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Nanostructure Stability and Wear of Binary Nanocrystalline Alloys

Blythe G. Clark, Sandia National Laboratories

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Co-Authors for this work

- **Nic Argibay**, Sandia National Labs
- **Tim Furnish**, Sandia National Labs
- **Mike Dugger**, Sandia National Labs
- **Brad Boyce**, Sandia National Labs
- **Mike Chandross**, Sandia National Labs
- **Ping Lu**, Sandia National Labs
- **Stephen Foiles**, Sandia National Labs
- **Fadi Abdeljawad**, Sandia National Labs
- **Christopher O'Brien**, Sandia National Labs
- **Chris Schuh**, MIT

The Land of Enchantment

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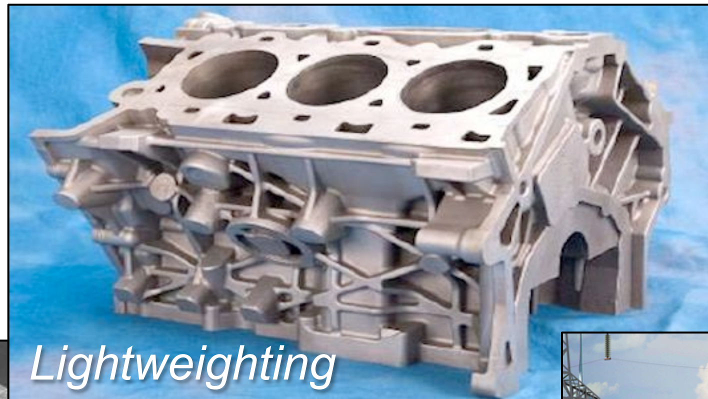
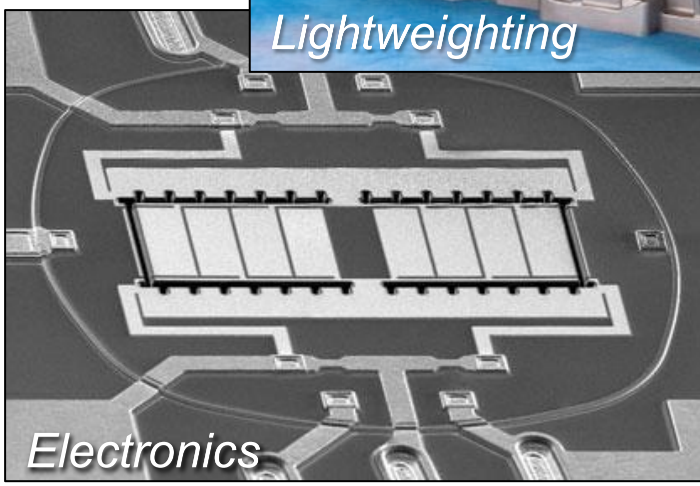
Outline

- Intro
- Prospects for Nanocrystalline (NC) Metals
- Challenges to Application of NC Metals
- Solute Segregation for Stabilization of NC Metal Alloys
- Stability under Wear in NC Ni-W
- Recent Stability Results in NC Pt-Au
- Future Outlook

Aren’t We “Done” with Metals?

Metals are Integral to Innovation





Strong demand to:
- Maximize performance
- Extend lifetimes
- Engineer properties ’by design’

Advanced experimental and computational methods are enabling *re-exploration* of decades-old questions and *new understanding* of complex phenomena in metals

eetimes.com; U.S. Department of Energy; elp.com

Achieving Properties 'By Design'

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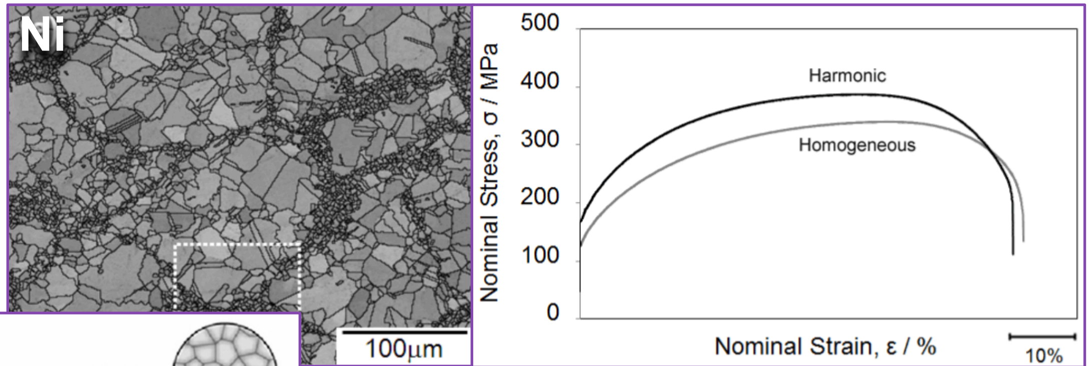
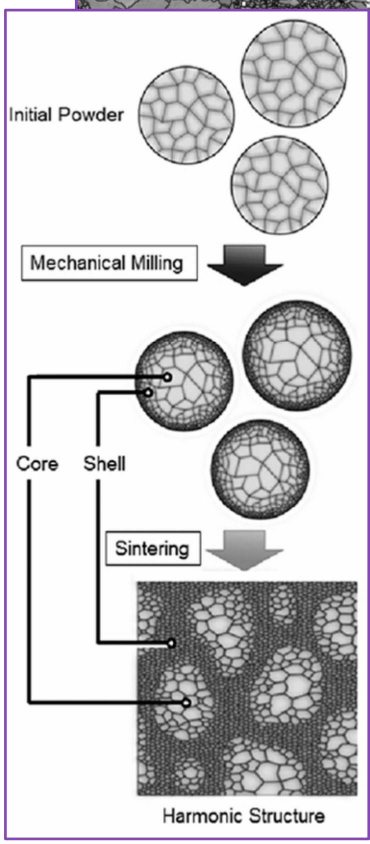
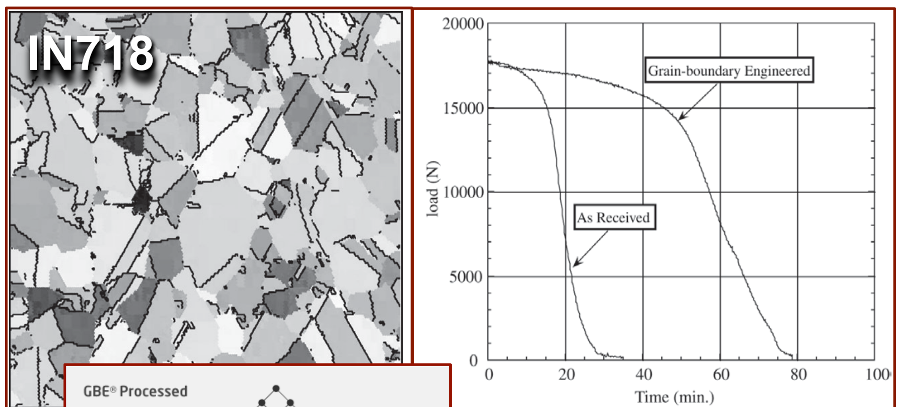
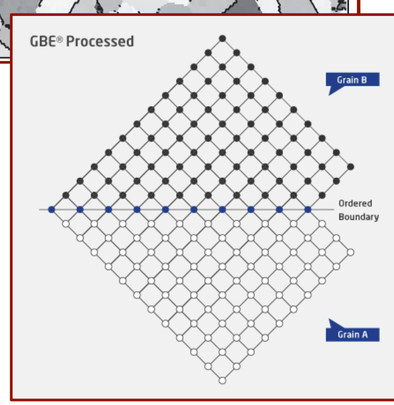
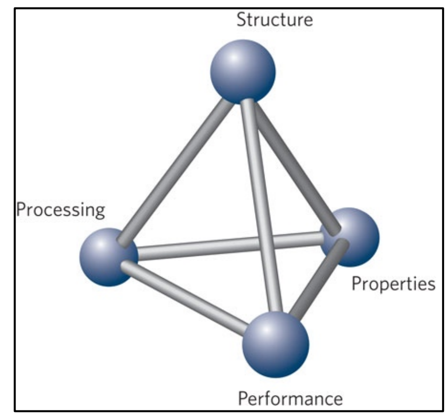






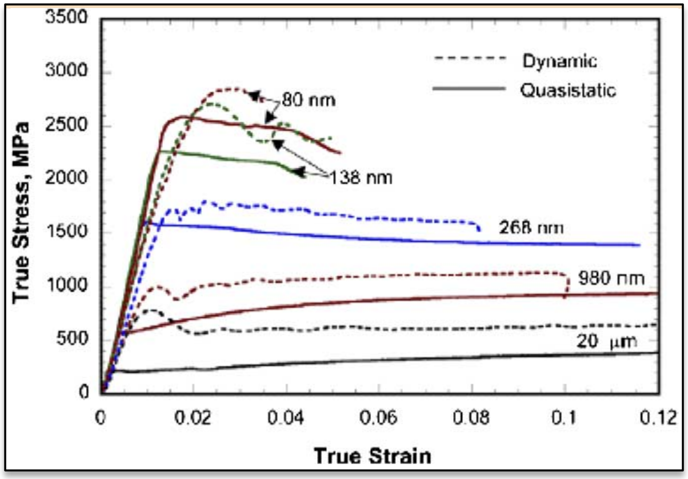




- Leveraging our physical understanding of fundamental interrelationships→ *properties 'by design'*

Advanced processing coupled with state-of-the-art microstructural analysis and *physical understanding* of the origin of properties is key

Nanocrystalline Advantages

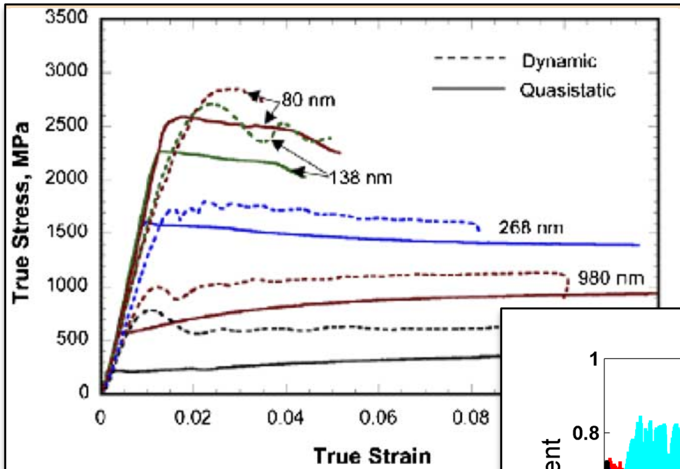


Increased strength

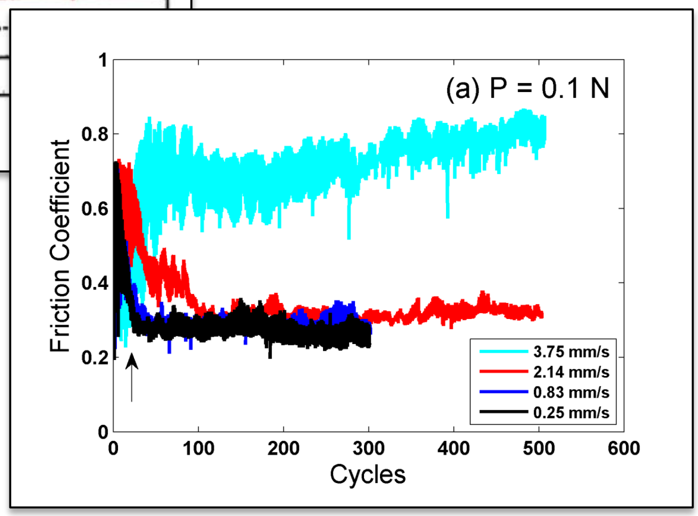
- Nanocrystalline (NC) metals have many advantages…

D. Jia, K. T. Ramesh, E. Ma, Acta Mater 2003.; H. A. Padilla, B. L. Boyce, C. Battaile, S. Prasad, Wear 2013.; B. L. Boyce, H. A. Padilla, Met Trans 2011.

Nanocrystalline Advantages



Increased strength



Lower friction coefficient

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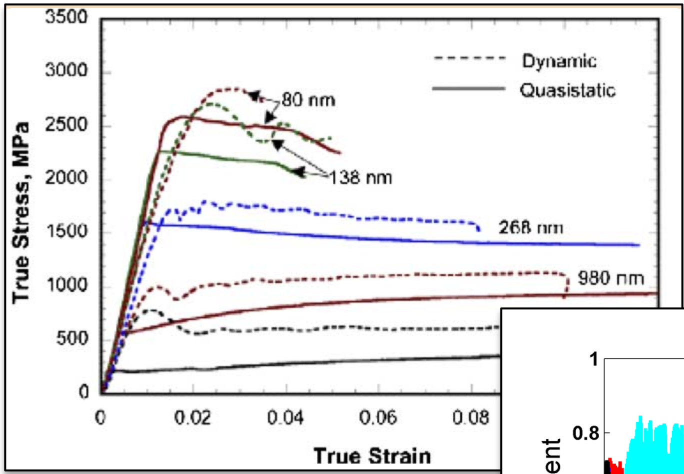
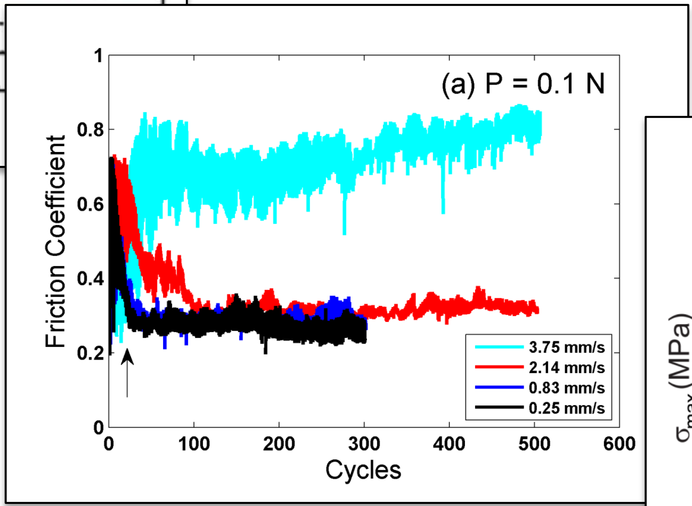
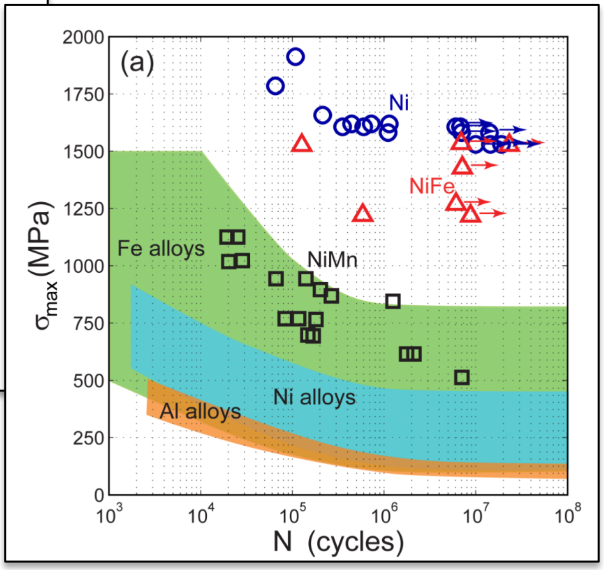


Increased strength

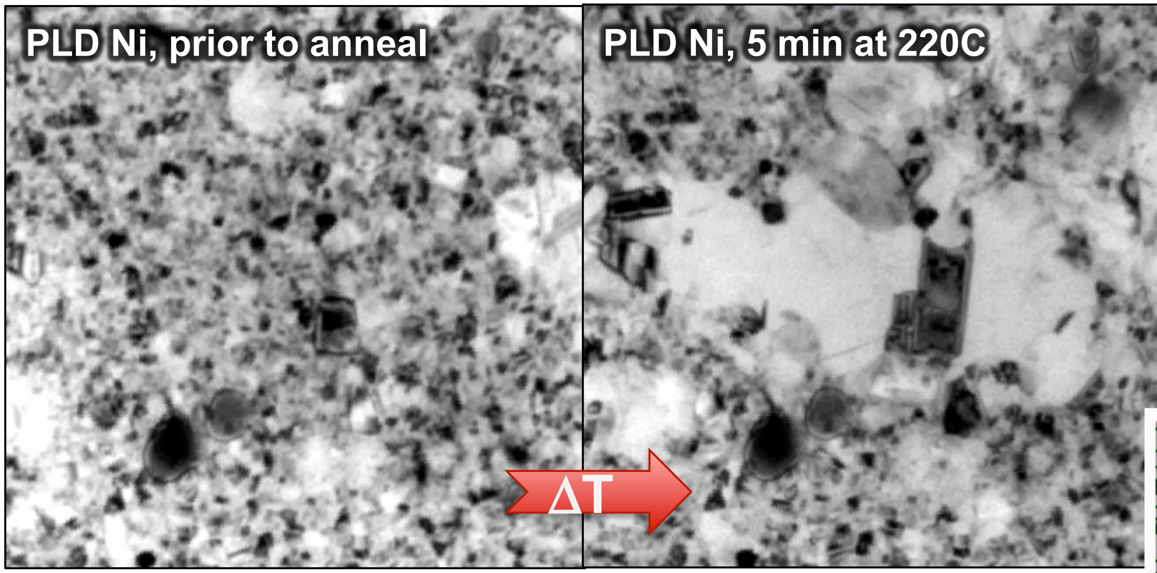


Lower friction coefficient



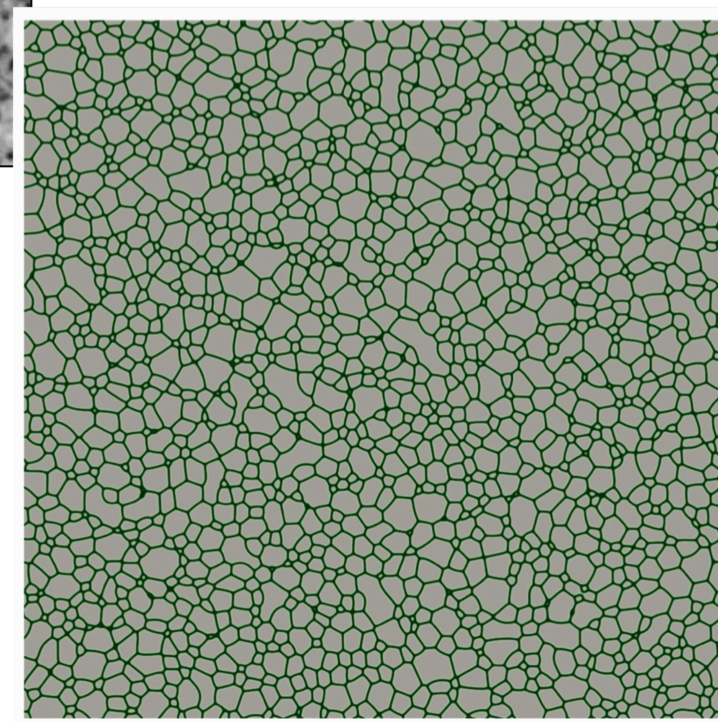
Enhanced fatigue performance

Challenge of Instability



NC Metals are driven to grain growth

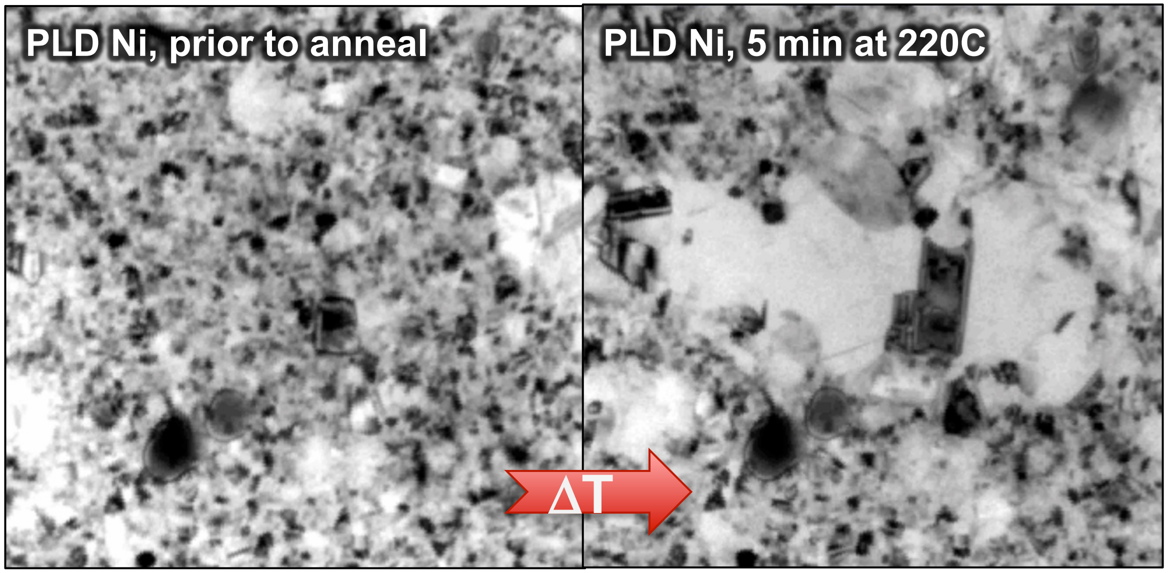
Thermally…



Video credit: Fadi Abdeljawad

S. Rajasekhara, K. Hattar, P. Ferreira, A. Kinghorn, B. G. Clark, unpublished.;H. A. Padilla and B. L. Boyce, Exp. Mech. (2010).

