman et al., *Acta Mater*, 2022

BIG SCIENCE AT THE NANOSCALE

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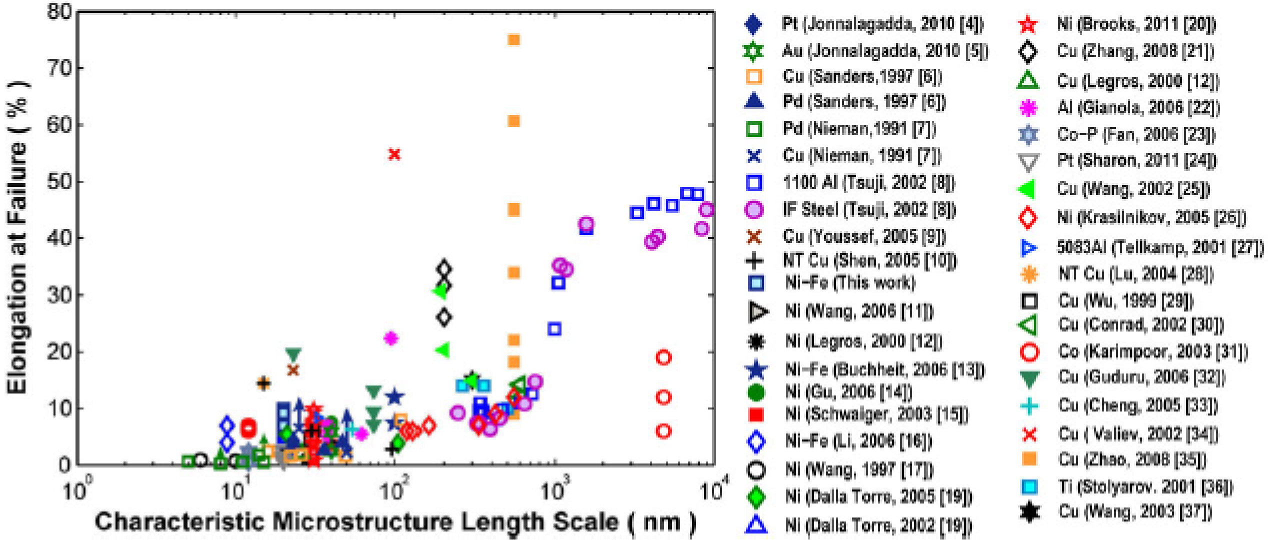
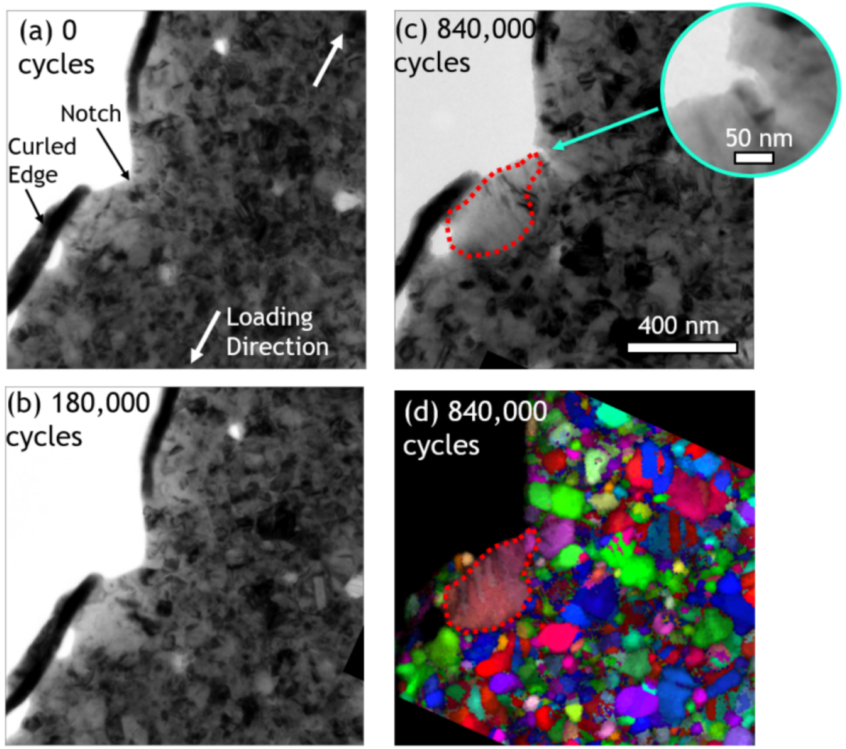
The limitations of pure nanocrystals

