SAND2022-3864C

Chemical gradients to control stability and mechanical behavior in nanostructured Pt-Au

PRESENTED BY

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Center for Integrated Nanotechnologies

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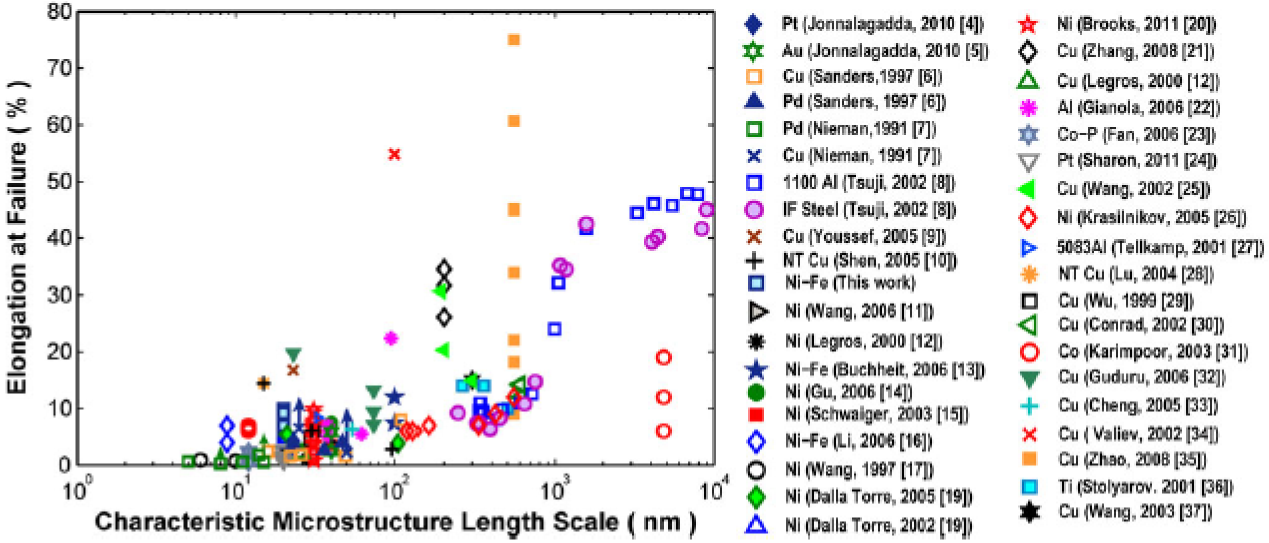
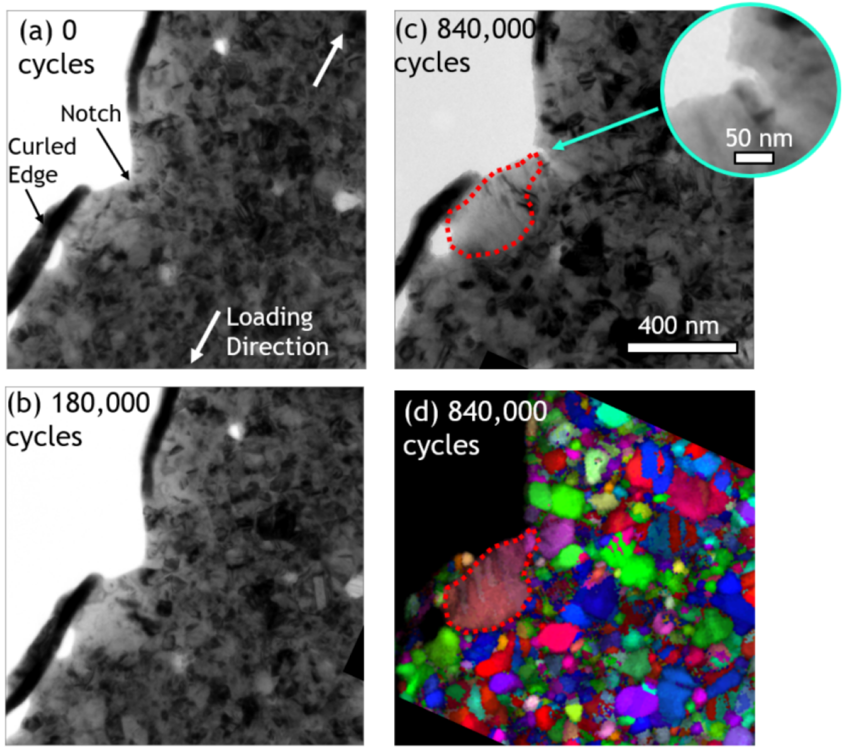
The limitations of pure nanocrystals

Ductility/toughness



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

Stability



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

Competing Priorities

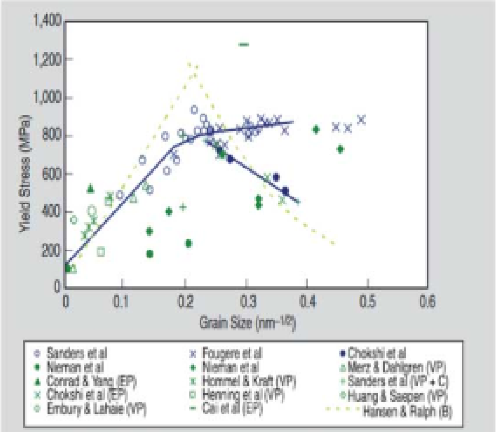
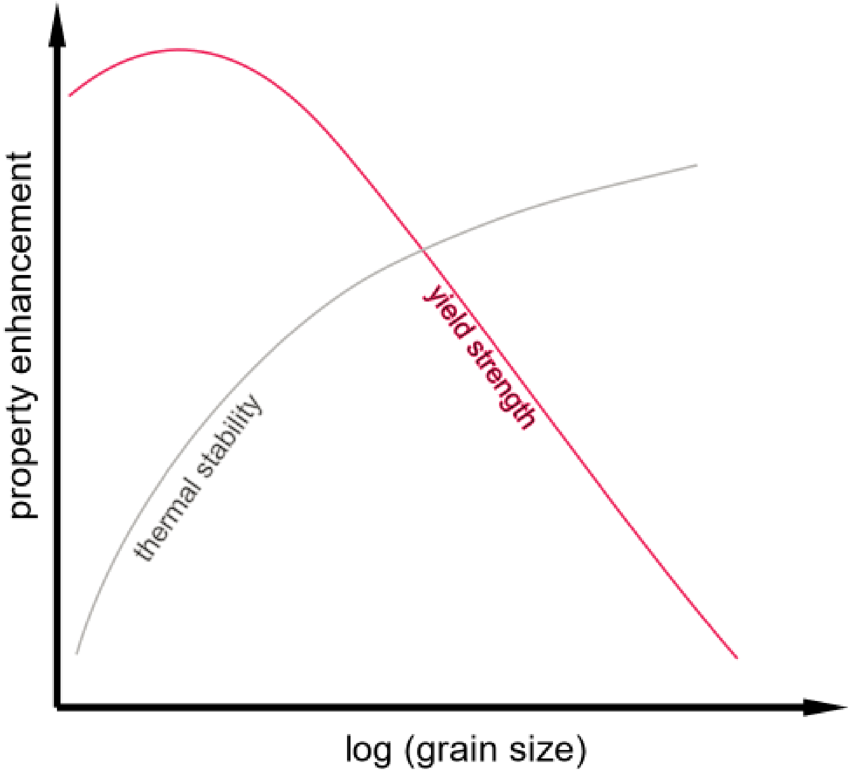


Figure A. The compiled yield stress versus grain size plot for copper from various sources ranging from coarse to nanograin size. The plots show different trend as the grain size falls below a critical size.

Meyers, Mishra, Benson, JOM, 2006



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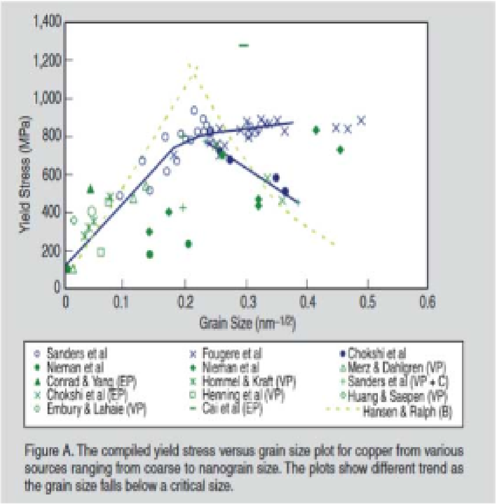
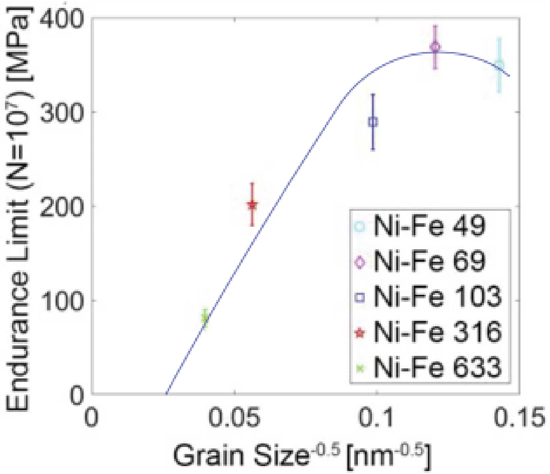
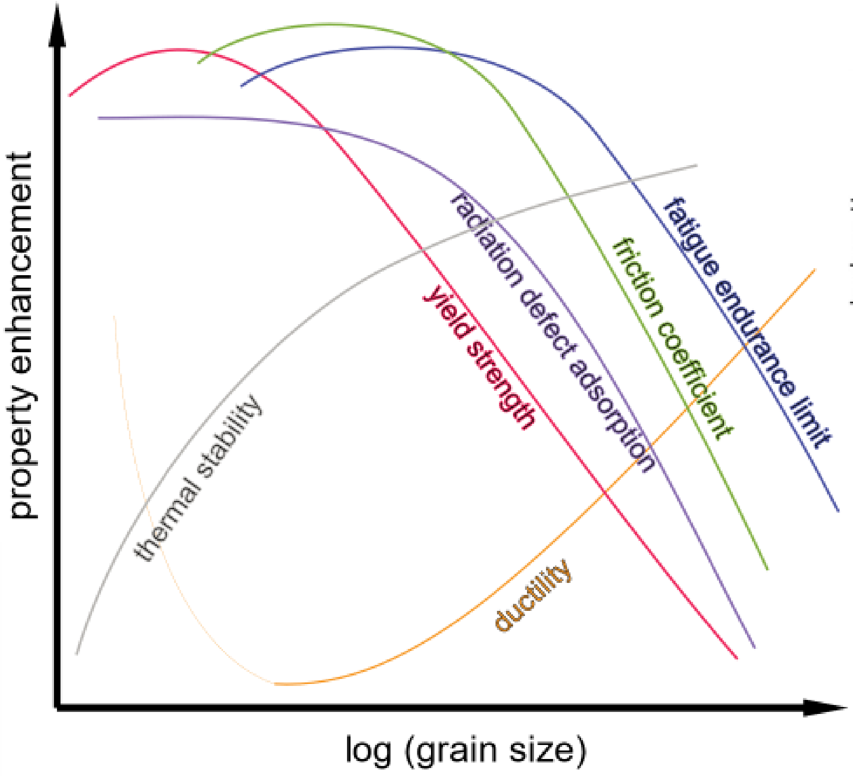
Competing Priorities