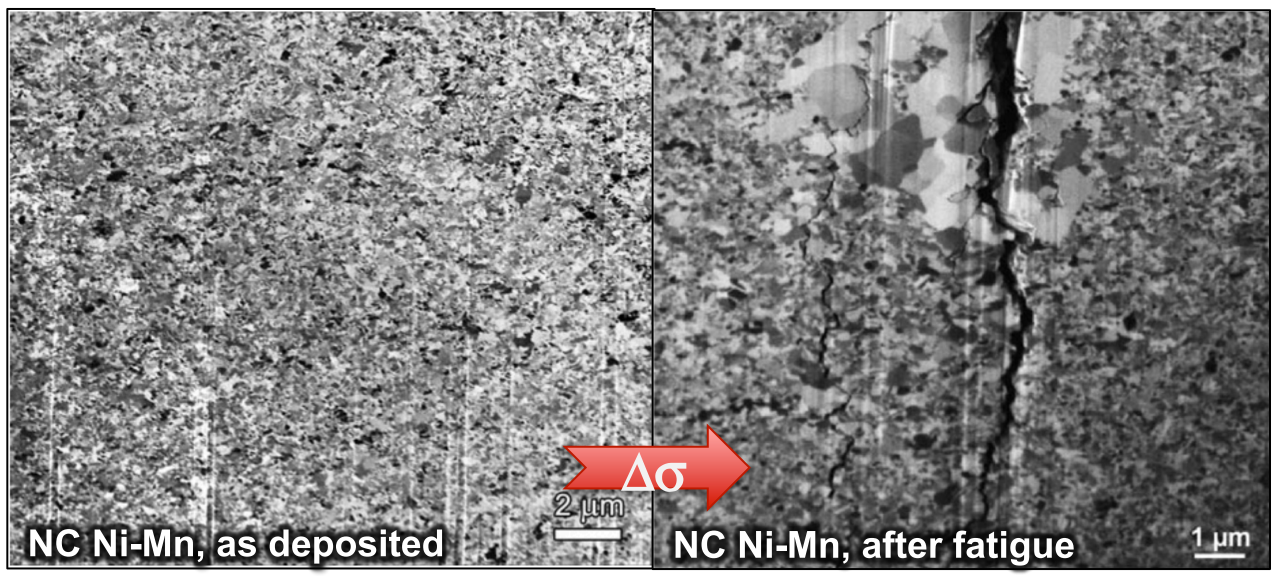
Challenge of Instability



NC Metals are driven to grain growth

Thermally…

…and Mechanically



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Two Routes to Stability

ref: Simoes et al., Nanotech. (2010)

Grain growth driven by boundary velocity, related to boundary mobility and applied stress →

$$v = M \cdot P = M_o \exp\left(-\frac{Q_m}{kT}\right) \cdot \frac{2\gamma_o}{r}$$

M = grain boundary mobility

P = pressure on grain boundary

γ_o = interfacial energy per unit area

r = mean grain radius

S. Rajasekhara, K. Hattar, P. Ferreira, A. Kinghorn, B. G. Clark, unpublished.;H. A. Padilla and B. L. Boyce, Exp. Mech. (2010).

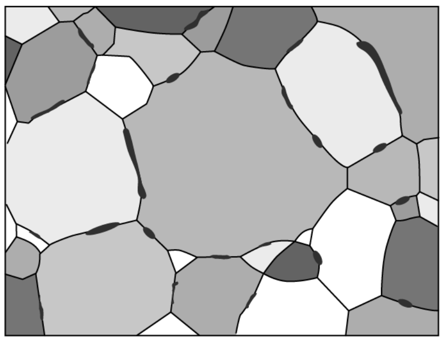
Two Routes to Stability

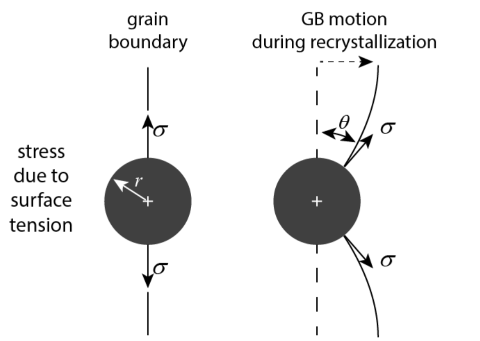
ref: *Simoes et al., Nanotech. (2010)*

$$v = M \cdot P = M_o \exp\left(-\frac{Q_m}{kT}\right) \cdot \frac{2\gamma_o}{r}$$

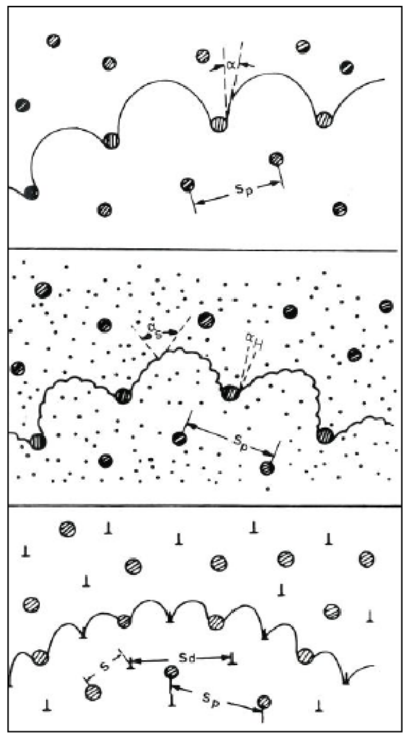
Limit the ***kinetics*** of recrystallization (traditional quasi-stability)

e.g. Zener pinning, solute drag, porosity





drag force: $f_D = 2\pi r\sigma \cos\theta \sin\theta$



M = grain boundary mobility

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Two Routes to Stability

ref: Simoes et al., Nanotech. (2010)

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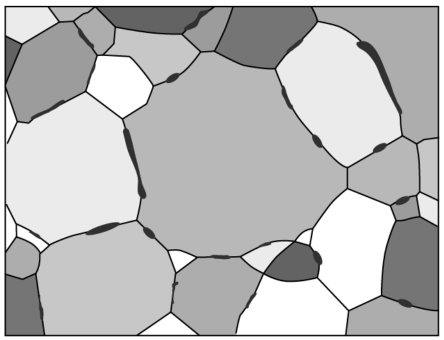

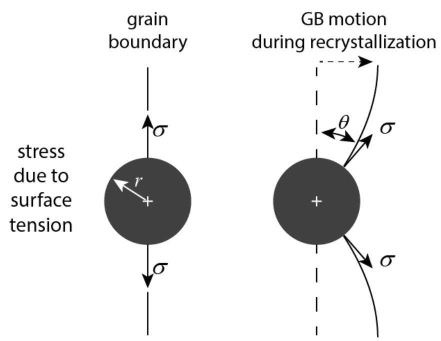

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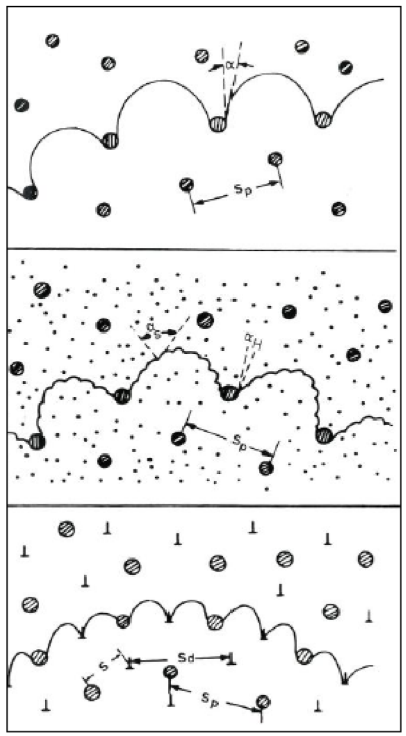


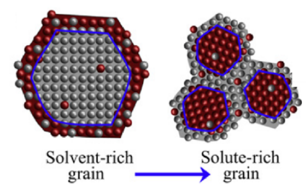
Weissmüller (1993), Kirchheim (2002), and Schuh (2012) have made significant contributions toward understanding and achieving ***thermodynamic*** stability by lowering grain boundary energy through solute segregation

Regular Nanocrystalline Solution (RNS) Model:
ref: Chookajorn et al., Science, 2012

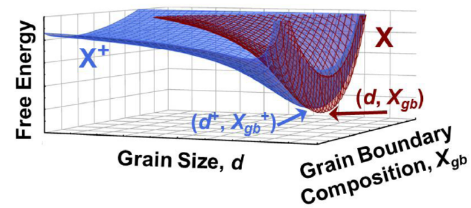
$$\Delta G^{mix} = (1 - f_{gb})\Delta G_c^{mix} + f_{gb}\Delta G_{gb}^{mix} + z\nu f_{gb}(X_{gb} - X_c)\left[(2X_{gb} - 1)\omega_{gb} - \frac{1}{zt}(\Omega^B\gamma^B - \Omega^A\gamma^A)\right]$$

$$dG = \left[\gamma - \frac{N_\beta}{A}\Delta G_{seg}\right]dA$$

Grain structure model:
segregated 2-phase metal system



ref: Murdoch et al., Acta Mat. (2013)



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Solute Segregation for Stabilization

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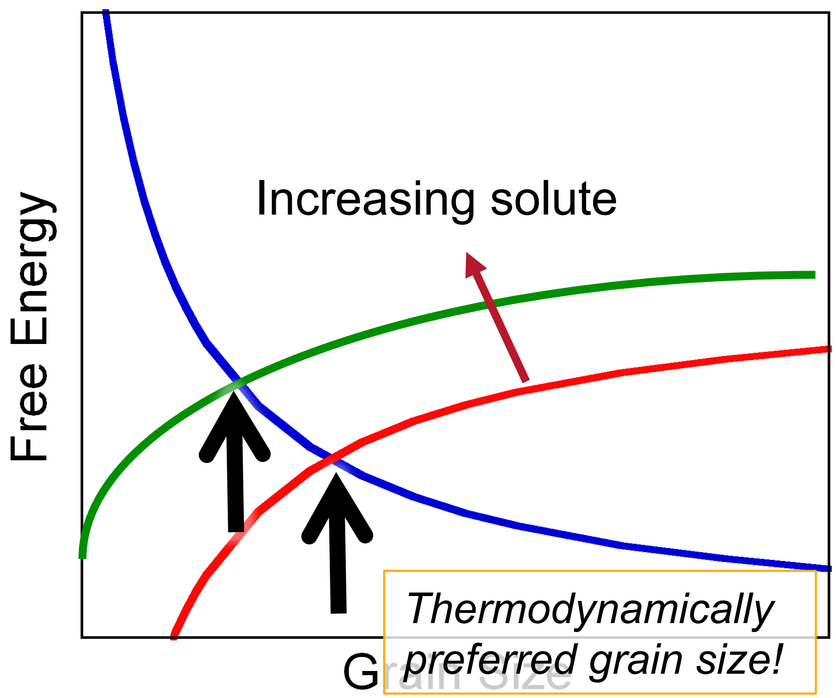

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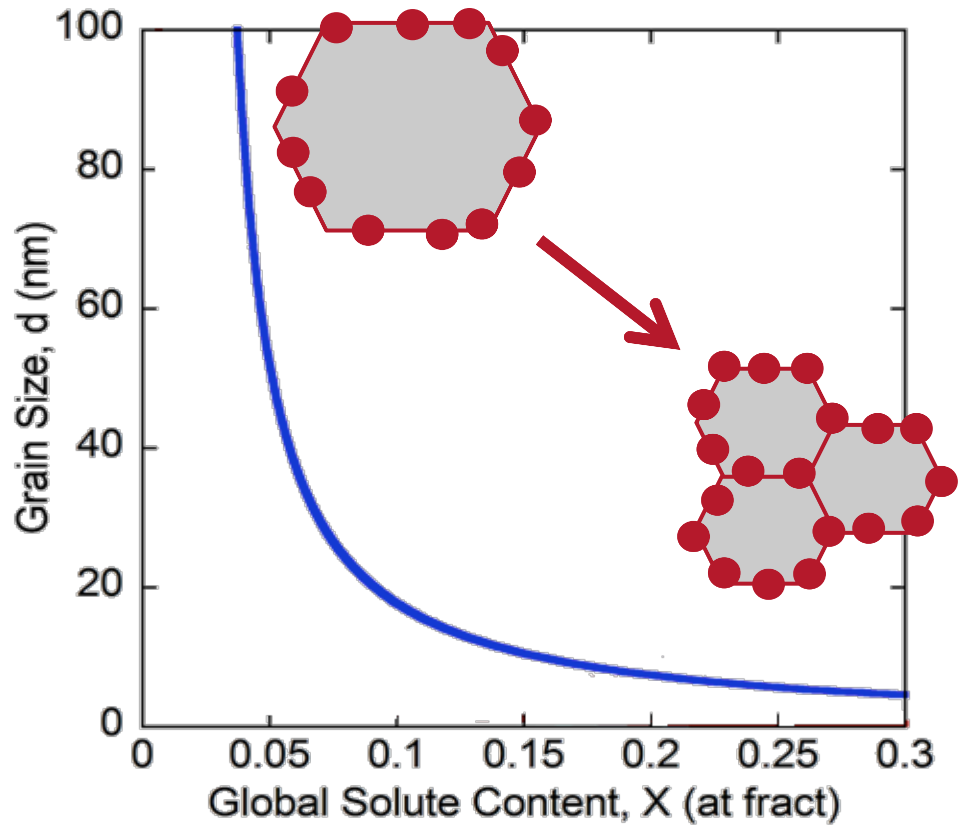
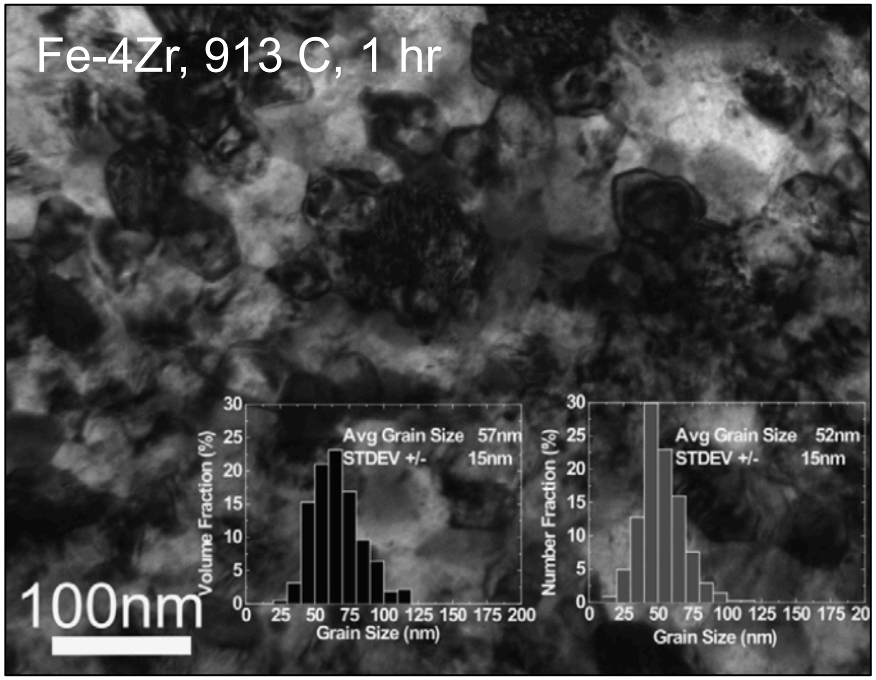


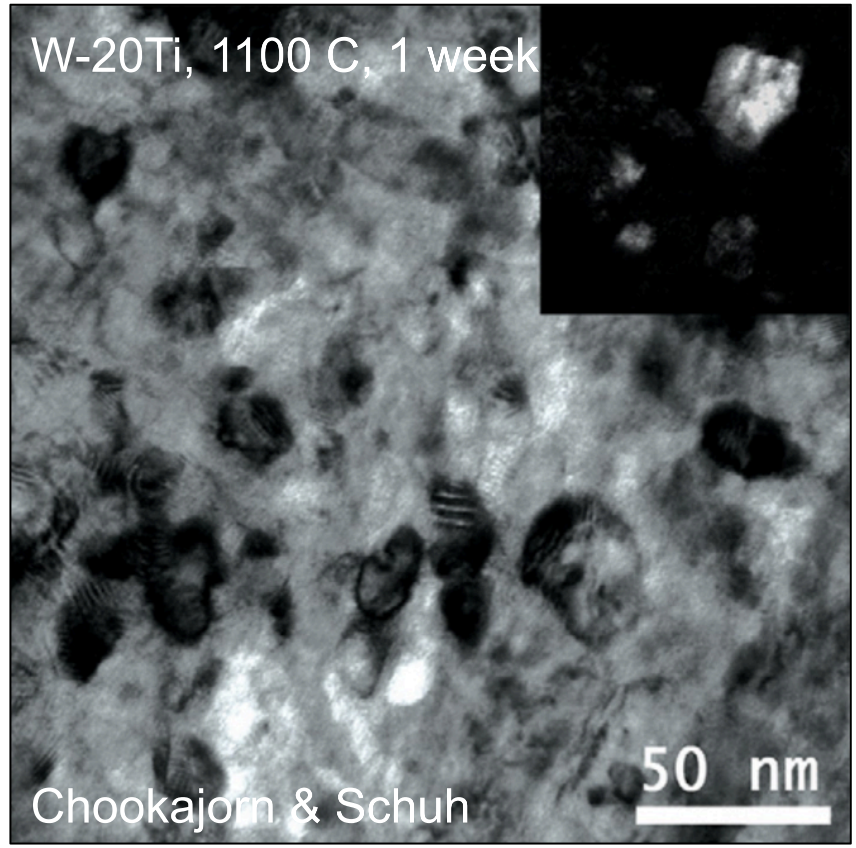
Increasing solute lowers the grain boundary energy and reduces the grain size

Murdoch and Schuh, 2012.

