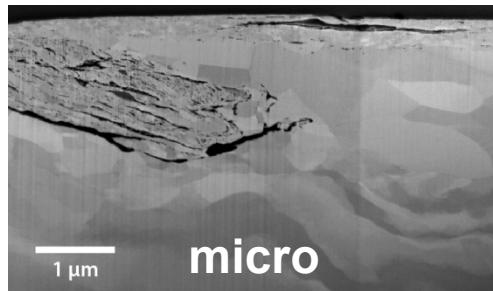
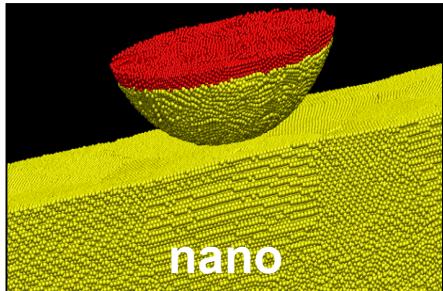


Pushing the Performance Limits of Electrical Contact Materials

Connecting Nano to Macro

Nicolas Argibay, Michael E. Chandross, Blythe G. Clark,
Michael T. Dugger and Somuri V. Prasad

*Materials Science and Engineering Center
Sandia National Laboratories
Albuquerque NM USA*



Sandia National Laboratories



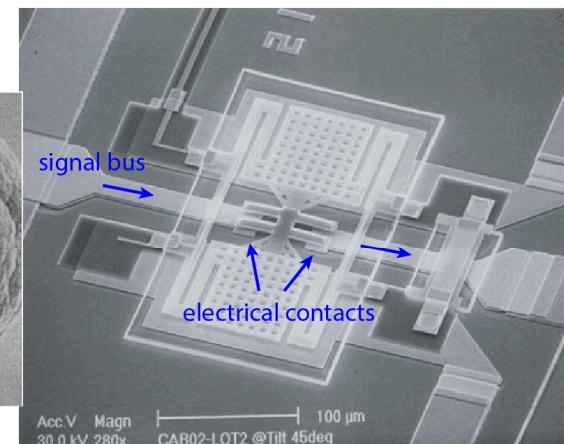
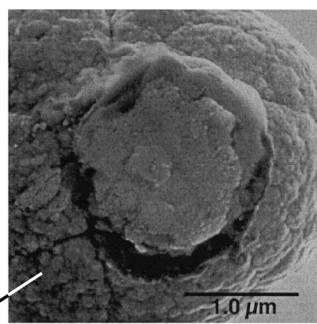
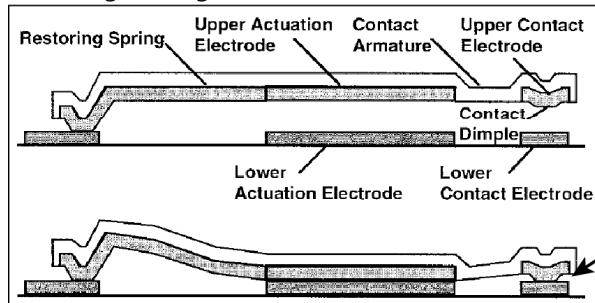
**U.S. DEPARTMENT OF
ENERGY**

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Metals are widely used tribological materials – electrical contacts

RF Micro Electromechanical Systems (MEMS)

switching GHz signals

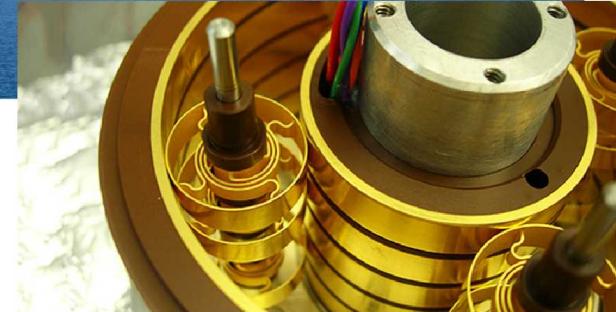


Source: D. Hyman and M. Mehregany, IEEE Trans. & Pack. Tech. 22-3, 1999

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



Aerospace and Energy



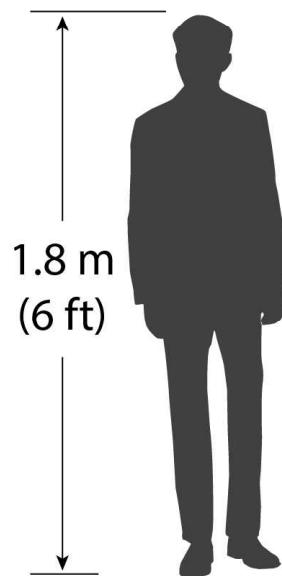
Source: Honeybee Robotics (<http://www.honeybeerobotics.com/portfolio/rolling-contact-connector/>)

The Gold Standard... how much gold you may ask? TONS per year

An estimated **300 metric tons/year** of gold used in electronics related applications, most of it in electroplated connectors and contacts (**11% of yearly amount mined**)

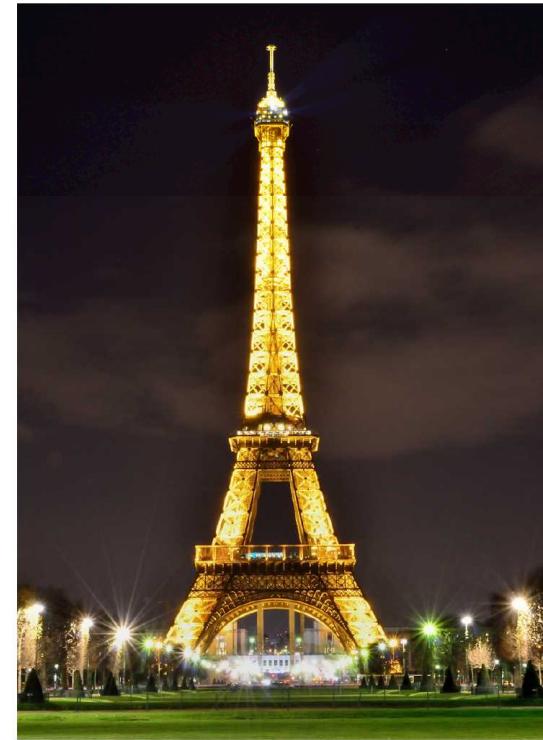
Equivalent to a cube comprised of ~25,000 standard gold bars (12 kg/26.4 lb each)...

2.6 m (8.5 ft) wide



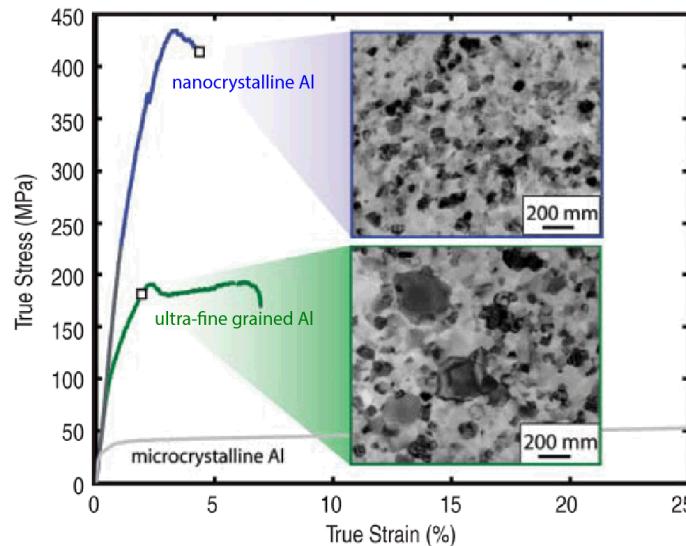
Reference: Gold Survey, Gold Fields Mineral Services Ltd., 2010

... or enough to clad the surface of the Eiffel Tower with 70 μm of pure gold *every year*

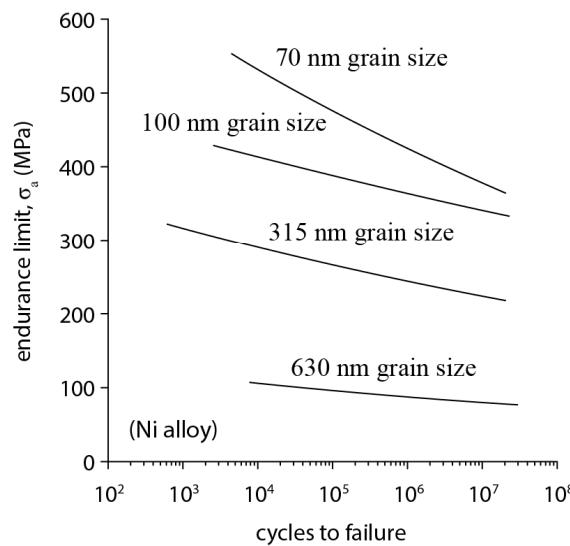


Engineering advantages of nanocrystalline (NC) alloys and metal-matrix composites

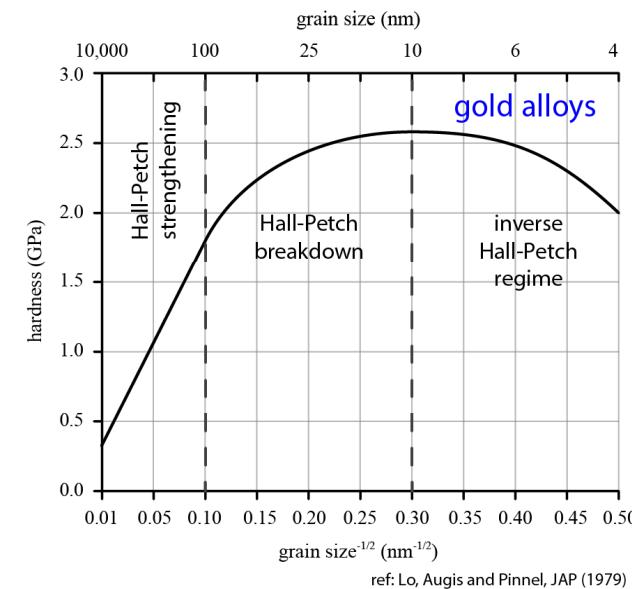
higher yield strength



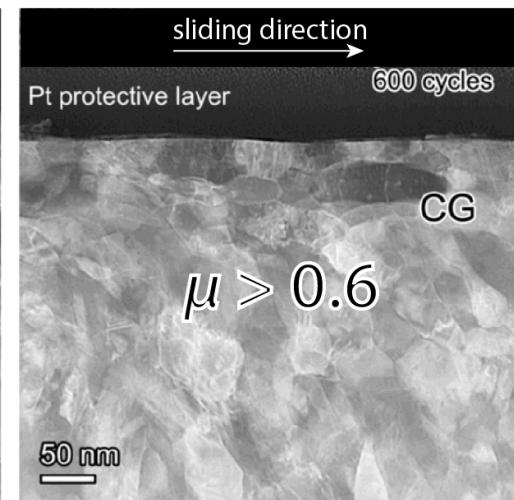
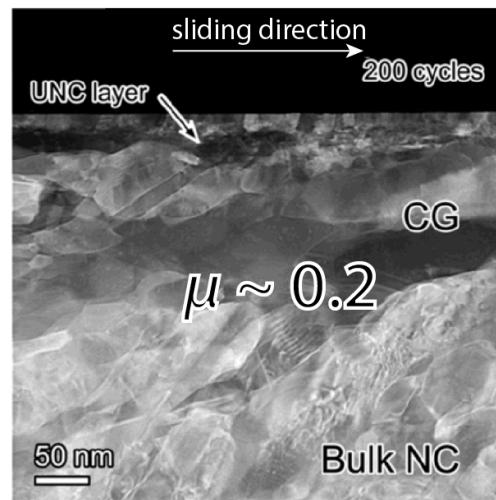
higher fatigue strength (endurance limit)



higher hardness



lower friction and wear rates -- *but why?*

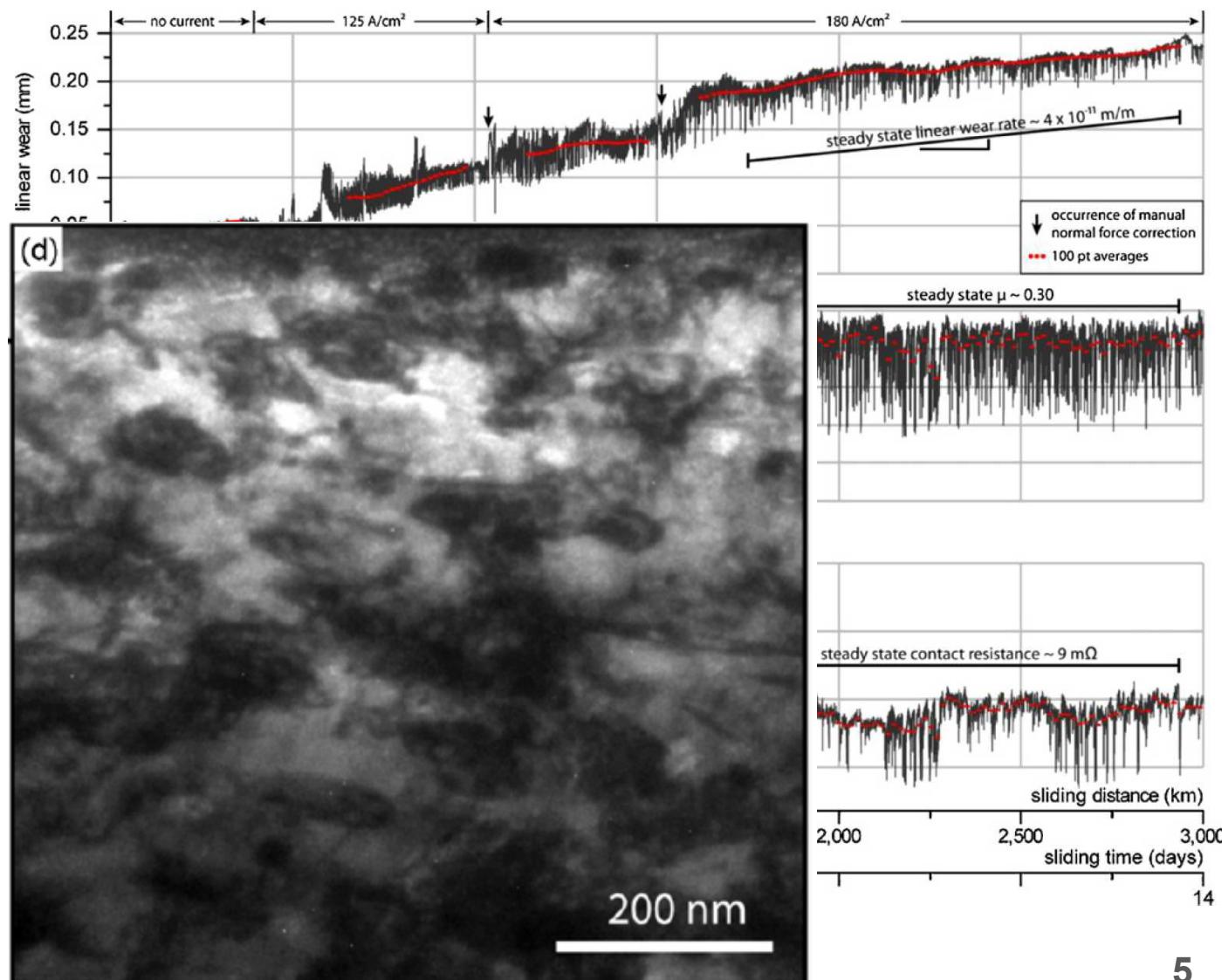


steady-state cross-sections of wear tracks

Low friction linked to nanocrystalline surface grain size – even with pure metals