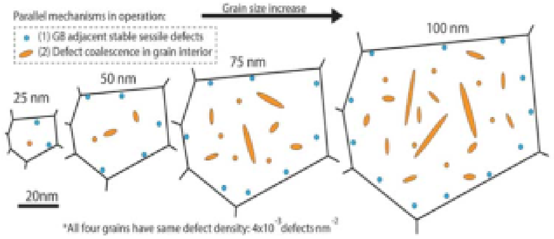


Meyers, Mishra, Benson, JOM, 2006

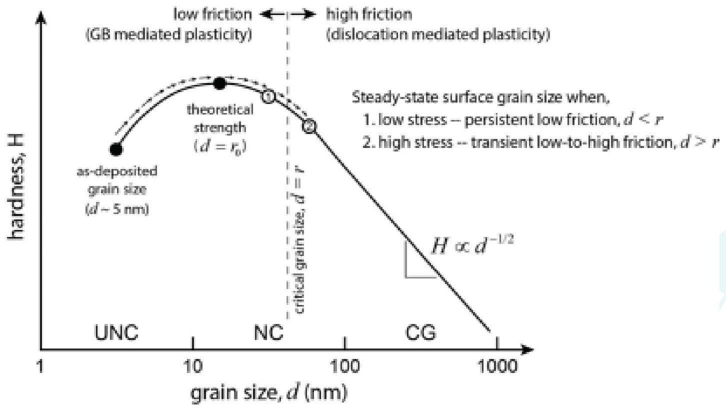


Heckman...Boyce, submittted, 2019

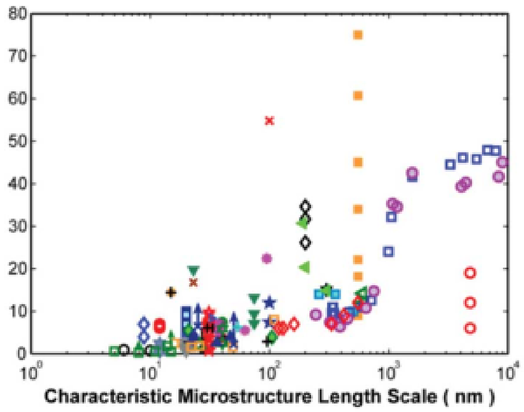




Barr, Li, Boyce, Hattar, Appl. Phys. Lett., 2018

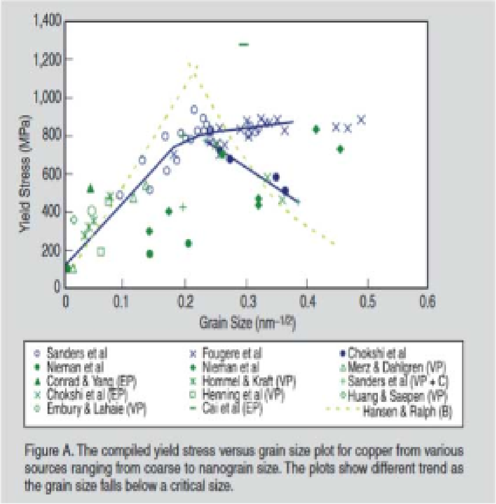


Argibay, Furnish, Clark, Boyce, Chandross, Scripta Mater, 2016

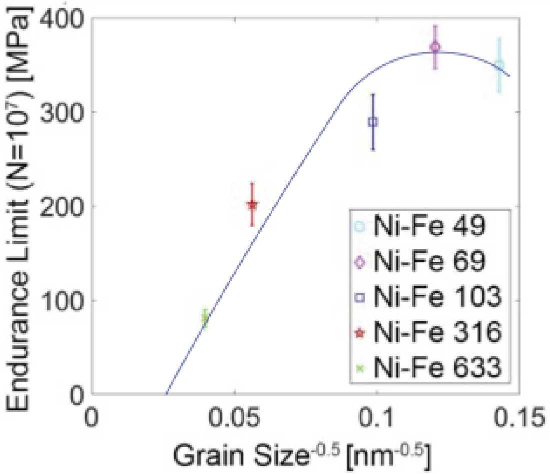


Sharon, Padilla, Boyce, J. Mater. Res., 2013

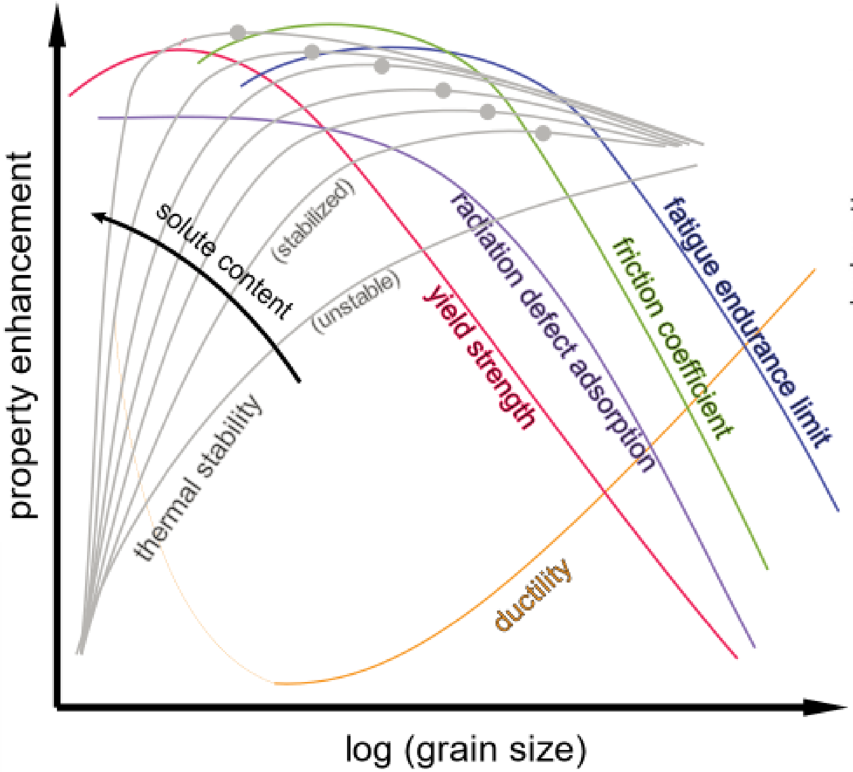
A gradient solute strategy…

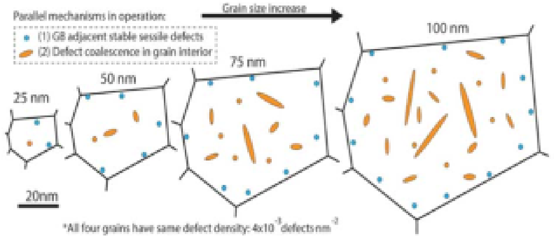


Meyers, Mishra, Benson, JOM, 2006

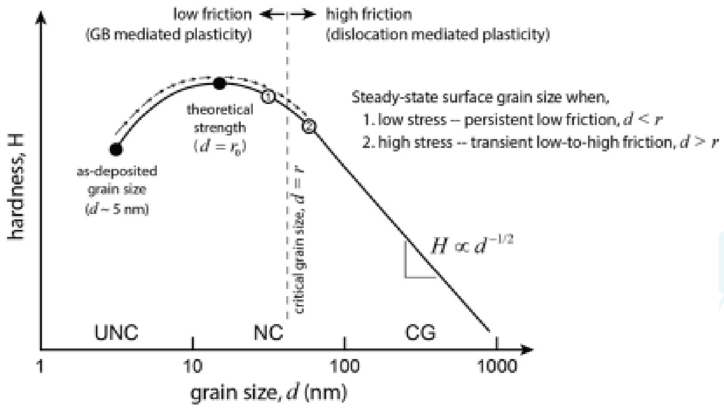


Heckman...Boyce, submittted, 2019

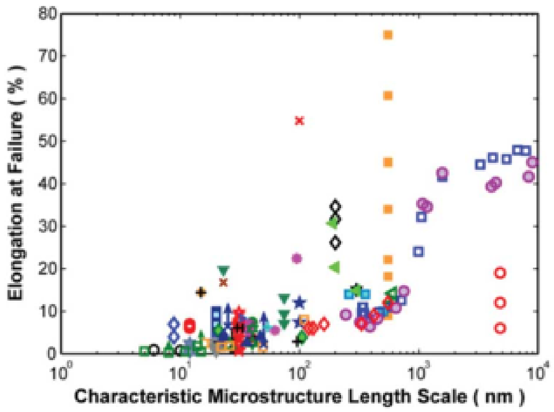




Barr, Li, Boyce, Hattar, Appl. Phys. Lett., 2018

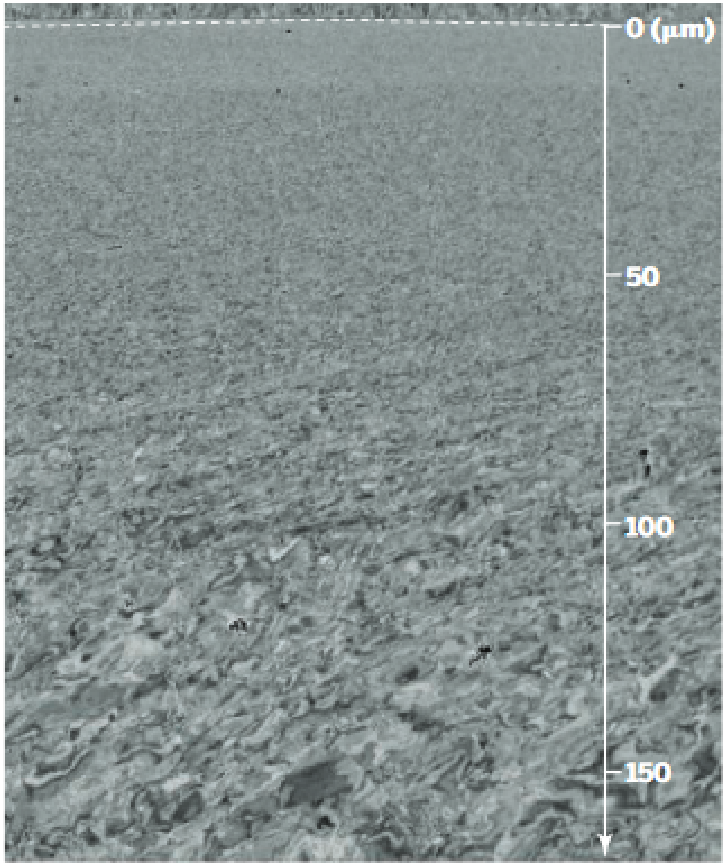


Argibay, Furnish, Clark, Boyce, Chandross, Scripta Mater, 2016

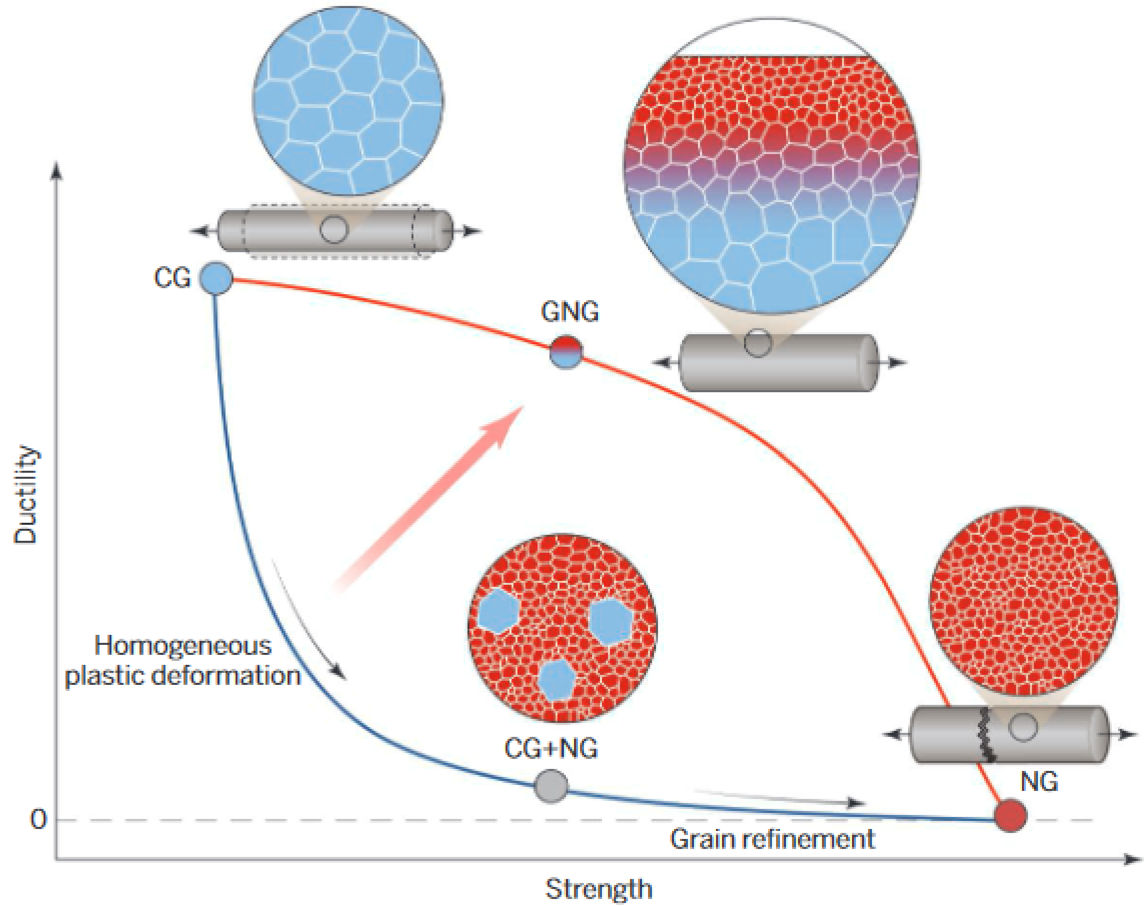


Sharon, Padilla, Boyce, J. Mater. Res., 2013

Gradients offer strength/ductility payoff

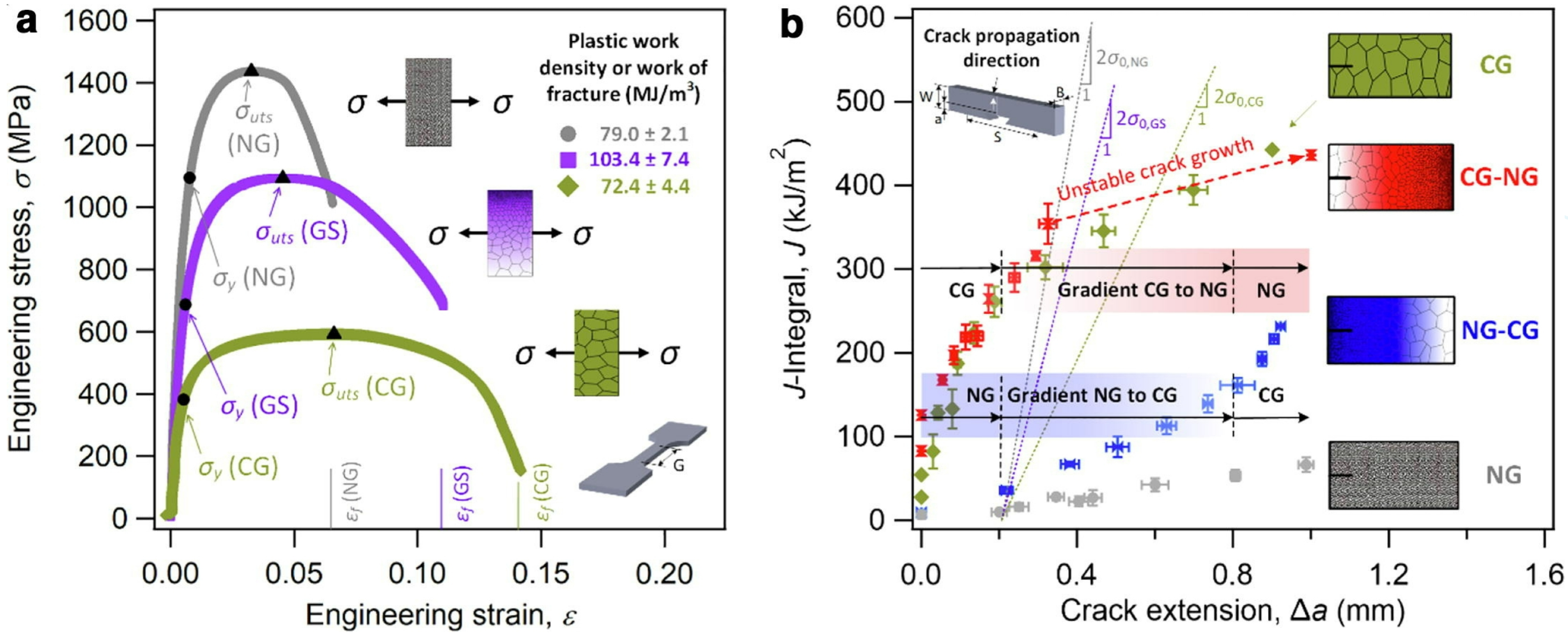


Gradient nanograined structure. After a surface mechanical grinding treatment to copper, grain sizes are about 20 nm in the topmost treated surface (outlined by dashed line) and increase gradually to the microscale with depth.