Binary NC Alloys with Improved Thermal Stability

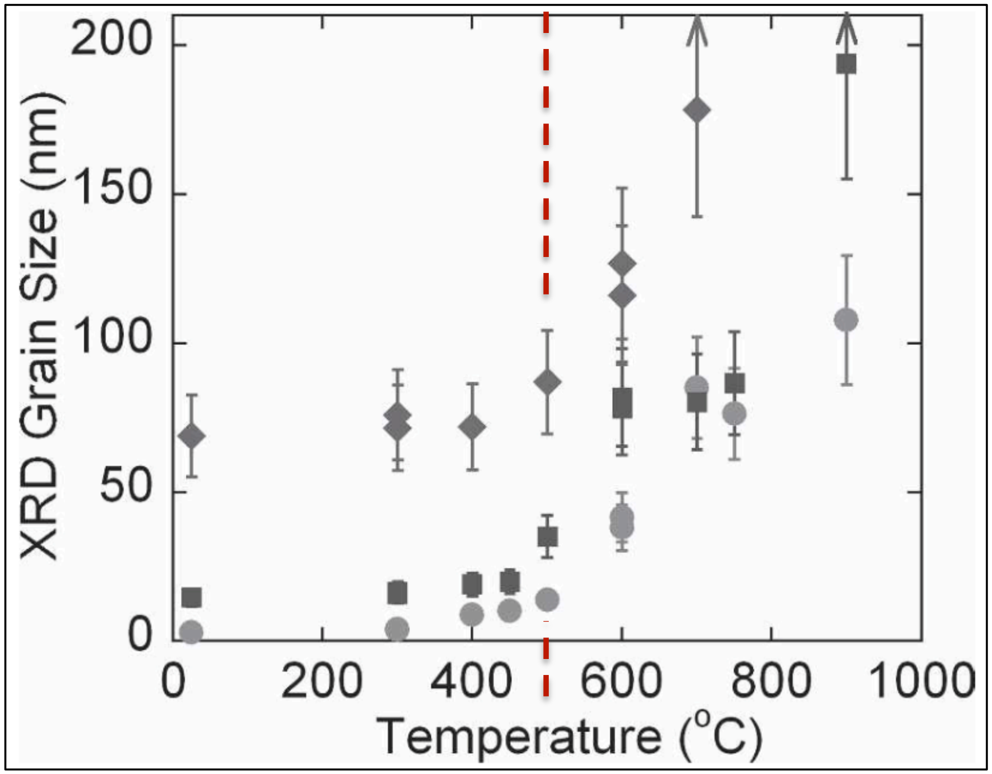


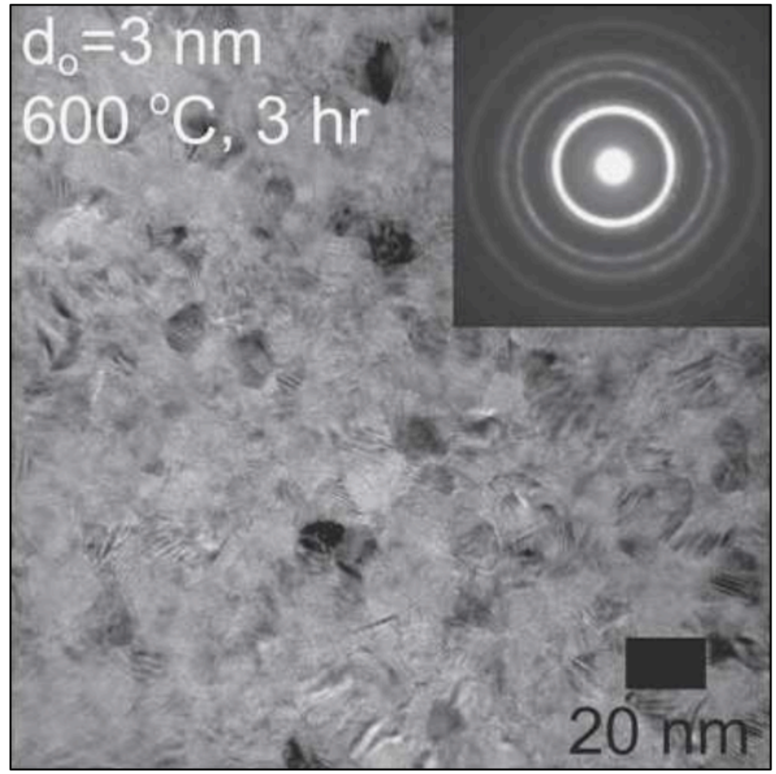
Darling et *al.*



…plus examples of improved thermal stability in other NC alloys: Ni-P, Cu-Ta, Ti-Cu, Pd-Zr, Fe-Mg, among others.

Ni-W: Improved Thermal Stability

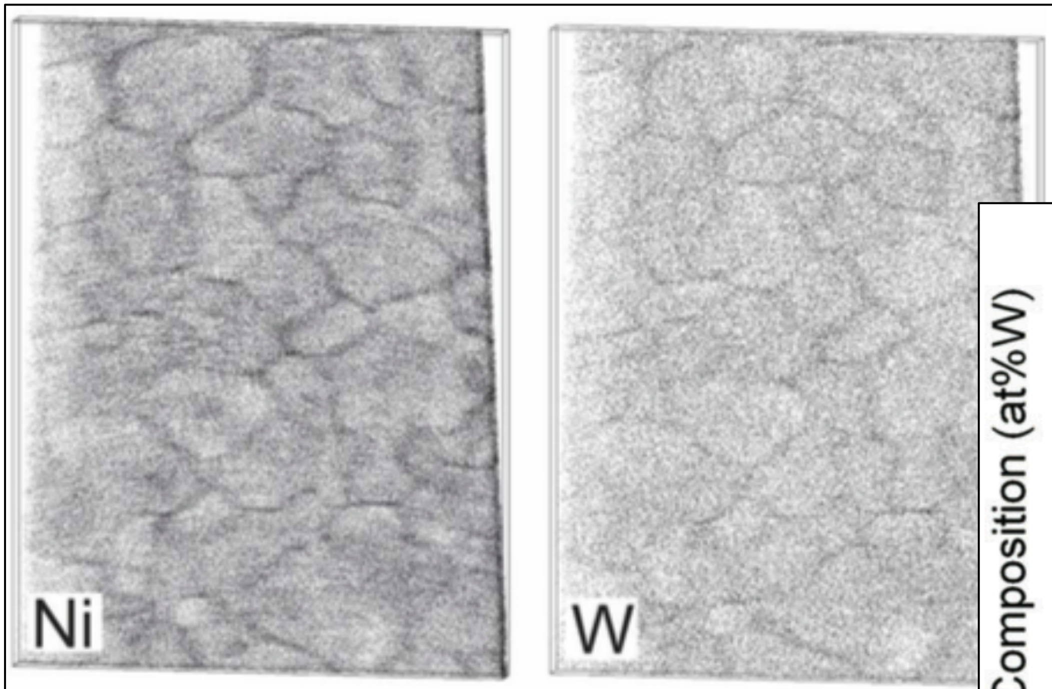


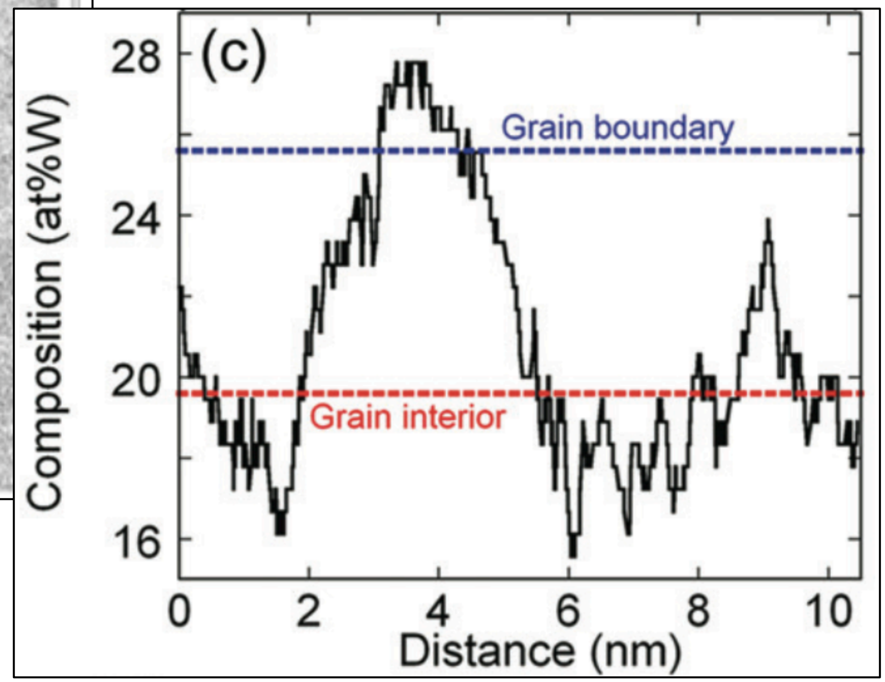


Grain size remains stable during 24 h anneals up to 500 °C

Detor & Schuh, JMR (2007)

Ni-W: Solute Segregation





Atom probe tomography shows W enriched at grain boundaries in Ni-W

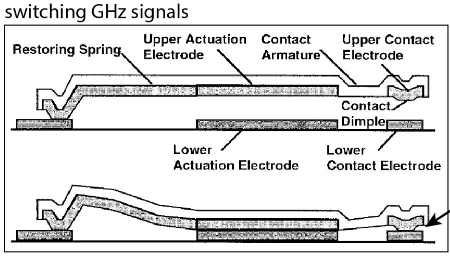
Ni-W demonstrated improved thermal stability…what about mechanical?

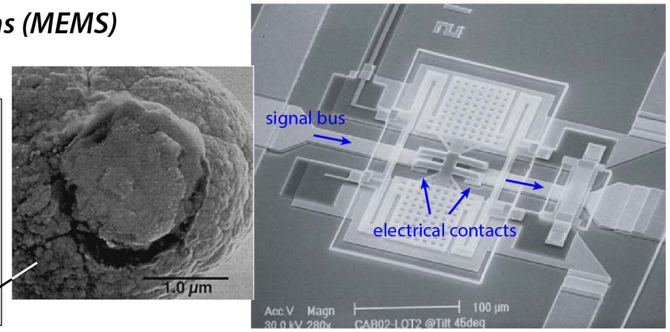
Does thermal stability correlate with stability under wear?

Motivation for Stability under Wear

RF Micro Electromechanical Systems (MEMS)

switching GHz signals



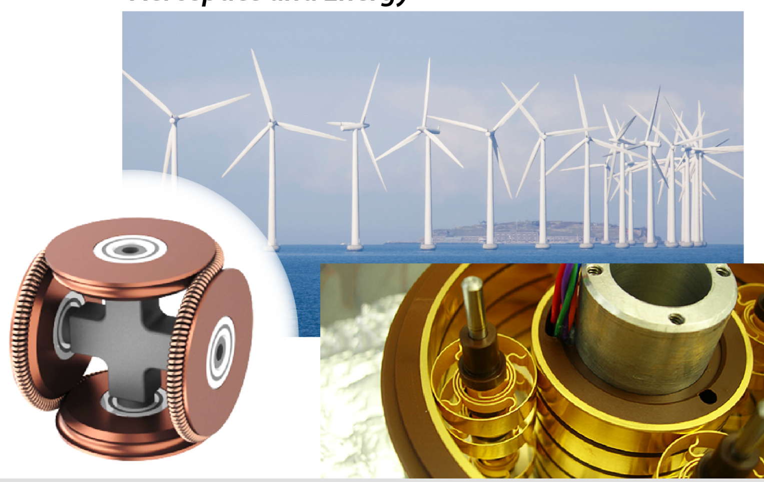


Source: D. Hyman and M. Mehregany, IEEE Trans. & Pack. Tech. 22-3, 1999

Source: Rockwell Scientific metal-metal switch

Electronics (e.g. PCB blade connectors):
200 - 500 nm thick electroless hard gold

Aerospace and Energy

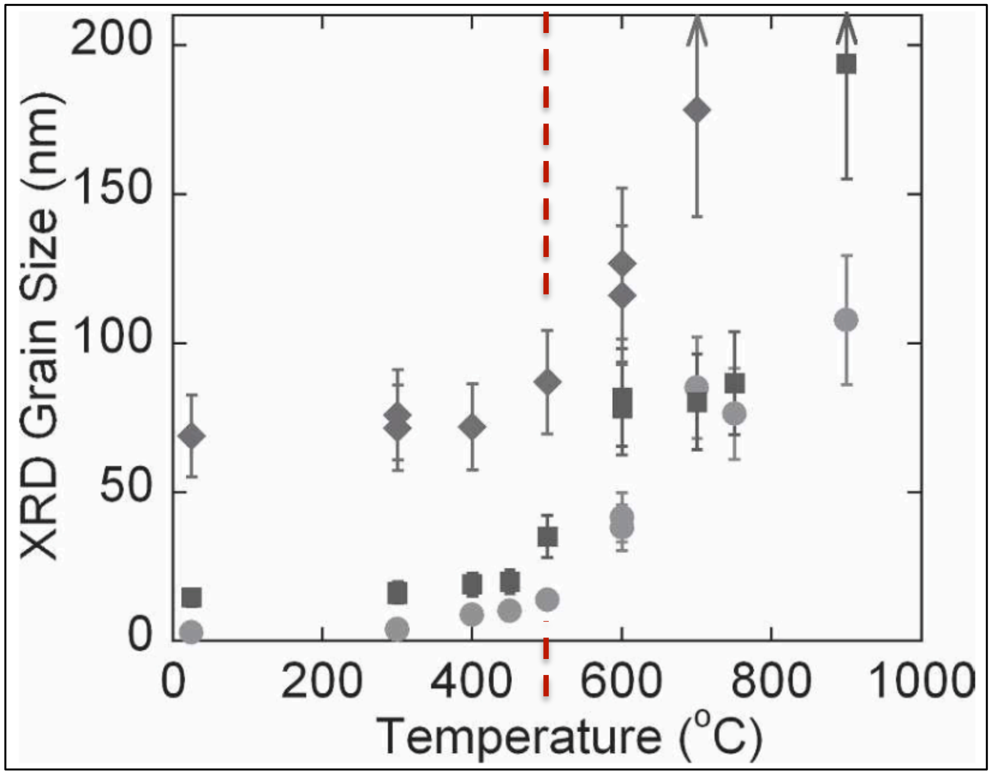


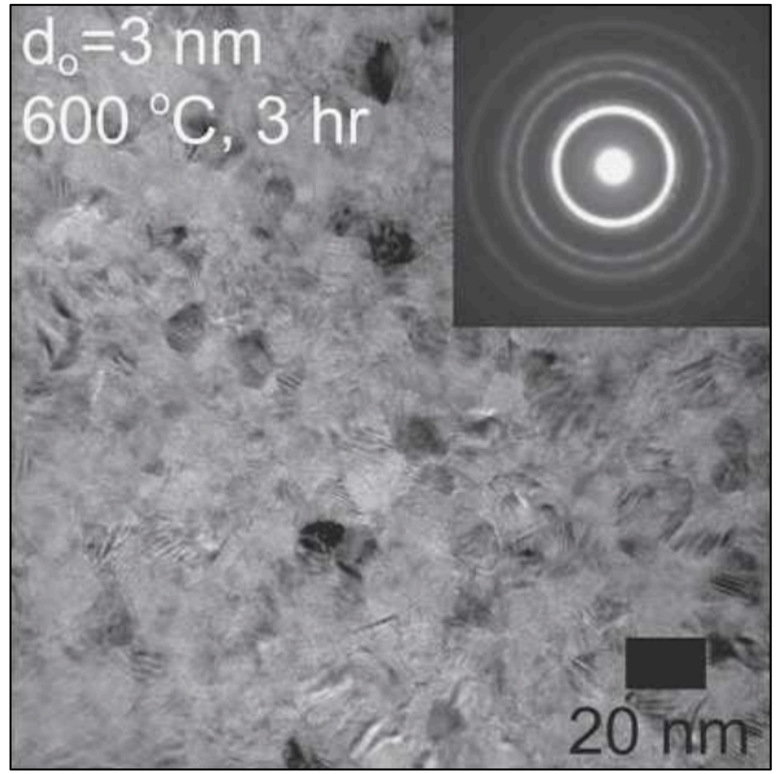
- Metals are widely used tribological materials

- Particularly for electrical contacts

Nanocrystalline metals well-suited for electrical contacts due to high hardness and thin film form
→ wear properties very important!

Ni-W: Improved Thermal Stability





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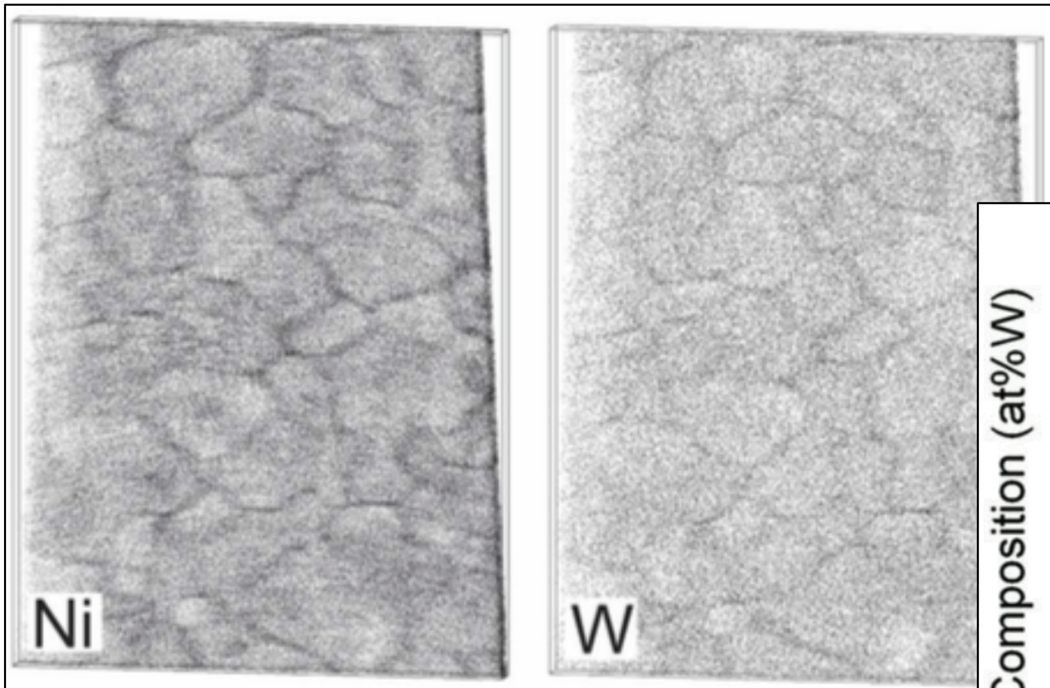
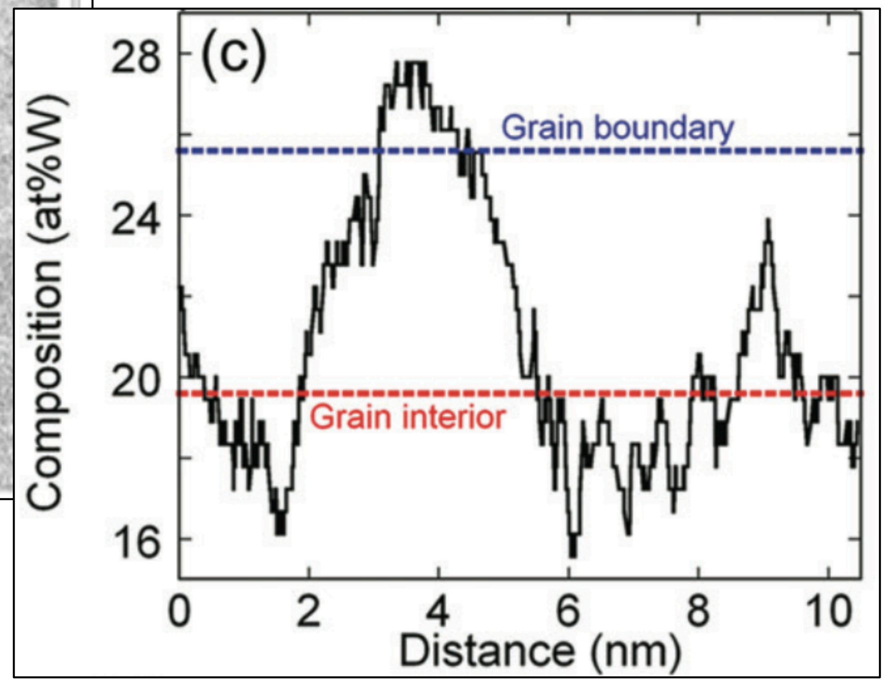
Ni-W: Solute Segregation





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Ni-W: Previous Wear Study

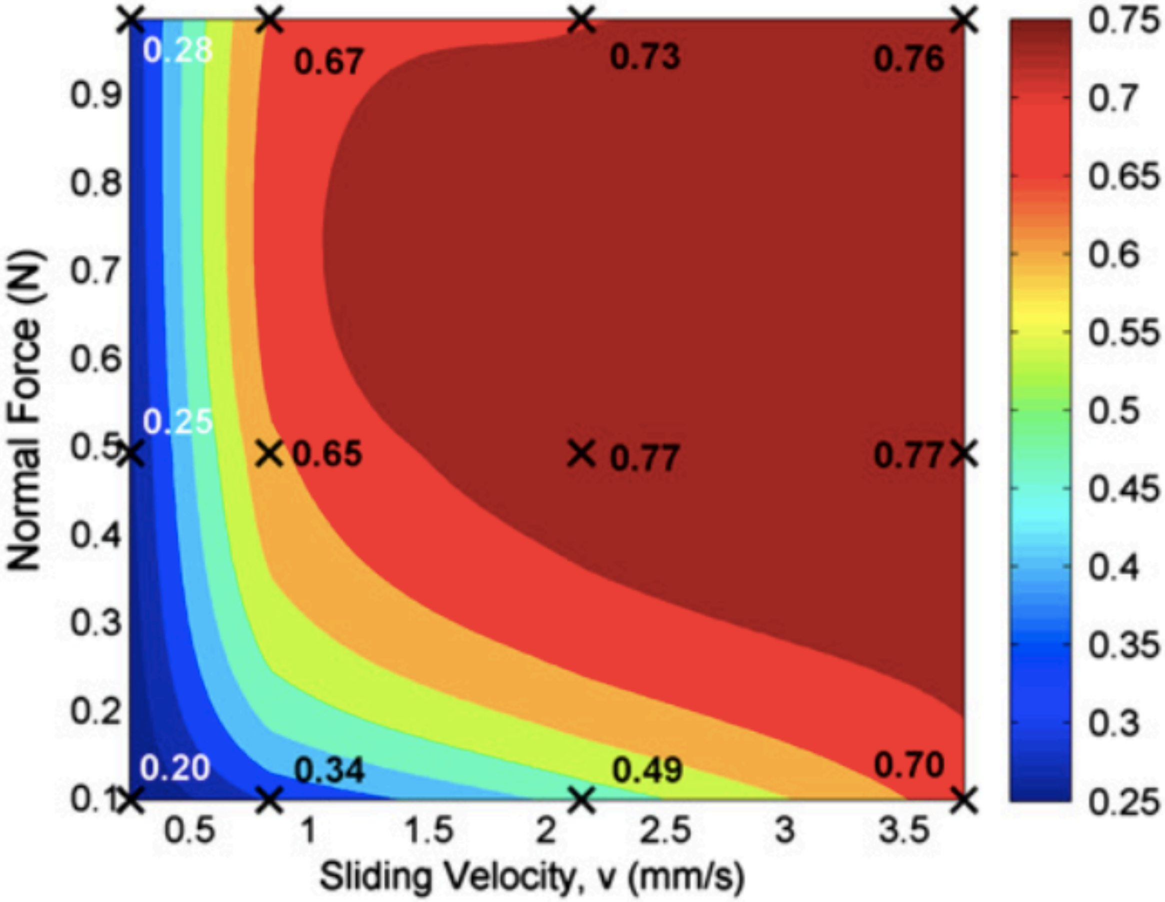
Microstructural and mechanical properties of Ni–W electrodeposits.