Ductility/toughness



Sharon, Padilla, Boyce, *J. Mater. Res.*, 2013

Stability



Lu, Pan, Hattar, Boyce, *MRS Bull.*, 2021

Competing Priorities

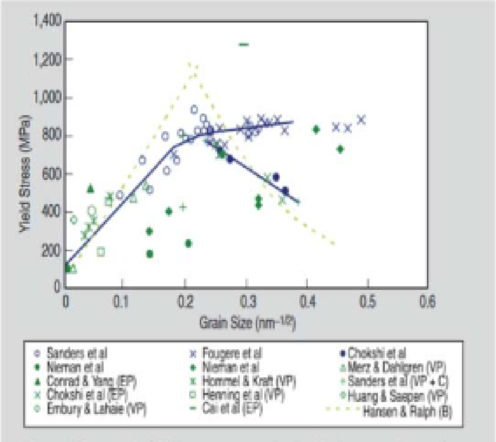
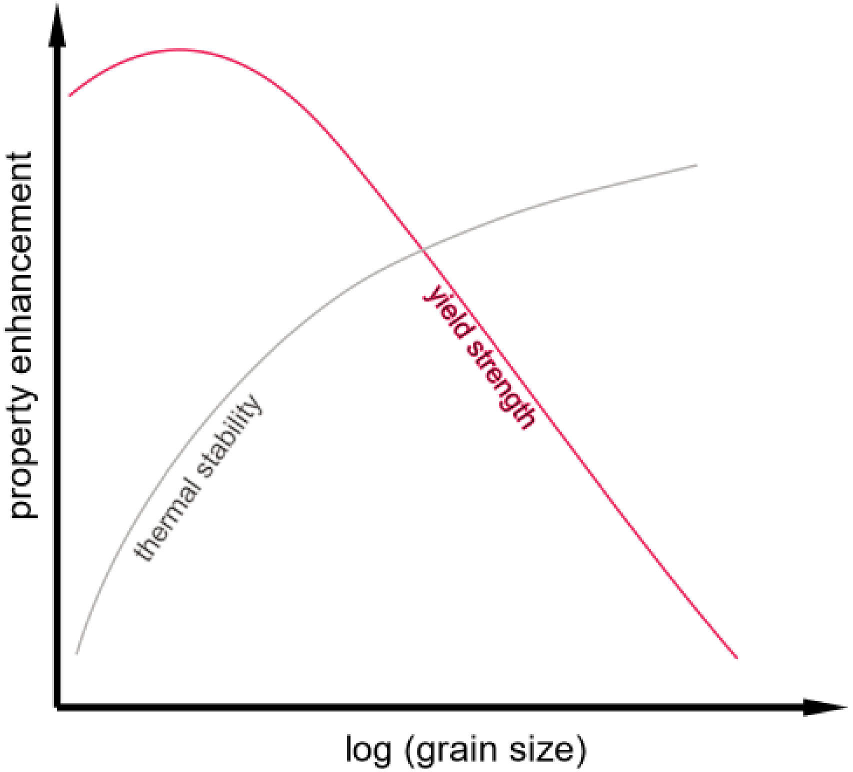
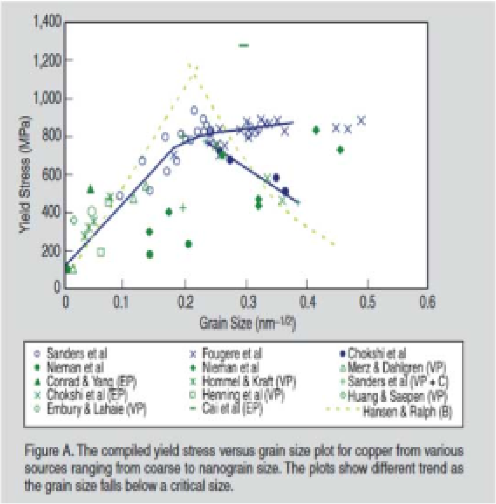


Figure A. The compiled yield stress versus grain size plot for copper from various sources ranging from coarse to nanograin size. The plots show different trend as the grain size falls below a critical size.

Meyers, Mishra, Benson, JOM, 2006



Competing Priorities



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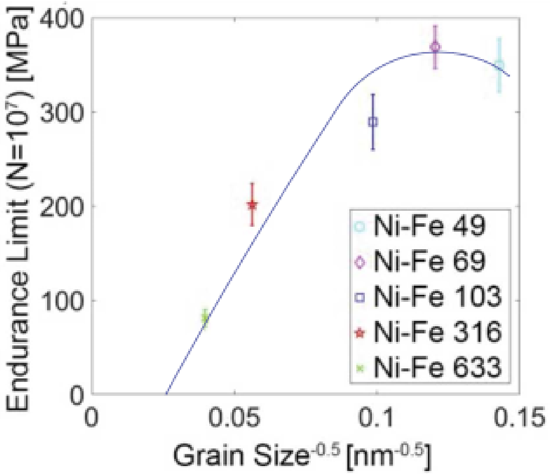
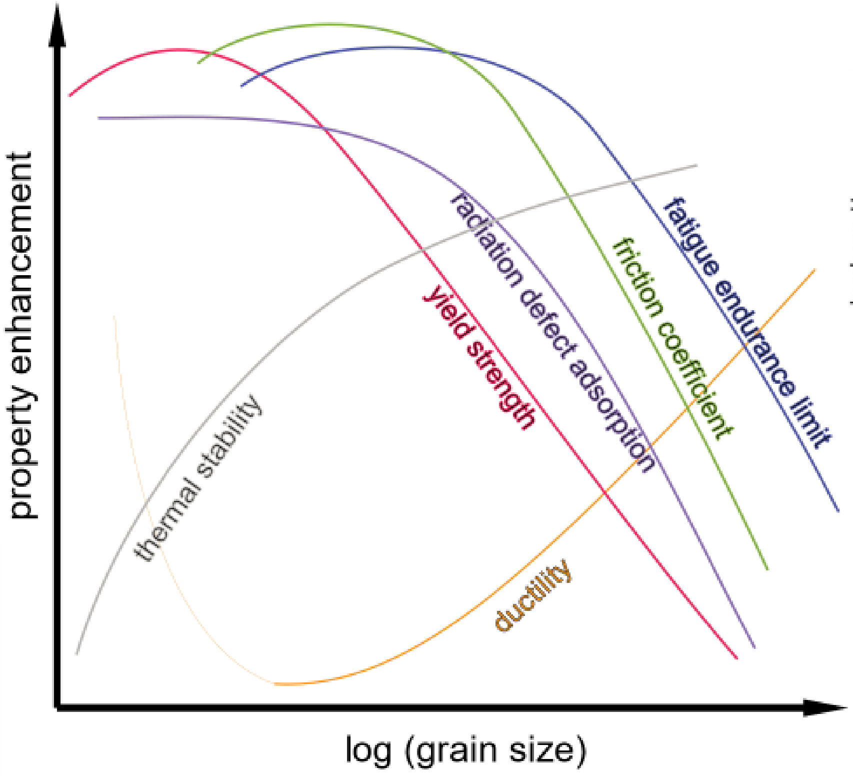
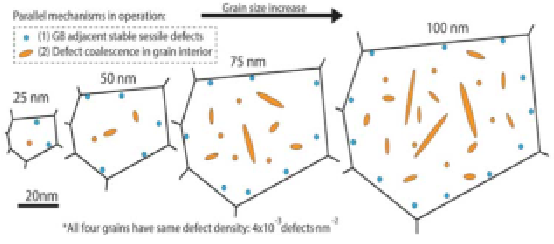
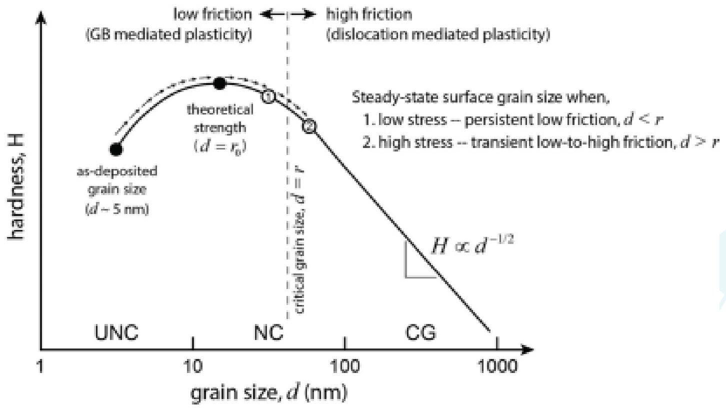