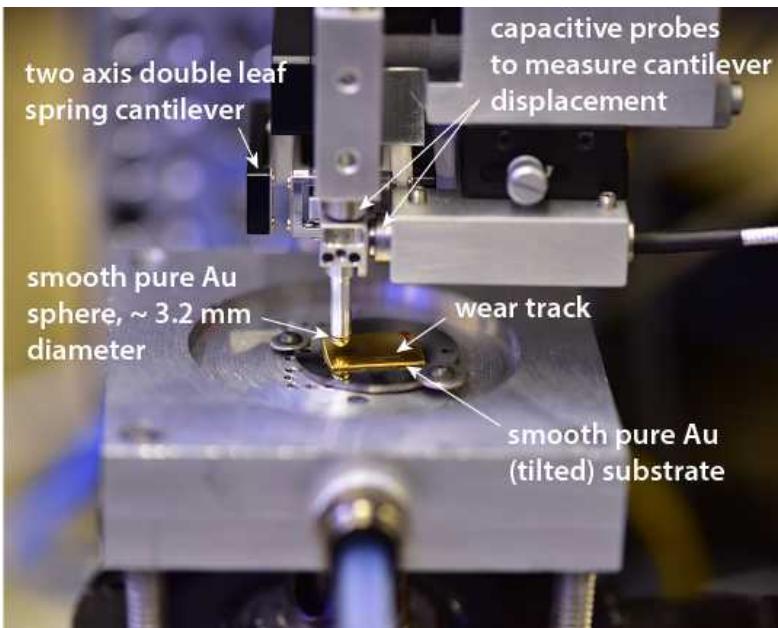
wear rate of $\sim 1 \text{ nm per kilometer}$
 $\mu_{ss} \sim 0.3$



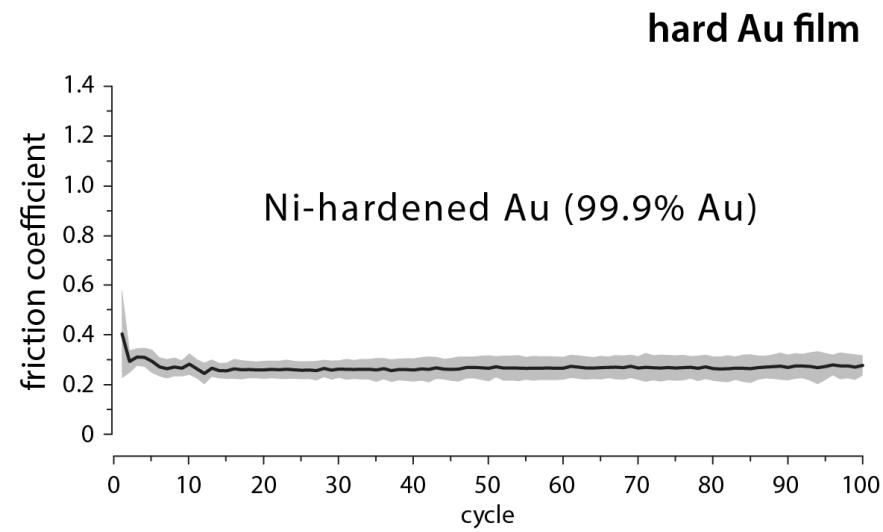
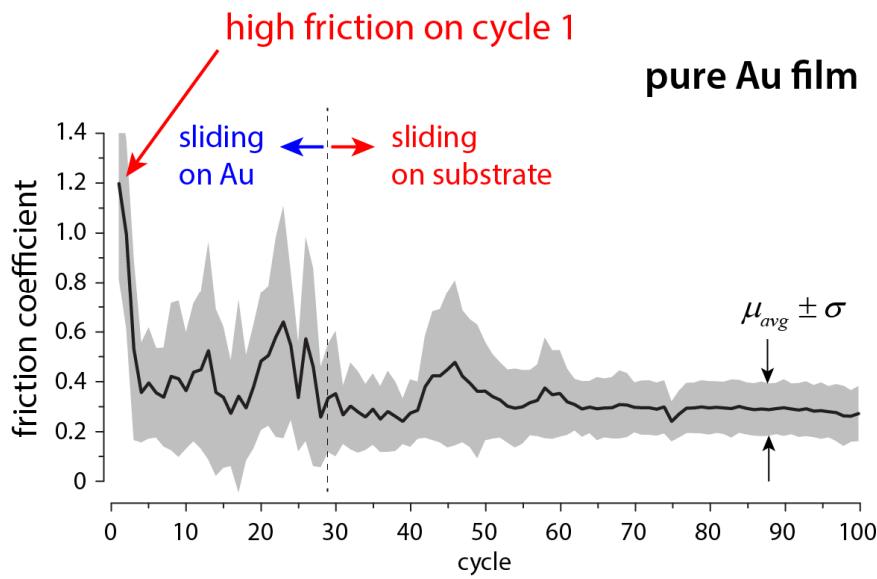
Low friction
associated with
nanocrystalline
surface for a Cu-Cu
system

ref: Argibay et al., Wear 2010

Example of **low friction** with unlubricated metal contacts – Hard Au vs Pure Au

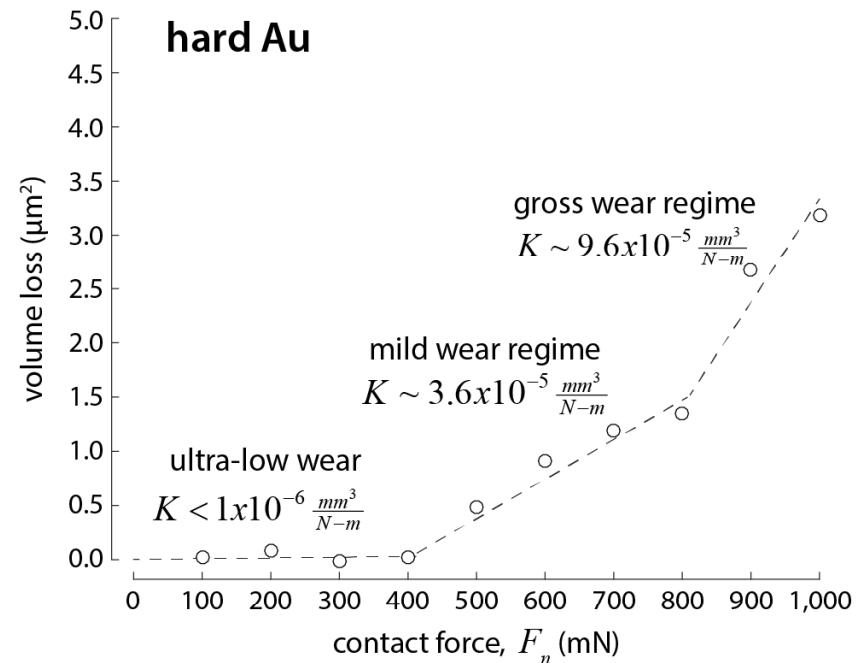
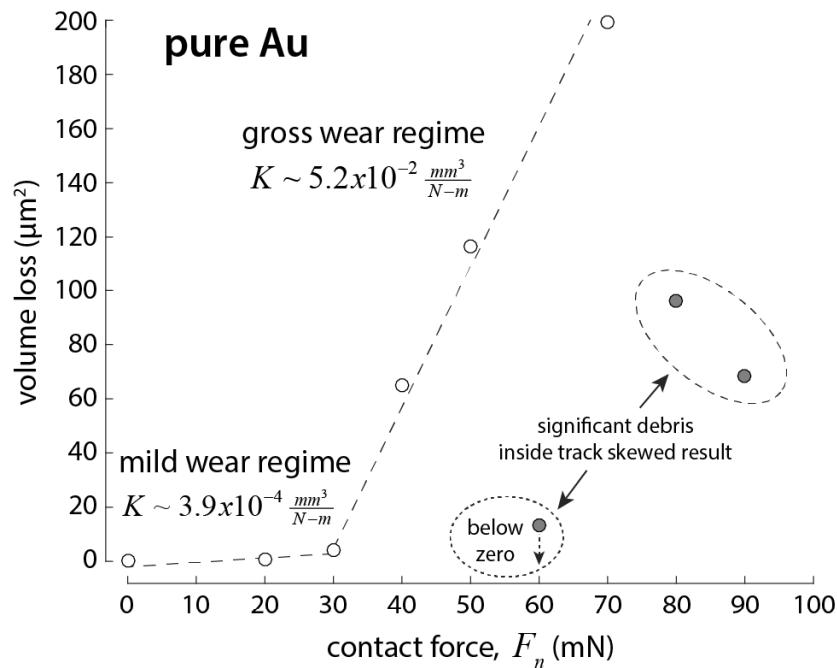


normal force = 100 mN
ball radius = 1.6 mm
speed = 1 mm/s



Example of **low wear** with unlubricated metal contacts – Hard Au vs Pure Au

Note x- and y-axis scale difference!

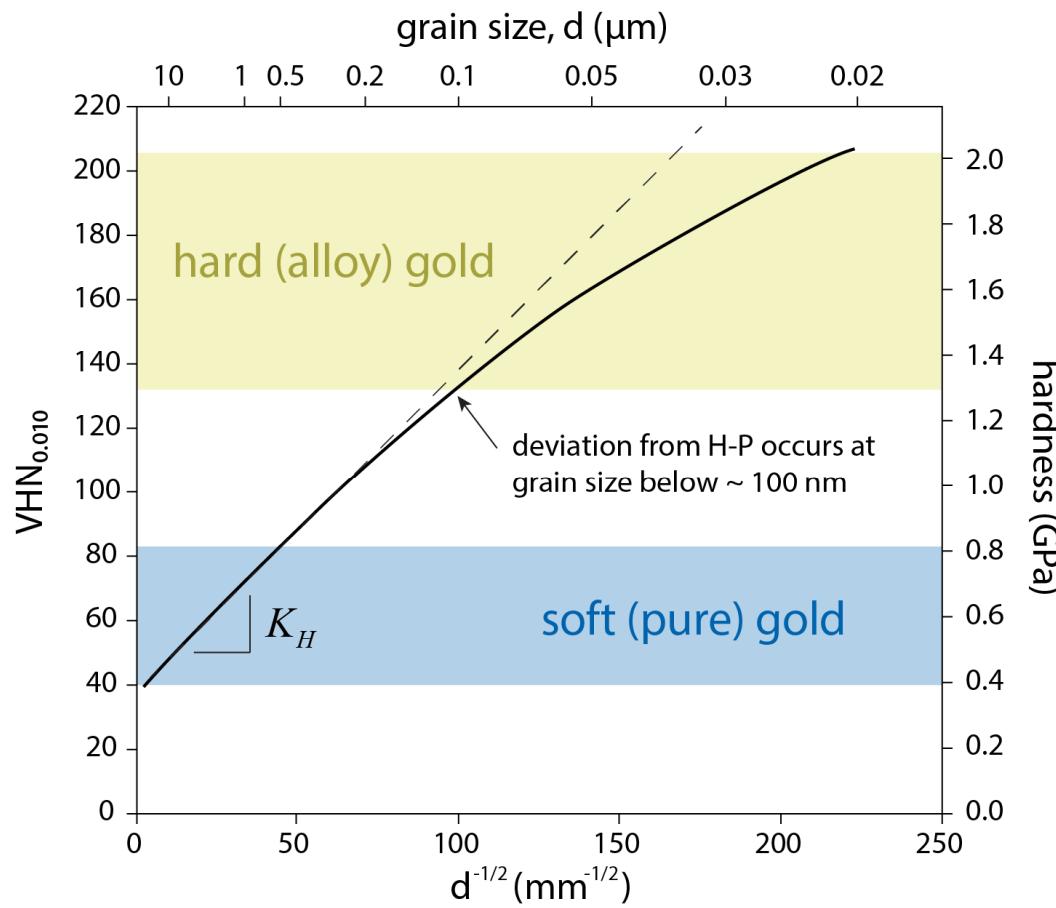


> 10,000x wear rate reduction with addition of 0.1% Ni

Archard wear = rate is linearly dependence to contact force

low wear and friction with pure Au is possible!