W content (at.%)	Average XRD grain size (nm)	Average TEM grain size (nm)	Hardness (GPa)	Wear volume (μm^3)	Friction coefficient
3.0	47		4.0	9.49×10^6	0.63
6.0	30		5.6	7.40×10^6	0.67
8.2	26	25	5.9	5.88×10^6	0.61
12.5	15		6.6	5.12×10^6	0.65
15.7	9		6.8	5.06×10^6	0.66
18.2	6	6	6.9	4.03×10^6	0.65
22.9	5		7.1	3.79×10^6	0.60
27.9	3	3	7.1	2.77×10^6	0.66

5N applied load, 150 mm/s → High friction measured across range of initial compositions and hardness values

Detor & Schuh, JMR (2007)

Friction Transition in Ni-20Fe



Data collected *via* unidirectional sliding in inert environment

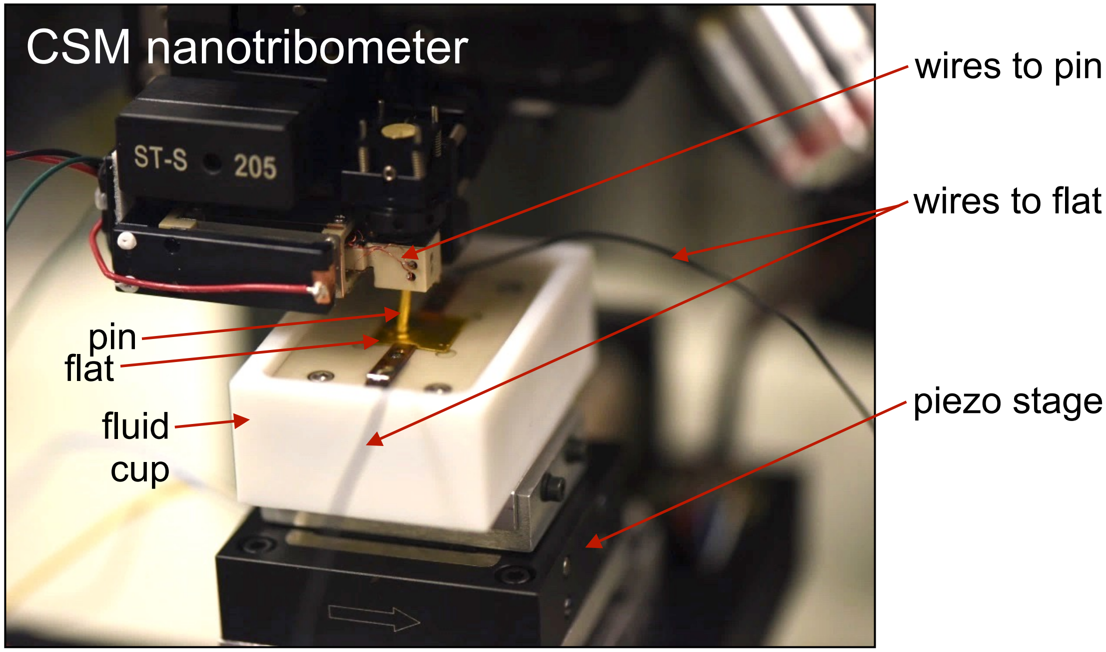
Friction coefficients measured plotted as X's

Contours by cubic interpolation

Low to high friction transition observed for increased normal force and sliding velocity

Is there a window of microstructural stability under wear for Ni-W?

Experimental Method



Goal to study microstructural stability under wear over a range of loads and cycles

Test parameters:

- 1 mm/s sliding speed
- Bidirectional sliding (to/from = 1 cycle)
- 1.6 mm **sapphire** ball (chosen to match H=9GPa)
- 2 mm track
- In air (10% humidity)

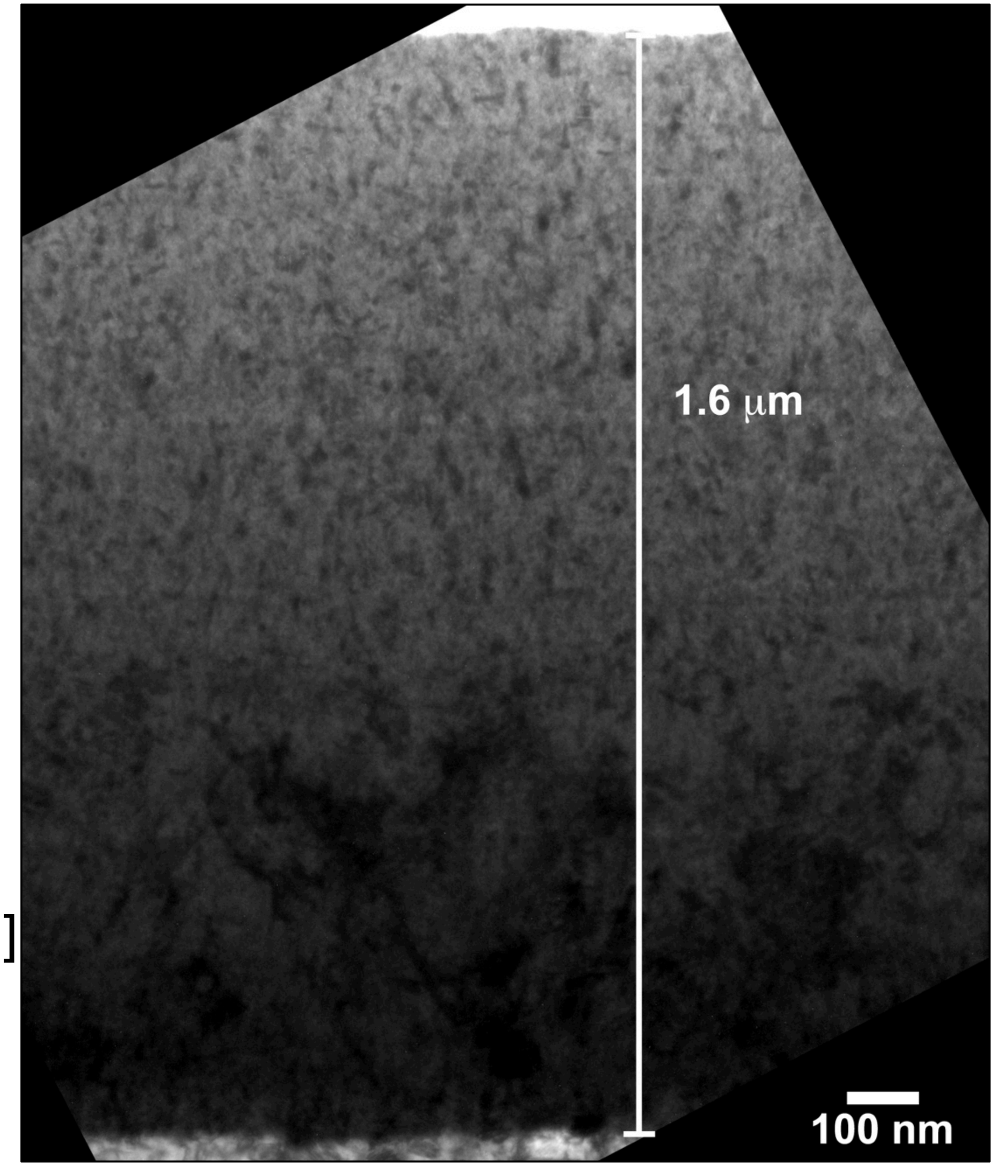
Three contact forces:

- 1 mN
- 10 mN
- 1000 mN

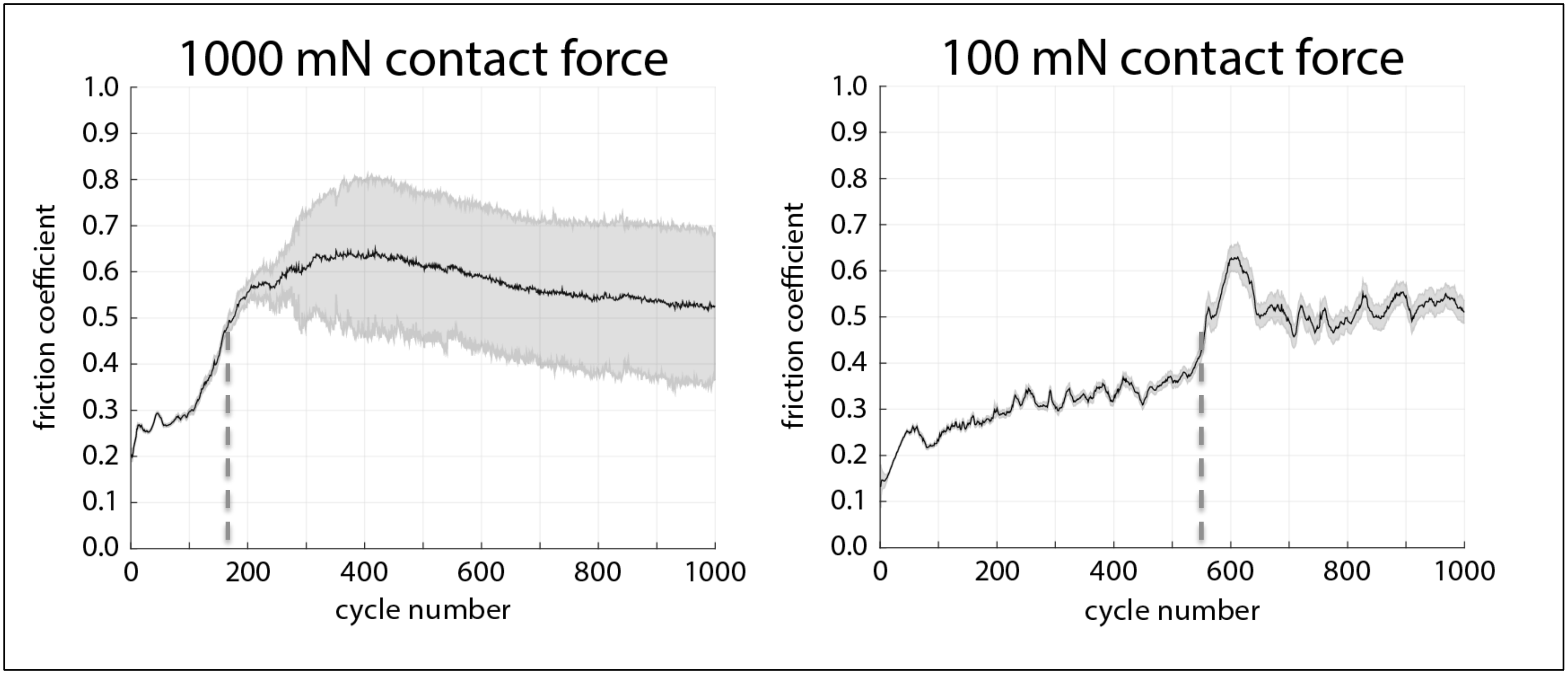
Cross-sectional samples for each wear track prepared for TEM via FIB milling

Initial Microstructure: Ni-40 wt.% W

- Electrodeposited Ni-40W, on brass substrate
- Film thickness of 1.6 um
- Starting grain size of 5.2 ± 0.2 nm, via XRD
- Demonstrated stability of grain size over 24 hours at up to 500 °C [Detor & Schuh]

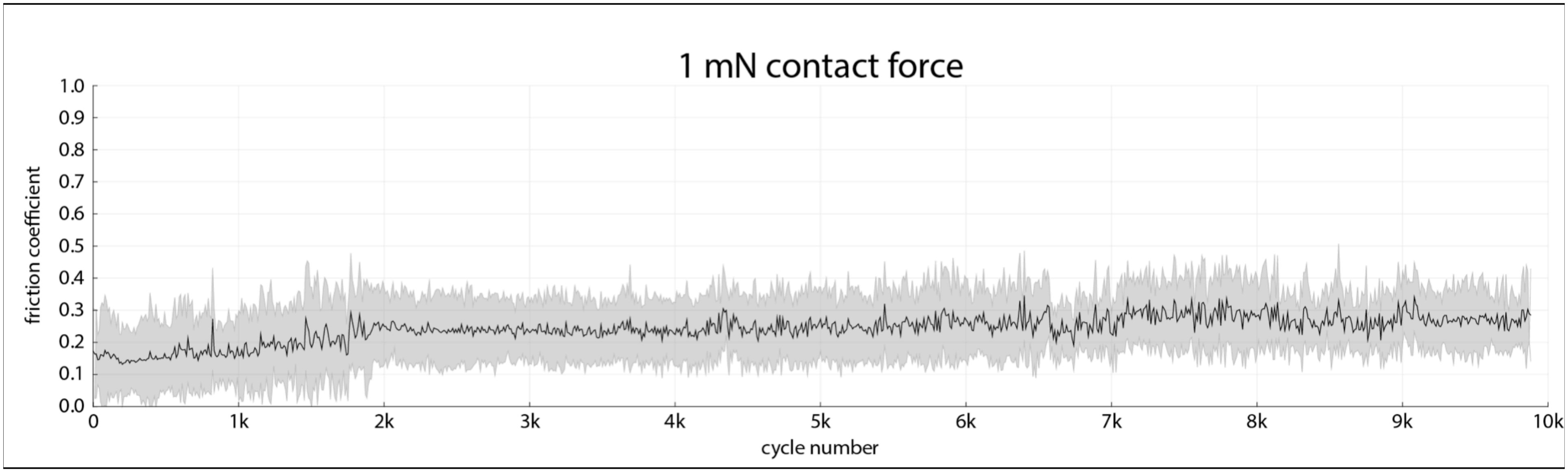


Higher Contact Force Results



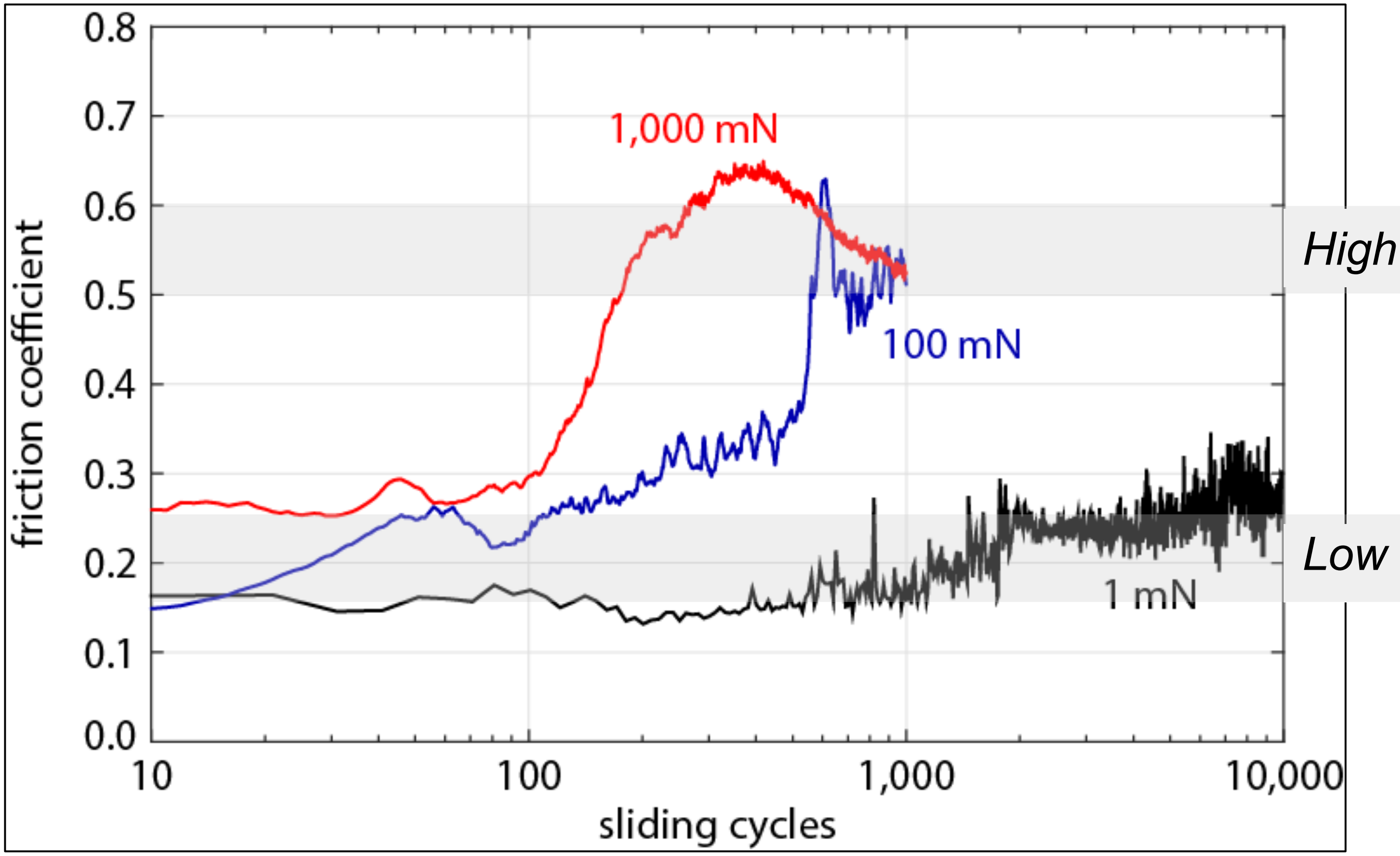
For higher applied contact forces, see transition from low COF (0.15-0.25) to high COF (0.5-0.6) within hundreds of cycles

Low Contact Force Results



For the lowest applied contact force case, friction coefficient remains low (0.15-0.25) for test duration over 10,000 cycles

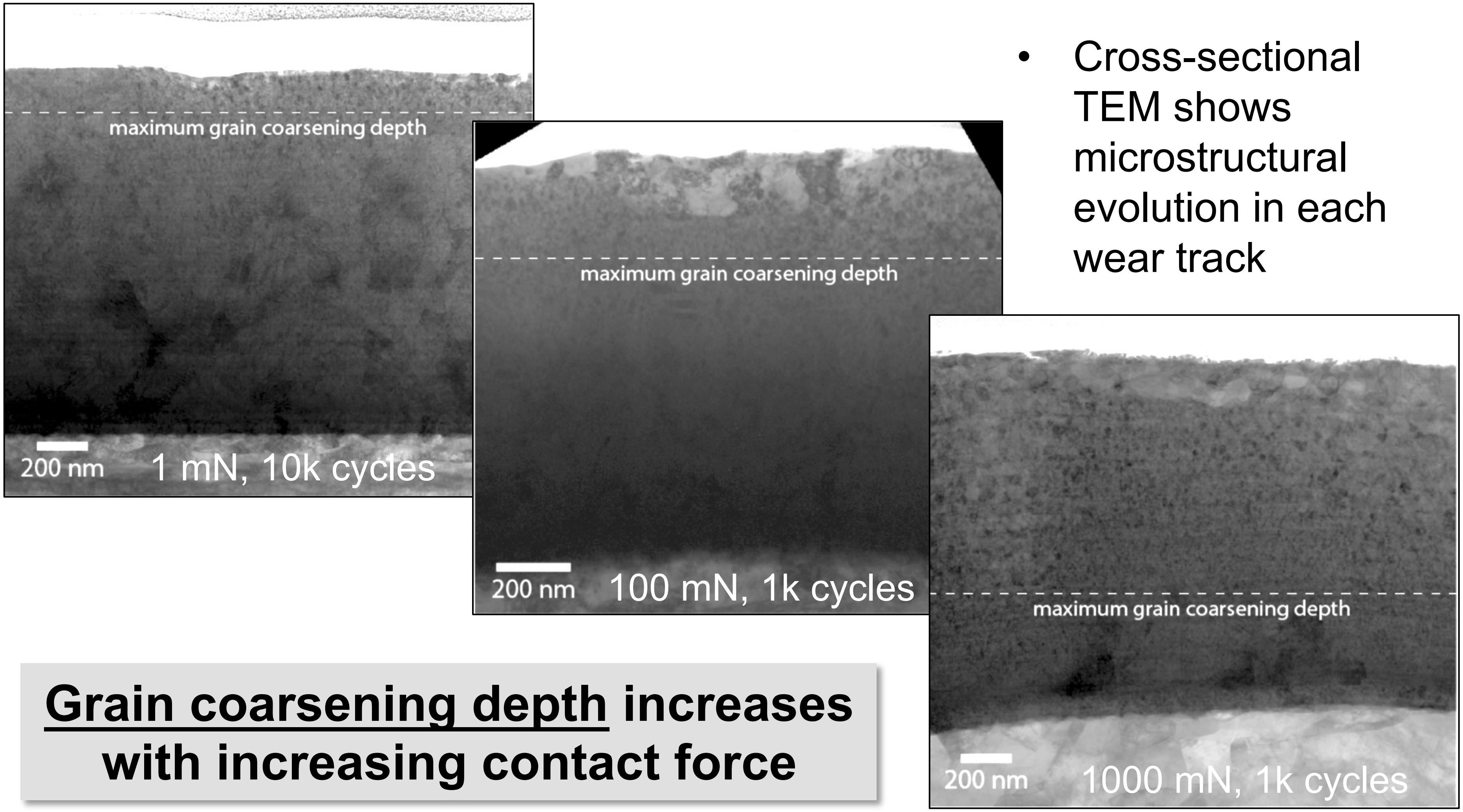
Friction Response as a Function of Contact Force for Ni-40W



- Friction coefficient low, 0.15-0.25, for first 100 cycles for all
- Transition to high friction, 0.5-0.6, for all but the 1 mN case

Argibay, Furnish, Boyce, Clark, and Chandross, Scripta Mat (2016).