K Lu, *Science*, 2014

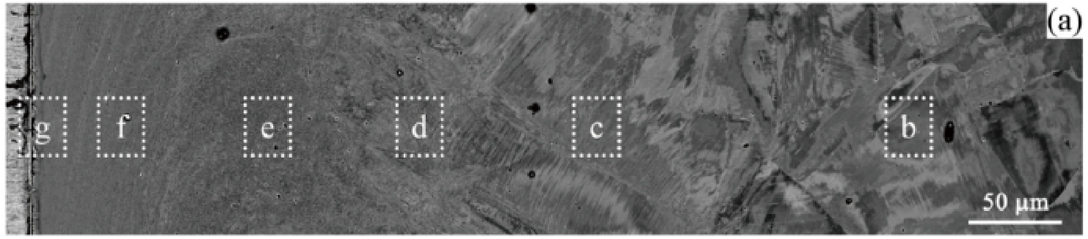
Gradients offer toughening

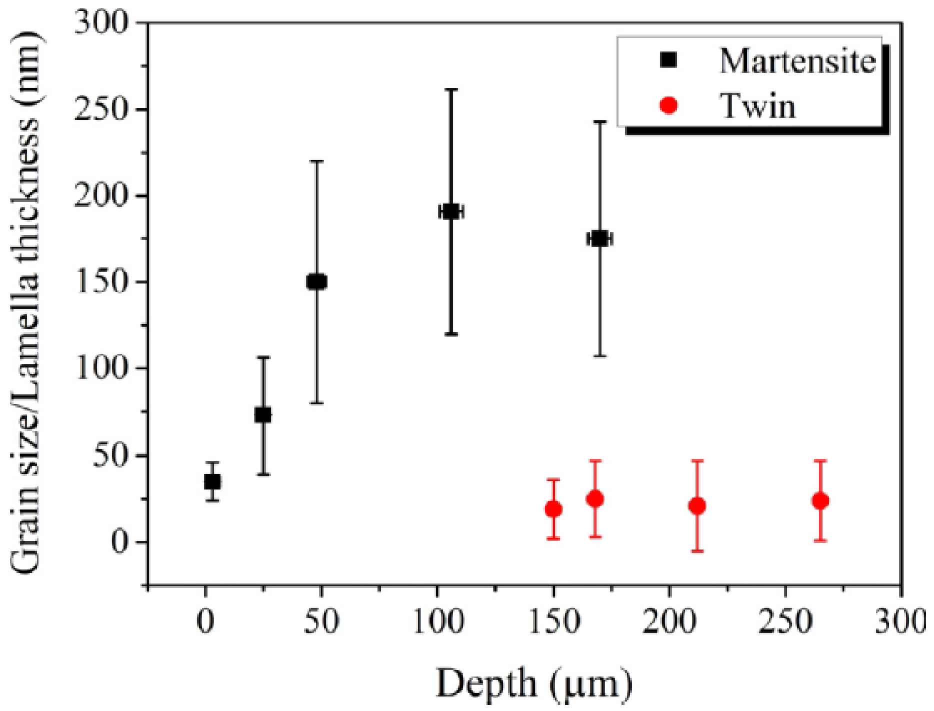


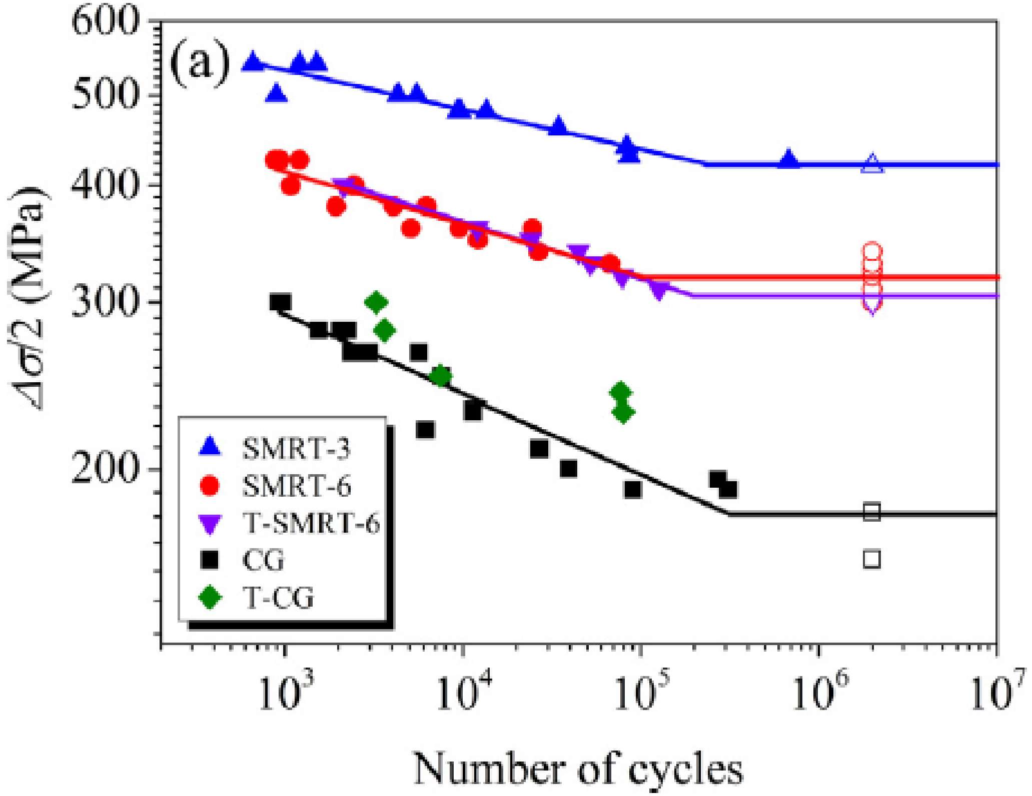
Cao…Ritchie, *Materials Today*, 2020

Gradients offer fatigue resistance

Gradient 316L by SMRT





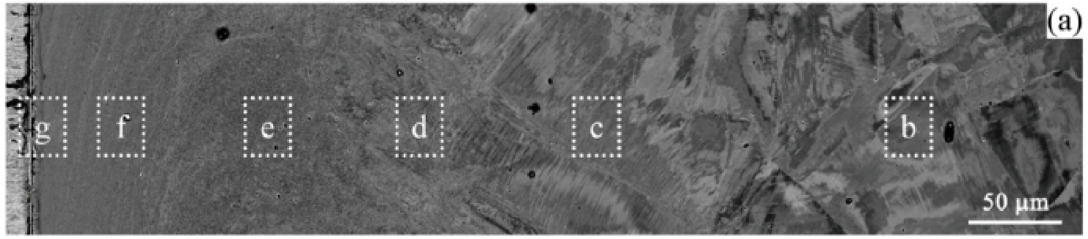


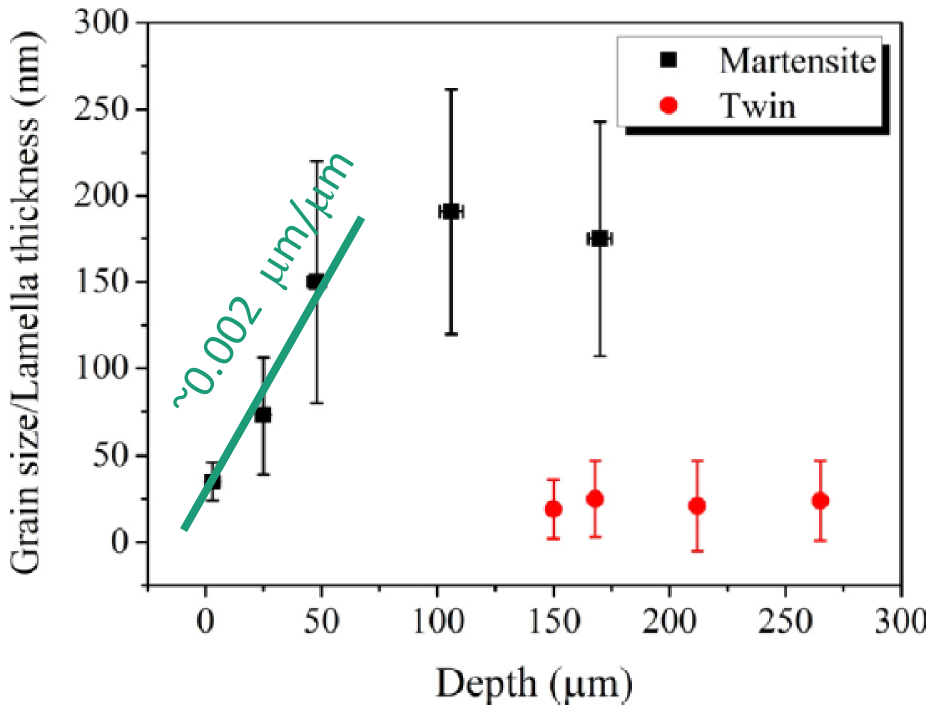
- Strain-induced martensite
- Compressive residual stresses of -1200 to -1500 MPa

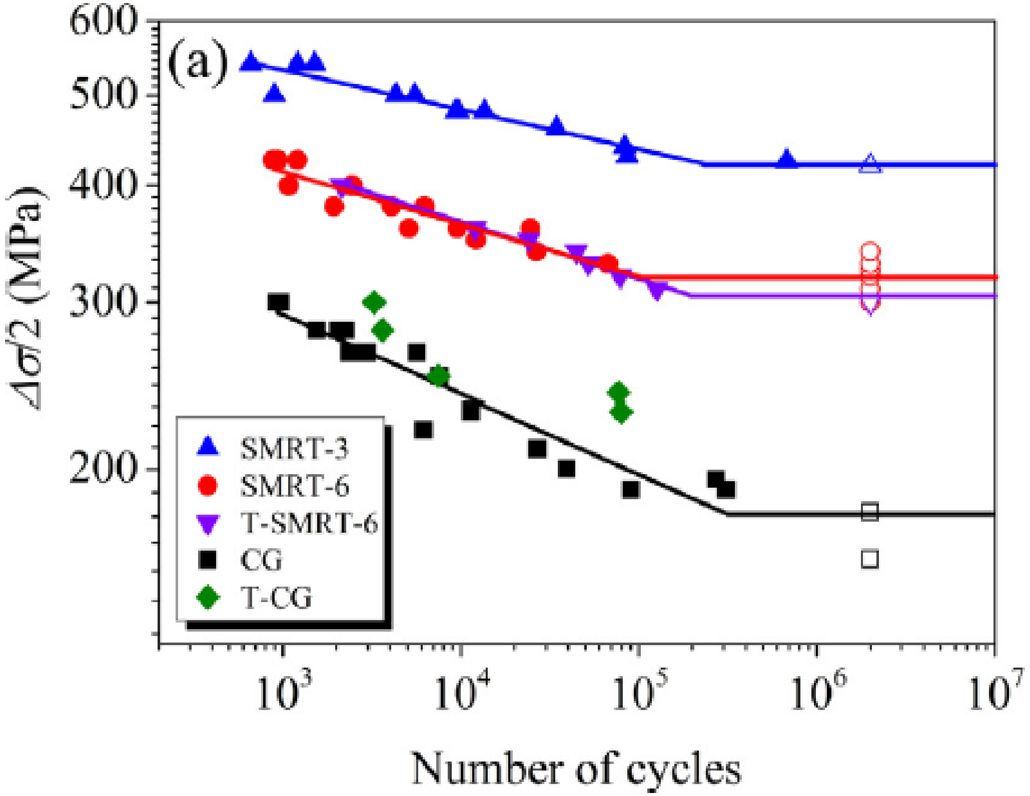
HW Huang, ZB Wang, J Lu, K Lu, *Acta Mater*, 2015

Gradients offer fatigue resistance

Gradient 316L by SMRT



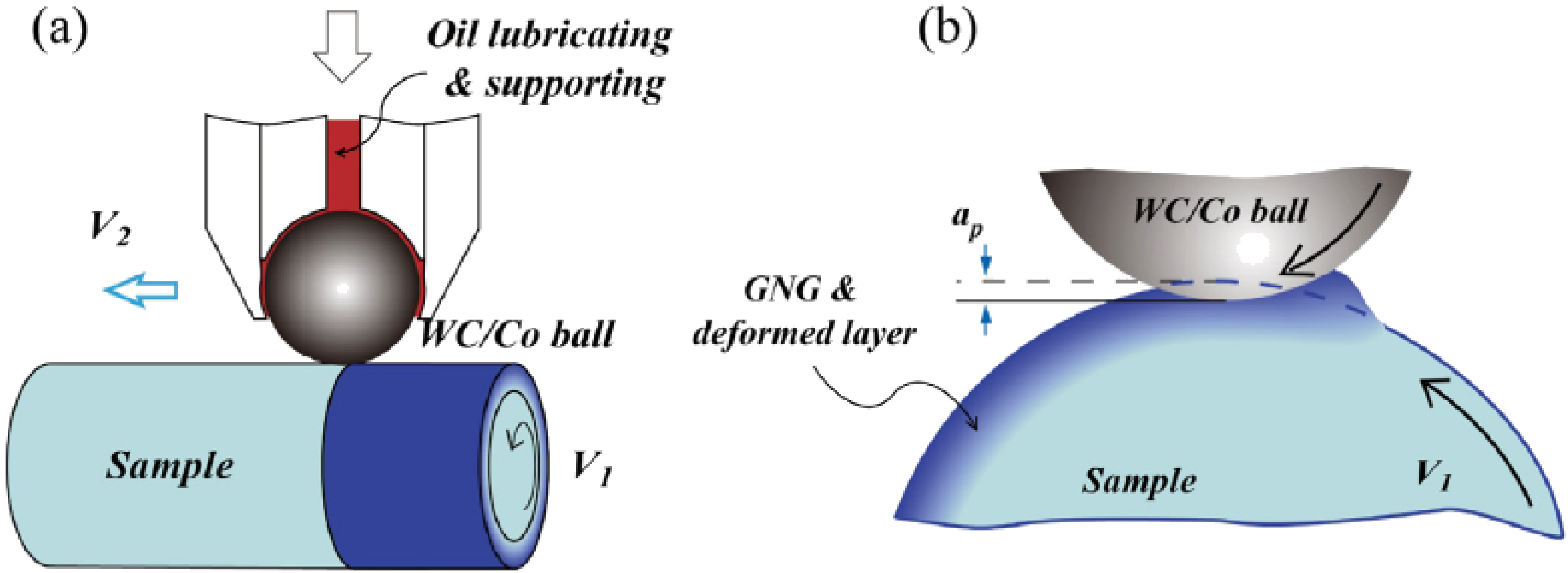




- Strain-induced martensite
- Compressive residual stresses of -1200 to -1500 MPa

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

SMRT, SMGT, SMAT

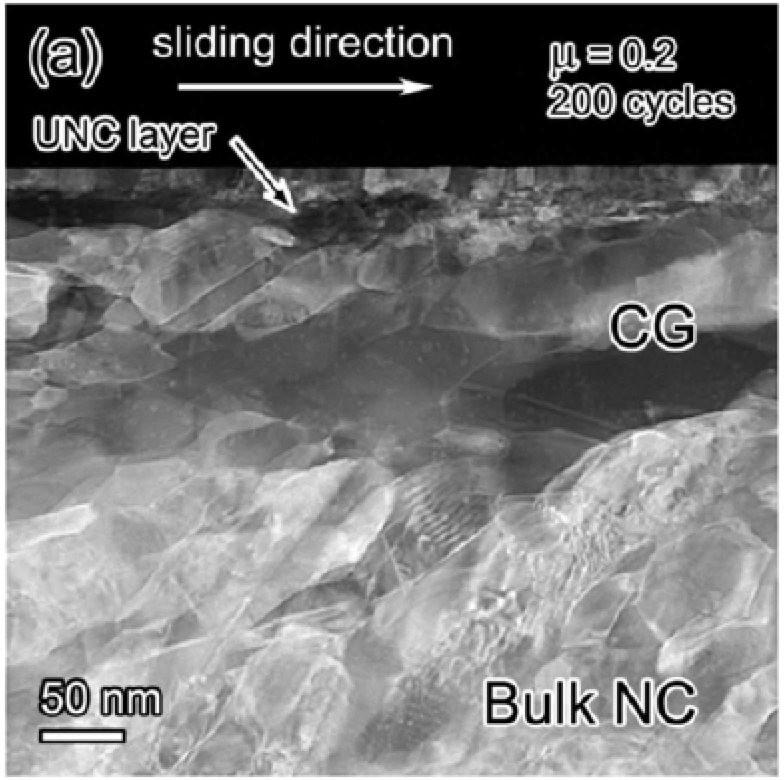


HW Huang, ZB Wang, J Lu, K Lu, *Acta Mater*, 2015

Gradient refinement vs coarsening

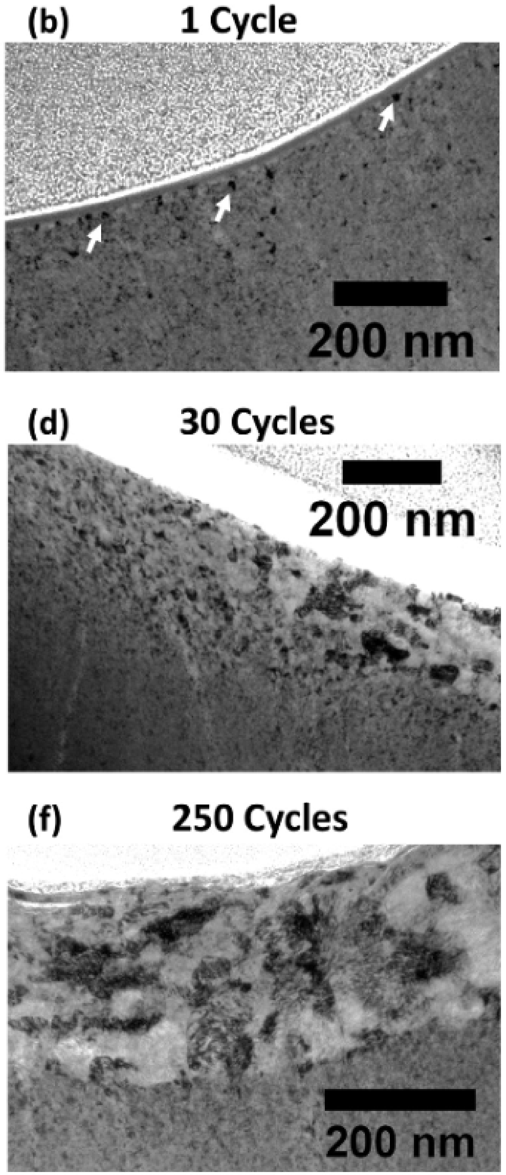
Cyclic sliding contact can surface grain refinement…