Heckman...Boyce, submittted, 2019

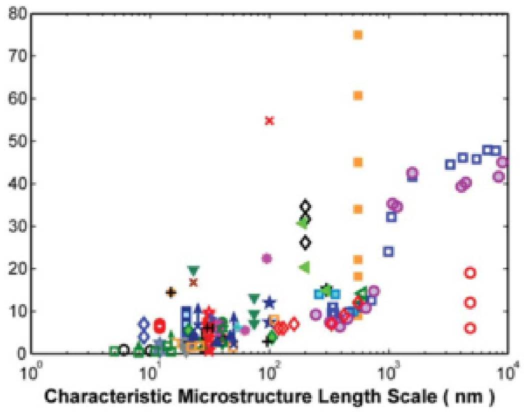




Barr, Li, Boyce, Hattar, Appl. Phys. Lett., 2018

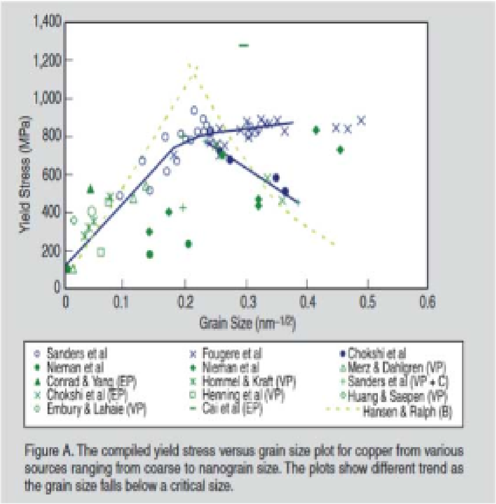


Argibay, Furnish, Clark, Boyce, Chandross, Scripta Mater, 2016



Sharon, Padilla, Boyce, J. Mater. Res., 2013

A gradient solute strategy…



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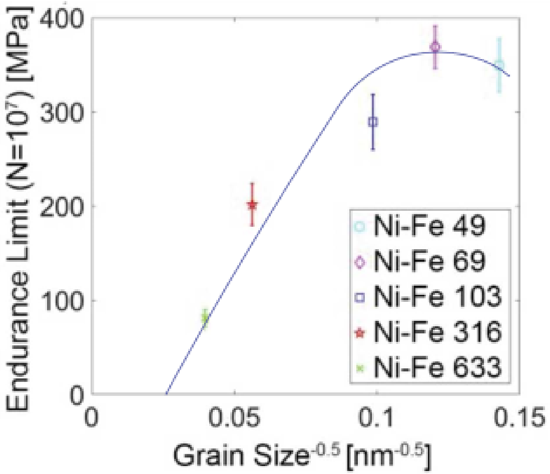
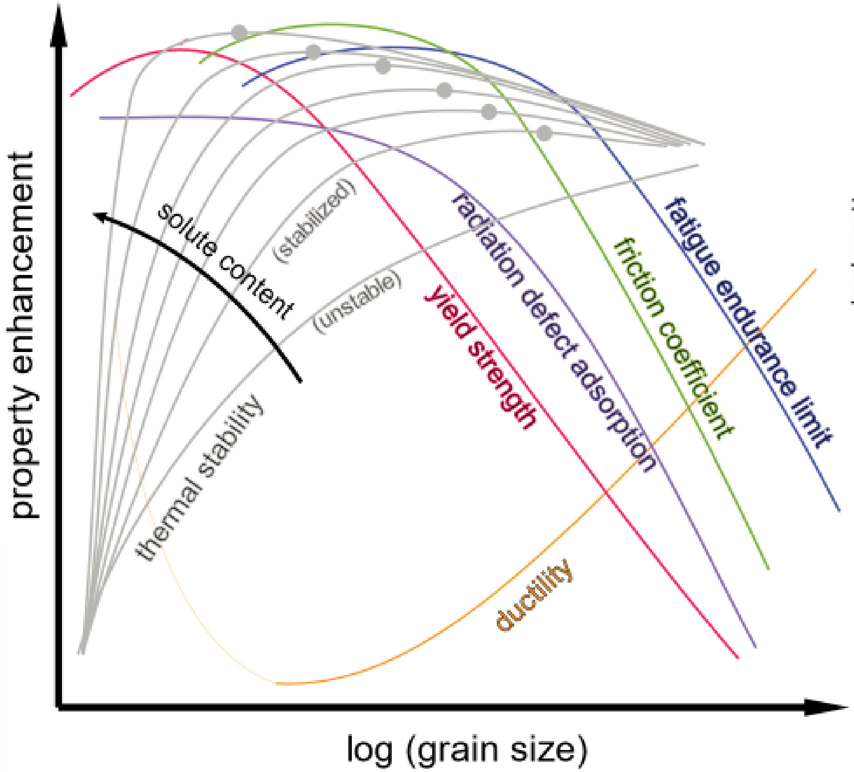
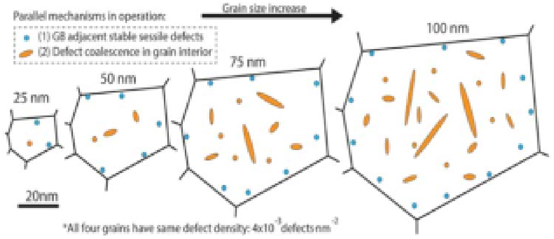
Meyers, Mishra, Benson, JOM, 2006