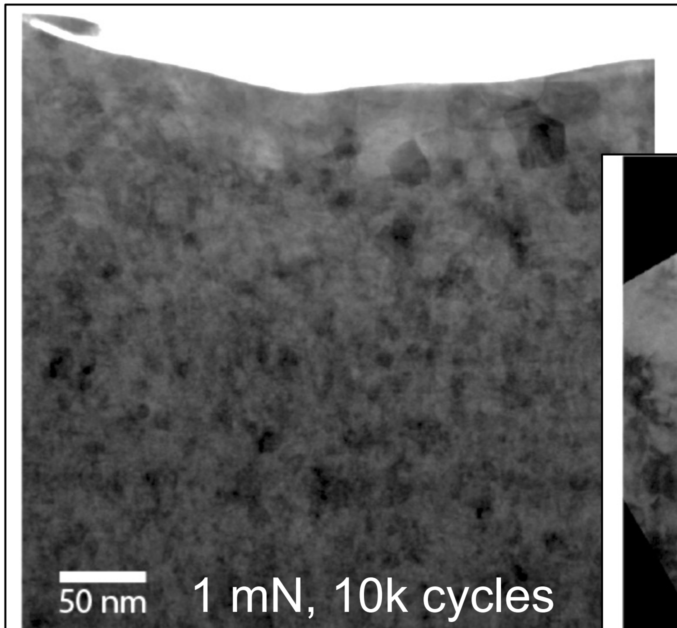
Microstructure in Ni-W Wear Tracks

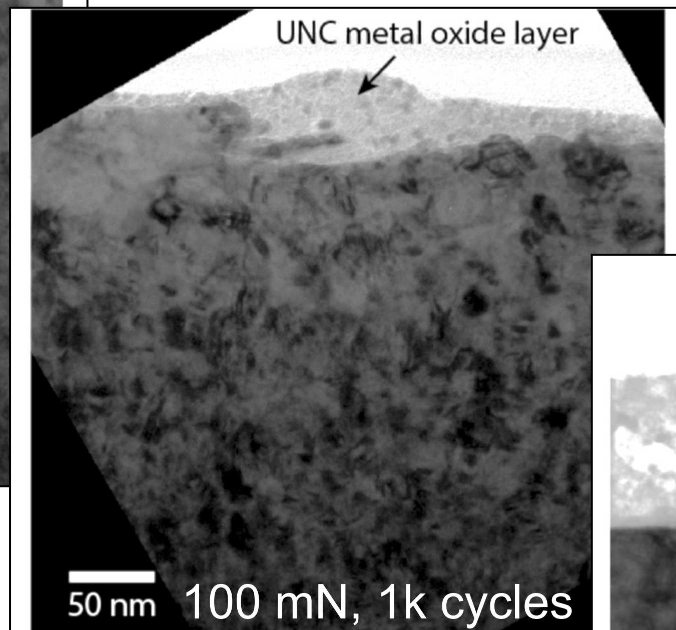


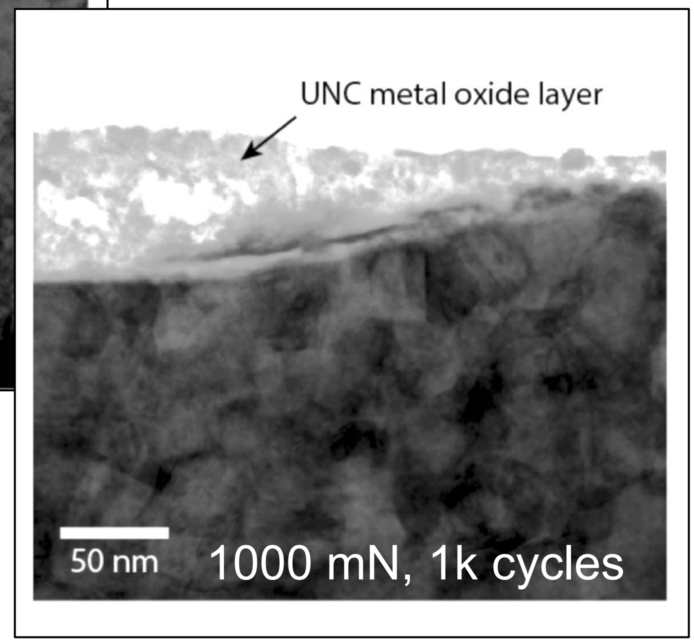
- Cross-sectional TEM shows microstructural evolution in each wear track

<u>Grain coarsening depth</u> increases with increasing contact force

Microstructure in Ni-W Wear Tracks





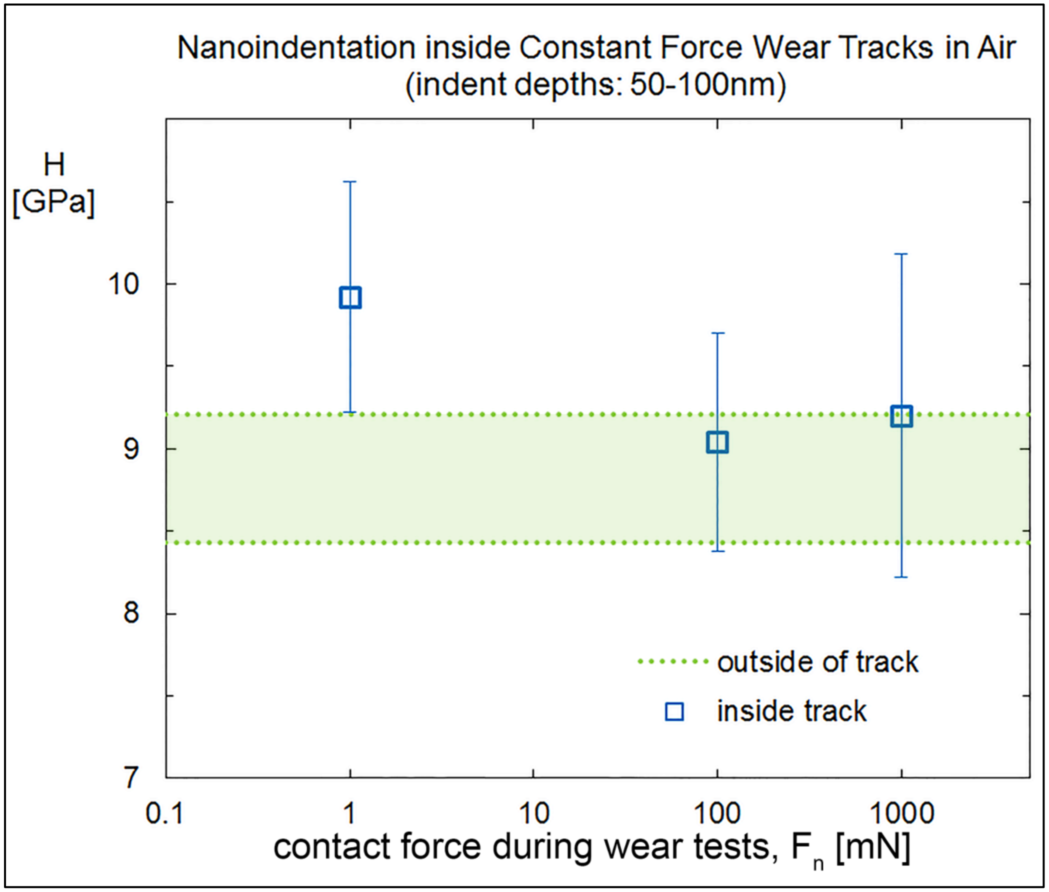


- Presence of metal oxide layer with increased wear

<u>Max grain size</u> increases with increasing contact force

Is the low friction hardness driven?

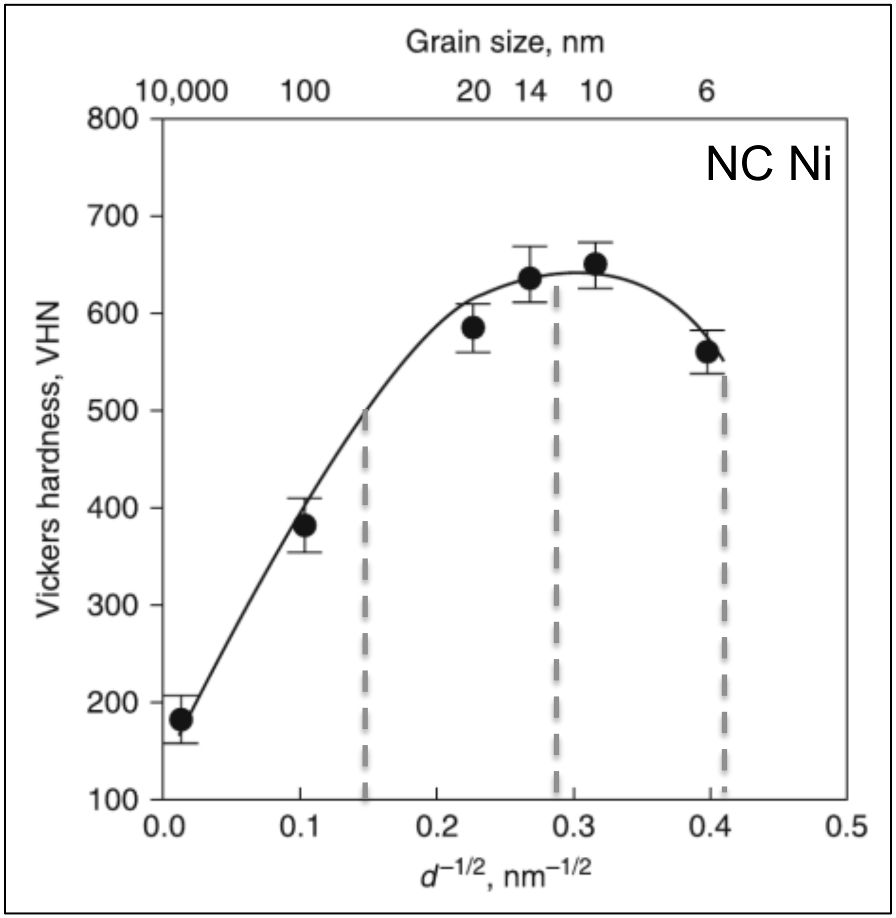
Increase in Hardness for 1mN Track

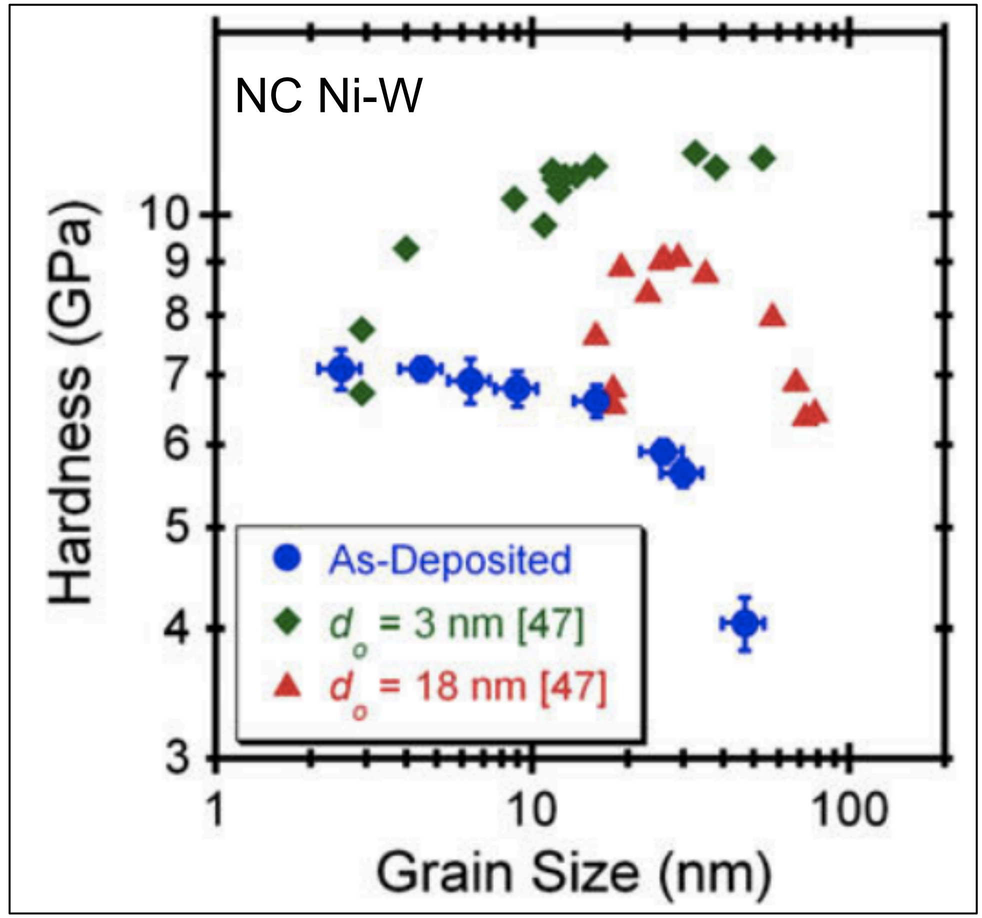


- Increase in hardness (13%) for 1 mN wear track
  - In comparison to higher force tests *and* to parent material
- Parent material
  ~ 5nm grains
- 100 and 1000 mN track
  ~ 50-100 nm grains
- 1 mN track
  - ~ 10-20 nm grains

Higher hardness in 1mN track consistent with low coefficient of friction – but why harder than as-dep'd?

Hardness for 1mN Track > As-Dep'd

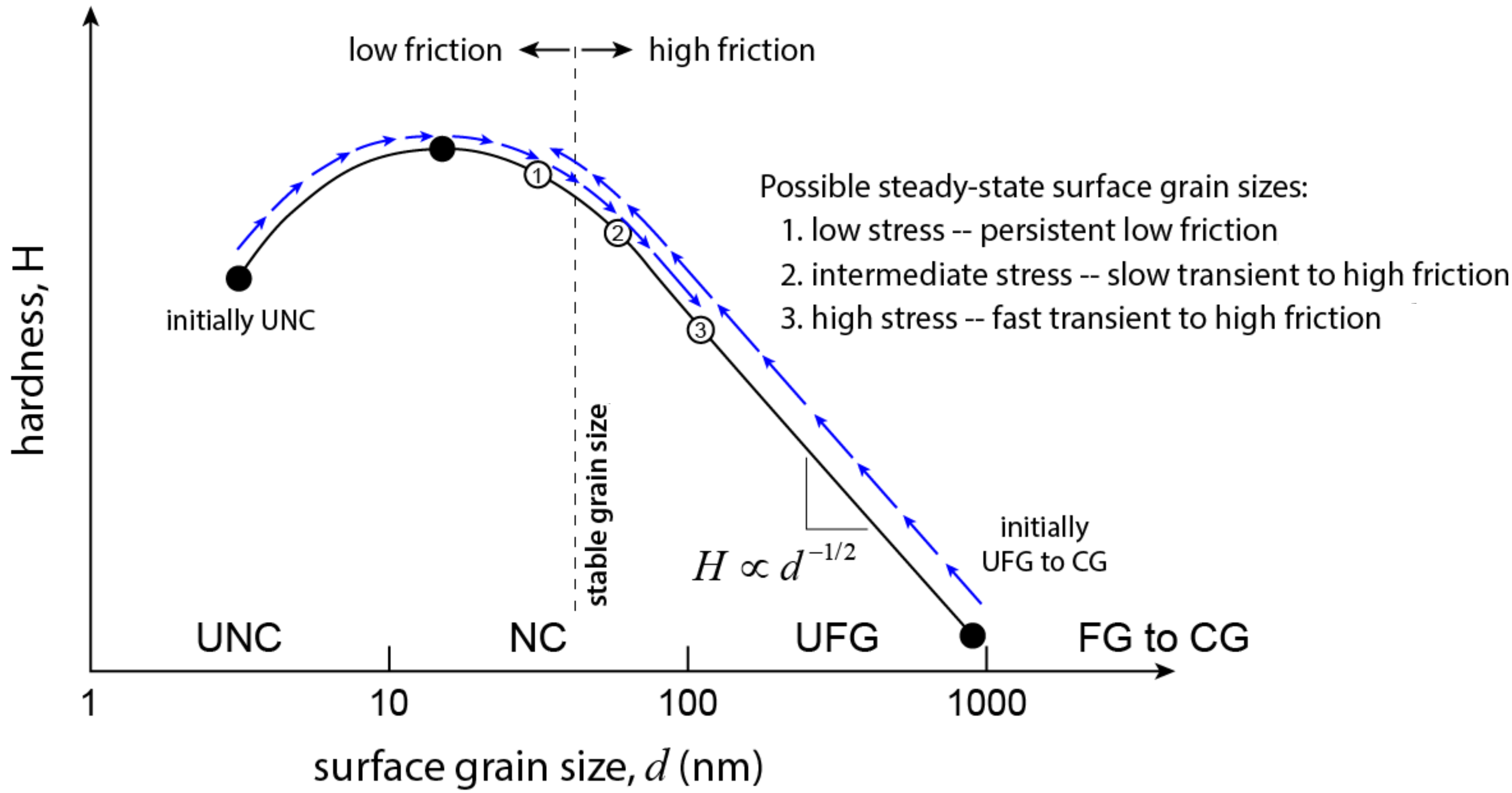




Higher hardness of evolved microstructure, compared to as-deposited microstructure, consistent with previous data

How to define a friction transition?