Ni



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

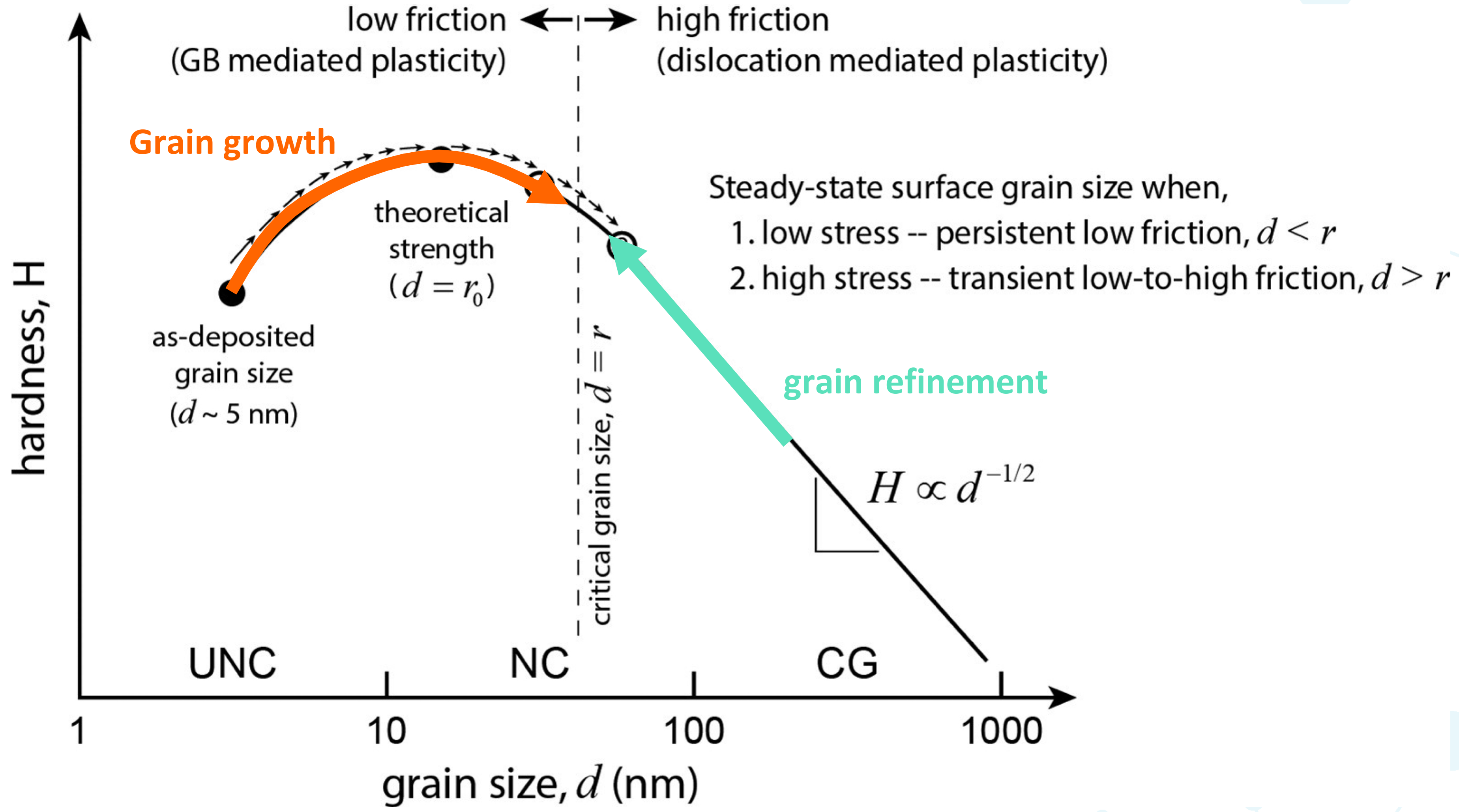
Ni-W



…or grain coarsening

Panzarino & Rupert, *Materialia*, 2018

The goldilocks zone for stability?



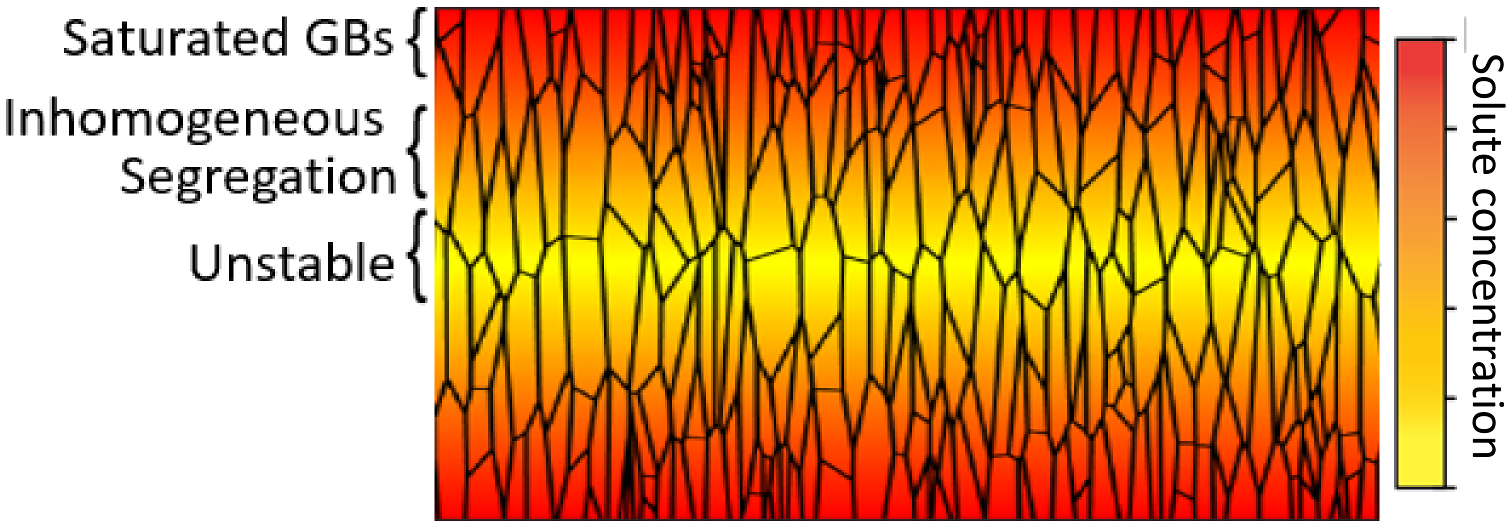
Argibay, Furnish, Boyce, Clark, Chandross, *Scripta Mater*, 2016

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

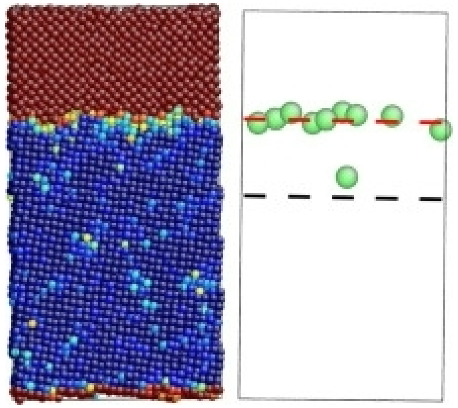


What is the role of solute in creating the microstructural gradient?

Solute effects on grain size stability

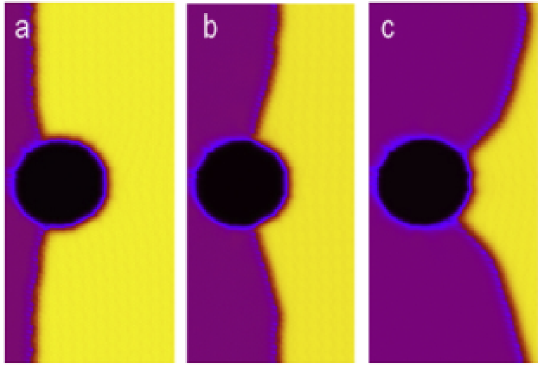
Kinetic

Solute drag



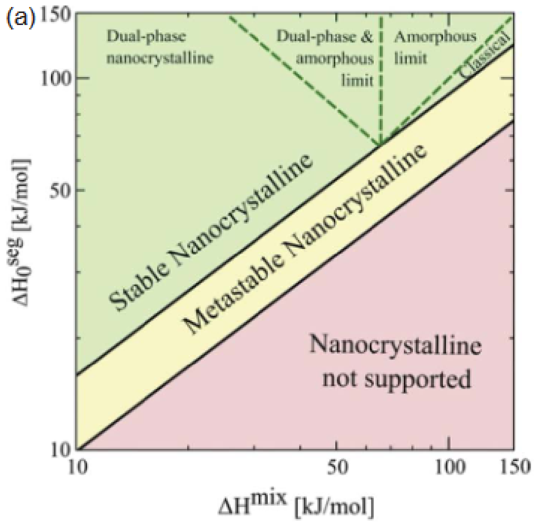
H Sun & C Deng, *Comp. Mater. Sci.*, 2014

Zener pinning



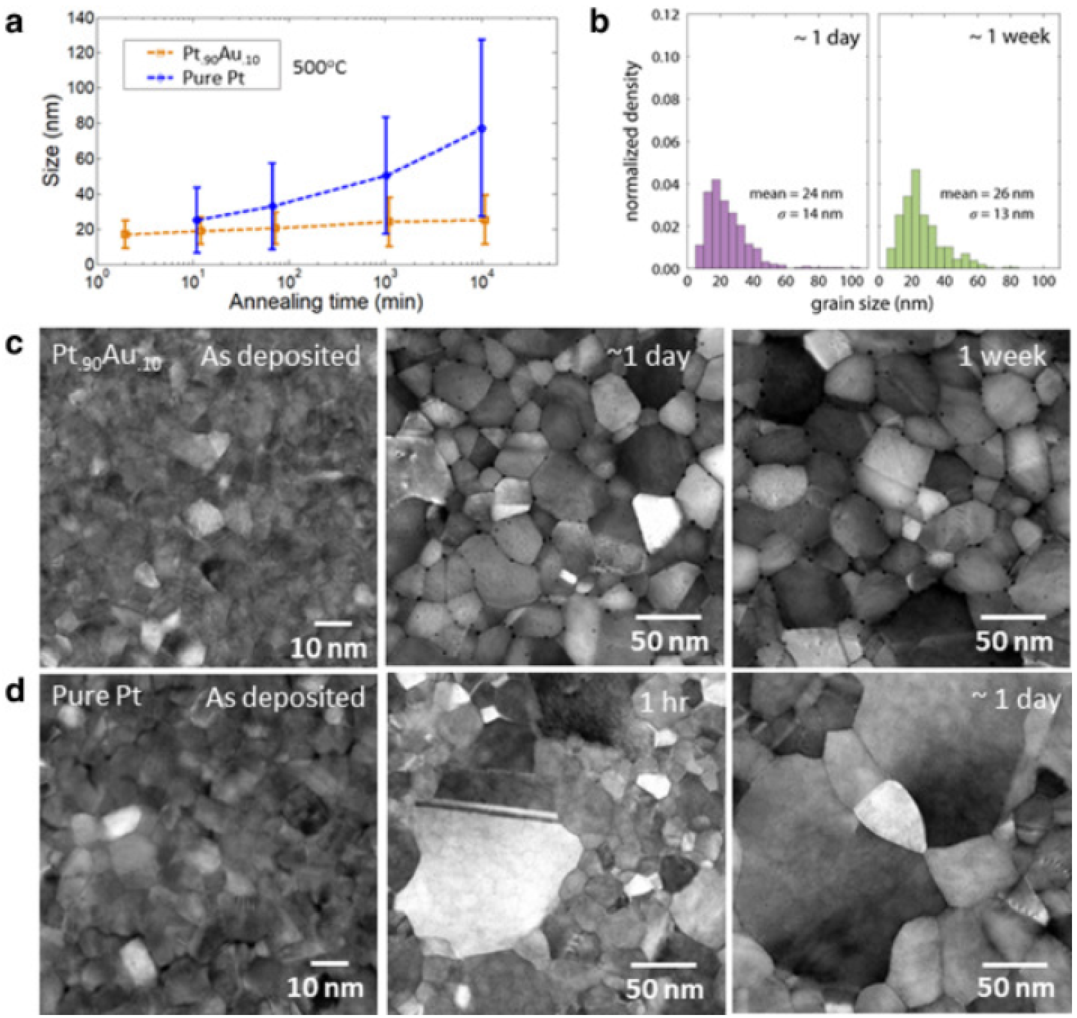
Wang, Ji, Wang, Wen, Chen, *Acta Mater*, 2017