Alloying produces stable NC metal in bulk... alloys -> low μ at higher stresses

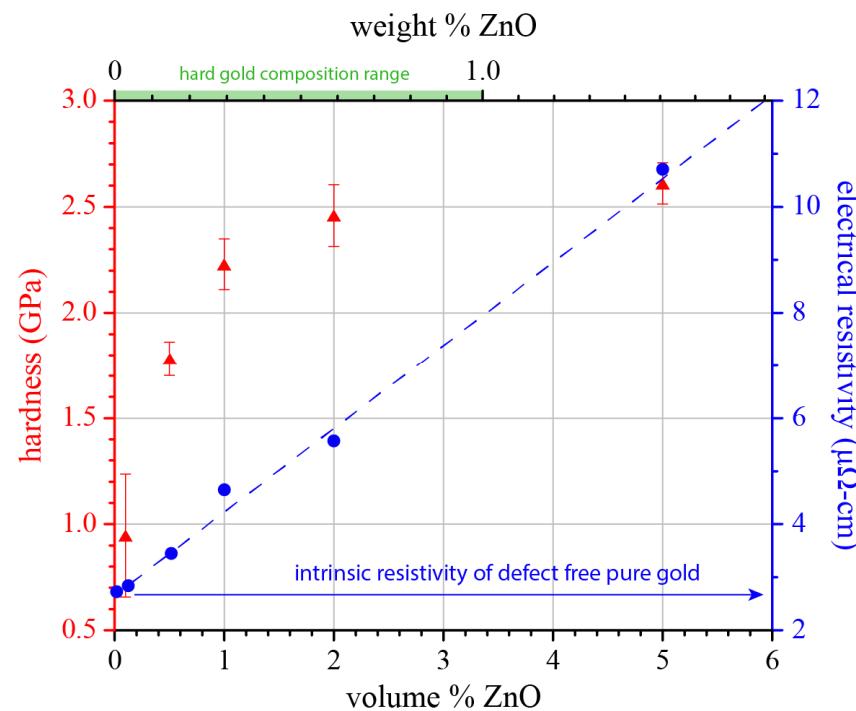
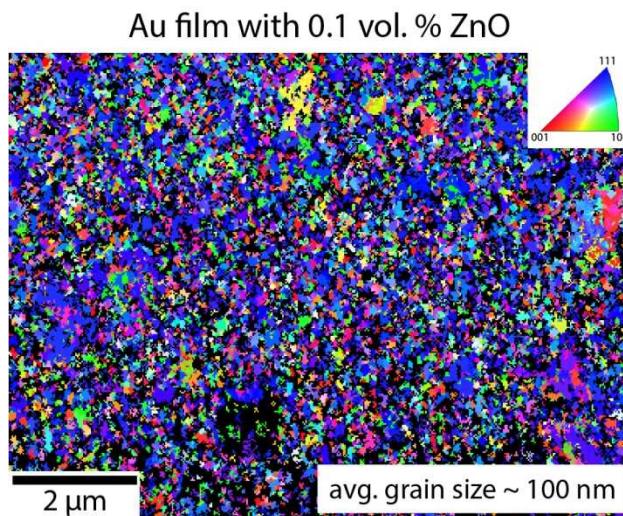
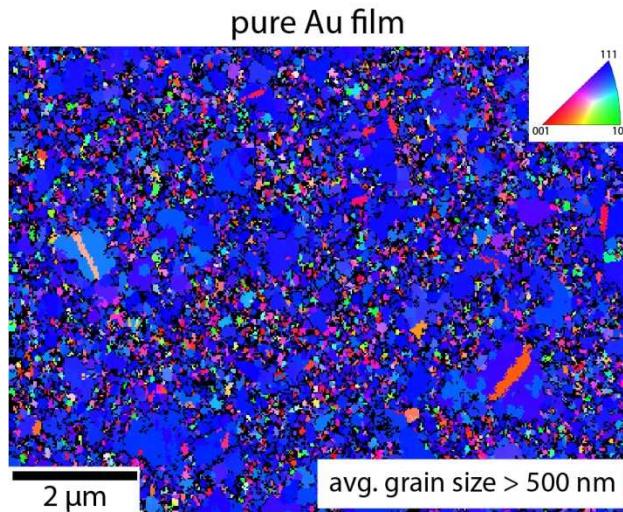


Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

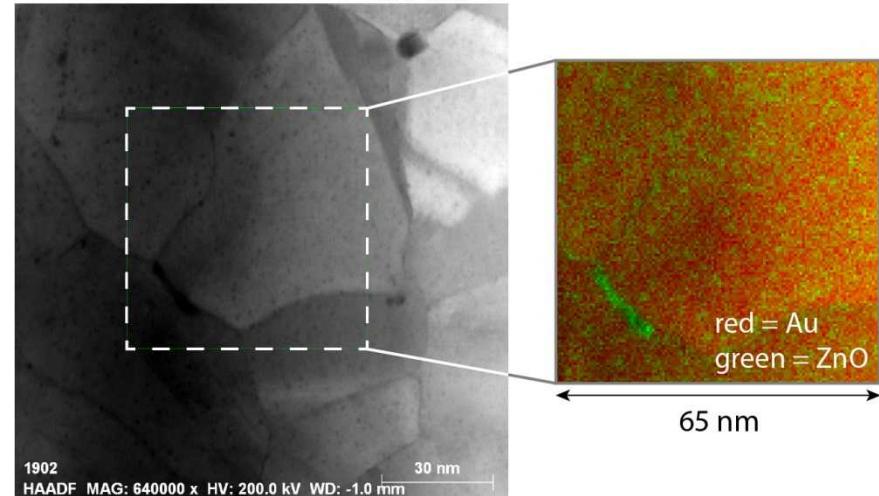
Stable NC grain size can be also achieved by adding **non-metal species**!

refs: Argibay et al. JAP (2015) and Wear (2013)

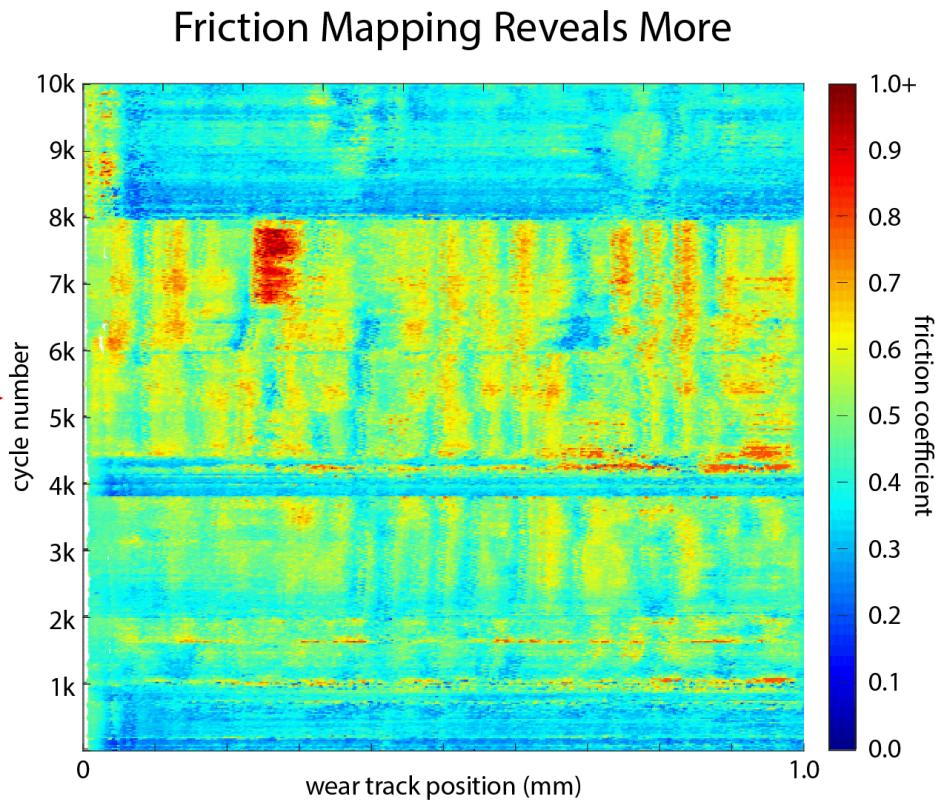
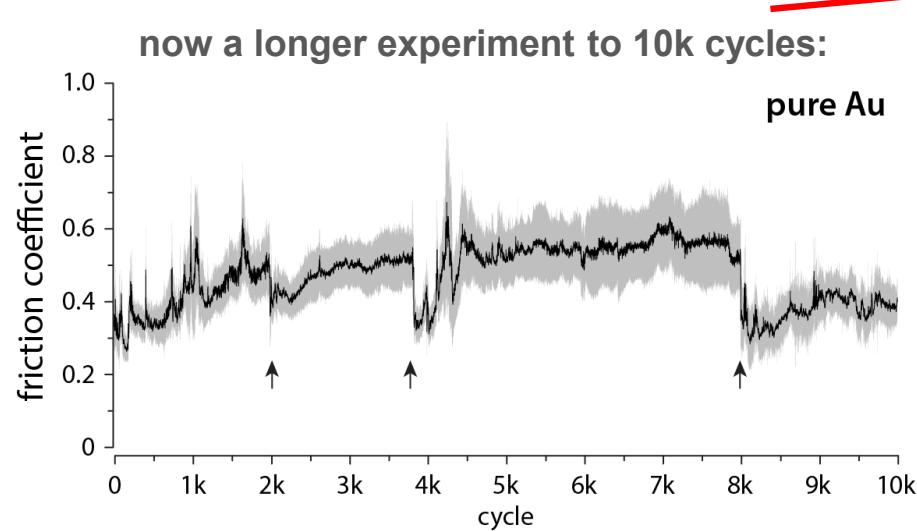
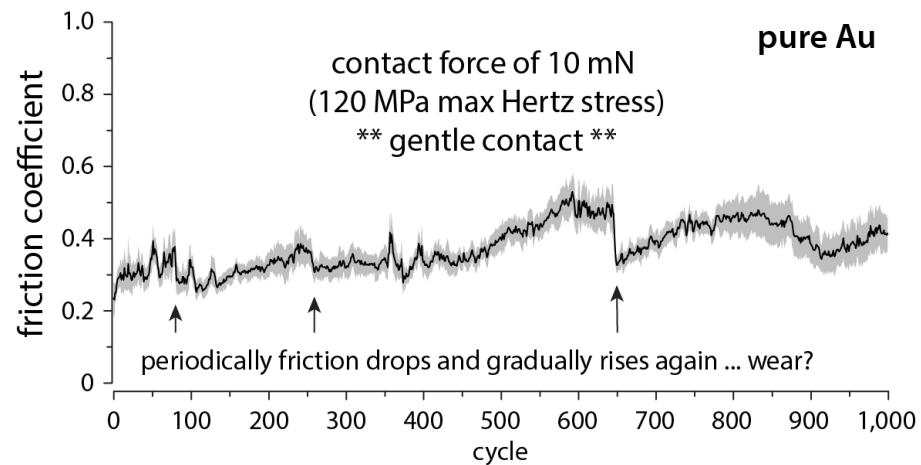
Surface-normal (planar) EBSD maps of e-beam deposited films:



Cross-sectional composition map of a Au- 5 vol. % ZnO film showing grain boundary segregated ZnO in a Au matrix