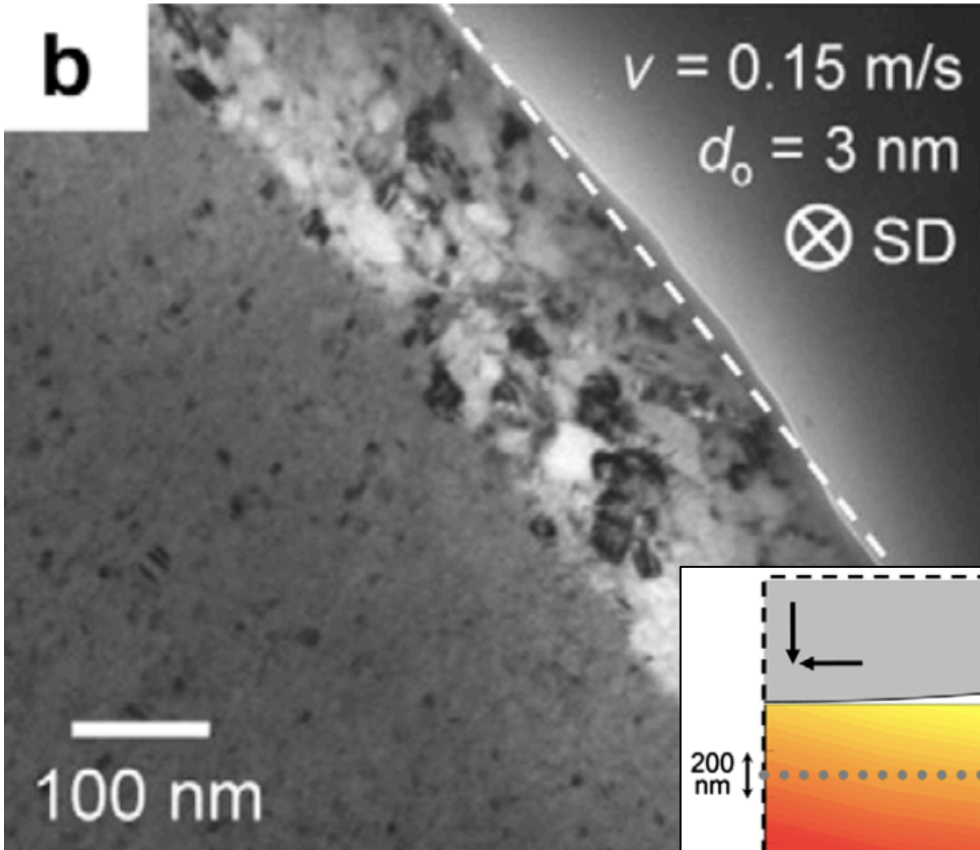
Stress-Dependent Stability?



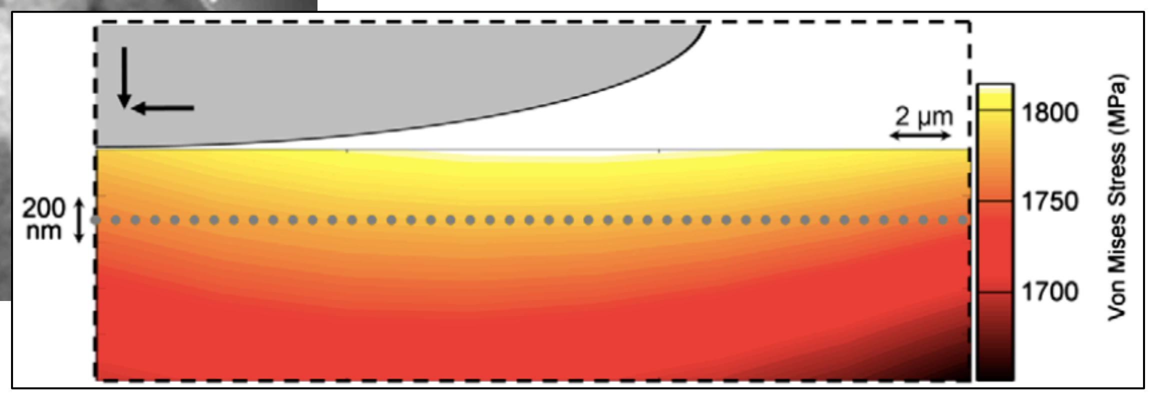
If true, then at the 'right' stress, you would drive ultra-NC material to be NC…and coarse grains to be NC!

Argibay, Furnish, Boyce, Clark, and Chandross, Scripta Mat (2016).

Evidence for Grain Coarsening under Wear

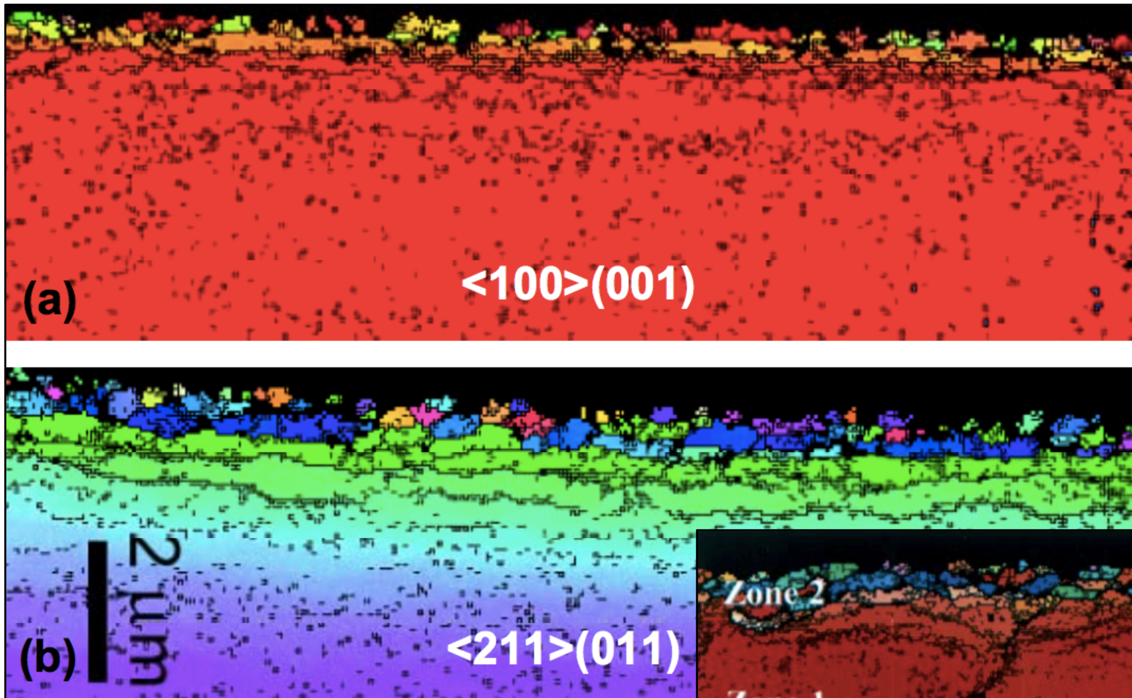


- Grain coarsening observed in previous study of Ni-W under sliding wear
- Coarsening depth correlated to depth of maximum von Mises stress

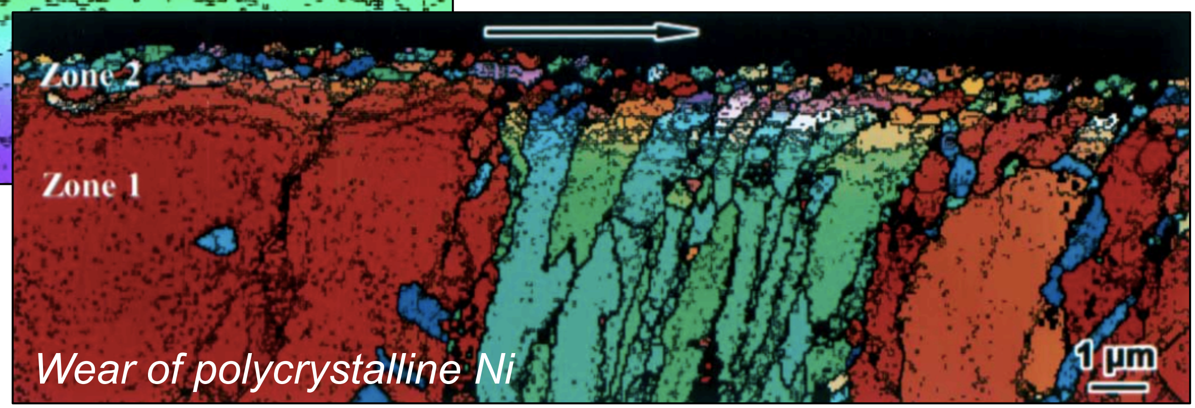


Stress-driven grain coarsening seems intuitive, but is grain *refinement* possible?

Evidence for Grain Refinement under Wear



Wear of single crystal Ni



Wear of polycrystalline Ni

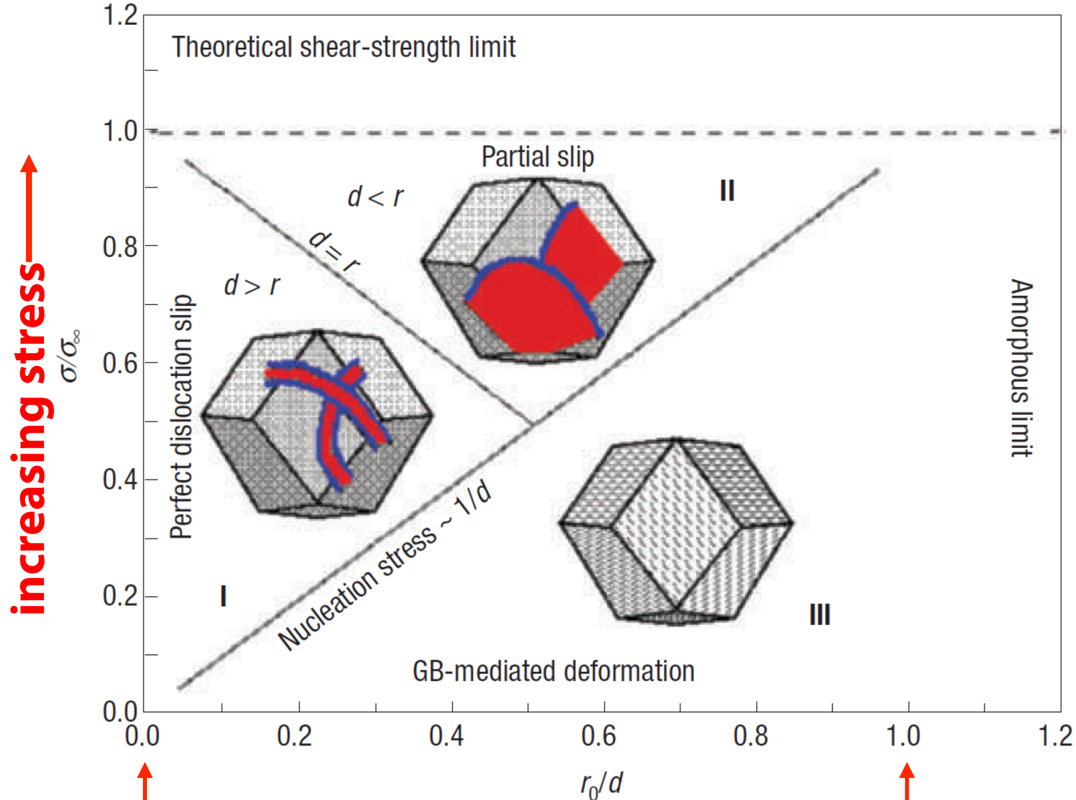
- Electron backscatter diffraction data of wear track cross-sections in Ni
- Grain refinement observed at wear track surface in both cases

Formation of ultrafine grains observed at wear track surfaces in single crystal and polycrystalline Ni

Prasad et al., Microscopy & Microanalysis (2008); Prasad, Michael, and Christenson, Scr. Mater (2003)

Can we Define a Stress-Dependent, Stable Grain Size under Wear?

Polycrystalline Plasticity Mechanisms



grain size goes to single crystal

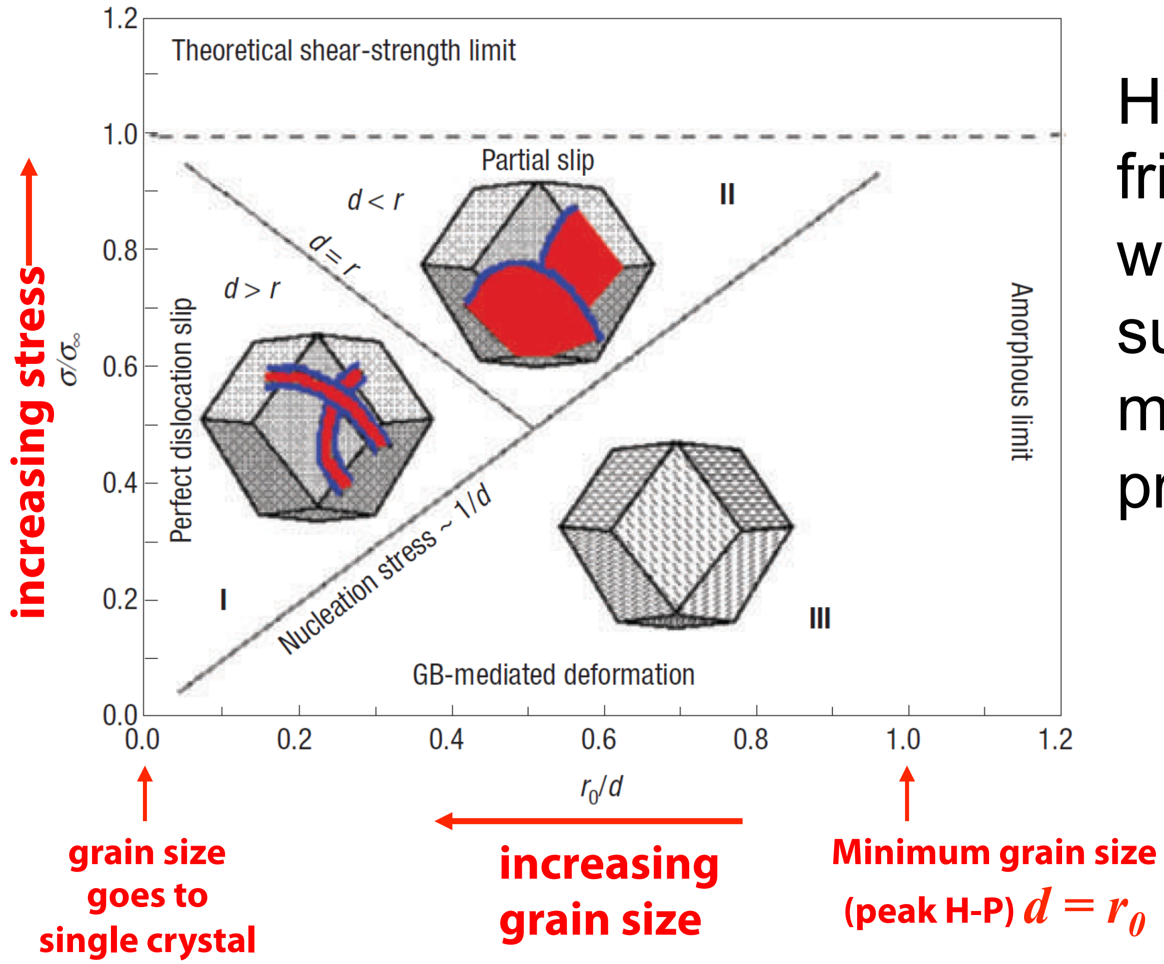
increasing grain size

Minimum grain size (peak H-P) $d = r_0$

Hypothesize that low friction stability occurs when microstructure supports grain boundary mediated deformation processes

Dominant plasticity mechanism linked to grain size AND stress

Polycrystalline Plasticity Mechanisms

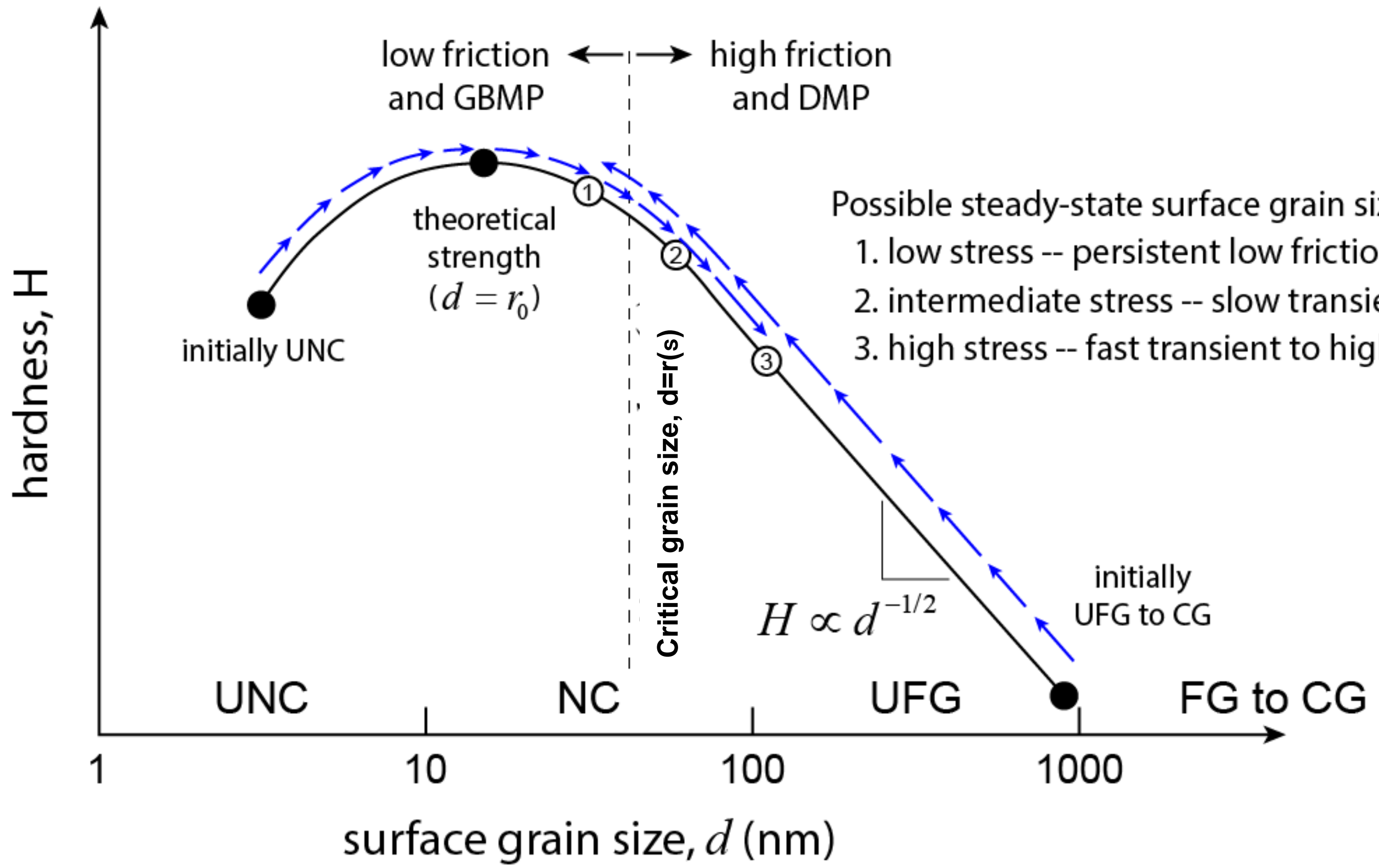


Hypothesize that low friction stability occurs when microstructure supports grain boundary mediated deformation processes

Dominant plasticity mechanism linked to grain size AND stress

Yamakov et al., Nat. Mat. (2004); Froseth et. al, Acta Mat. (2004).

Stress-Dependent Stable Grain Size



Critical grain size hypothesized to be equal to the stress-dependent dislocation splitting distance

Stress-Dependent Splitting Distance

Stress-dependent splitting distance:

$$r = \frac{r_0}{1 - \sigma_a / \sigma_\infty}$$

Equilibrium (zero stress) dislocation splitting distance:

$$r_0 = \frac{(2+\nu)Gb^2}{4\pi(1-\nu)\gamma_{sf}}$$

Theoretical strength (grain size where Hall-Petch reaches max):

$$\sigma_\infty = \frac{2\gamma_{sf}}{b}$$

- Function of zero-stress, equilibrium splitting distance, and the ratio of applied stress (to theoretical strength
- Aside from applied stress, all other parameters are materials dependent (G, b, v, SFE)

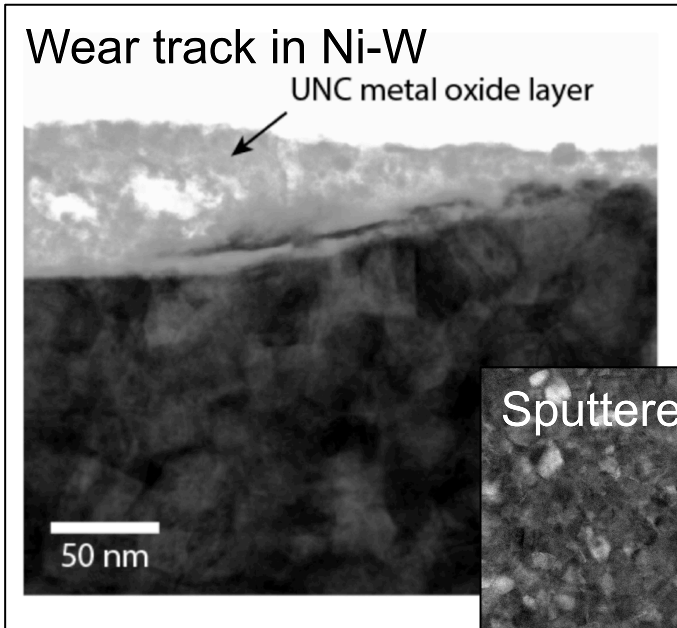
Hamiltonian applied stress (von Mises surface stress):

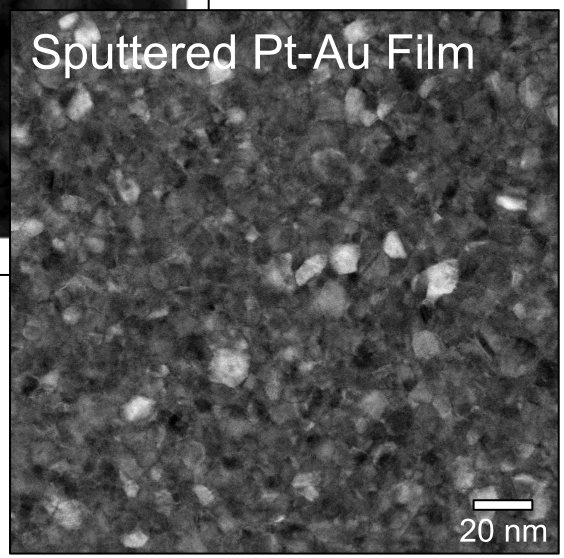
$$\sigma_\infty = \frac{3F_n}{2\pi a^2}\left[\frac{1-2\nu}{3} + \frac{(4+\nu)}{8}\pi\mu\right]$$

Normal forces during wear above 5-10 mN would drive evolution beyond critical 37 nm grain size in Ni-W, consistent with our data

Yamakov et al., Nat. Mat. (2004); Froseth et. al, Acta Mat. (2004).