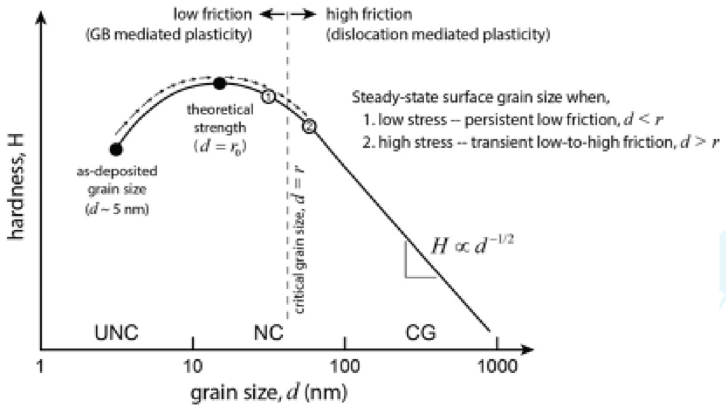


Heckman...Boyce, submittted, 2019

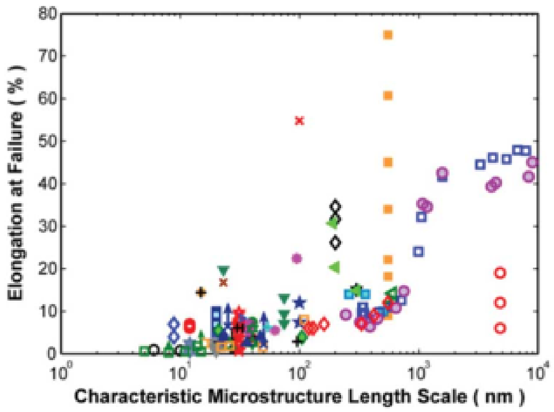




Barr, Li, Boyce, Hattar, Appl. Phys. Lett., 2018

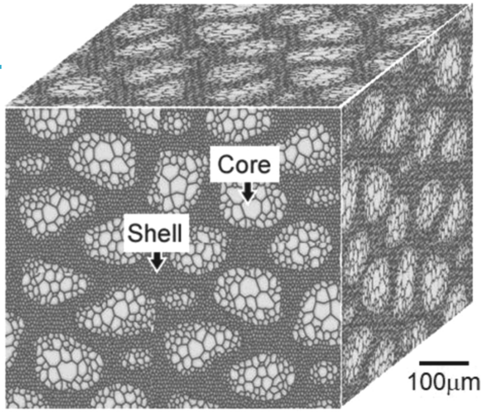


Argibay, Furnish, Clark, Boyce, Chandross, Scripta Mater, 2016

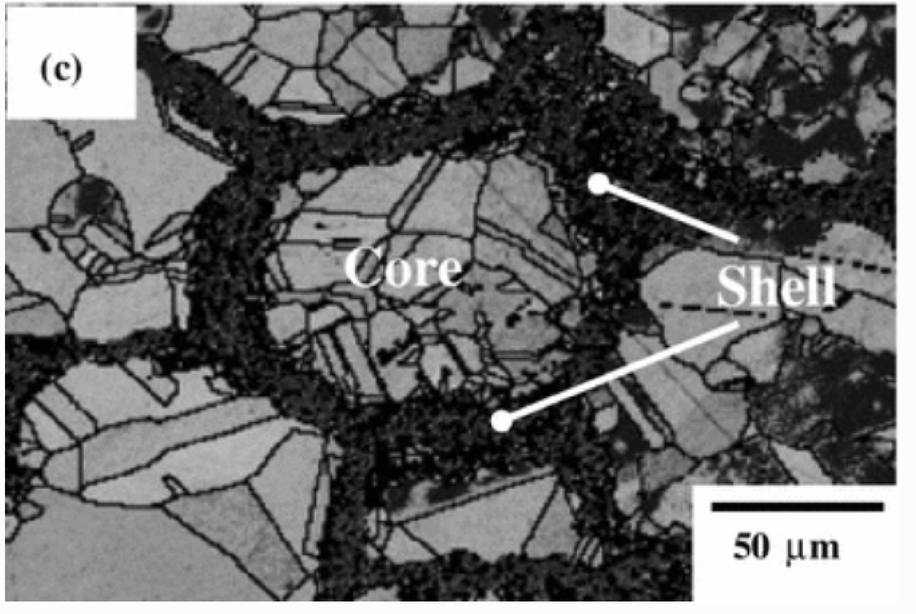


Sharon, Padilla, Boyce, J. Mater. Res., 2013

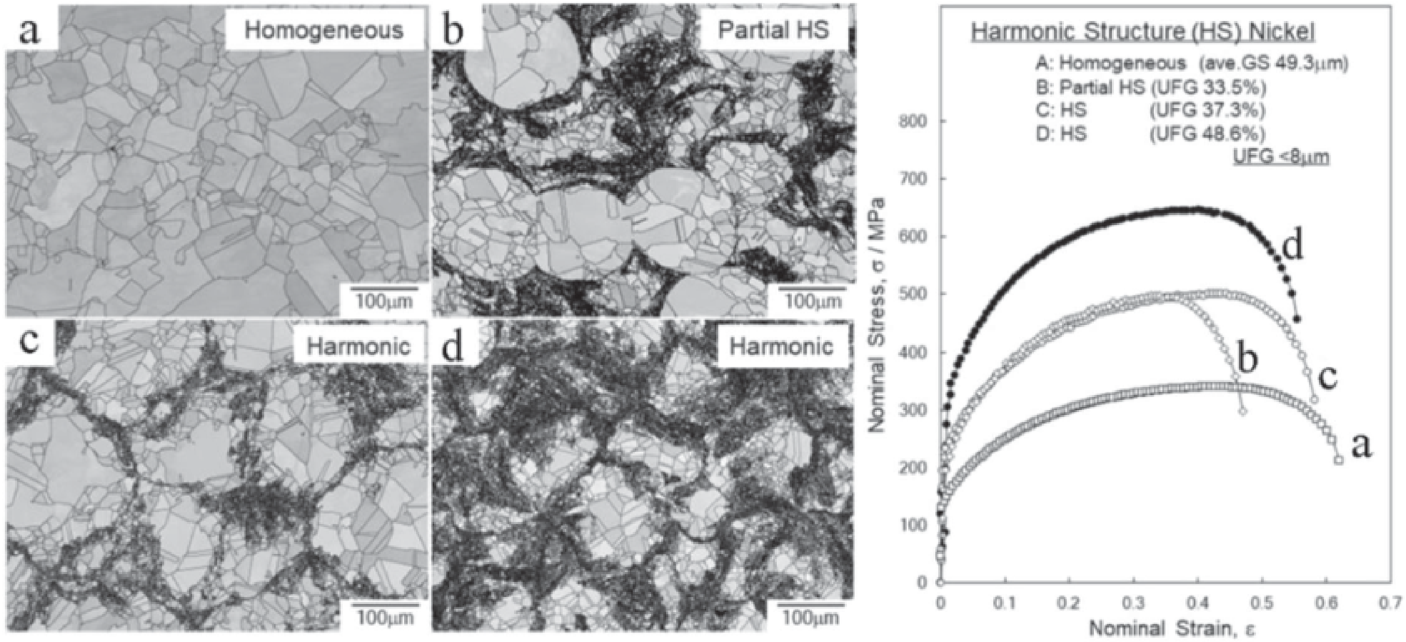
Gradients are not just from the surface



Manufactured via powder metallurgy
e.g. ball milling & sintering



Sawangrat et al, *J. Mater. Sci*, 2014



Y. Zhu et al, *Mater. Res. Lett*, 2020

Grain growth with segregation

Combined grain growth and segregation model: Abdeljawad and Foiles