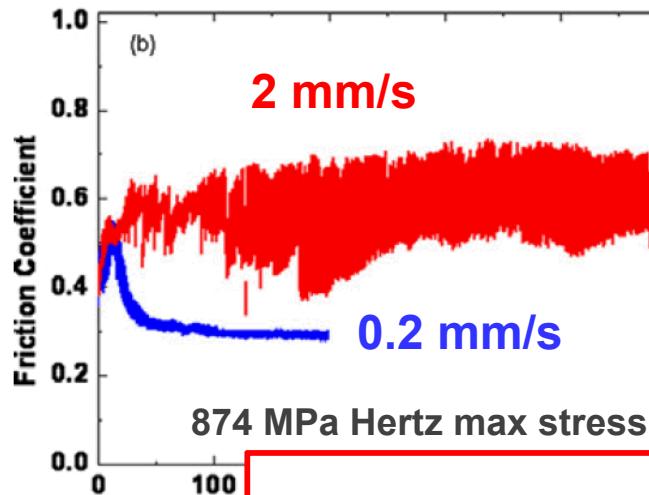


However, low friction IS possible even with **pure Au** sliding against hard Au

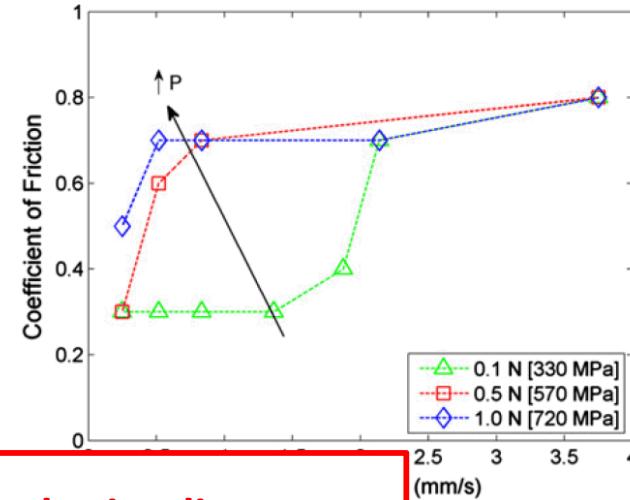


Evidence of threshold stress and speed for low friction to prevail

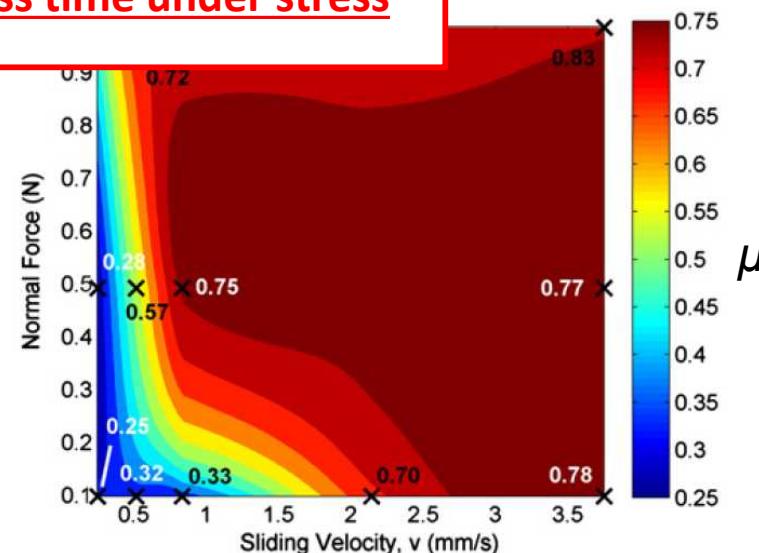
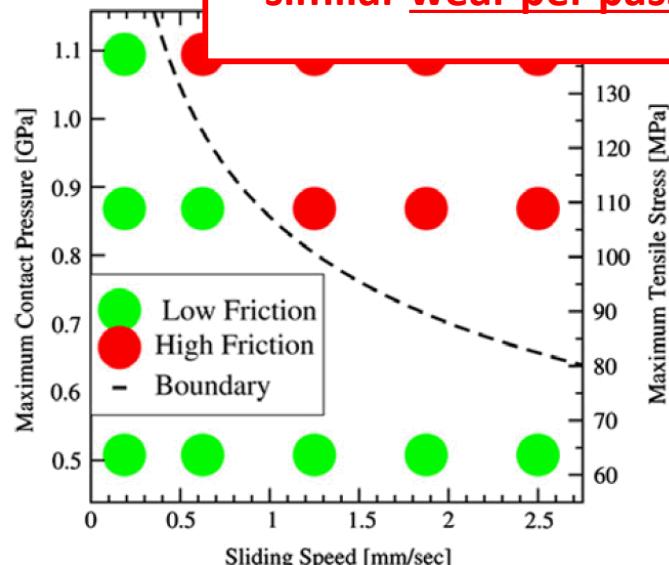
pure Ni data from S. V. Prasad et al., Scripta Mat. (2011)



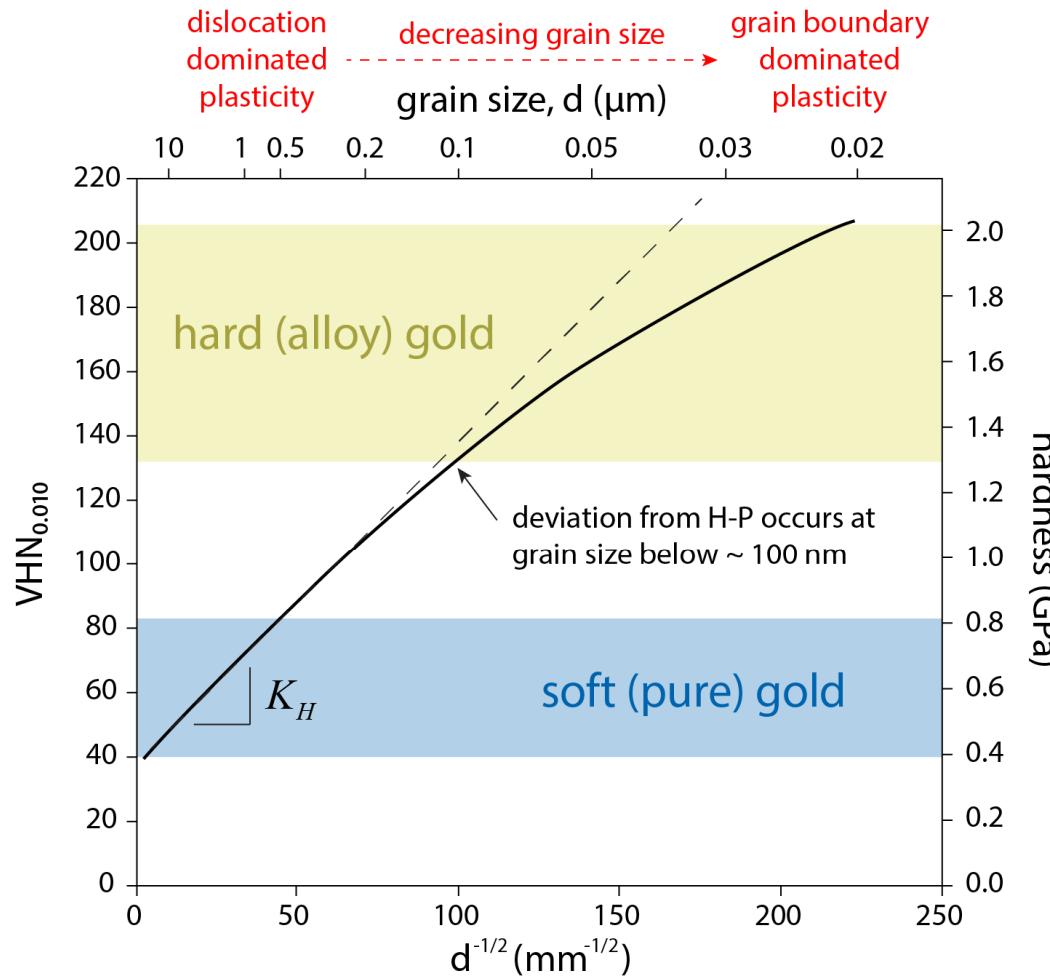
Ni-Fe data from H.A. Padilla et al., Wear (2013)



Higher speed but same cycles implies
similar wear per pass but less time under stress



Why “hard” Au? Hardness increase associated primarily with grain size reduction



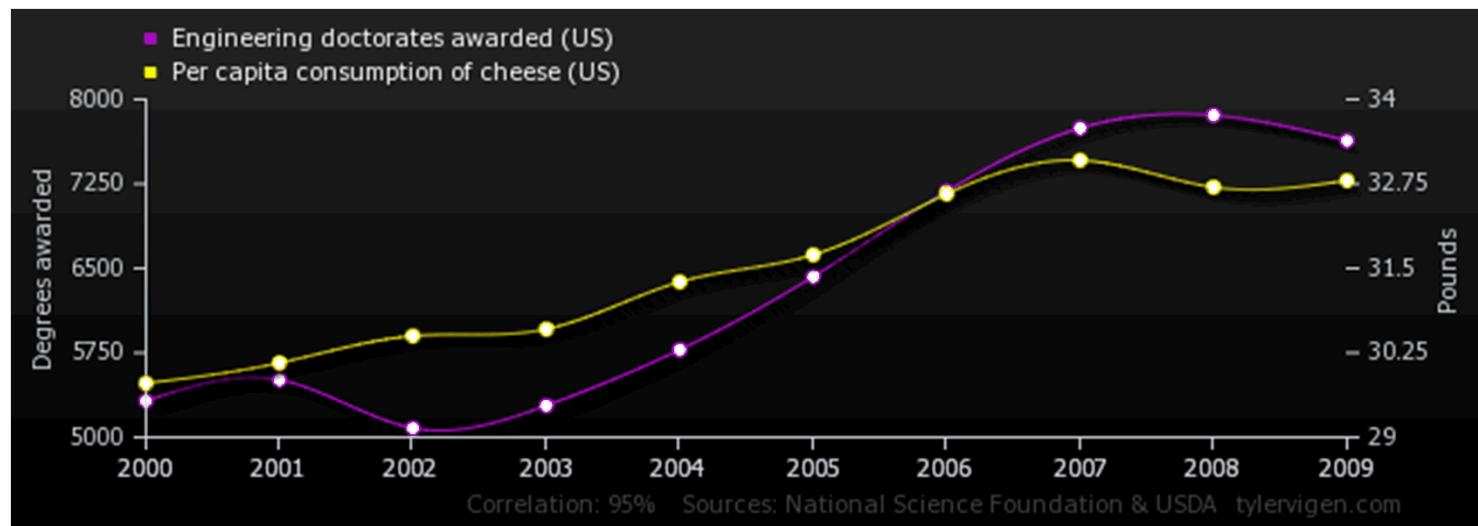
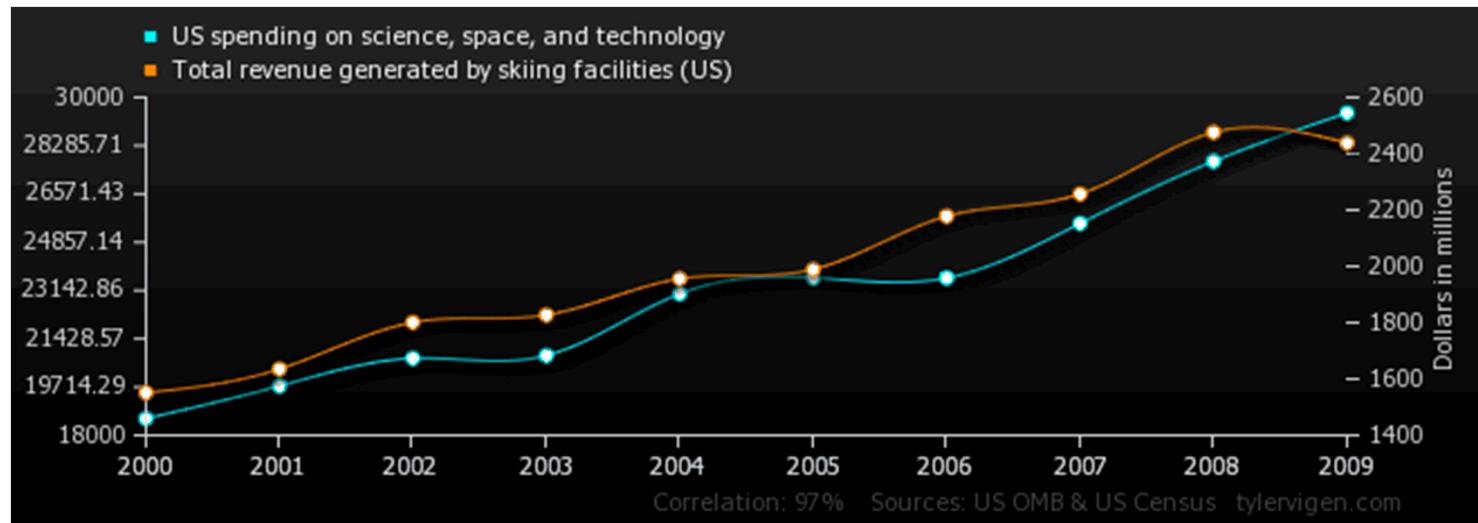
Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

The widely held misconception that hardness increase is the source of low wear and friction is loosely attributed to the notion that real contact area drops with hardness:

$$A_r \cong \frac{F_n}{H}$$

... for metal contacts the real area is a function of hardness and contact force.
(Bowden & Tabor, 1939)

Correlation is not causation...

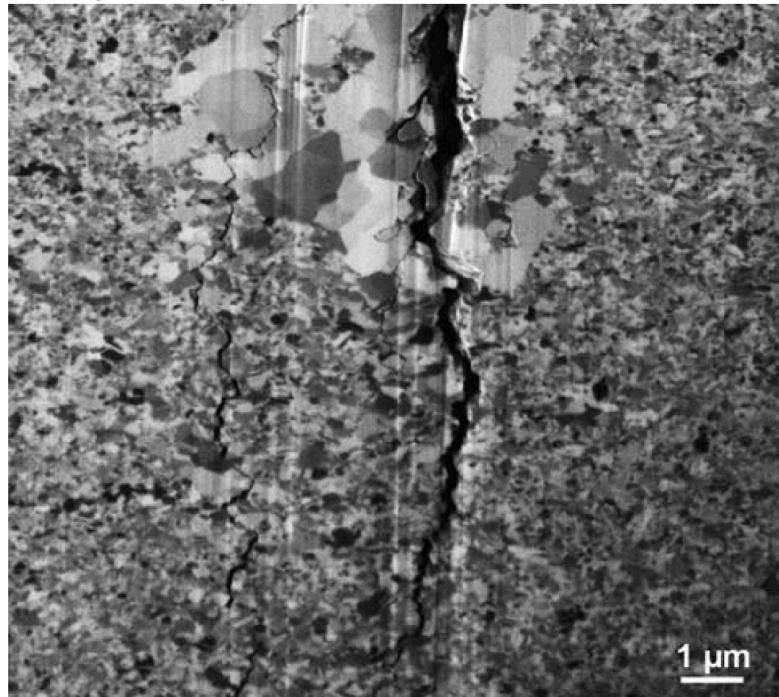


hardness is not the answer
(the answer seems to be grain boundary stability
and grain size evolution)

Grain size **stability** remains the key challenge to widespread adoption of NC metals

stress-driven grain growth

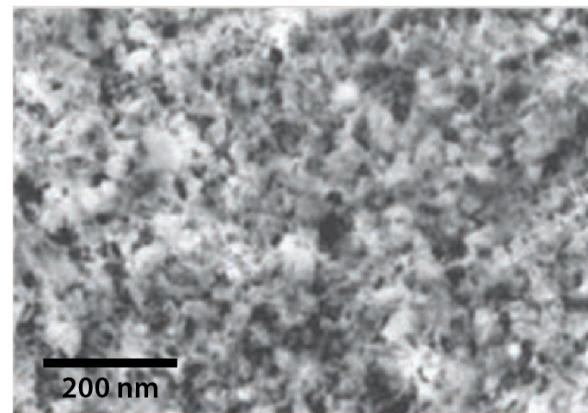
initially nanocrystalline Ni-Mn



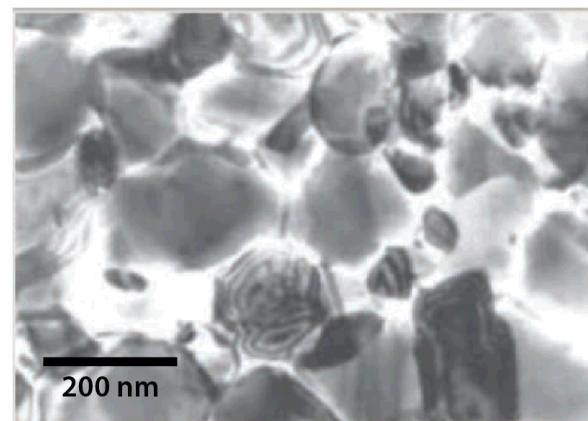
ref: Padilla & Boyce, *Exp. Mech.* (2010)

thermally-driven grain growth

initially nanocrystalline Ni



after anneal at 300°C for 30 minutes



This implies contact stress can drive coarsening...