Future Work: Isolate Solute Effects





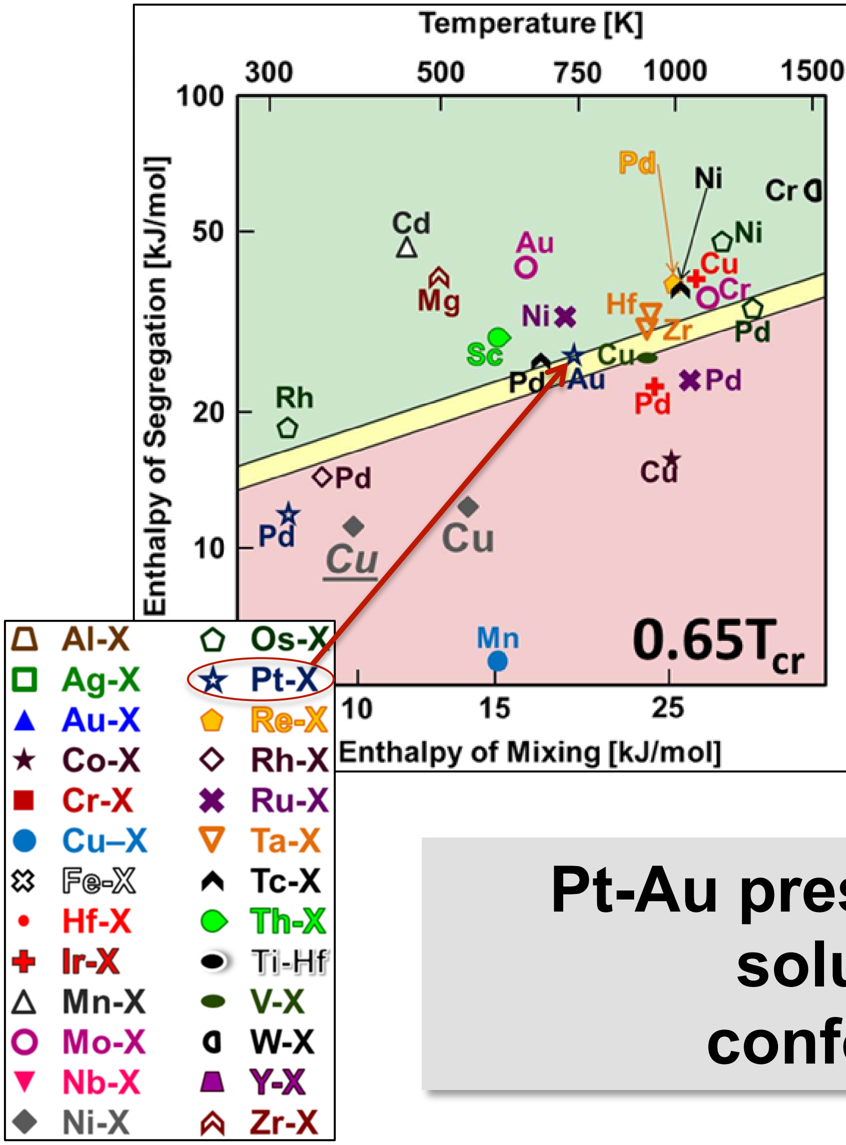
- Recall the surface oxide layer…
- Interested in better isolating the contribution of solute segregation on mechanical stability of NC alloys

- Pt-Au synthesis routes optimized
- As-deposited grain size of 5-6 nm

Studies in the noble metal binary system of Pt-Au are underway for thermal & mechanical stability

Selection of Pt-Au

Sandia National Laboratories



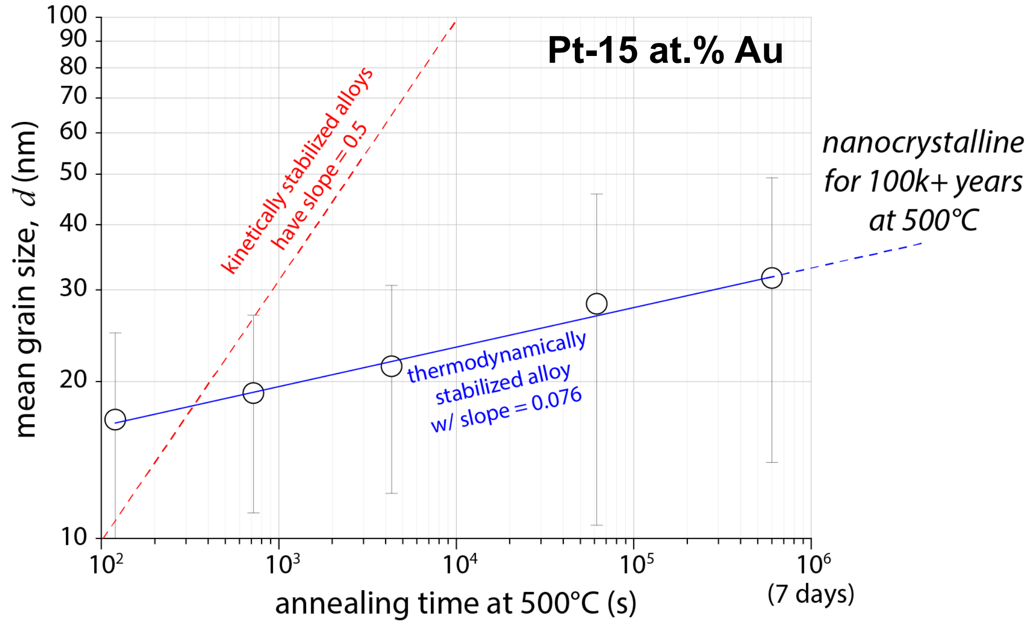
- Alloy selection driven by predictions of Murdoch & Schuh
- Wanted to avoid oxidation:
  - No oxidation in air
  - Chemically inert elements
- Pt-Au predicted to fall just at boundary of thermally-stable, solute stabilized region

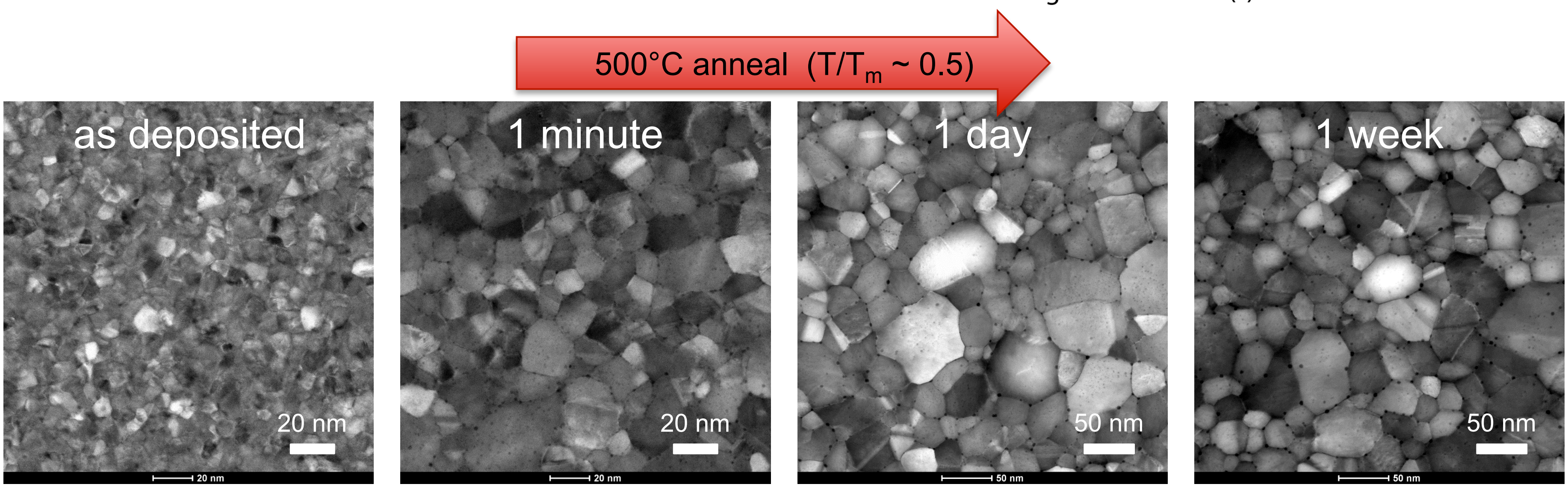
Pt-Au presents an opportunity to study solute segregation without confounding effects of oxide

Evidence of Thermodynamic Stability

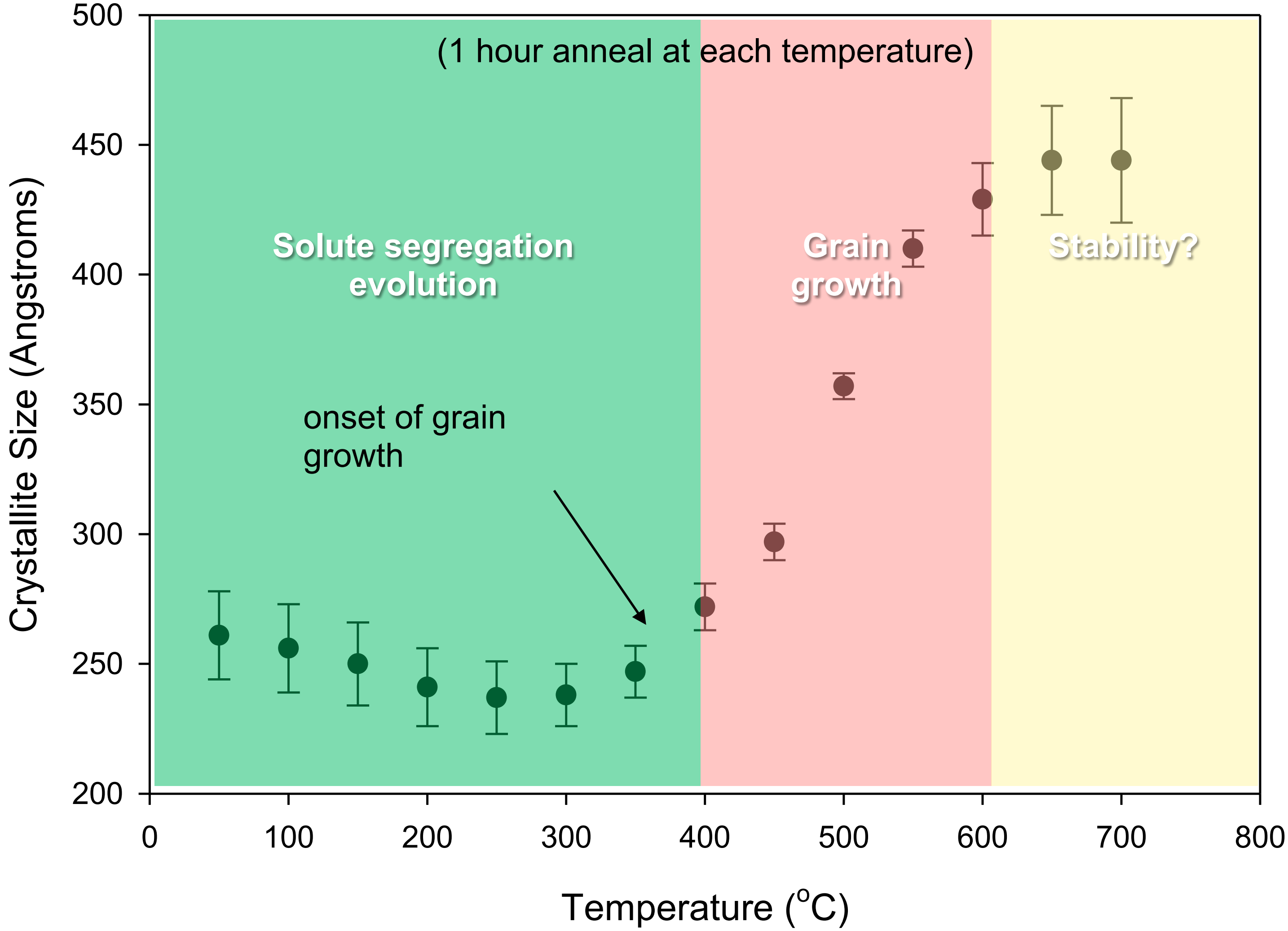
Sandia National Laboratories

- Constant temperature interrupted TEM annealing at 500°C, free-standing sputtered **Pt -15 at.% Au** films lifted from salt crystals
- Abnormal grain growth observed
- Grain growth trend does not follow time$^{1/2}$ trend (characteristic of kinetic stabilized alloys)

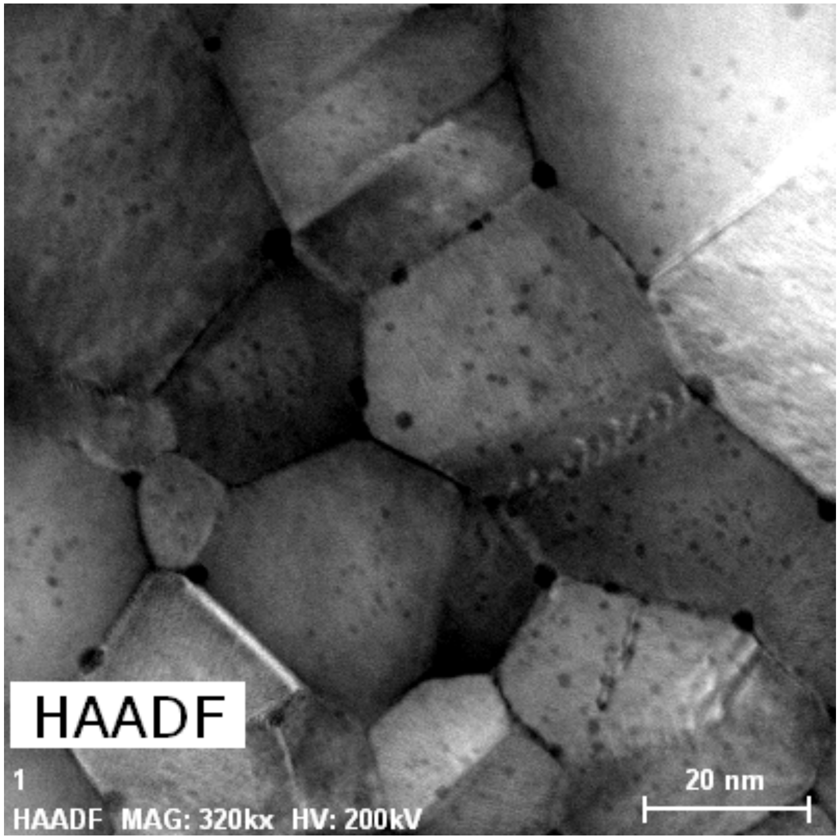


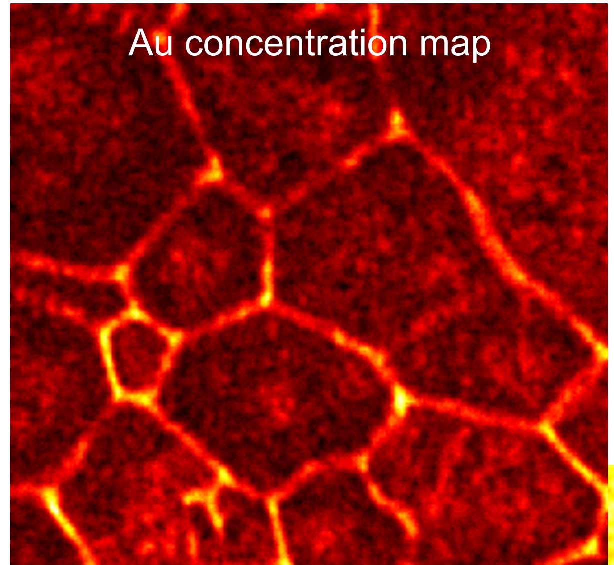


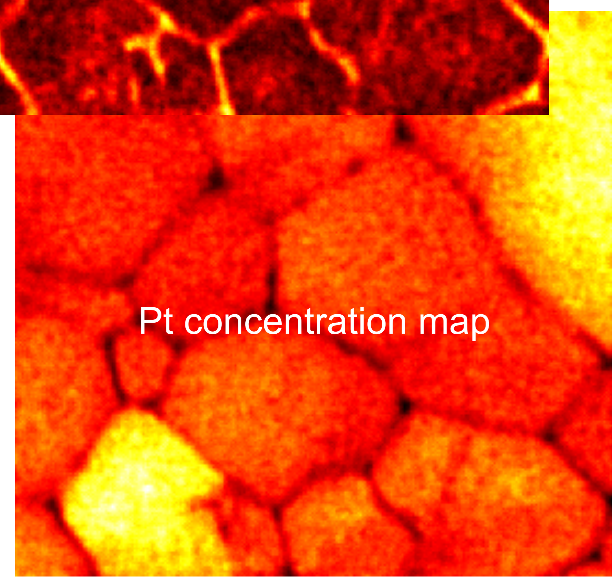
Evolution of 10 um thick Pt-Au Films



Preferential Segregation of Au at Triple Junctions



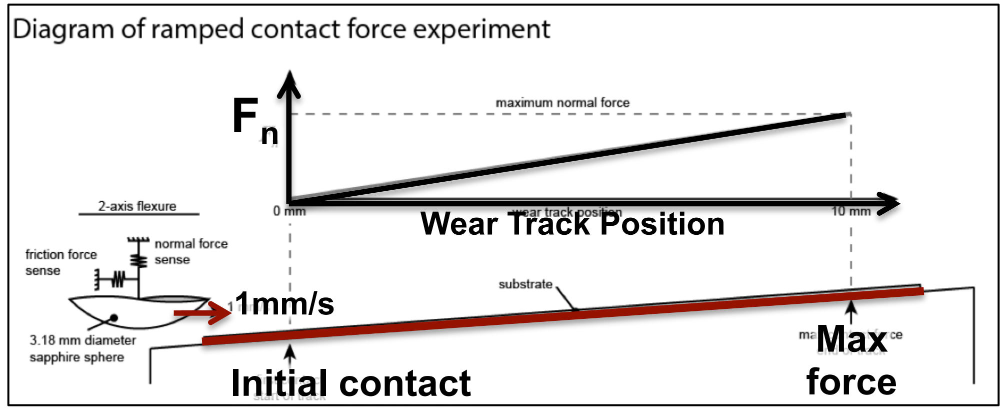




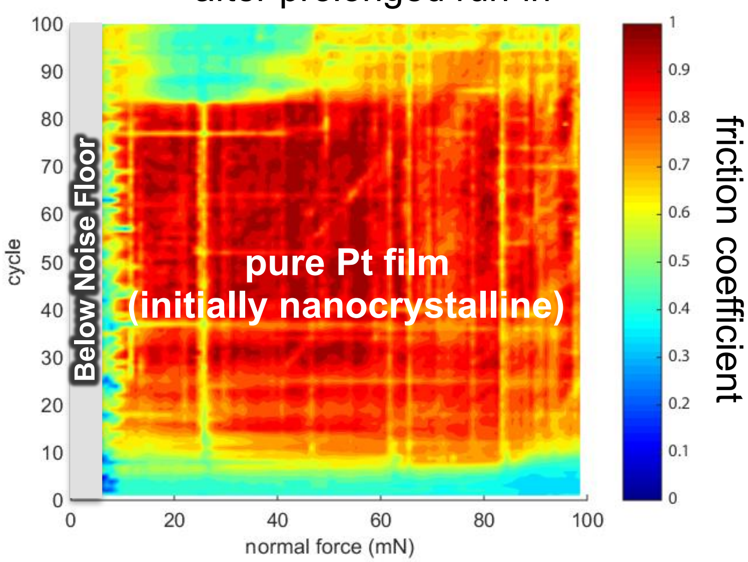
Tribological Testing – Evidence of Mech. Stability