$$\mathcal{F}_{tot} = \int dV \left[f_{loc}(c, T, \{\vec{\phi}\}) + \sum_{i}^{n_{\max}} \frac{\varepsilon^2}{2} |\nabla \phi_i|^2 + \frac{\kappa^2}{2} |\nabla c|^2 \right]$$

Grain boundary width

$$f_{loc}(c, T, \{\vec{\phi}\}) = f_b(c, T) + [W - \xi_1 c - \xi_2 c^2] g(\vec{\phi})$$

Bulk concentration

Grain dynamics

$g(\vec{\phi})$ varies smoothly between 0 (bulk) and 1 (grain boundary)

Abdeljawad et al., *Acta Mat. 126* 2017

Grain growth with segregation

$$f_{loc}(c,T,\{\vec{\phi}\}) = f_b(c,T) + [W - \xi_1 c - \xi_2 c^2]g(\vec{\phi})$$

Bulk concentration — Grain dynamics

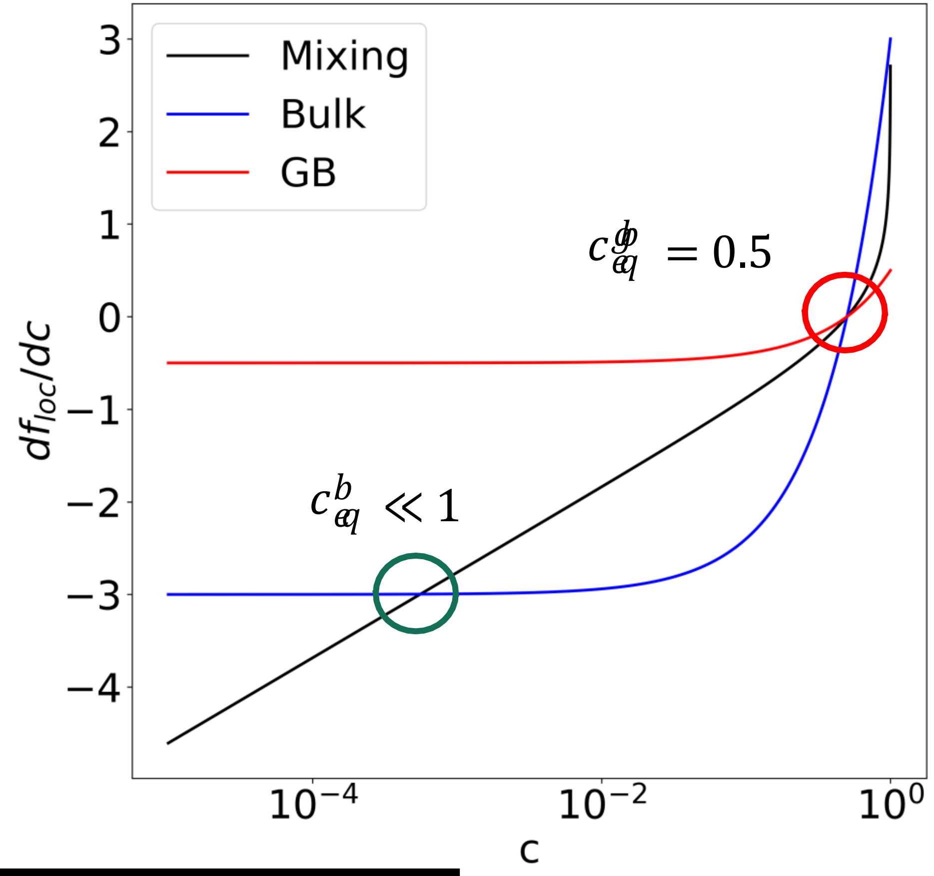
$$f_b = G_b^B c + (1-c)G_b^A + \Omega_b c(1-c) + \frac{RT}{V_m}[c \ln c + (1-c)\ln(1-c)]$$