... and contact heating can drive coarsening
(Blok, Jaeger, Archard, Lim and Ashby)

Two routes to stabilize nanocrystalline metals – kinetic and **thermodynamic**

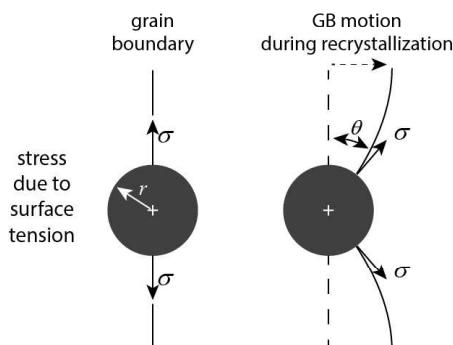
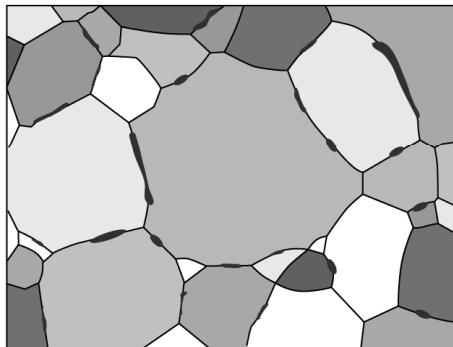
ref: Simoes et al., Nanotech. (2010)

Grain growth is essentially driven by grain boundary described by speed of grain boundary motion (speed), v

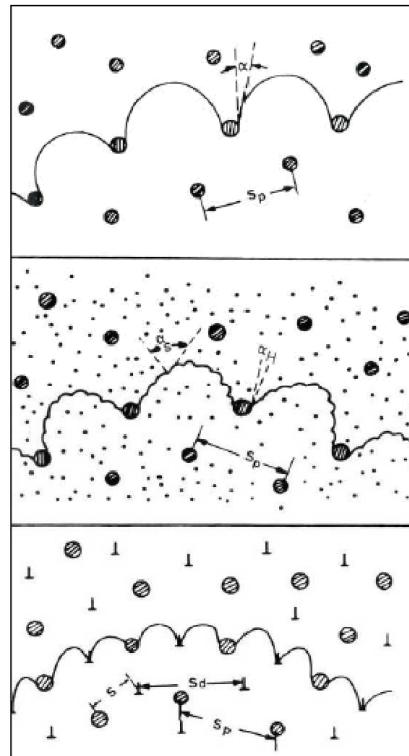
$$v = M \cdot P = M_o \exp\left(-\frac{Q_m}{kT}\right) \cdot \frac{2\gamma_o}{r}$$

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

e.g. Zener pinning, solute drag, porosity



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



M = grain boundary mobility

P = pressure on grain boundary

γ_o = interfacial energy per unit area

r = mean grain radius

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

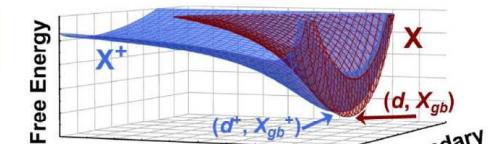
Regular Nanocrystalline Solution (RNS) Model:

ref: Chookajorn et al., Science, 2012

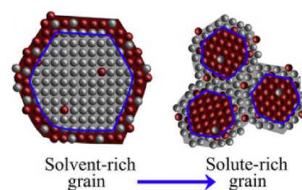
$$\Delta G^{\text{mix}} = (1 - f_{\text{gb}})\Delta G_c^{\text{mix}} + f_{\text{gb}}\Delta G_{\text{gb}}^{\text{mix}} + zVf_{\text{gb}}(X_{\text{gb}} - X_c) \left[(2X_{\text{gb}} - 1)\omega_{\text{gb}} - \frac{1}{zT}(\Omega^B \gamma^B - \Omega^A \gamma^A) \right]$$

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

Grain structure model:
segregated 2-phase metal system



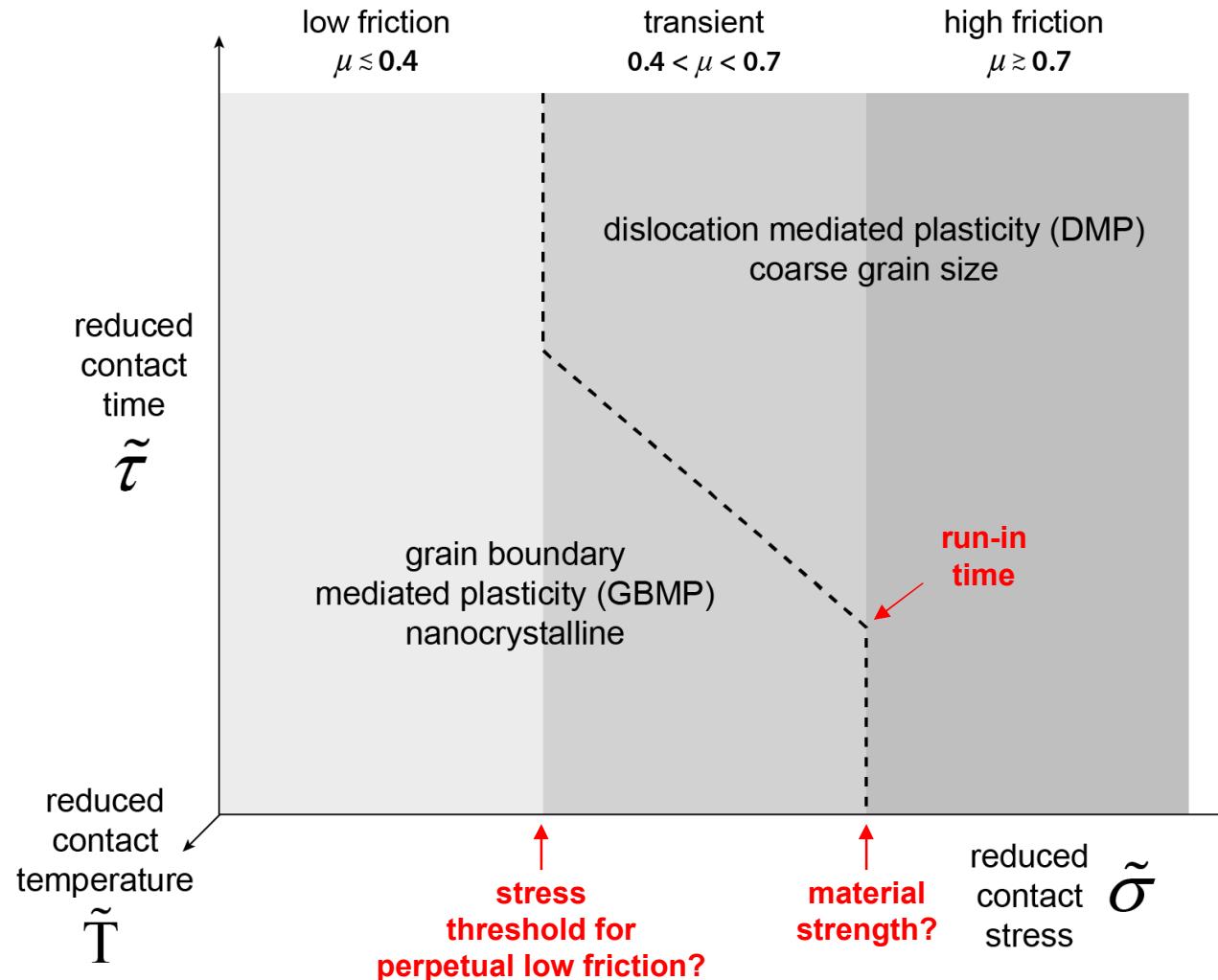
ref: Murdoch et al., Acta Mat. (2013)



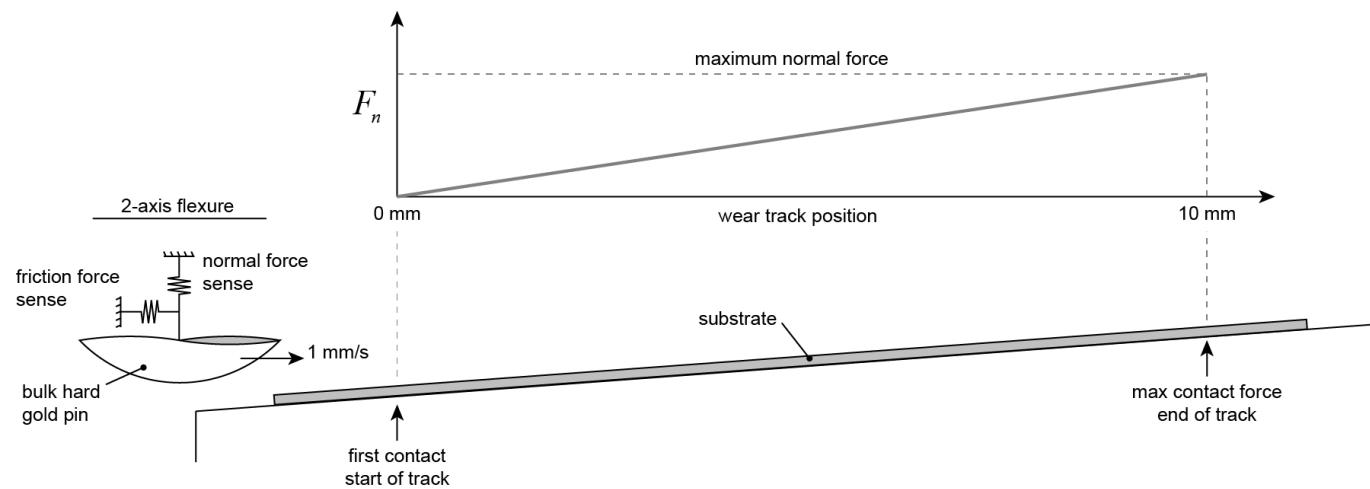
ref: Murdoch et al., Acta Mat. (2013)

What does a microstructure-based friction regimes model look like?

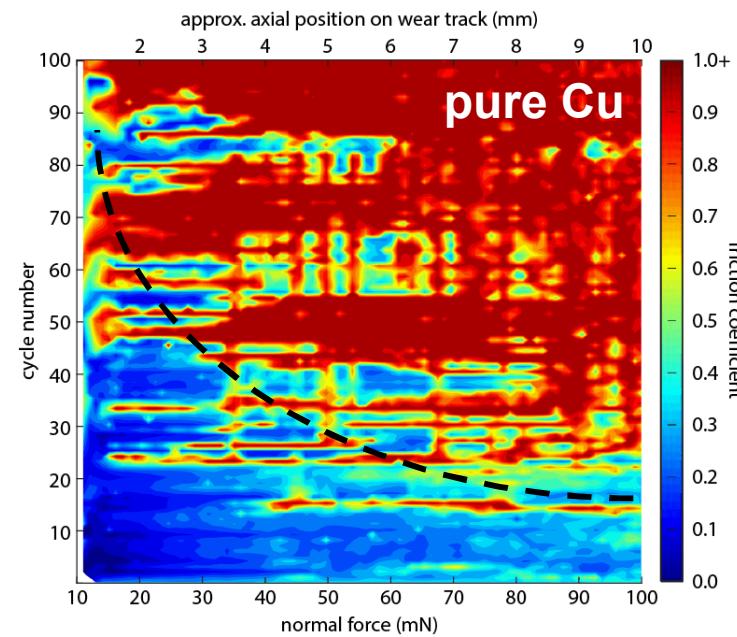
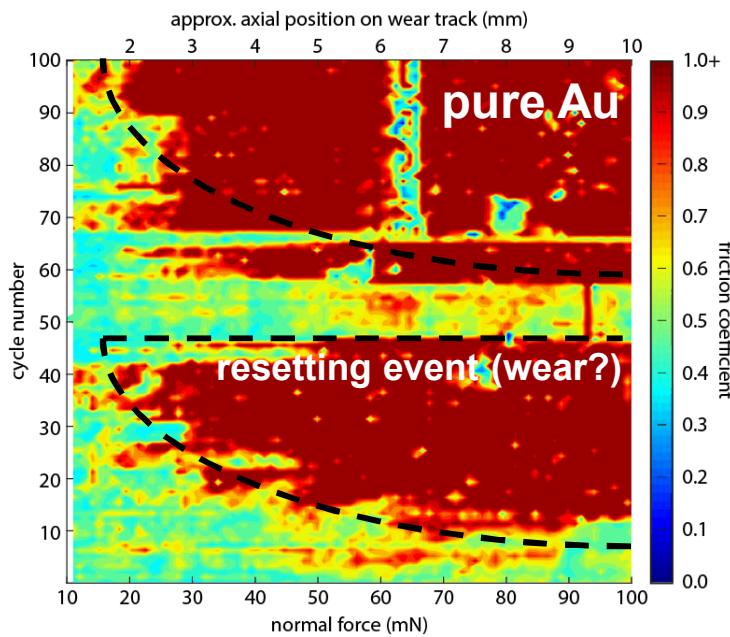
Based on recent experimental and MD simulation results, we arrived at a new model that predicts (some) friction behavior regimes based **exclusively on materials parameters and microstructure evolution models**