(Right) Contact force is ramped along the length of the wear track with continuous friction measurement:

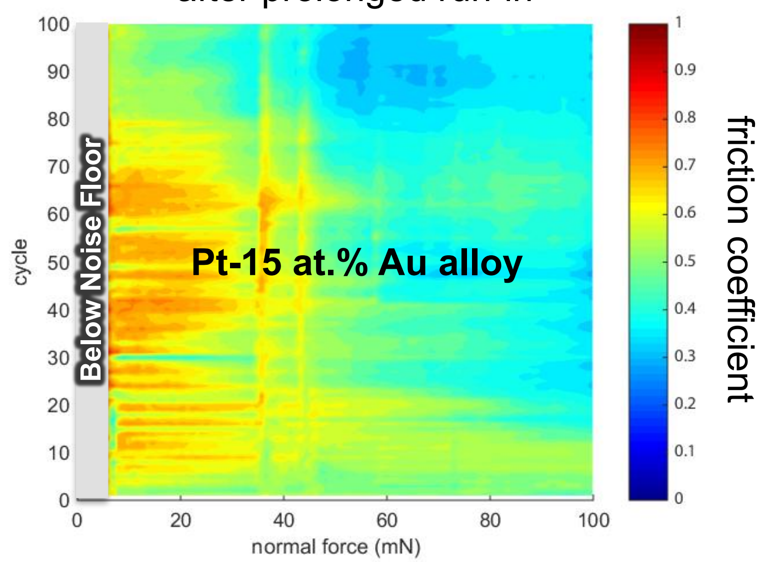
(Below) Using a Au-alloy tip rastered on pure and alloyed Pt we measure the following friction data:



high friction (> 0.8)
after prolonged run-in



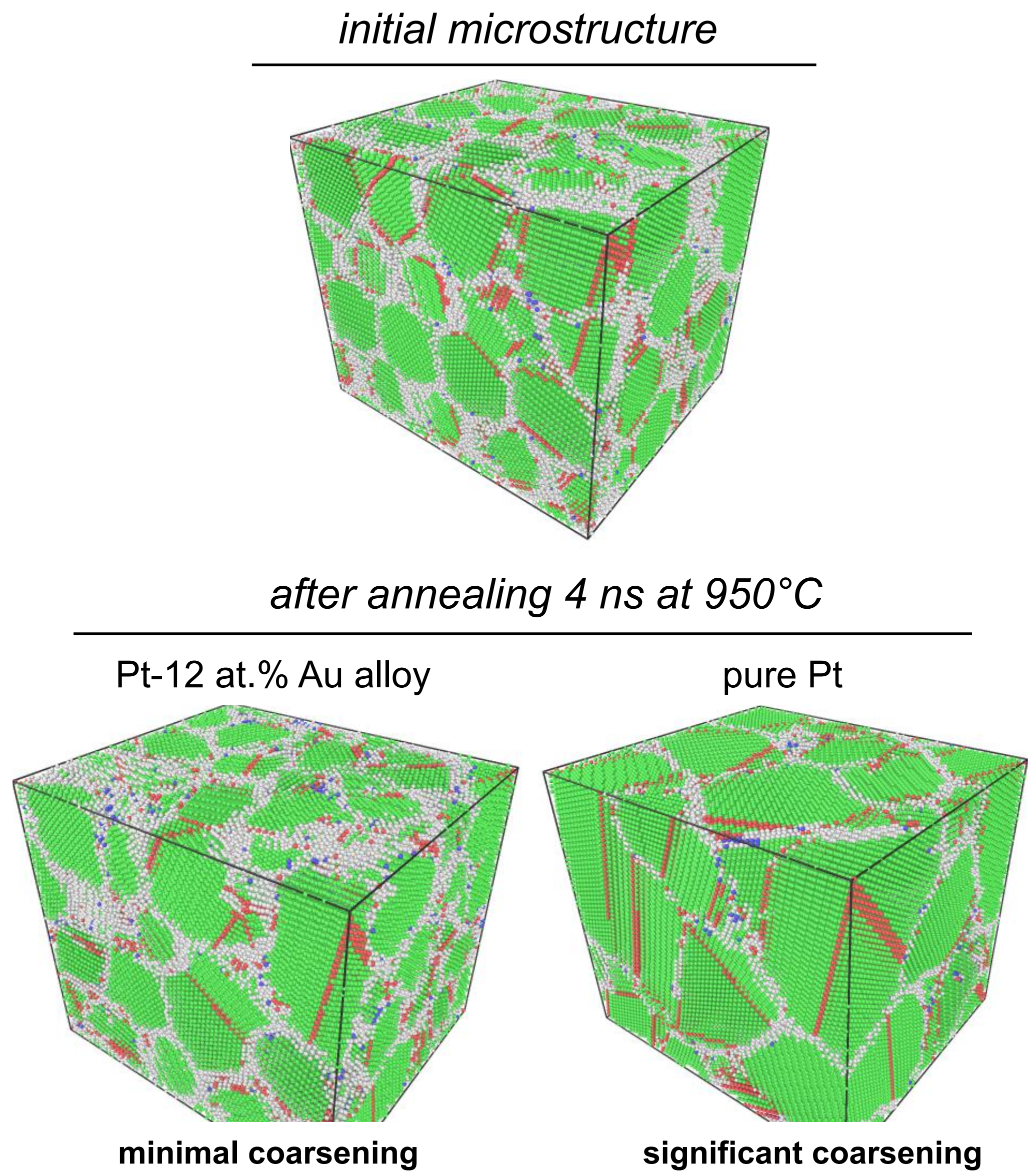
low friction (< 0.3)
after prolonged run-in



Pt-Au films showed low friction & negligible wear

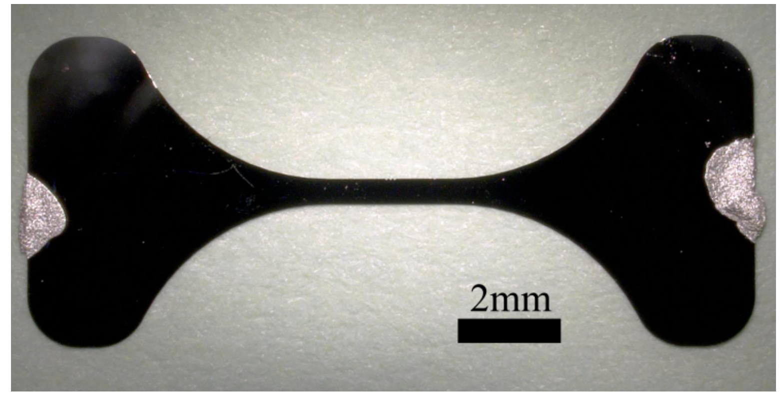
MD Supports Shows High Thermal Stability

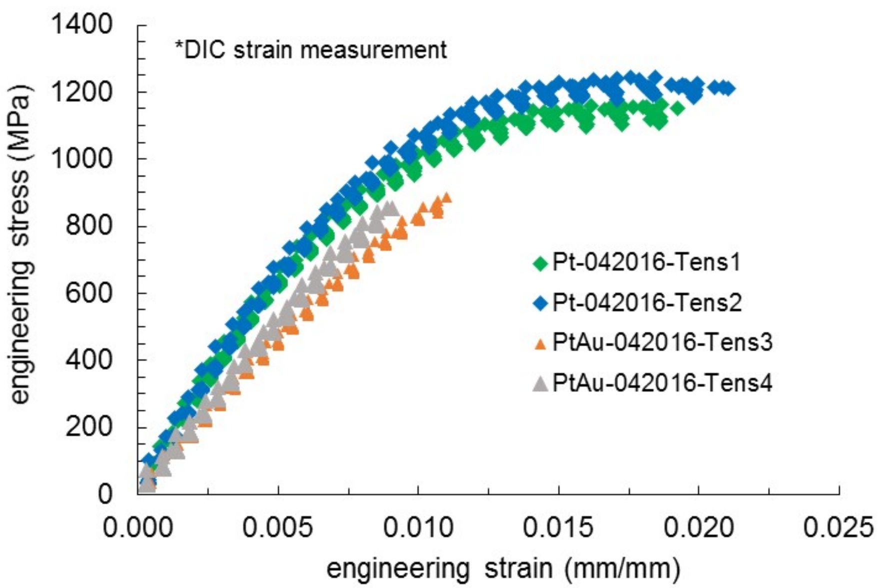
- Potentials for Pt-Au completed and vetted, results shown here – Pt-Au is highly stable, little change in microstructure
- Pt-Pd potentials completed, no preliminary data yet
- Pure Pt shows significant grain coarsening
- Capability to investigate stress-induced grain growth via MD has been developed

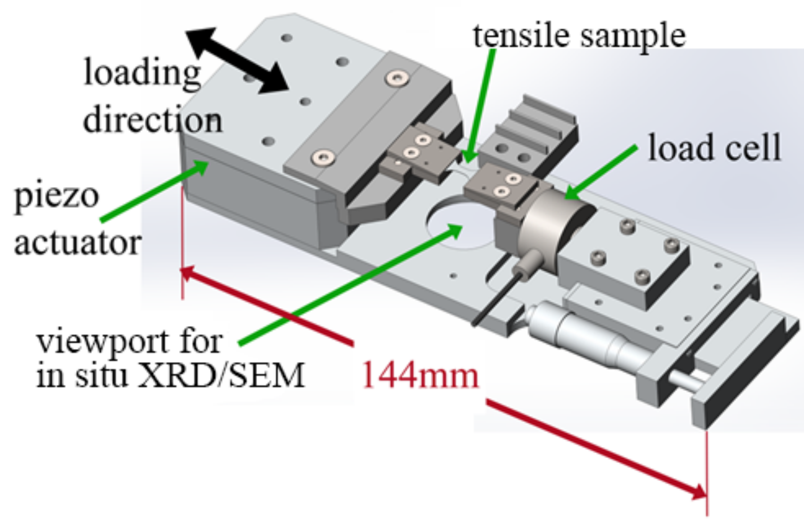


Tensile Testing Underway – Preliminary Data Here

- Developed method for fabricating free-standing “thin film dogbones” (10 μm thick) via laser cutting of sputtered films
- Micro-tensile fatigue tests underway







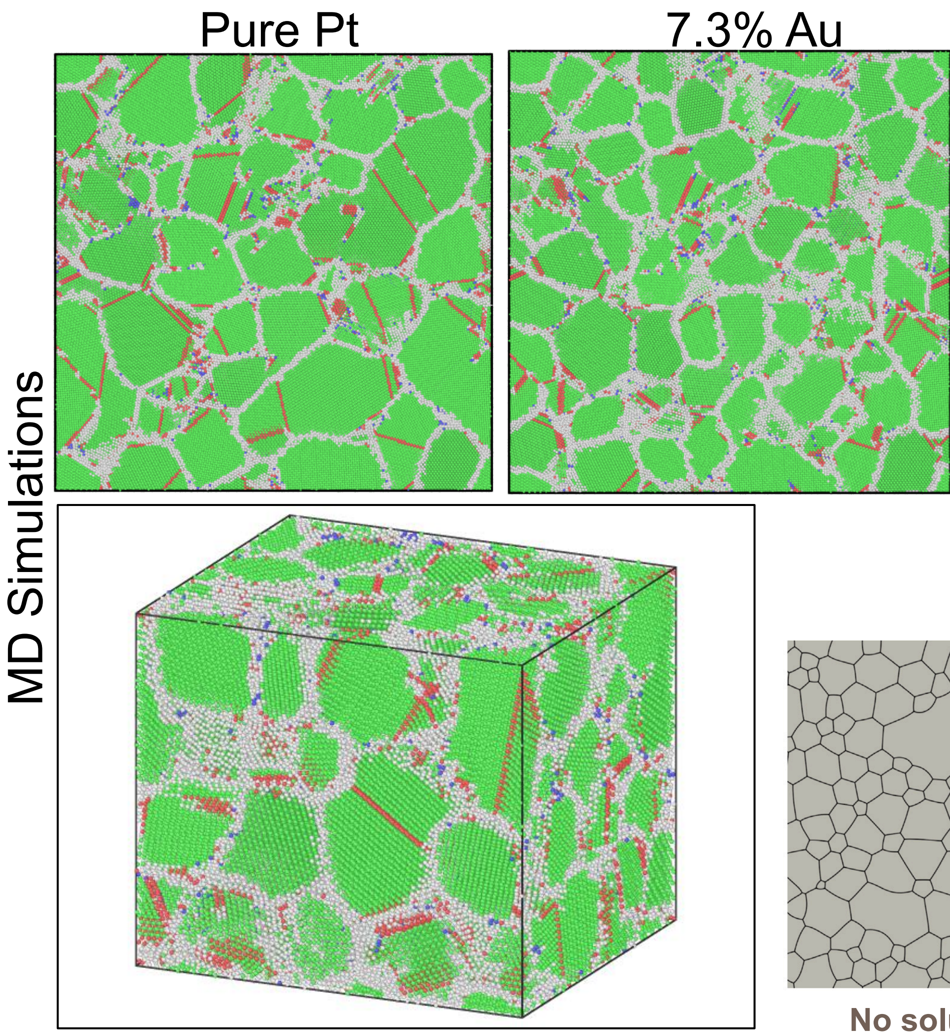
Summary

- Microstructural stability of Ni-W studied under sliding wear over a range of contact forces and cycles
  - Significant grain coarsening observed for 100 and 1000 mN, transition to high friction in 100s of cycles
  - Minimal grain coarsening for 1 mN, measured hardness increase and no transition to high friction to *10000* cycles
- Proposed presence of a stress-dependent stable grain size in nanocrystalline alloys under wear
  - Hypothesize low friction, stable microstructure in grain-boundary mediated plasticity regime
  - Potentially related to dislocation splitting distance
- Future work underway to:
  - Isolate solute segregation effects
  - Develop predictive framework for mechanical stability

Does Thermal Stability Lead to Stability under Wear?

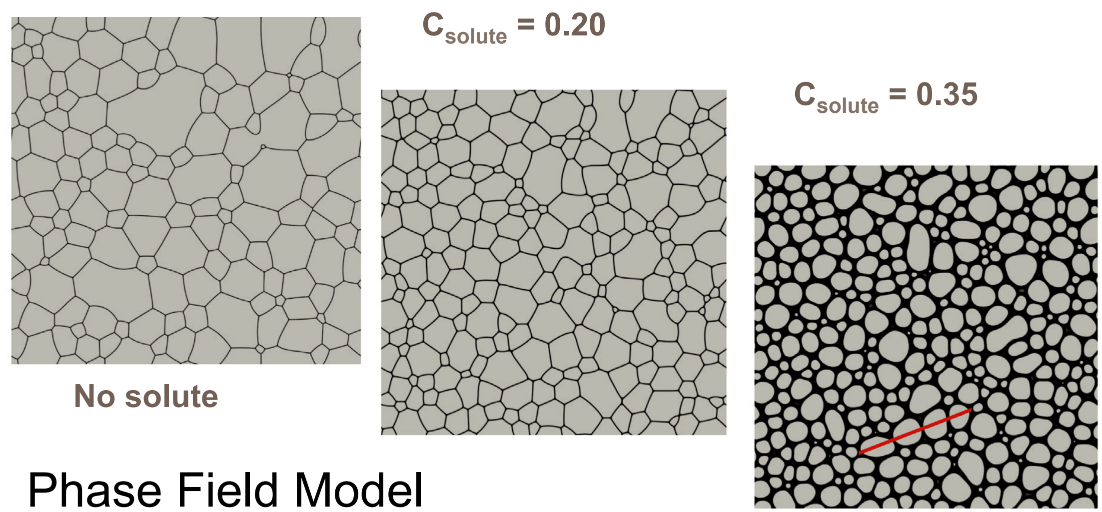
What Do We Know about Stability of Nanograins under Wear Anyway?

Future Work: Pair with Modeling



Combining experiments with modeling to further explore:

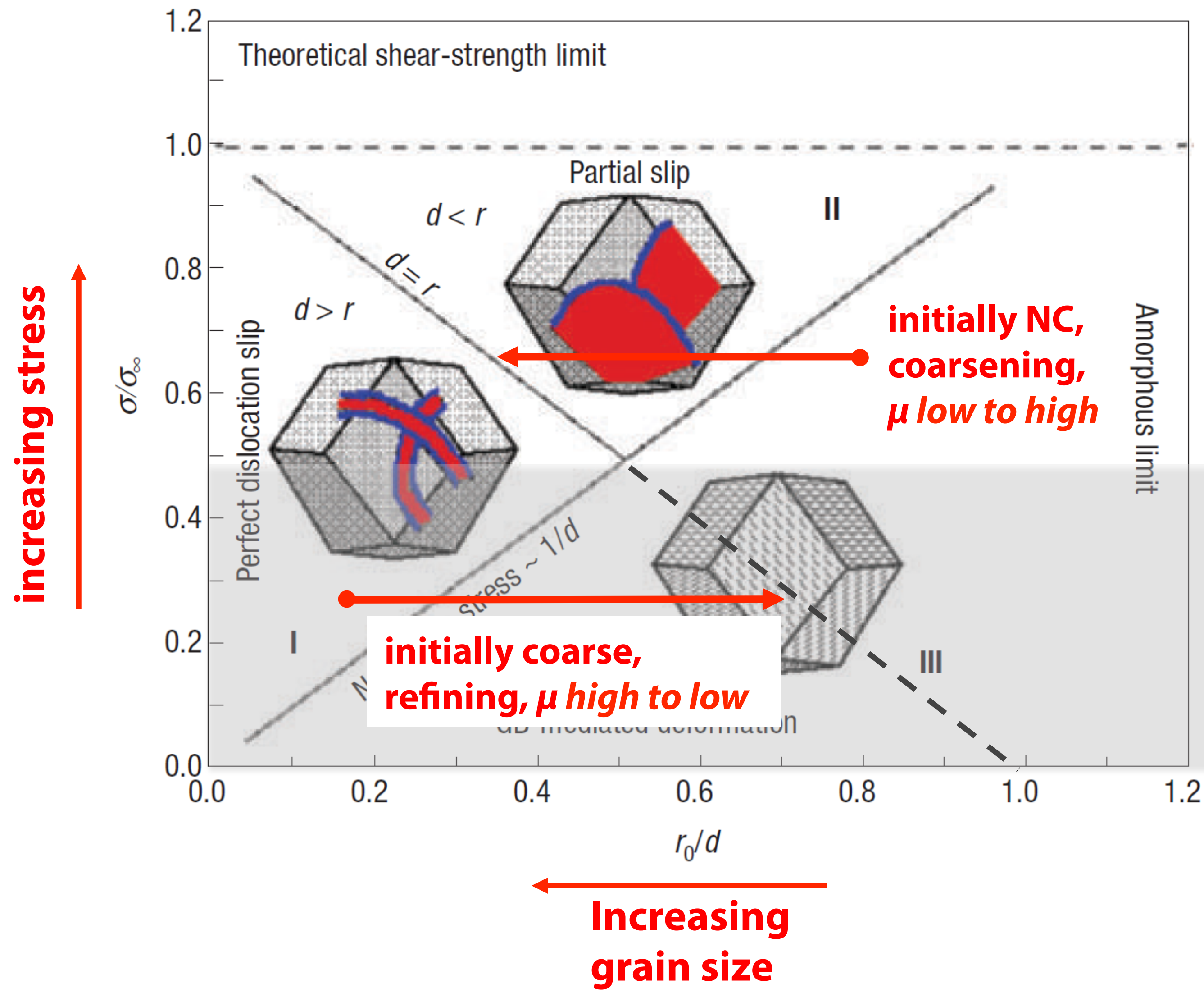
- Role of solute segregation in determining stability
- Competition between thermodynamics and kinetics
- Contributions of other variables (e.g. boundary type, film stress)



Phase Field Model

S. Foiles, unpublished. M. Chandross, unpublished.; F. Abdeljawad, unpublished.

Consider Stability



Low friction response would be expected for stresses in this grain boundary-mediated plasticity range

Yamakov et al., Nat. Mat. (2004)