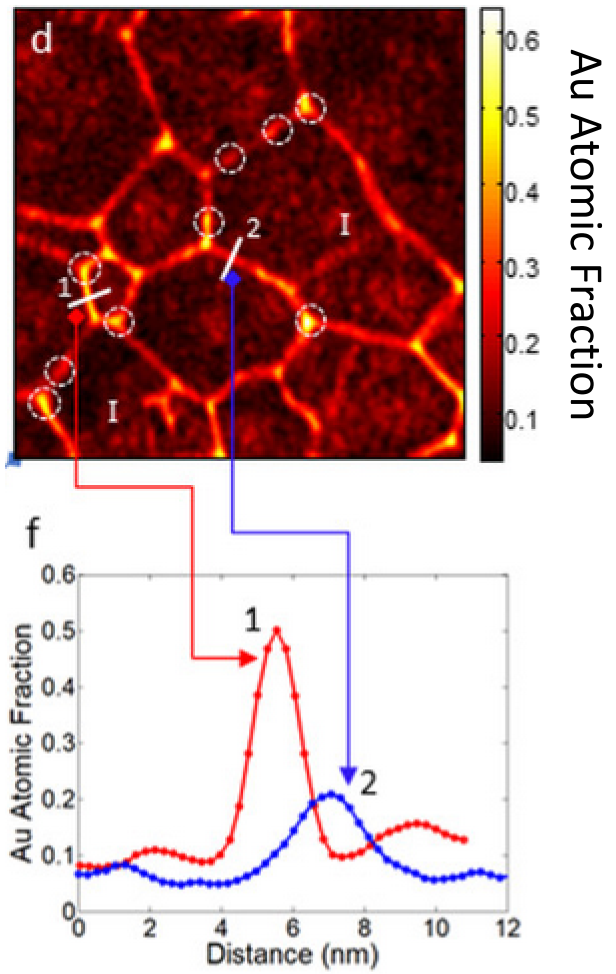
Thermodynamic



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

The Pt-Au nc system

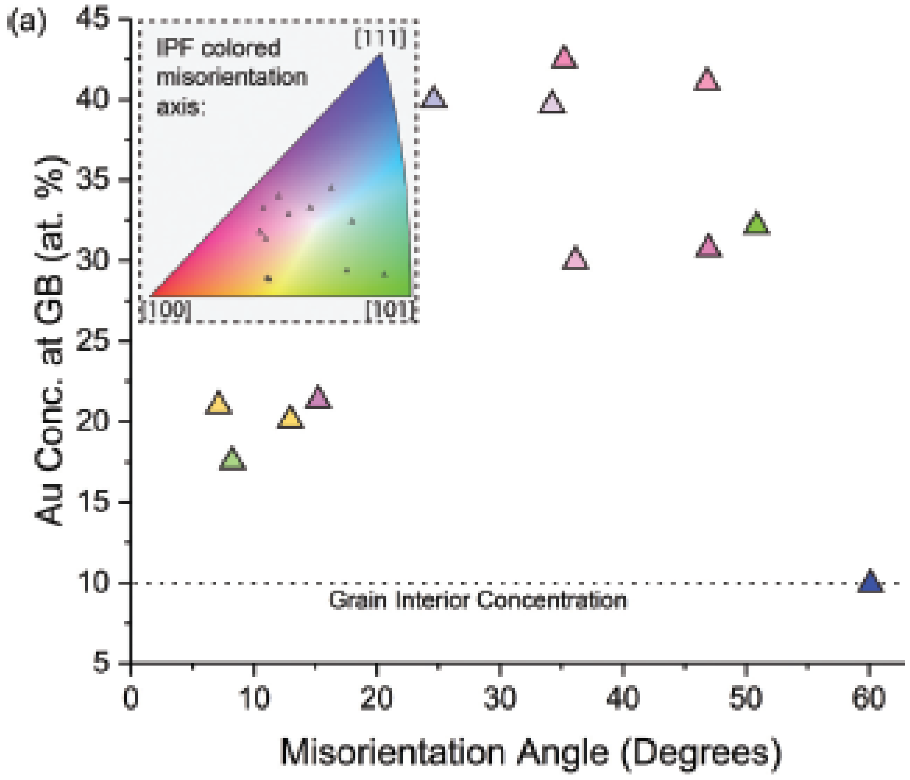




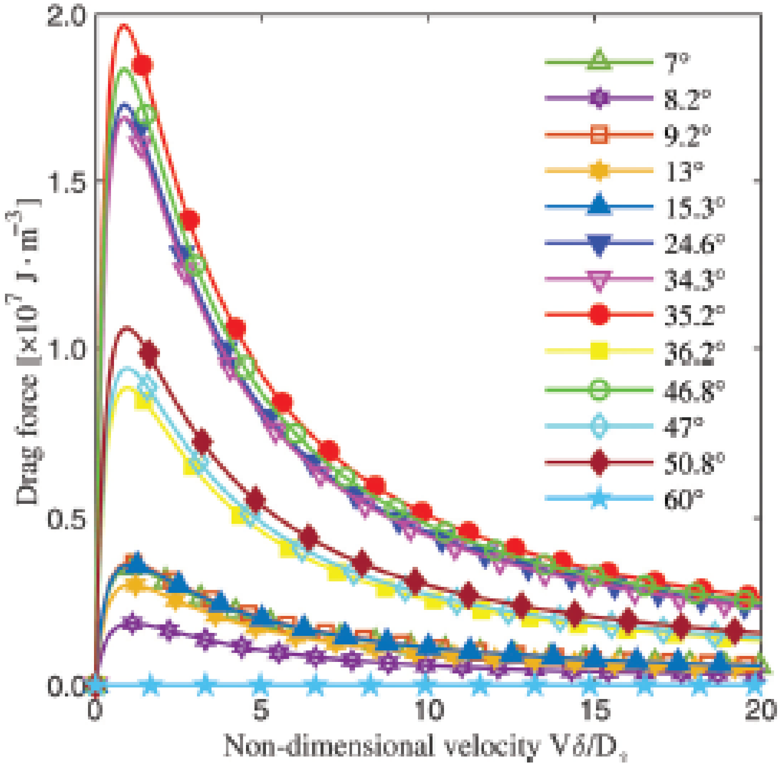
P. Lu, et al., *Materialia*, 2019

More details on Pt-Au

Au does not segregate uniformly…



Au plays both a thermodynamic & kinetic role



Another TMS presentation

Defect and Phase Transformation Pathway Engineering for Desired Microstructures — Invited Presentations

Sponsored by: TMS Materials Processing and Manufacturing Division, TMS: Phase Transformations Committee
Program Organizers: Yufeng Zheng, University of Nevada-Reno ; Rongpei Shi, Lawrence Livermore National Laboratory; Yipeng Gao, Idaho National Laboratory; Timofey Frolov, Lawrence Livermore National Laboratory; Stoichko Antonov, Max-Planck-Institut für Eisenforschung GmbH; Jessica Krogstad, University of Illinois at Urbana-Champaign; Bin Li, University of Nevada, Reno

Tuesday AM **March 16, 2021**

9:50 AM Invited
Grain Boundary Segregation in Immiscible Alloys: Anisotropy and Trijunction Effects: A. Barnett[1]; M. Cox[1]; D. Moore[1]; M. Alghalayini[1]; C. Barr[2]; K. Hattar[2]; B. Boyce[2]; *F. Abdeljawad*[1]; [1]Clemson University; [2]Sandia National Laboratories

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

Phase field model development…

Segregation-enhanced thermal stability via a phase-field model

Free energy functional

- $c(\mathbf{r},t)$: alloy concentration
- $\boldsymbol{\phi}_i(\mathbf{r},t)$, $\{i = 1, \ldots, n_{\boldsymbol{\phi}}\}$: 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.

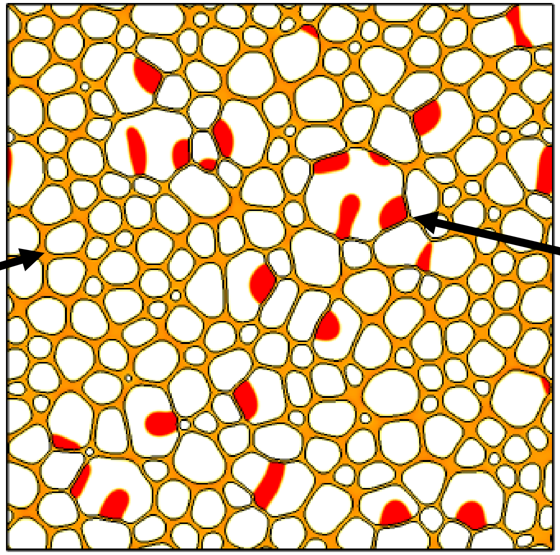
GB energy vs. concentration

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

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)



Solute drag

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

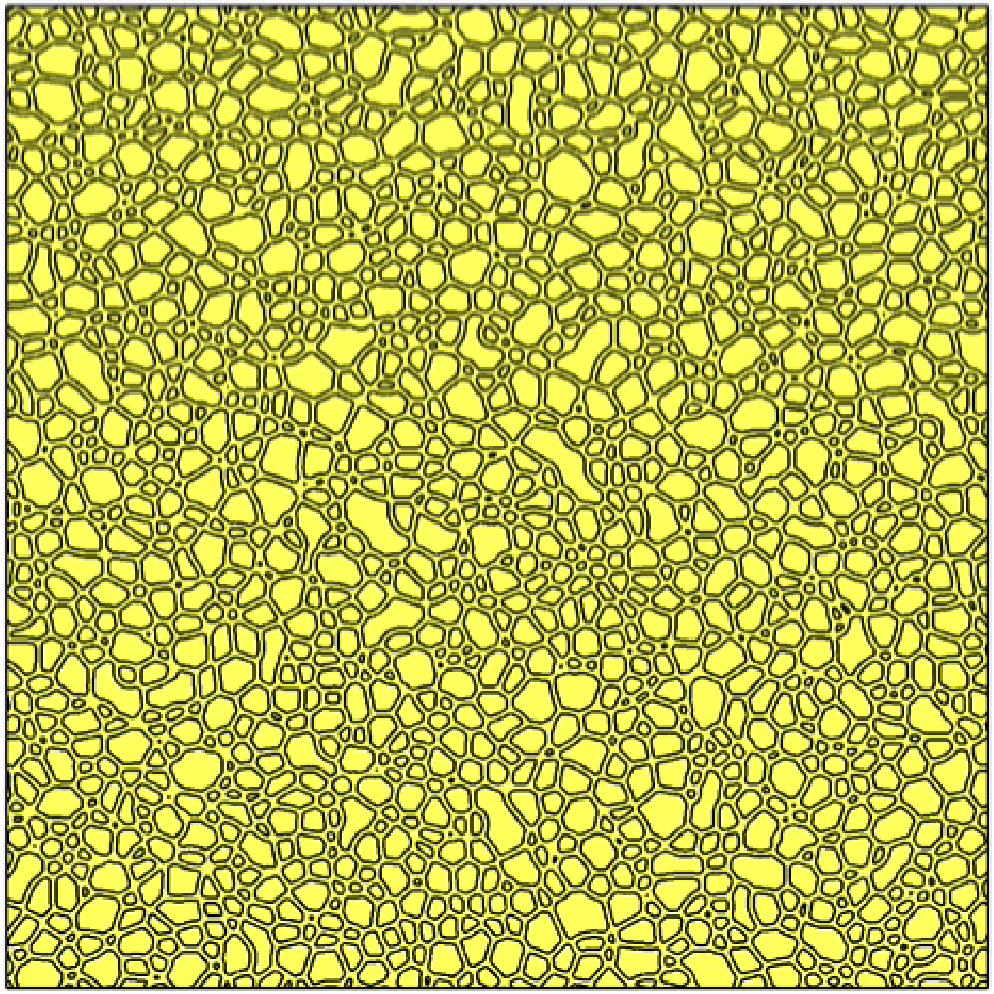
Zener pinning

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



Improvements:
Anisotropic Mobility
Anisotropic Energy
Heterogeneous solute segregating behavior
Adaptive grain tracking algorithm

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 — $f_b(c, T)$

grain boundary — $[W - \xi_1 c - \xi_2 c^2] g(\vec{\phi})$

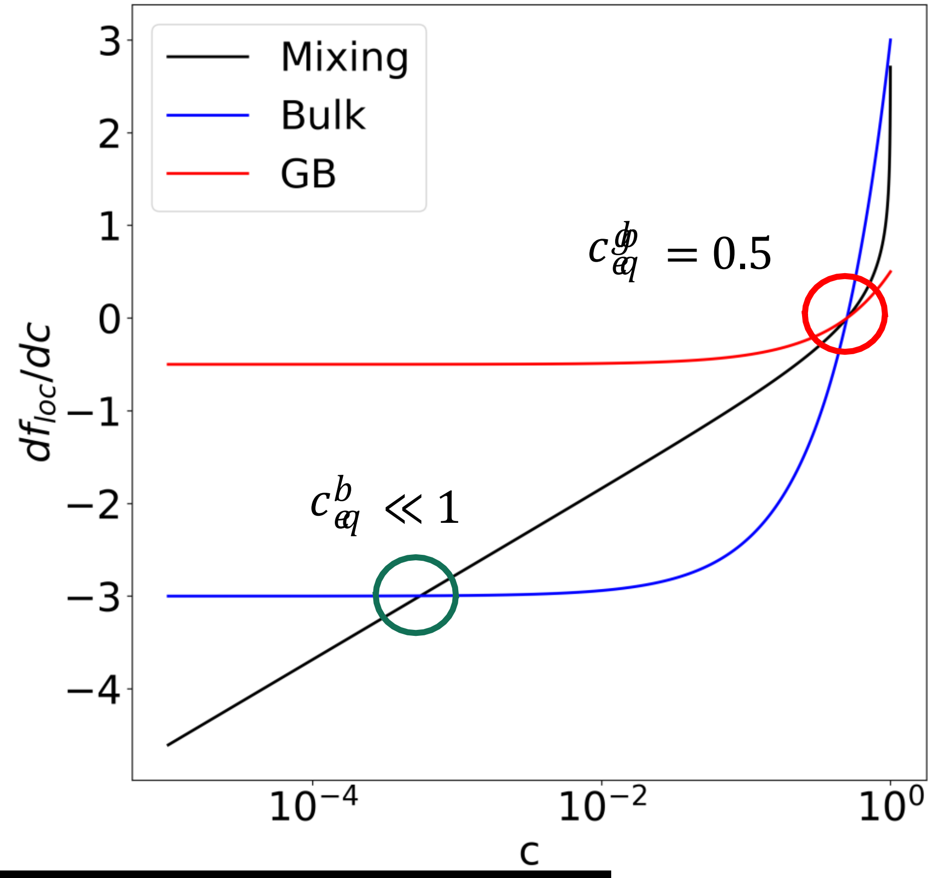
$$f_b = G_b^B c + (1-c) G_b^A + \Omega_b c(1-c) + \frac{RT}{V_m}[c \ln c + (1-c)\ln(1-c)]$$