$$W = W_\phi + (G_{gb}^A - G_b^A)$$

$$\xi_1 = (G_{gb}^A - G_b^A) - (G_{gb}^B - G_b^B) - (\Omega_{gb} - \Omega_b)$$

$$\xi_2 = (\Omega_{gb} - \Omega_b)$$

Anti-segregating parameters



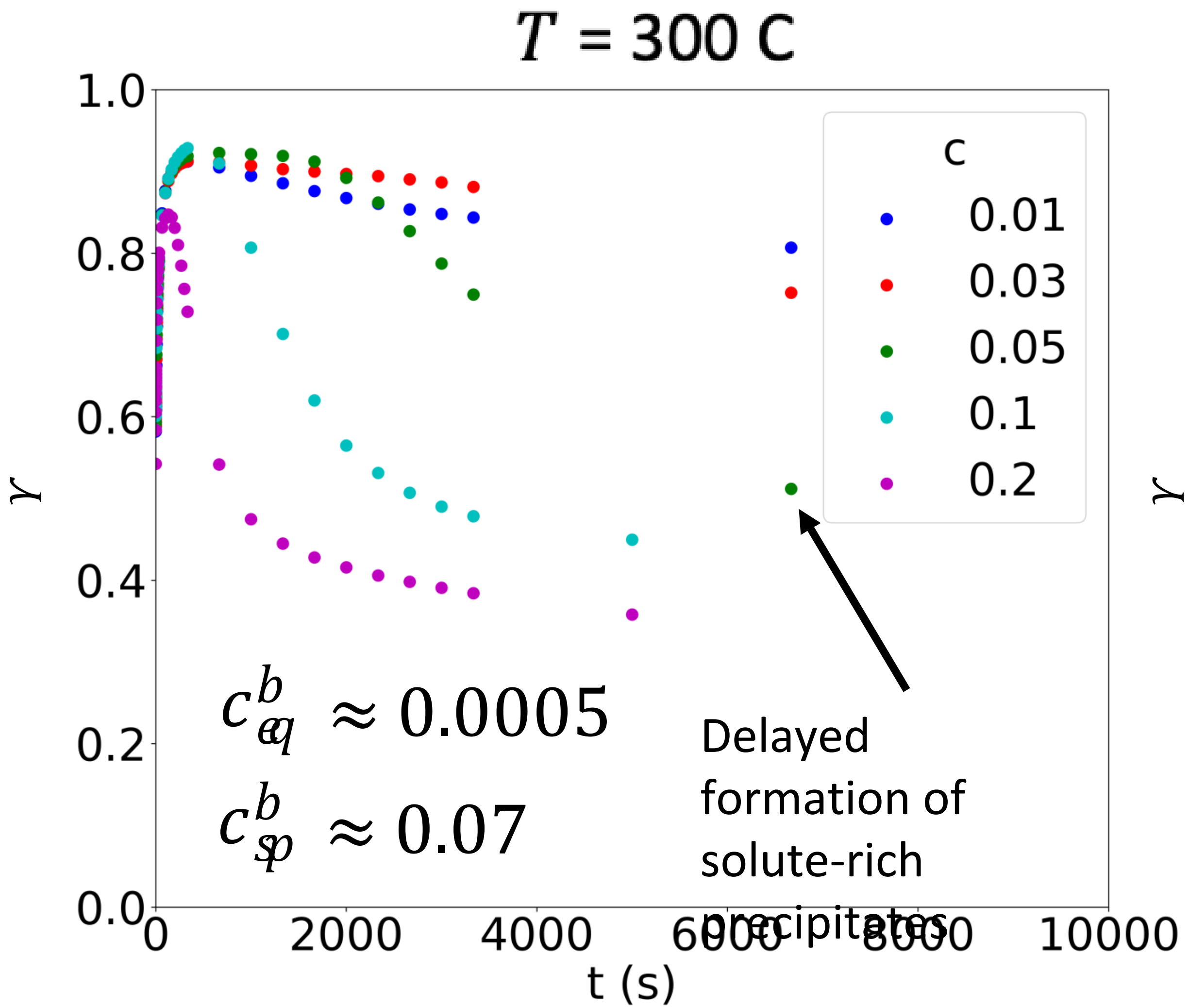