Ramped contact force experiments and friction mapping reveals much



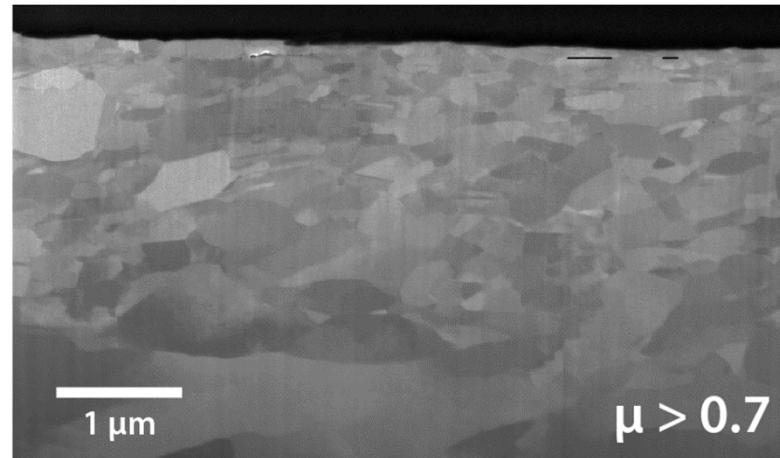
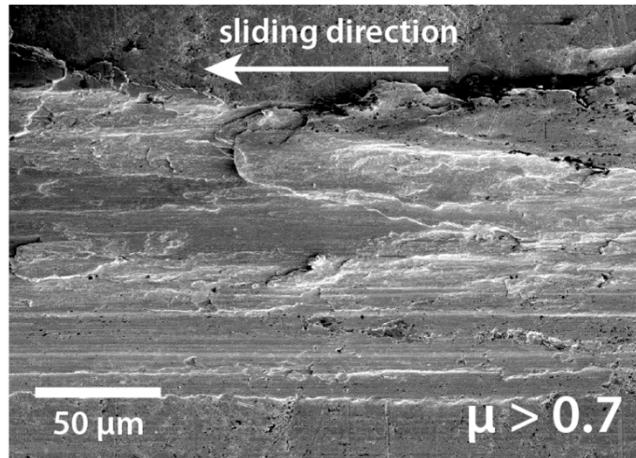
Messy (tribology...), but there is stress dependent envelope!



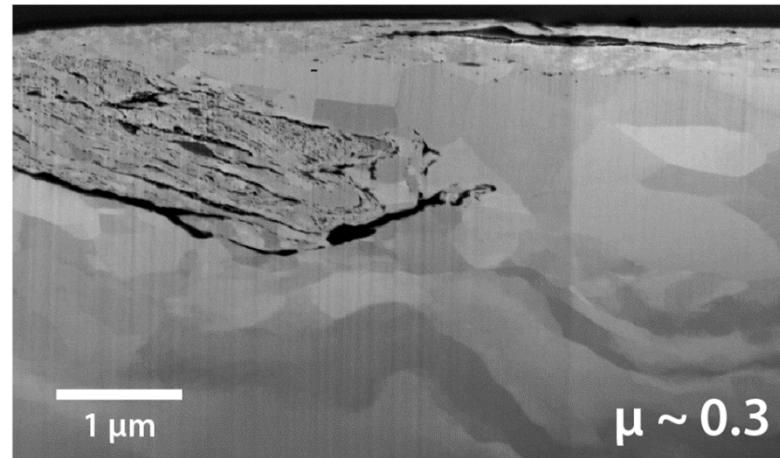
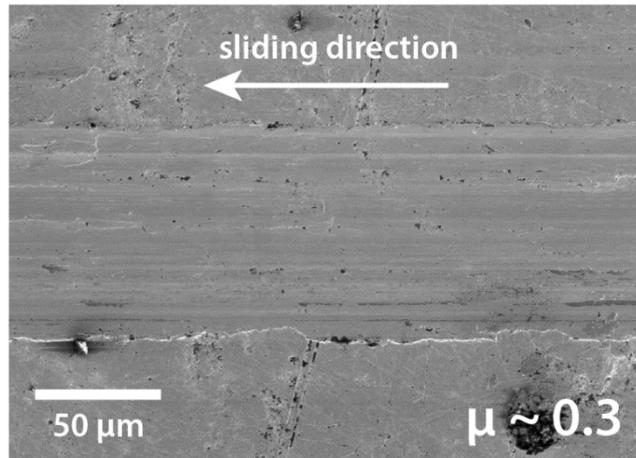
Again, low friction associated with nanocrystalline surface.. see shear banding too

comparing pure Au surfaces and microstructures where low and high friction were measured:

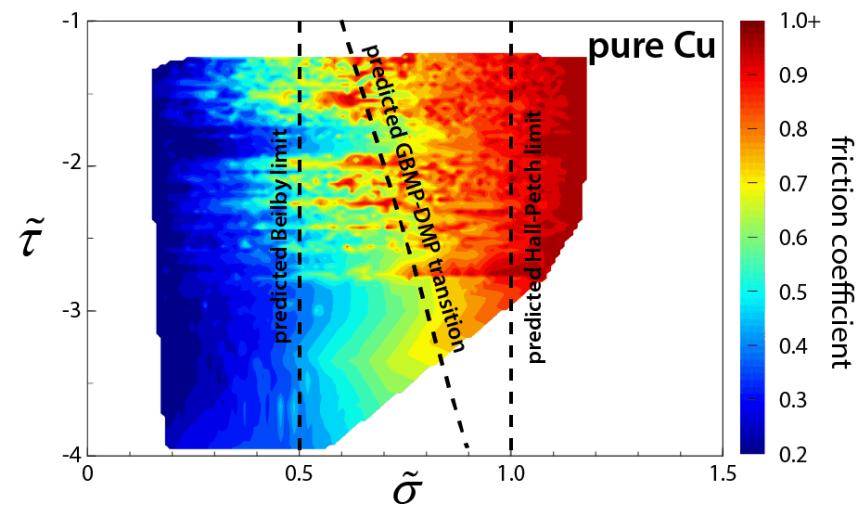
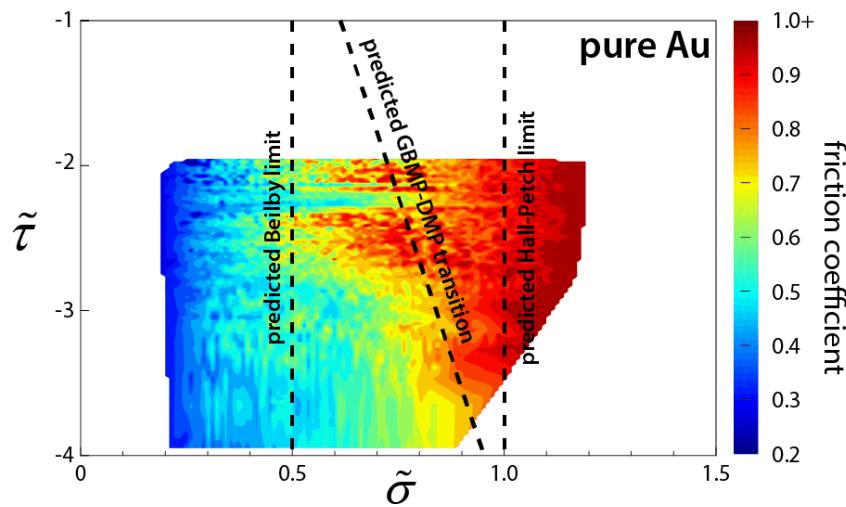
high
friction



low
friction

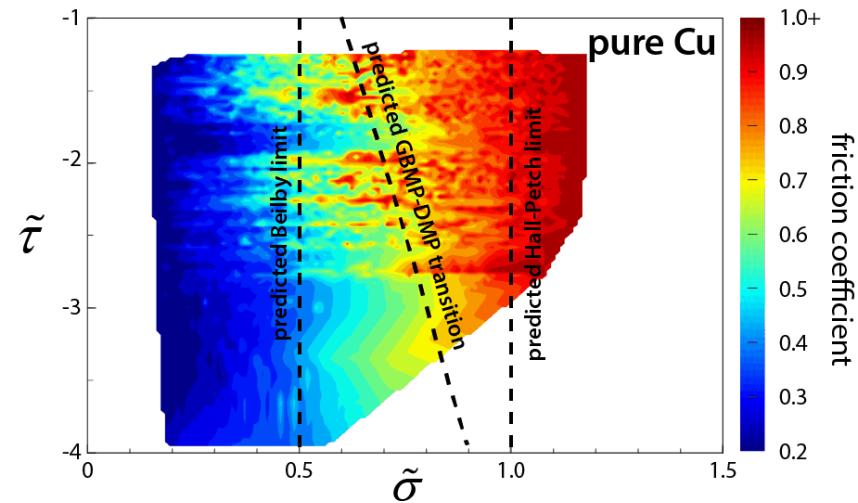
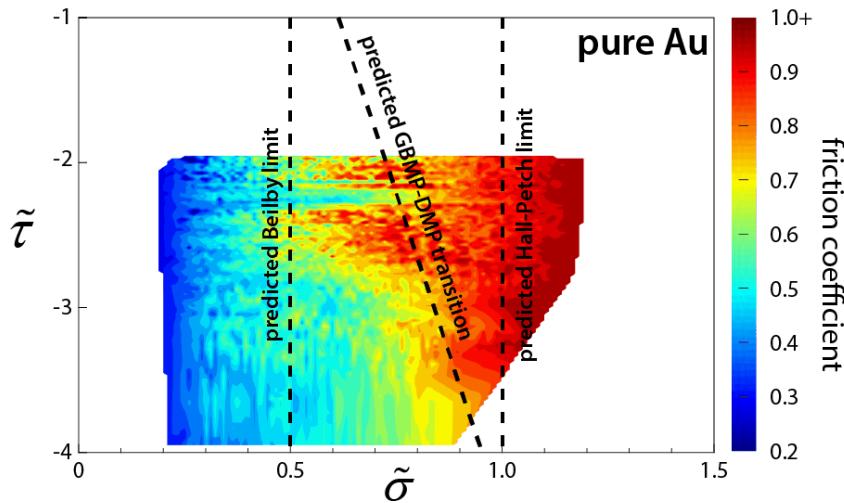


The punchline first: this is what the reduced data looks like



Predictions are pretty good... Note: no fitting or fudging, all bounds

predicted!

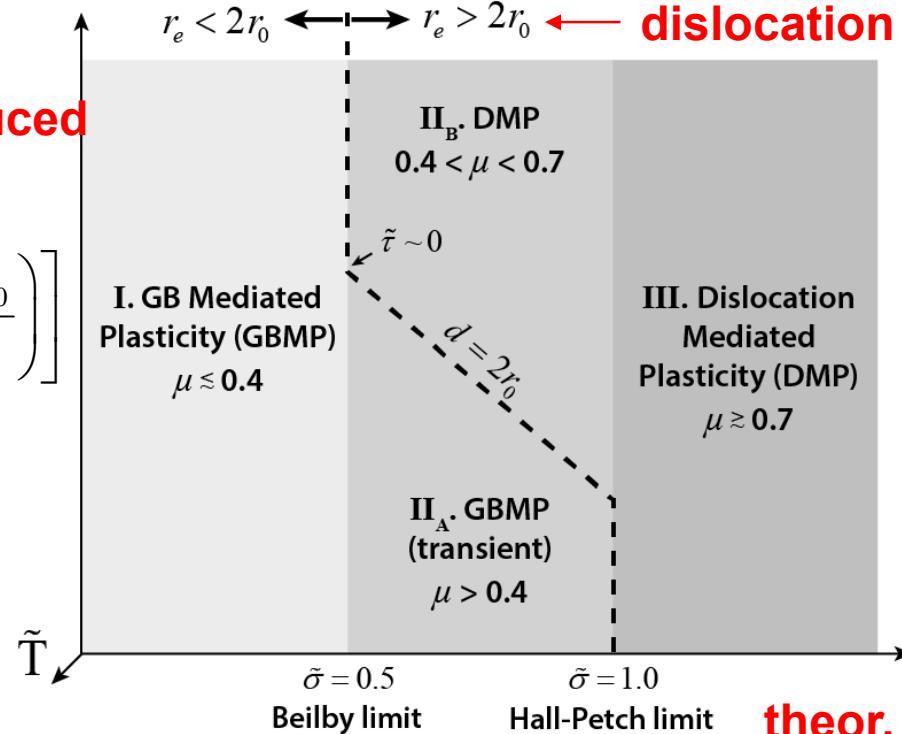


dislocation splitting distance is key

and formulated reduced time parameter:

$$\tilde{\tau} = \log_{10} \left[\left(\frac{2a_c}{v_s} \right) \left(\frac{4\gamma_{gb} M_0}{r_0^2} \right) \right]$$

contact time
grain growth



Found reduced stress parameter:

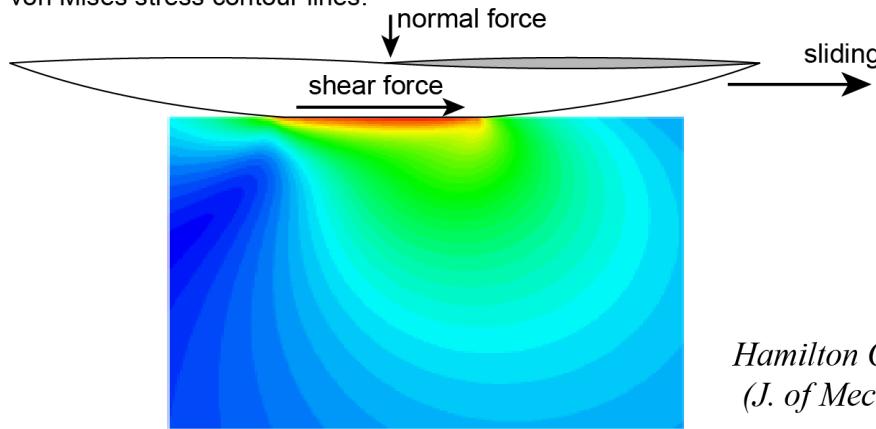
Hamilton Contact Model

$$\tilde{\sigma} = \frac{\sigma_{surf,max}}{\sigma_{\infty}}$$

theor. strength

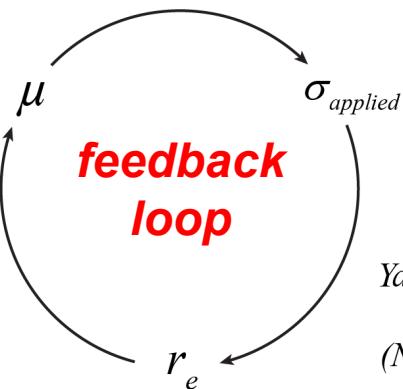
The connection between friction and microstructure evolution

von Mises stress contour lines:

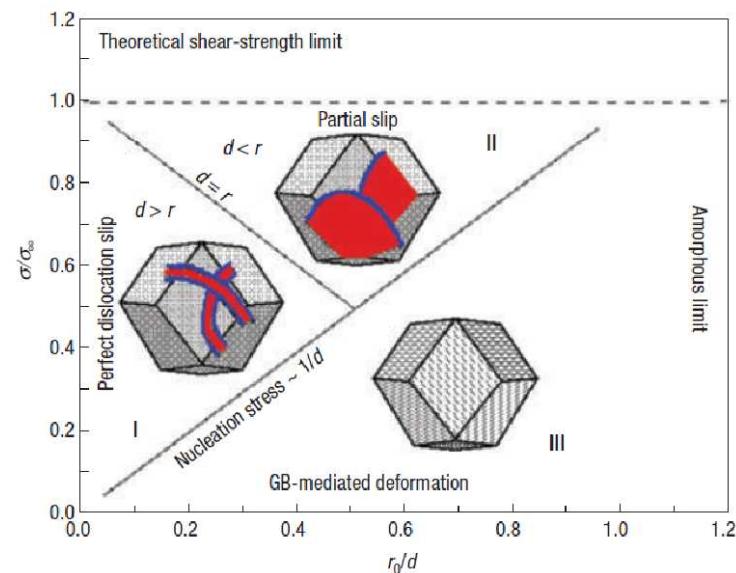
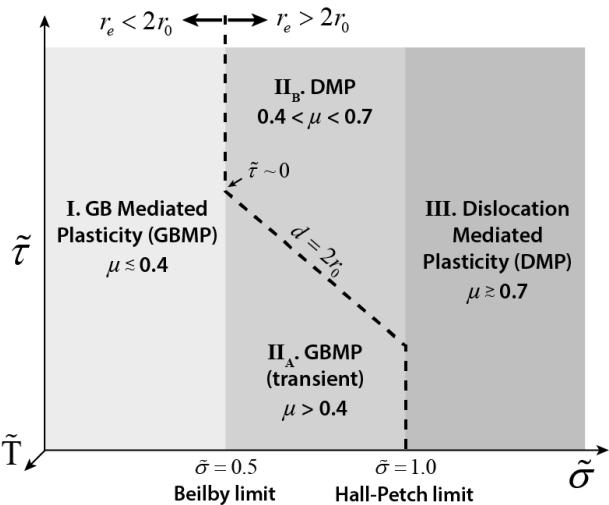


$$\sigma_{a,\max} = \frac{3F_n}{2\pi a^2} \left[\frac{1-2\nu}{3} + \frac{(4+\nu)}{8} \pi \mu \right]$$

Hamilton Contact Model
(J. of Mech. Eng. 1983)



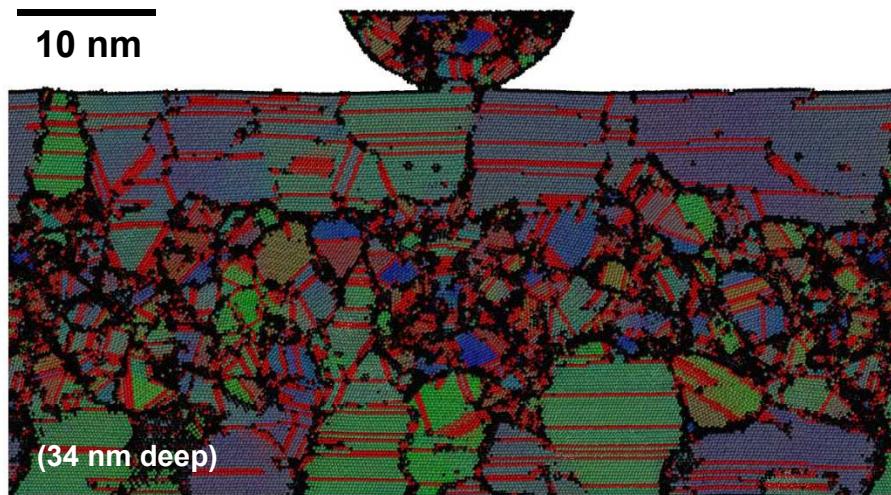
proposed
model



Yamakov et al.
model
(Nature 2004)

What did we learn from MD simulations...

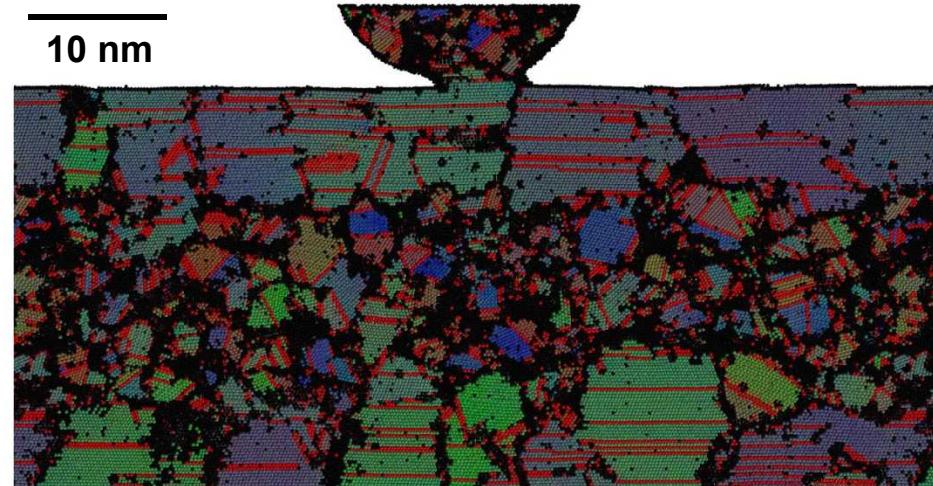
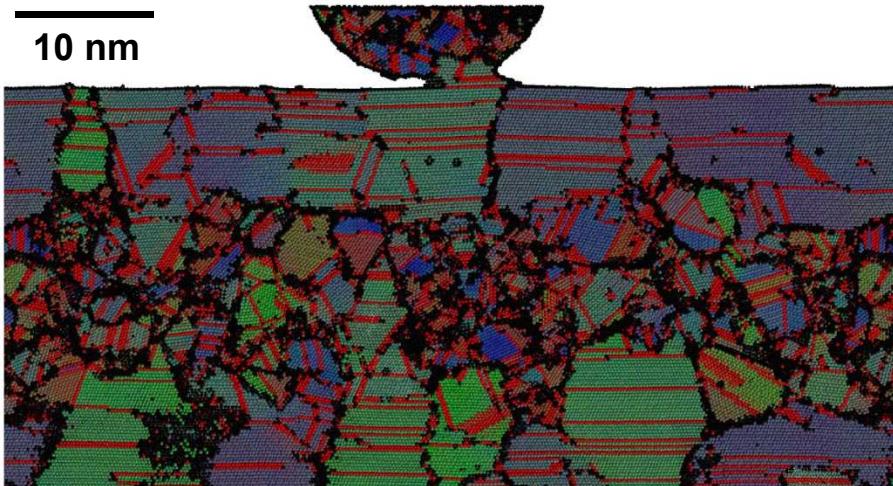
initial microstructure
of Ag and Ag-Cu alloy
(no sliding yet)

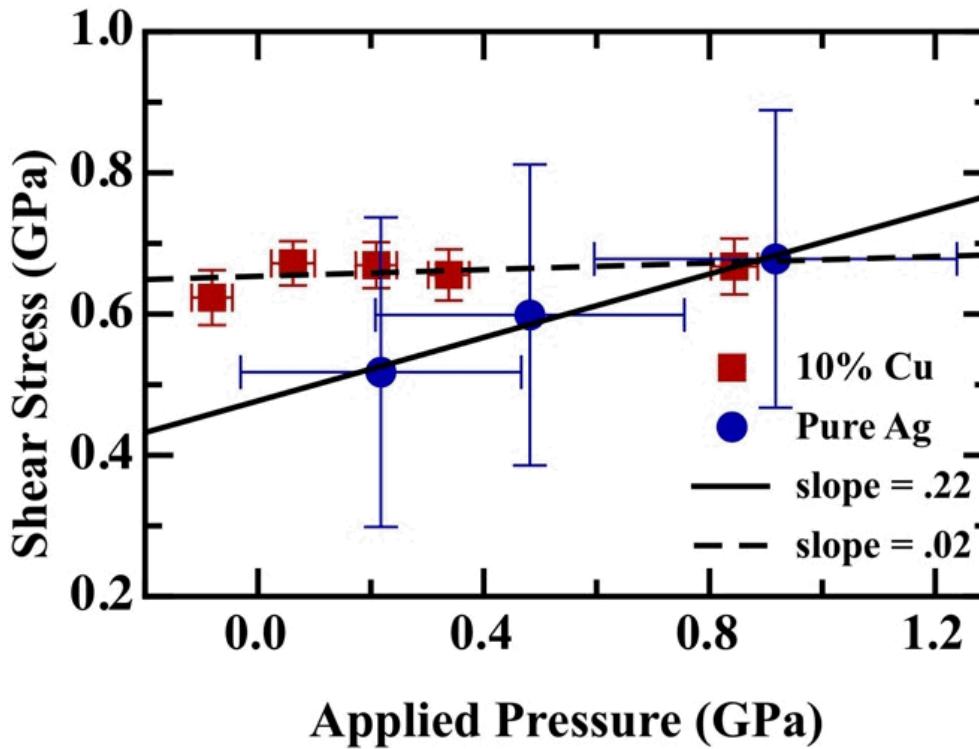


300 MPa contact stress
300 K temperature
2 m/s sliding speed

pure Ag after 4 nm of sliding

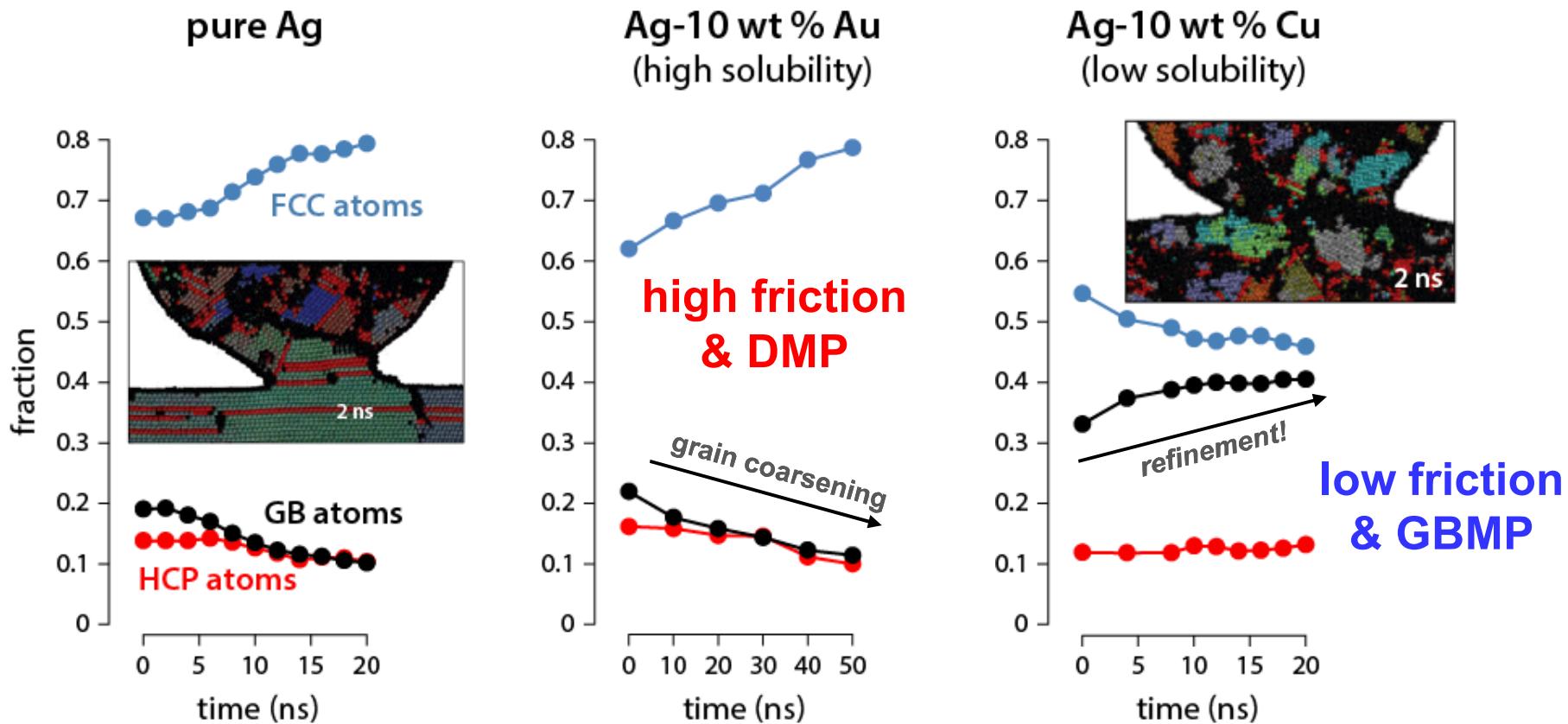
Ag-10% Cu alloy after 4 nm of sliding





- AgCu is similar to hard gold (AuNi, AuCo...)
- Friction coefficient is the slope of line
- Change in shear accommodation changes the friction