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

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

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

Anti-segregating parameters



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

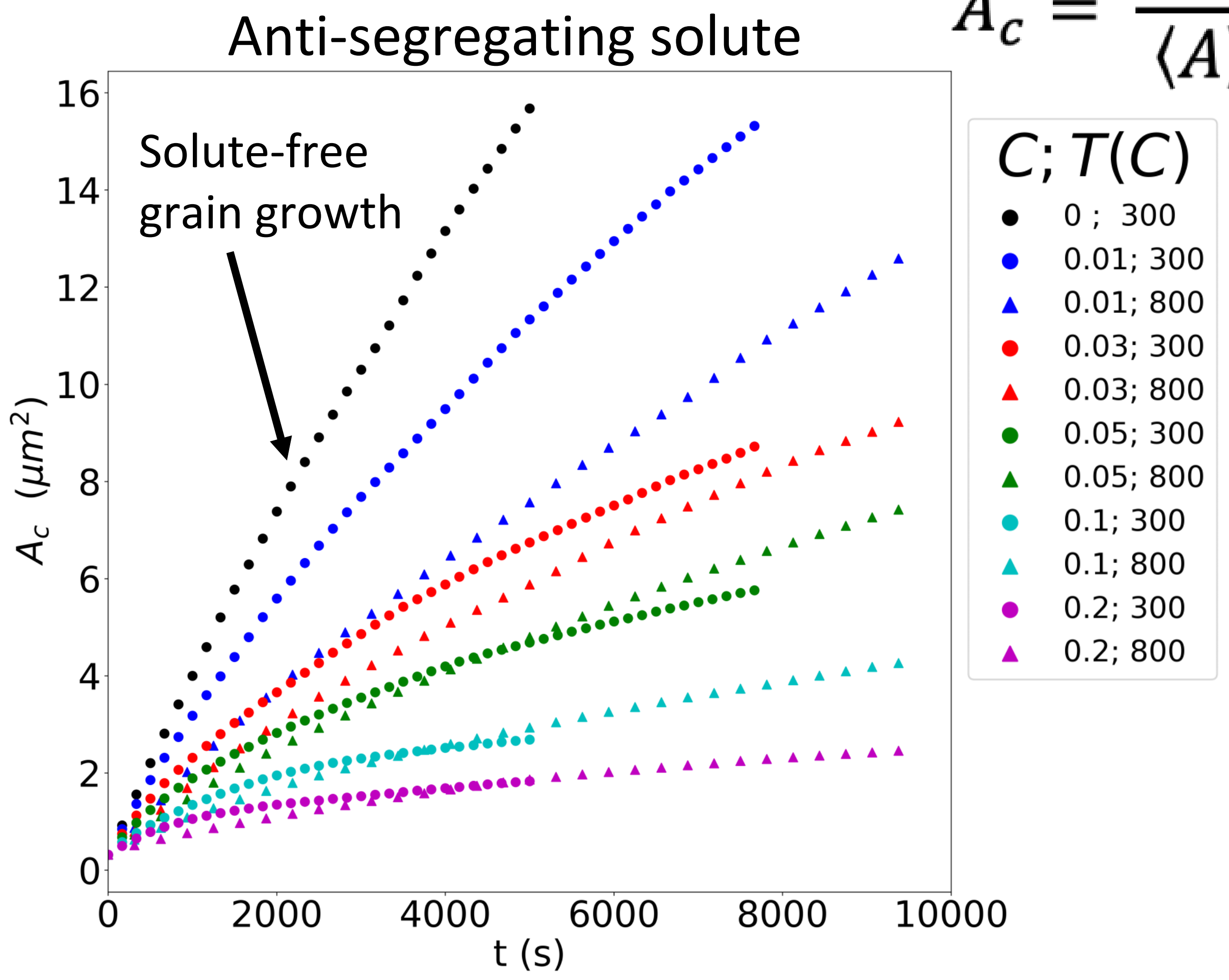
GB segregation: $\Omega_{gb} - \Omega_b < 0$

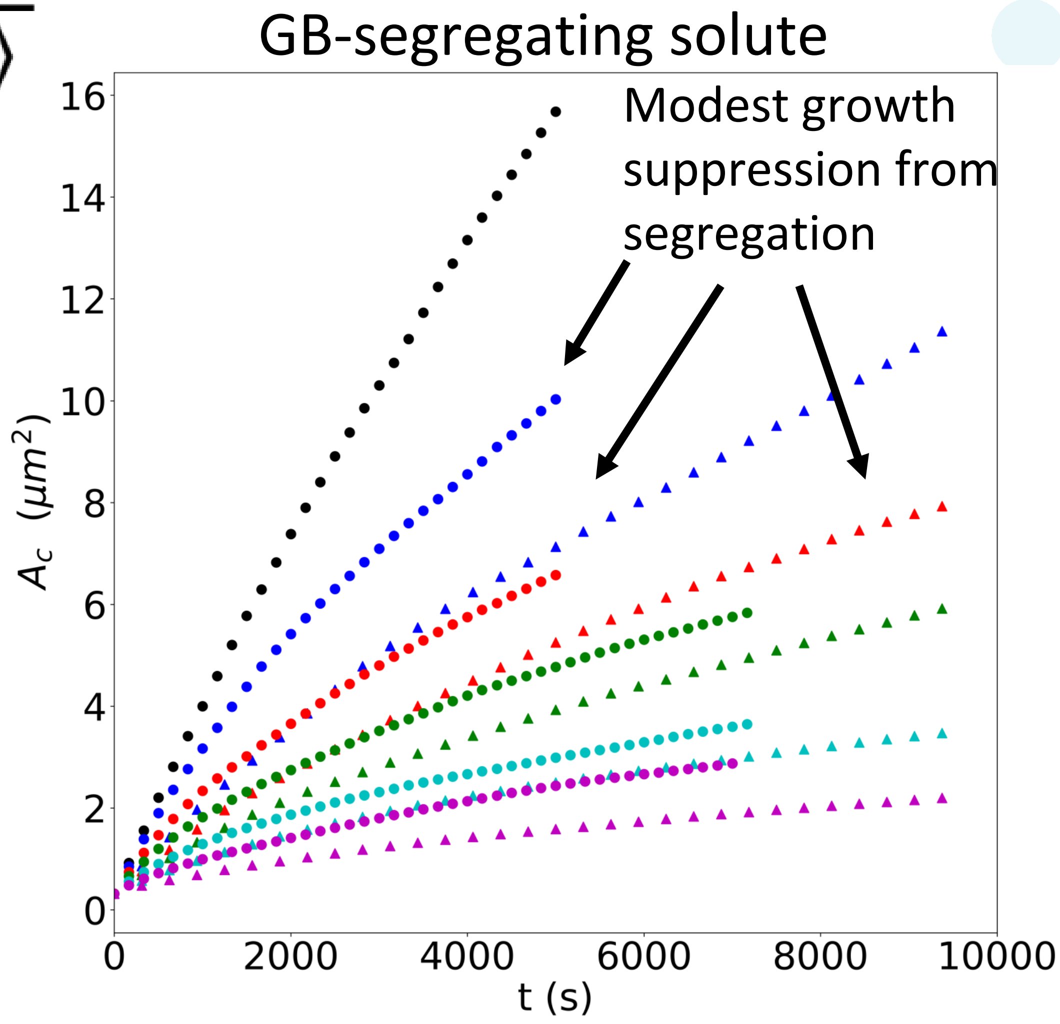
Abdeljawad and Foiles, *Acta Mat.* 101, 2015

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

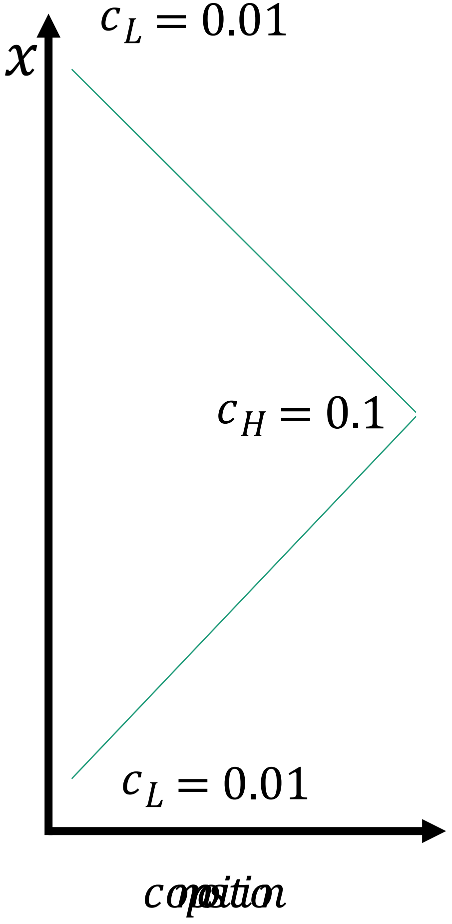
Solute impedes grain growth even without segregation