Anti-segregation: $\Omega_{gb} > 0$

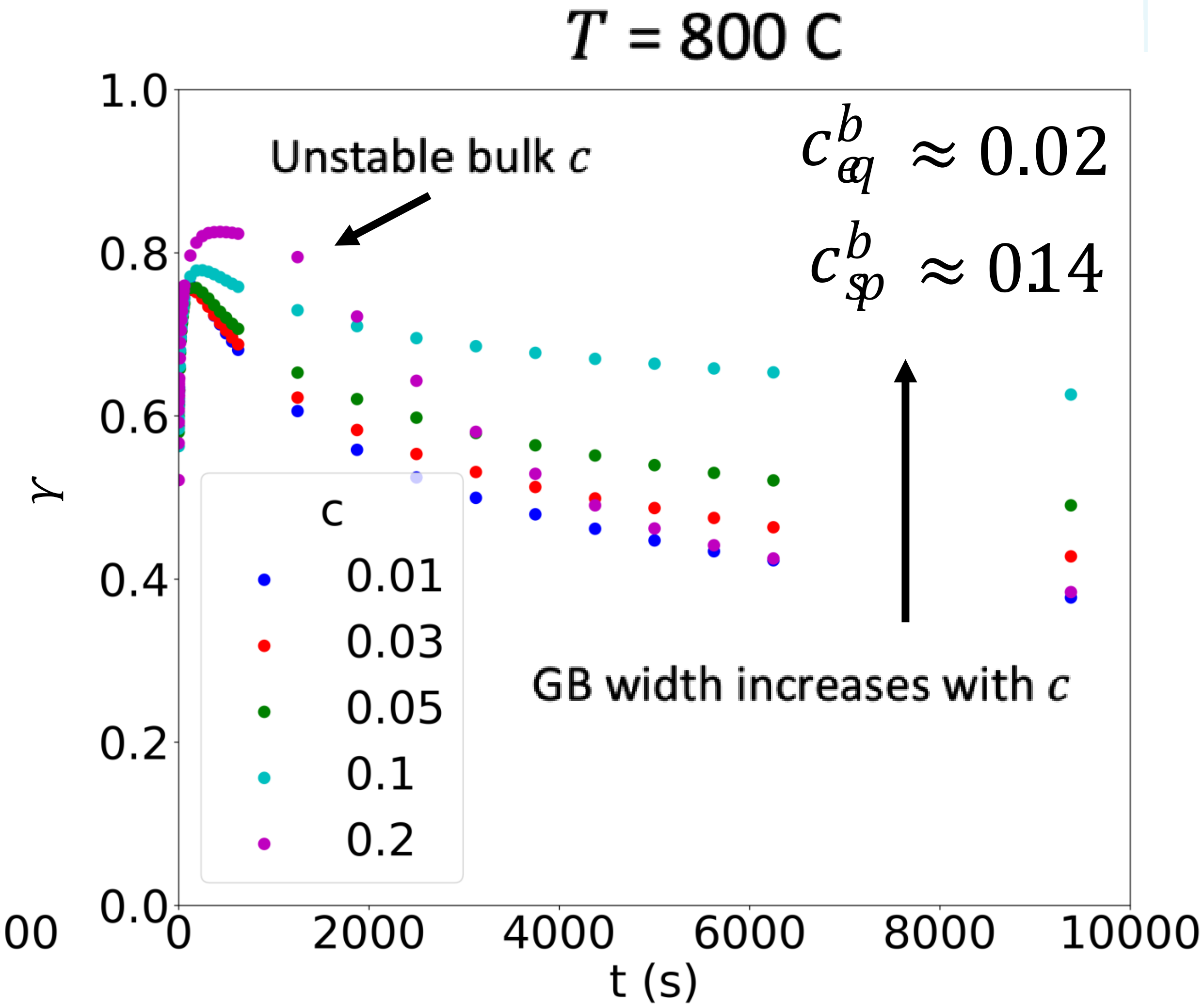
GB segregation: $\Omega_{gb} < 0$

Abdeljawad and Foiles, *Acta Mat.* 101, 2015

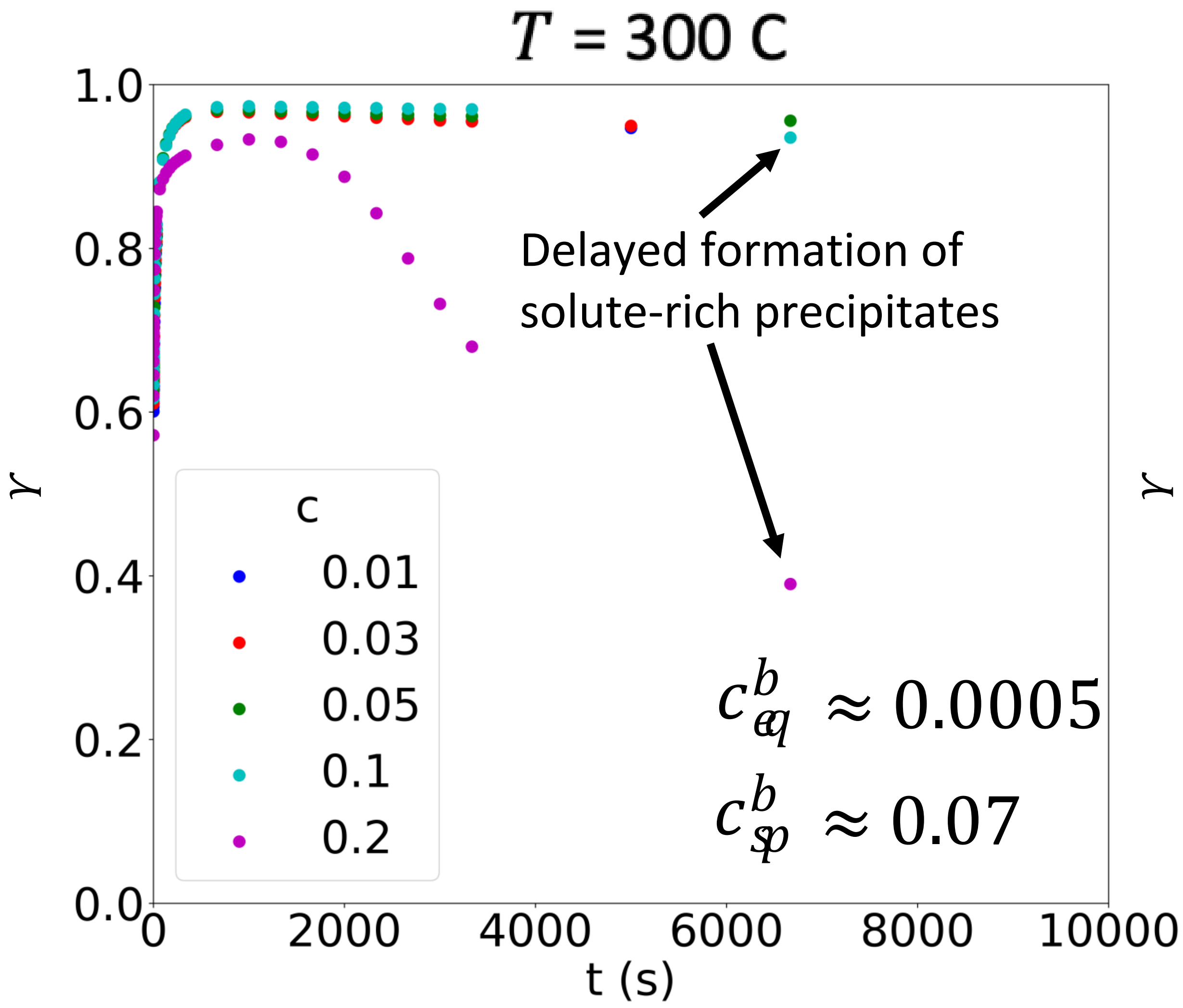
Abdeljawad et al., *Acta Mat. 126* 2017

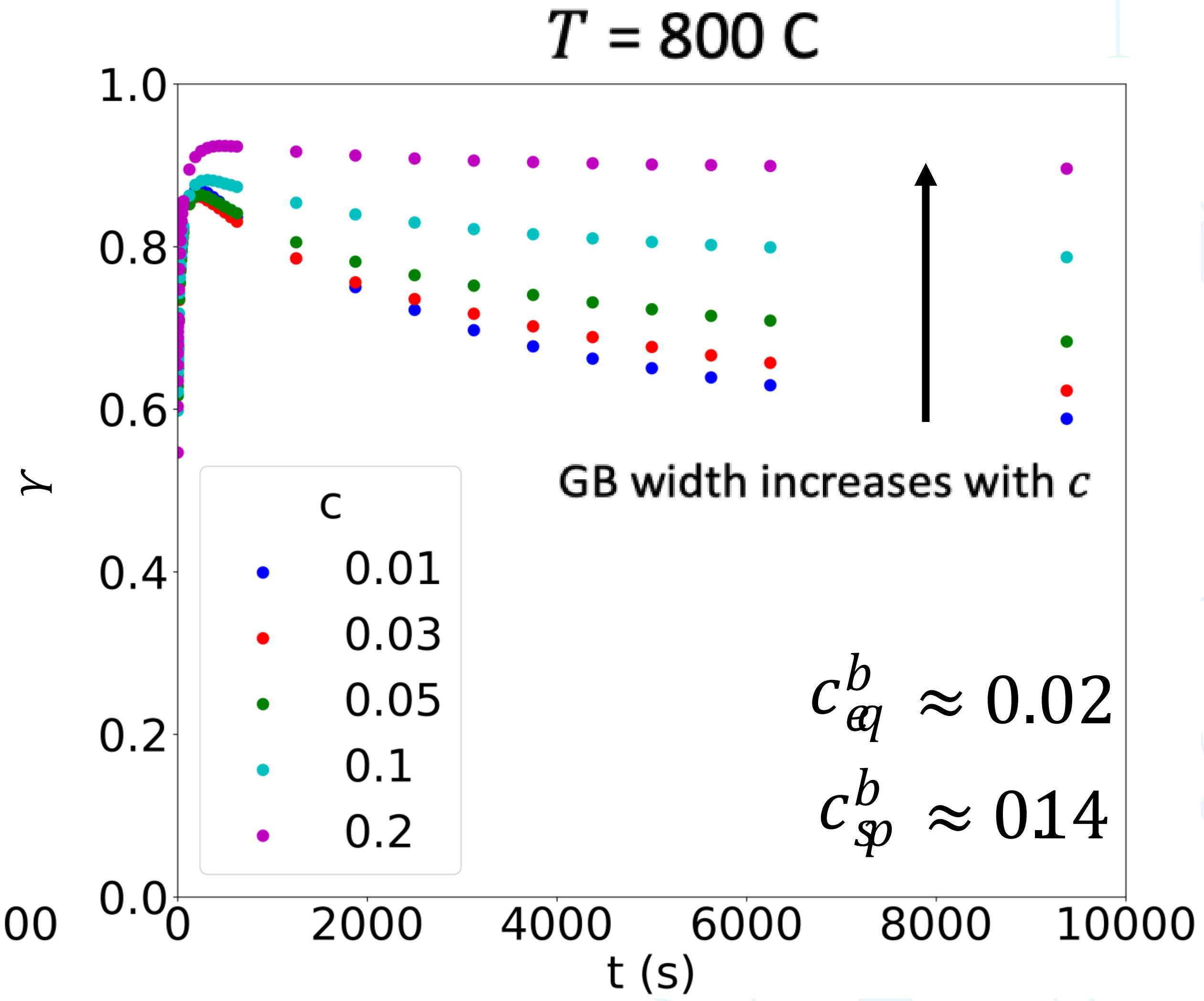
Anti-segregating solute population





GB-segregating solute population





Segregants impede grain growth

$$A_c = \frac{\langle A^2 \rangle}{\langle A \rangle}$$