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



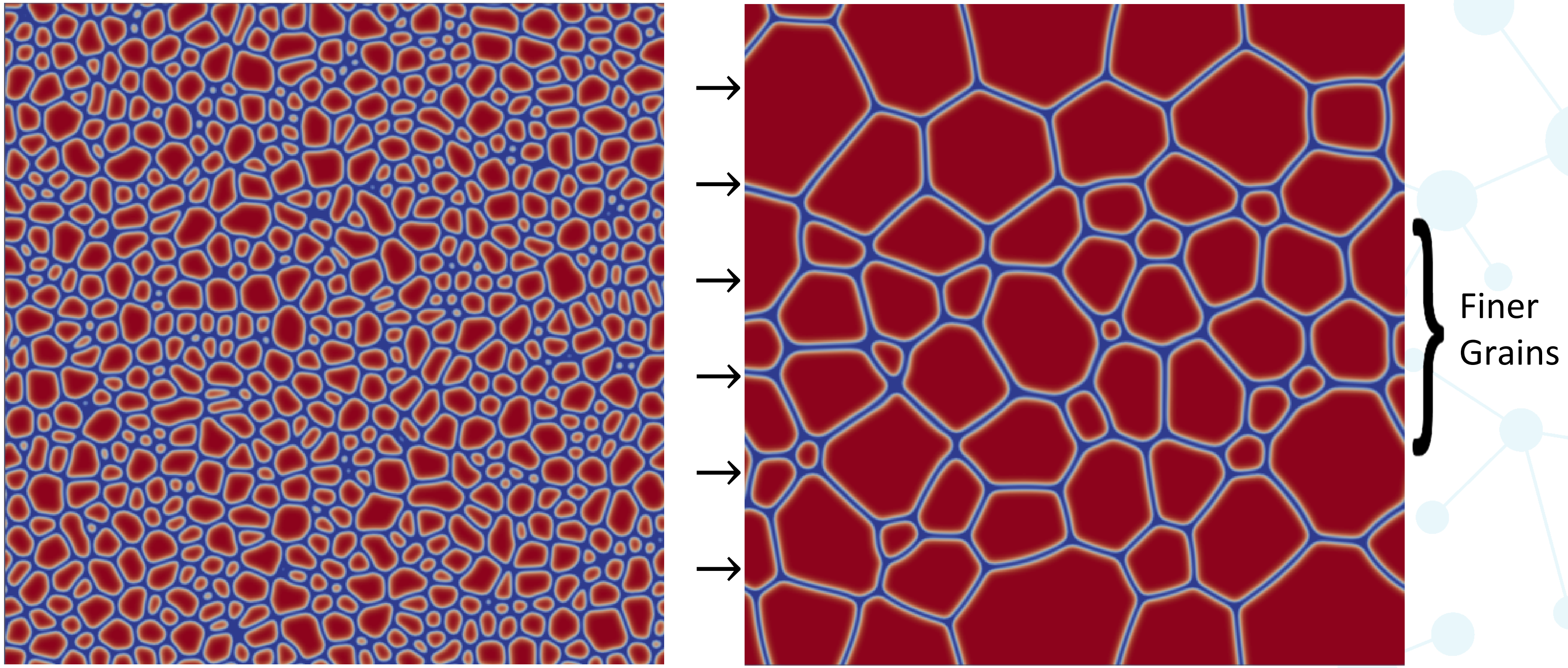


Using concentration gradient to trigger grain size gradient



Initial microstructure

After annealing



Annealing experiments

800˚C Anneal

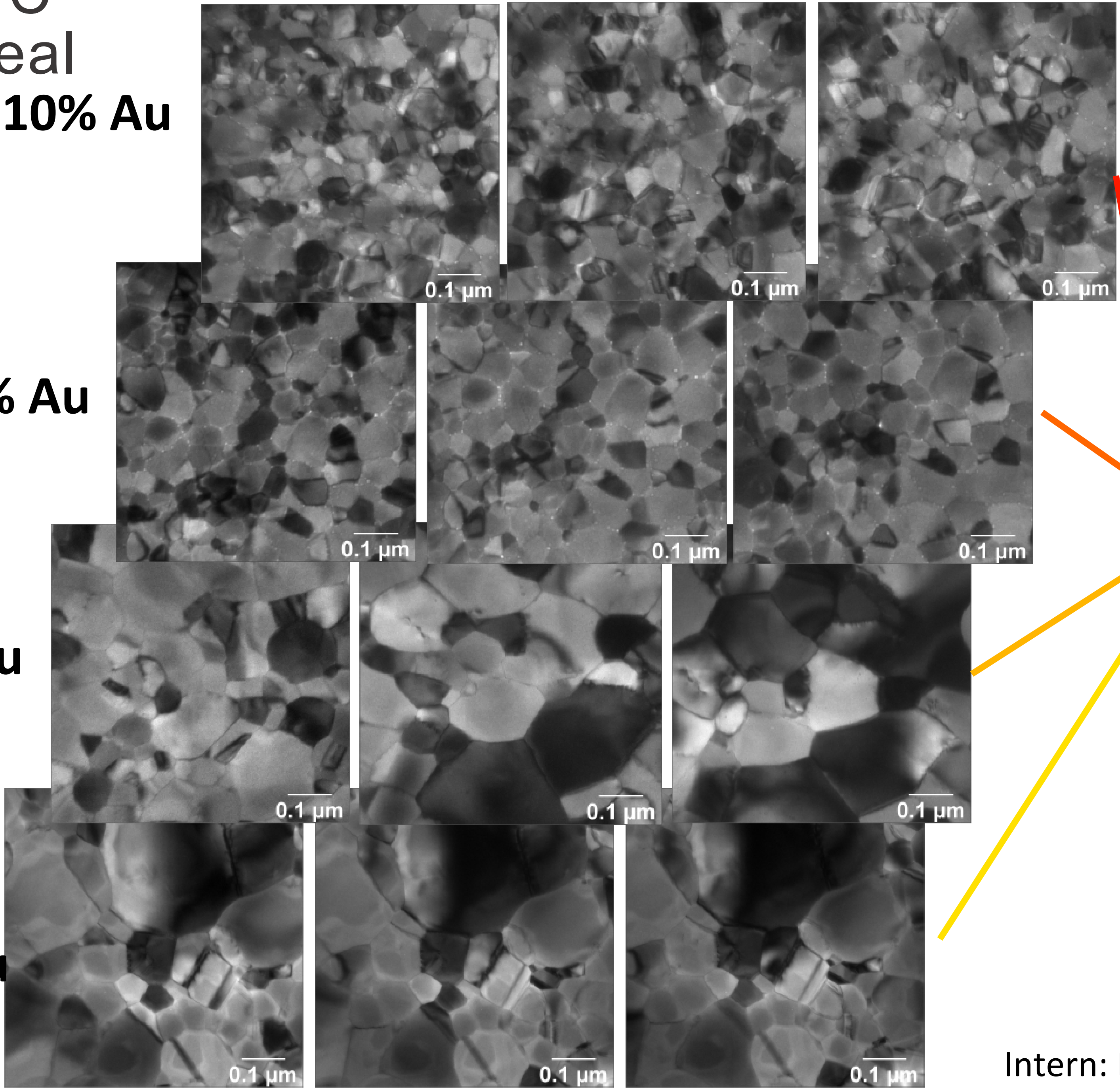
0 min | 5 min | 10 min

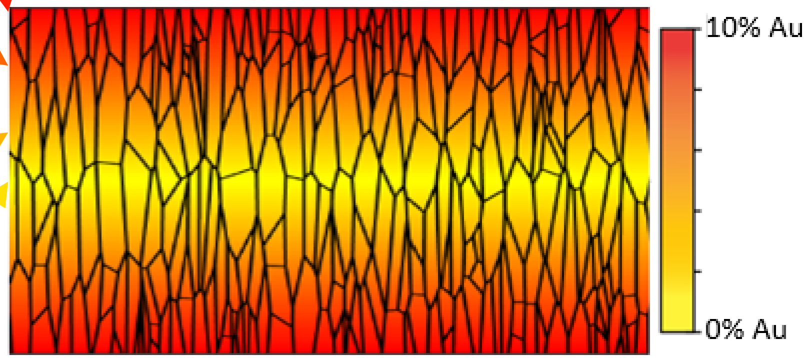
10% Au

3% Au

1% Au

0% Au

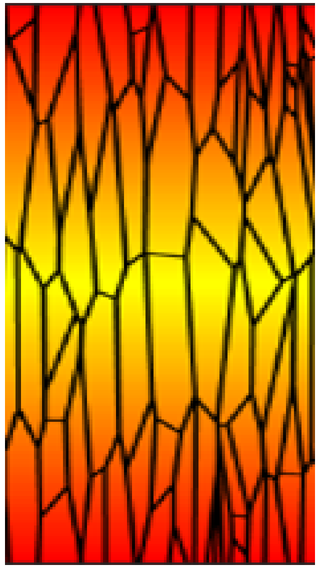




Intern: Emily Hopkins, JHU

Step-wise compositional gradient

PVD deposition



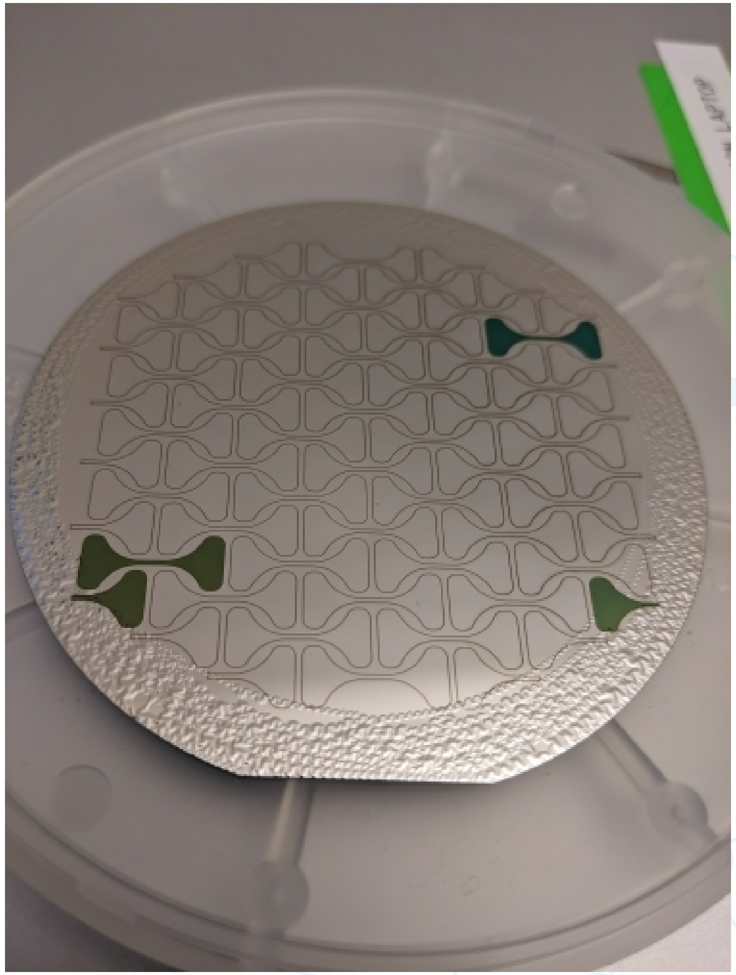
Pt-10Au	0.2 um
Pt-3Au	0.2 um
Pt-1Au	0.2 um
Pt	0.8 um
Pt-1Au	0.2 um
Pt-3Au	0.2 um
Pt-10Au	0.2 um

Across Thickness (2 um)

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

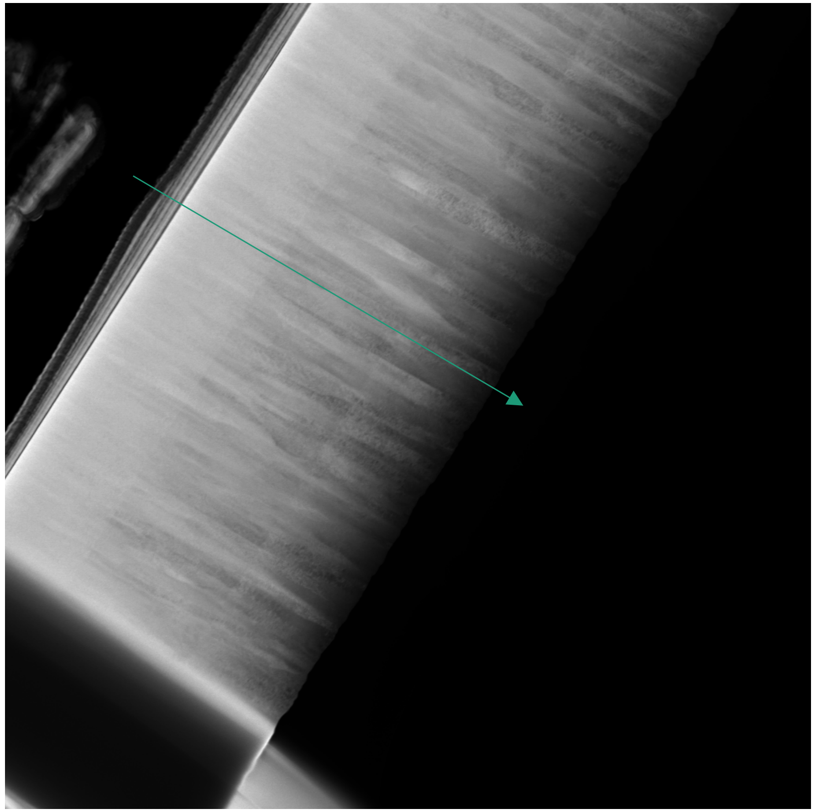
Deposited on Si/SiO wafer

Films femtolaser cut into dogbones

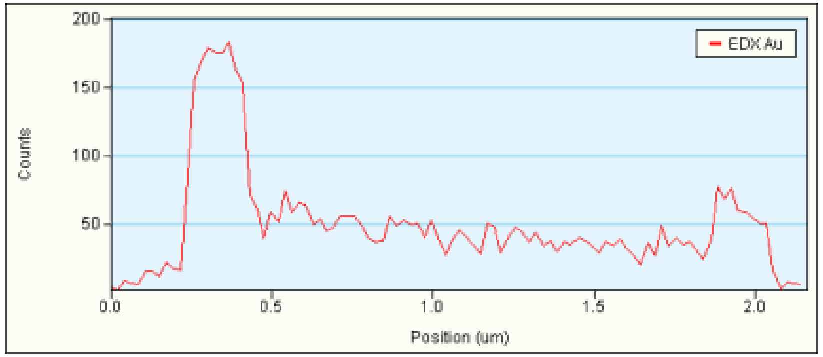


Preliminary results: EDS compositional gradients

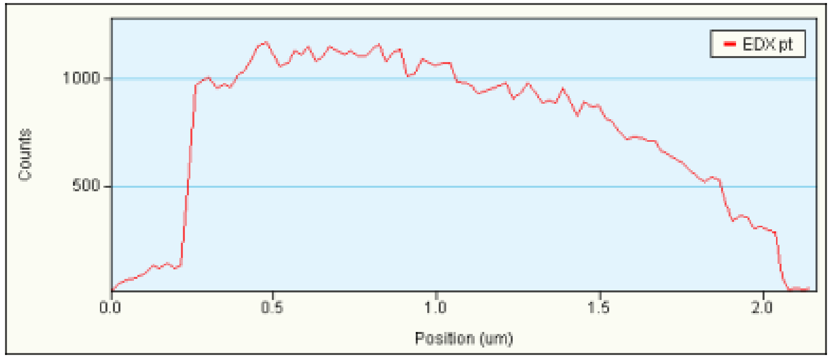
HAADF



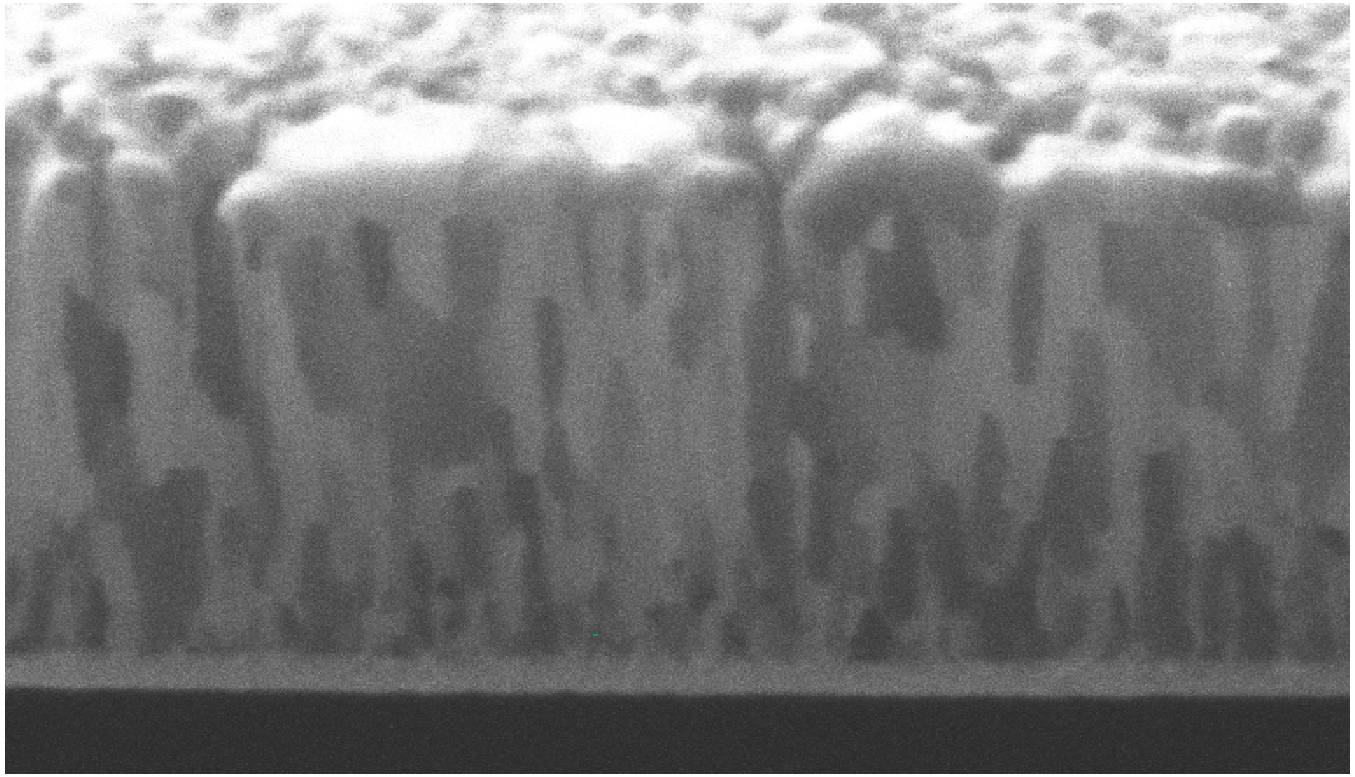
Au



Pt



Example ion channeling of gradient Pt-Au



∇ PtAu 071320, 500C, 10 min

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.
- Can we achieve steeper gradients (1 μm/μm)?
- Can steep microstructural gradients be manipulated to control tensile, fracture, fatigue resistance, wear resistance, radiation tolerance?

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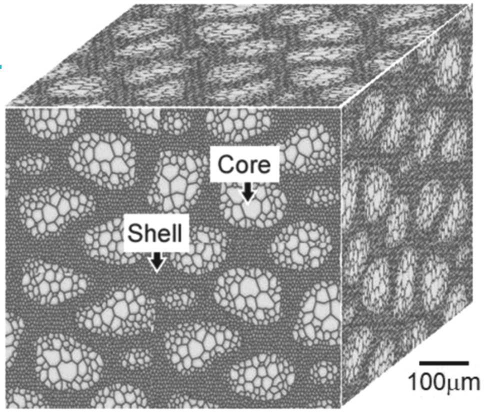
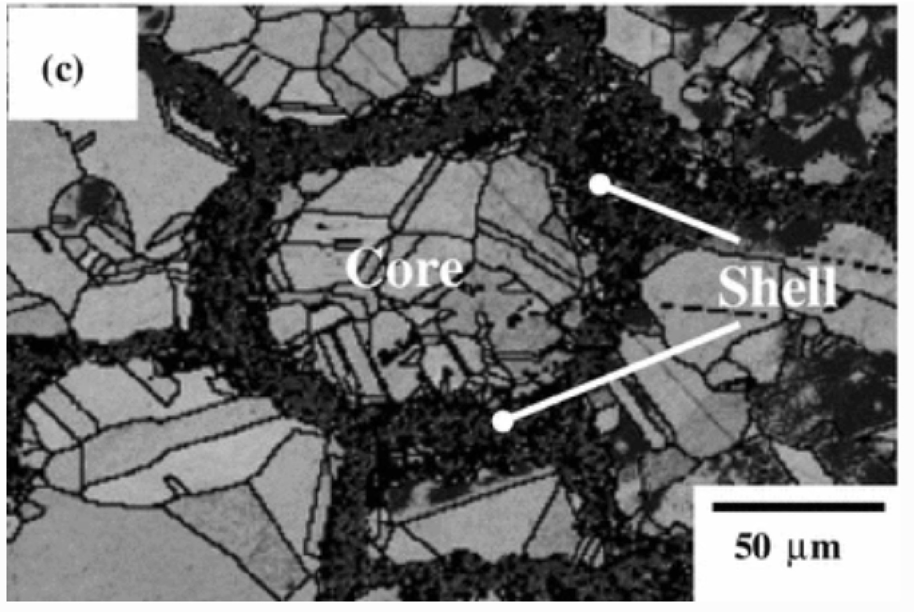
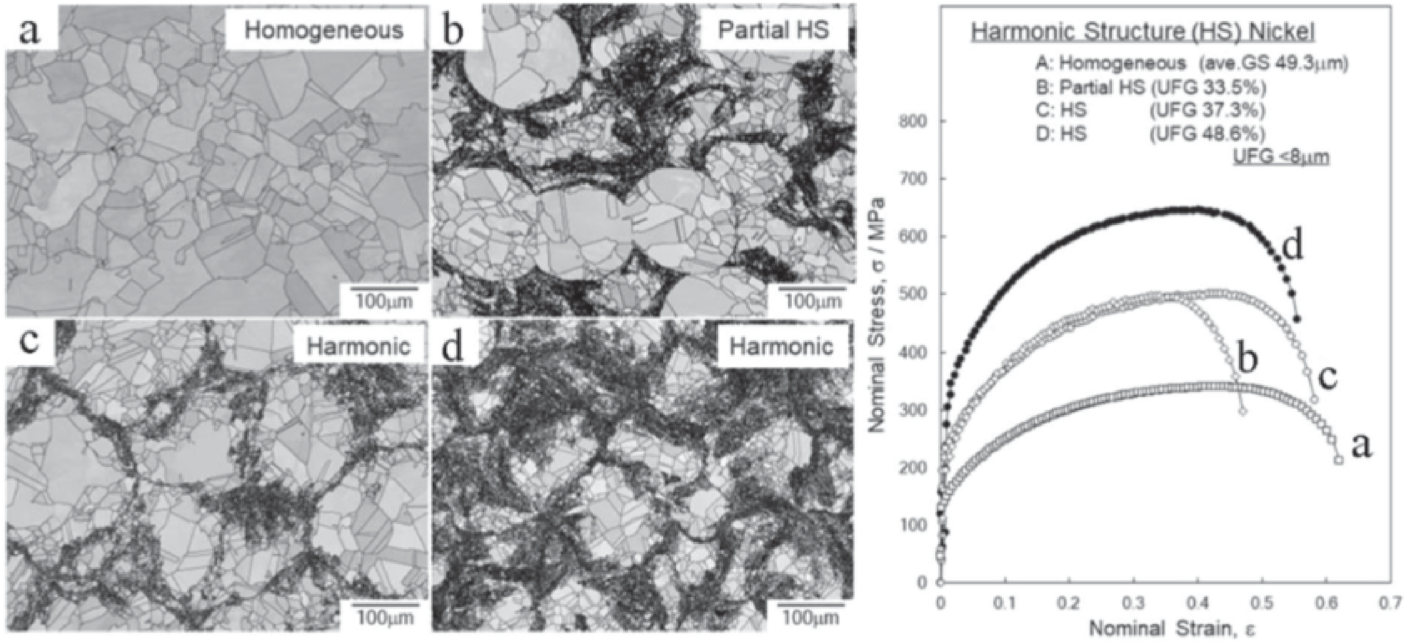
Gradients are not just from the surface



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

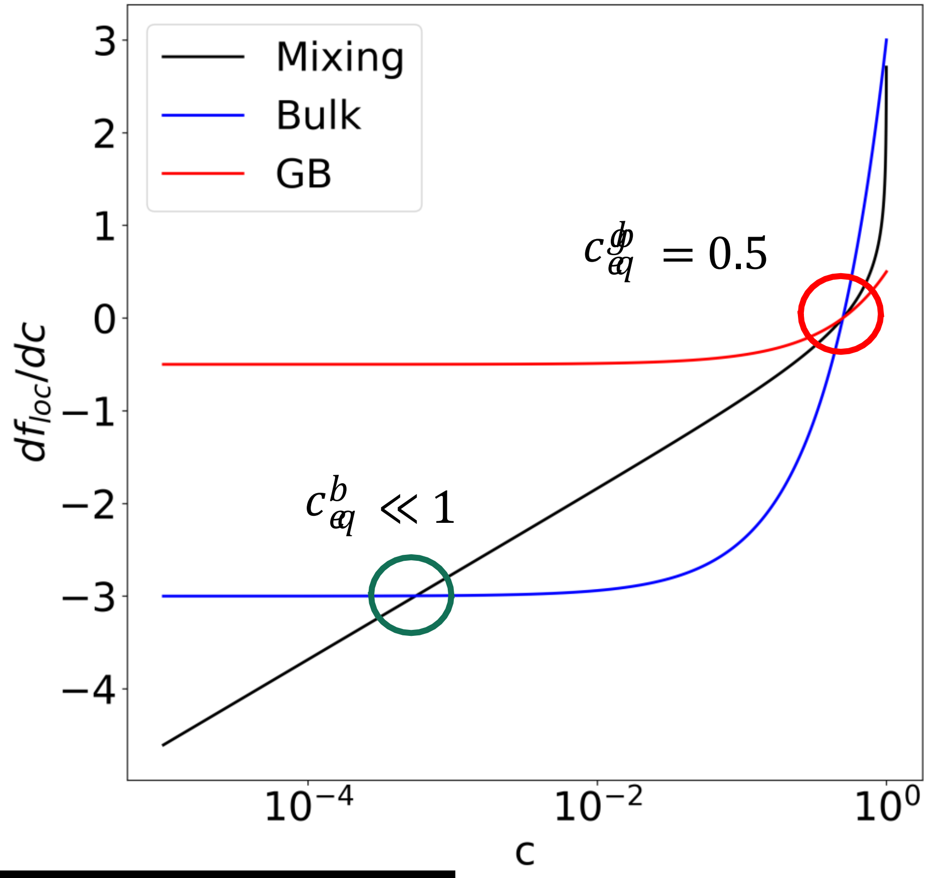
$$f_b = G_b^B c + (1-c)G_b^A + \Omega_b c(1-c) + \frac{RT}{V_m}[c \ln c + (1-c)\ln(1-c)]$$

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

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

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

Anti-segregating parameters

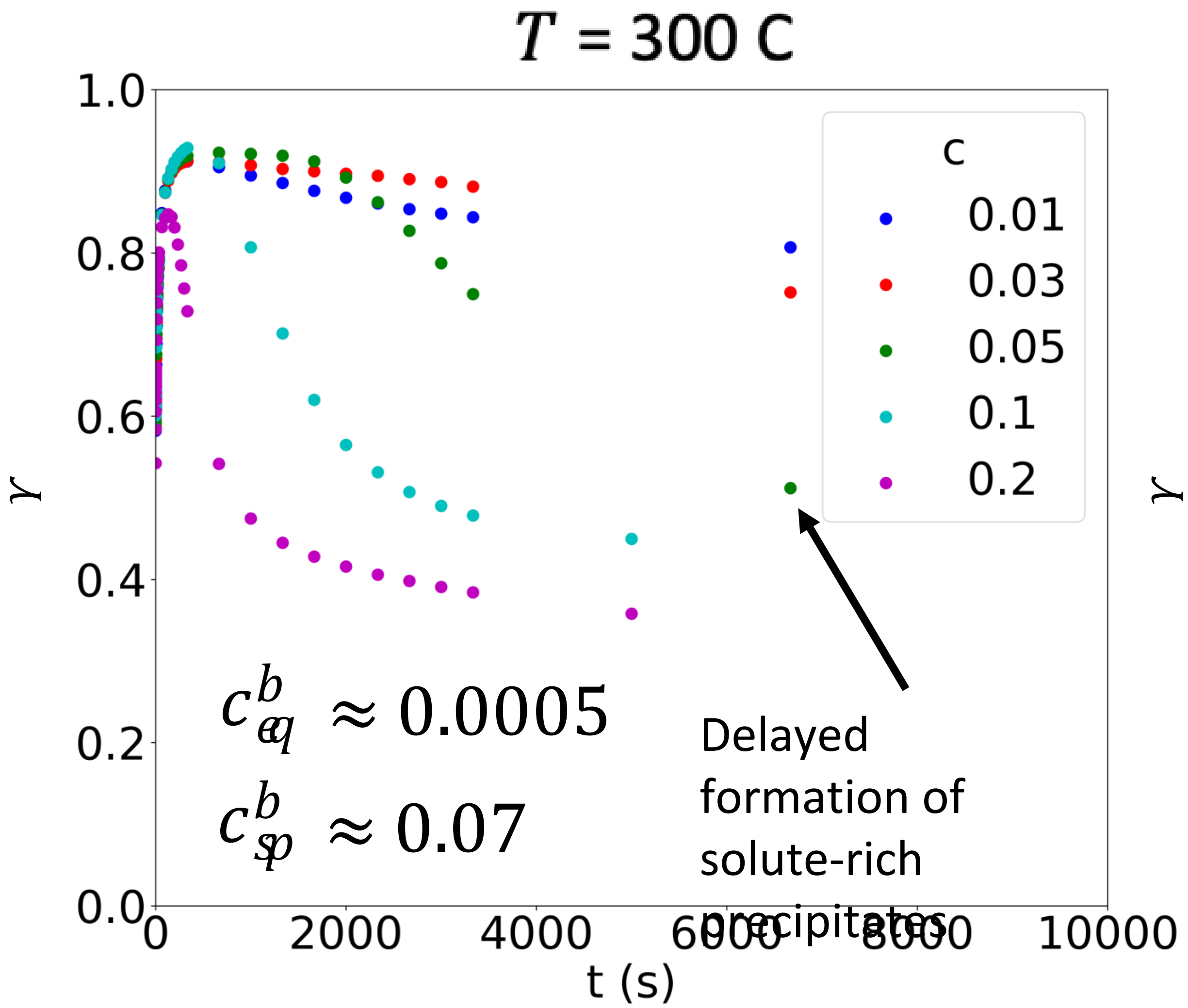


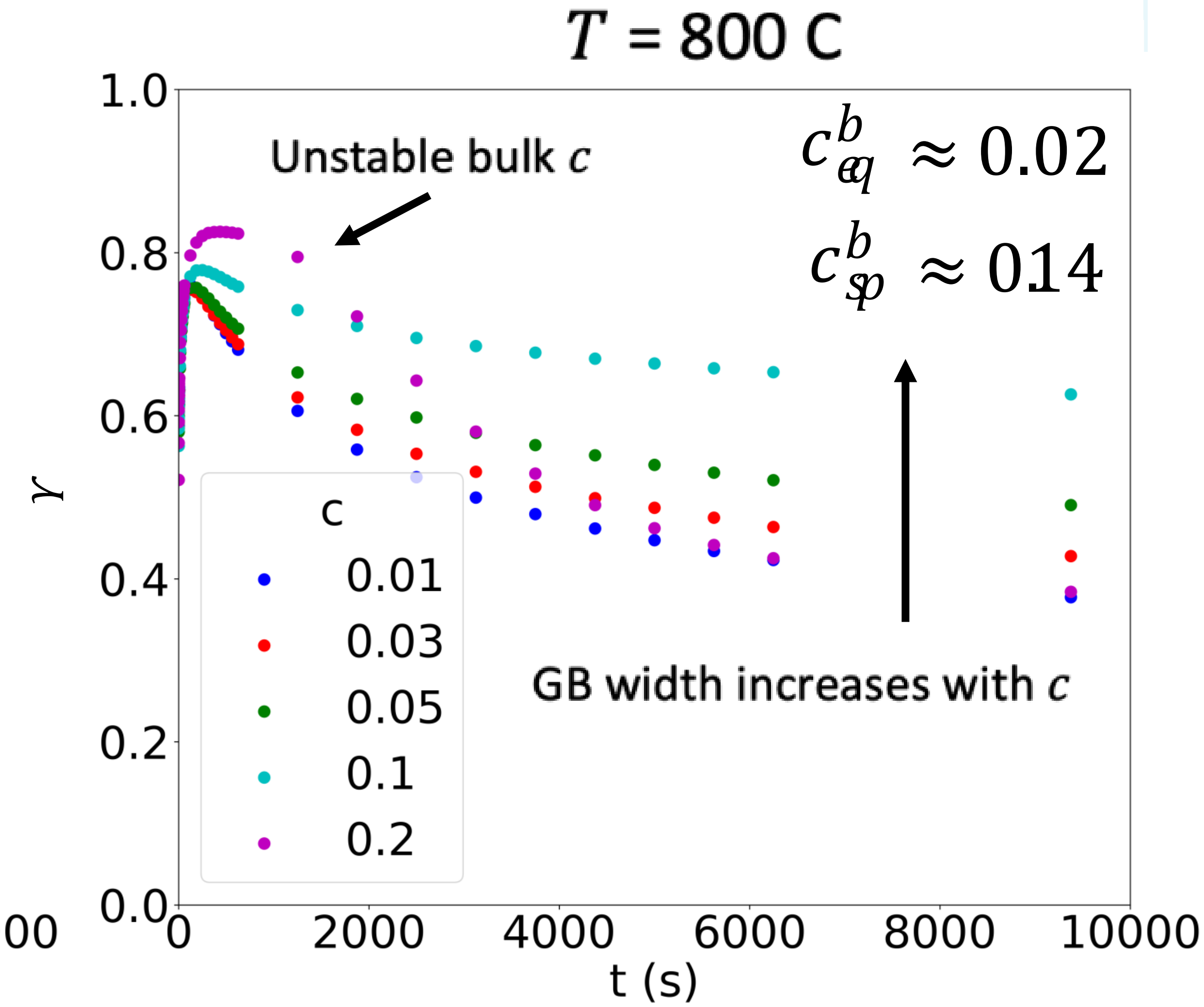
Anti-segregation: $\Omega_{gb} > 0$

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

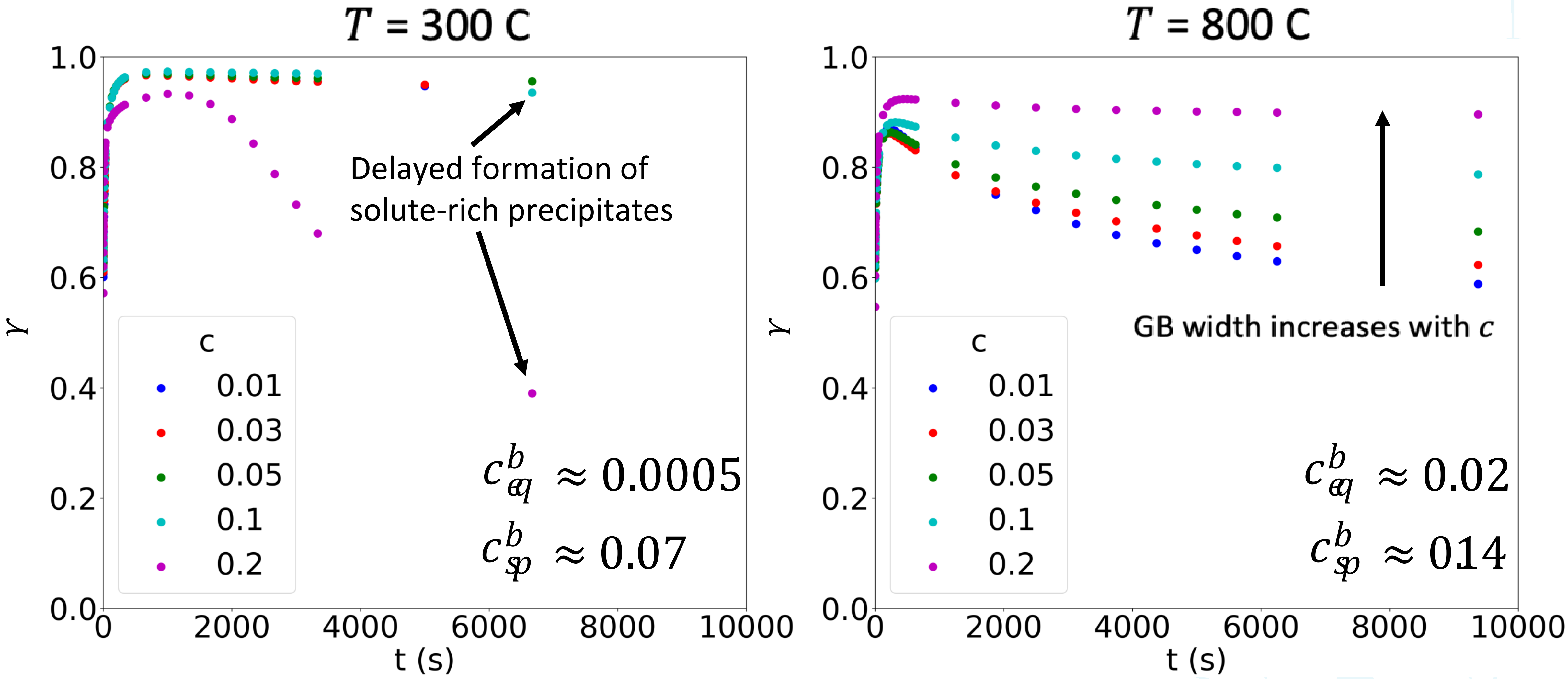
Abdeljawad and Foiles, *Acta Mat.* 101, 2015
Abdeljawad et al., *Acta Mat. 126* 2017

Anti-segregating solute population





GB-segregating solute population



Segregants impede grain growth

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