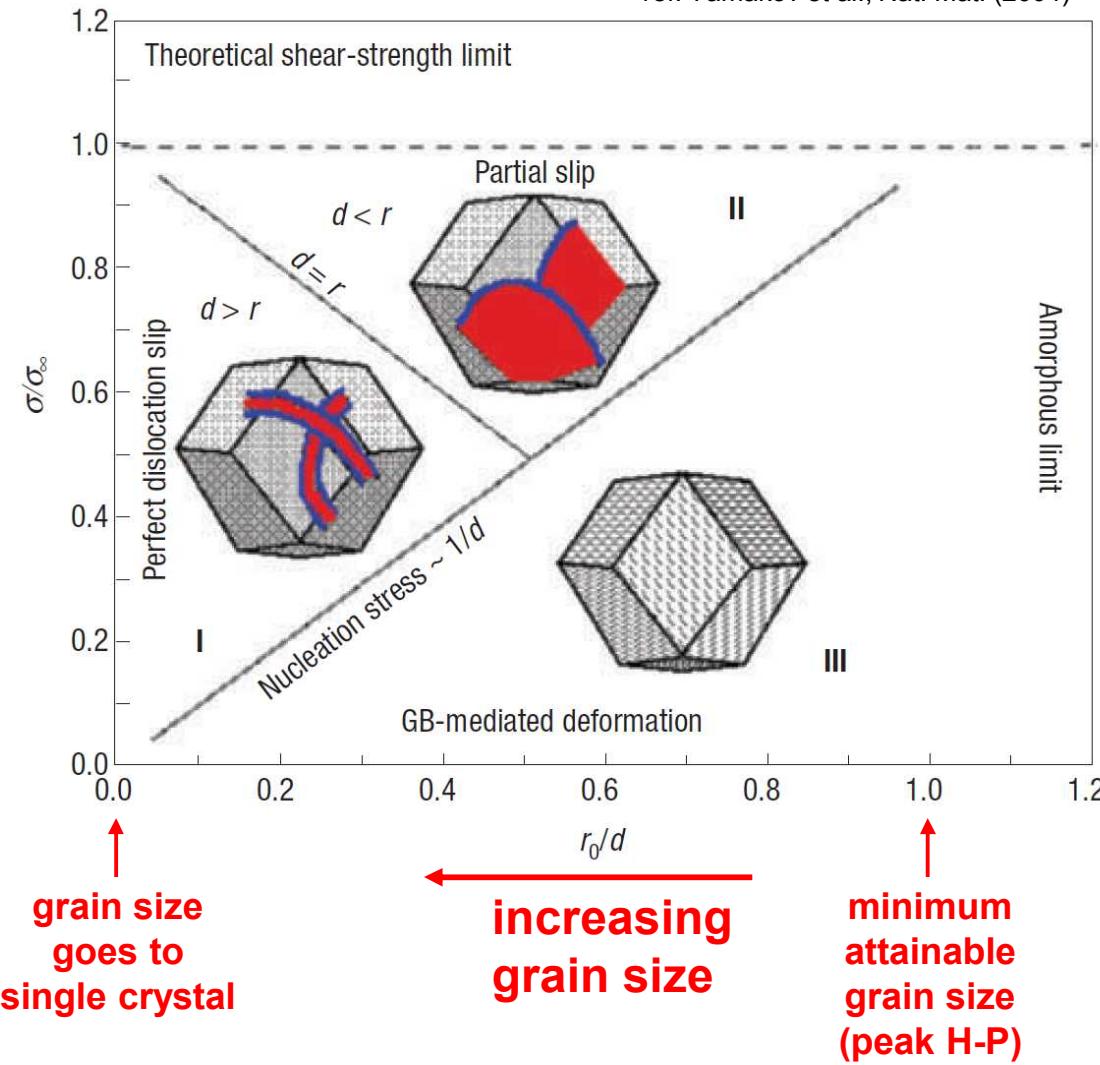
Alloying also impacts microstructural evolution



- Experiments: alloying reduces grain size and stabilizes grain boundaries
- Simulations: alloying mitigates stress-driven grain growth at interface and promotes defect (primarily GB) mediated plasticity
- Connection: stabilizing grain boundaries reduces friction

Evolution of the Yamakov et al. (Nat. Mat. 2004) deformation mechanisms model

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



Equilibrium (zero stress) dislocation splitting distance:

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

Stress-dependent splitting distance:

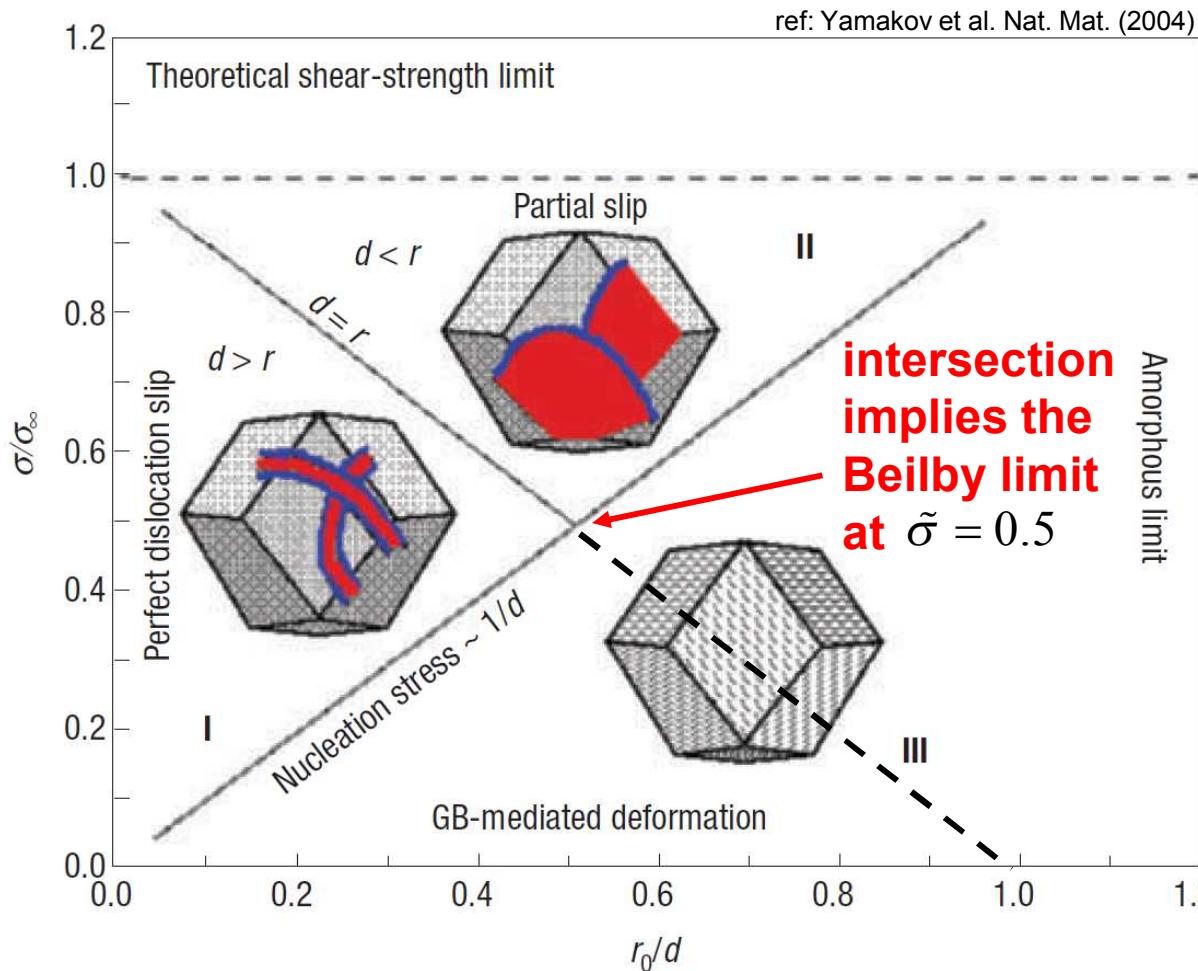
$$r_e = \frac{r_0}{1 - \sigma_a / \sigma_\infty}$$

Theoretical strength, grain size where Hall-Petch reaches max:

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

Ref: Froseth et al., Acta Mat. (2004)

Evolution of the Yamakov et al. (Nat. Mat. 2004) deformation mechanisms model

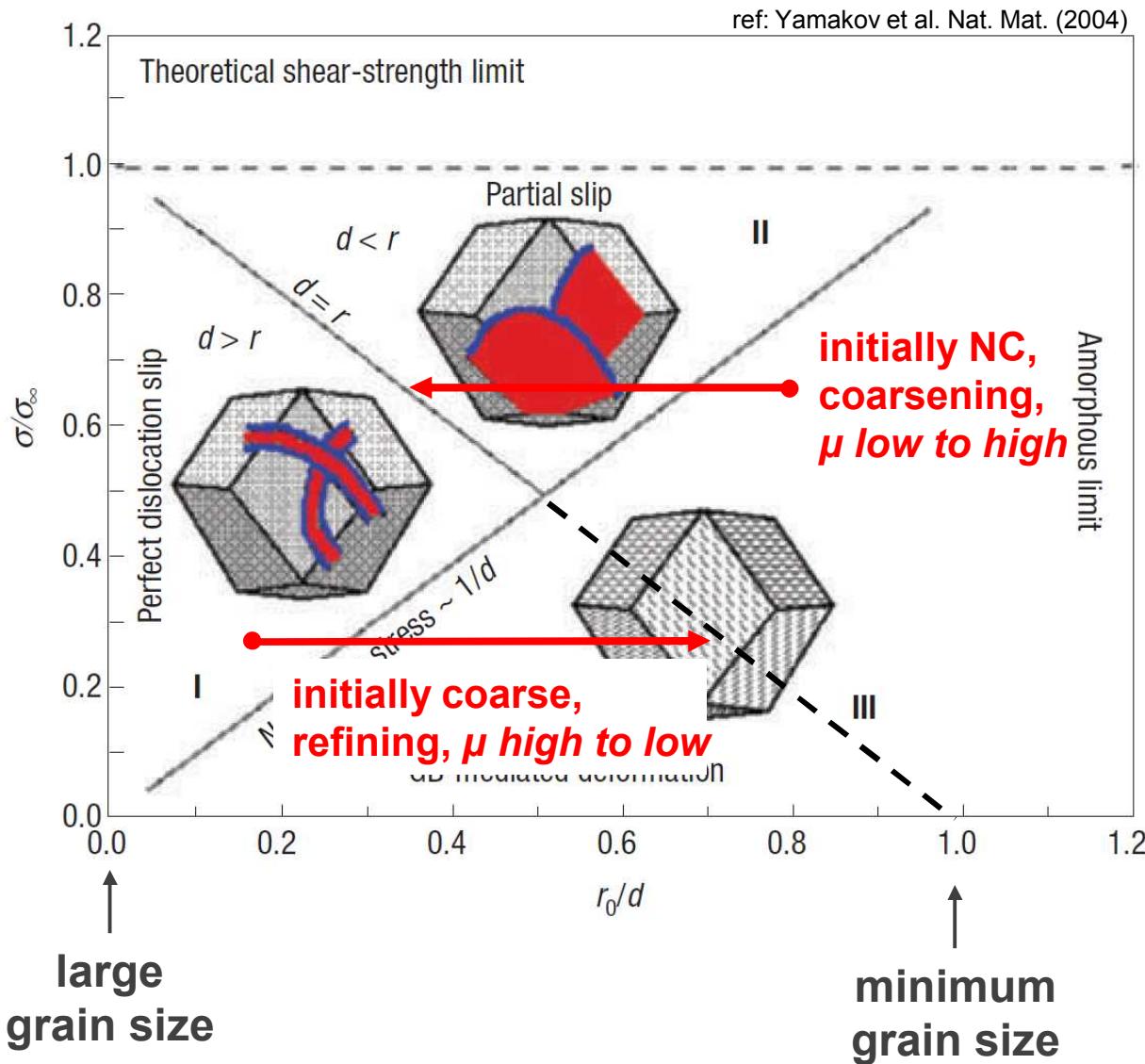


Assumptions:

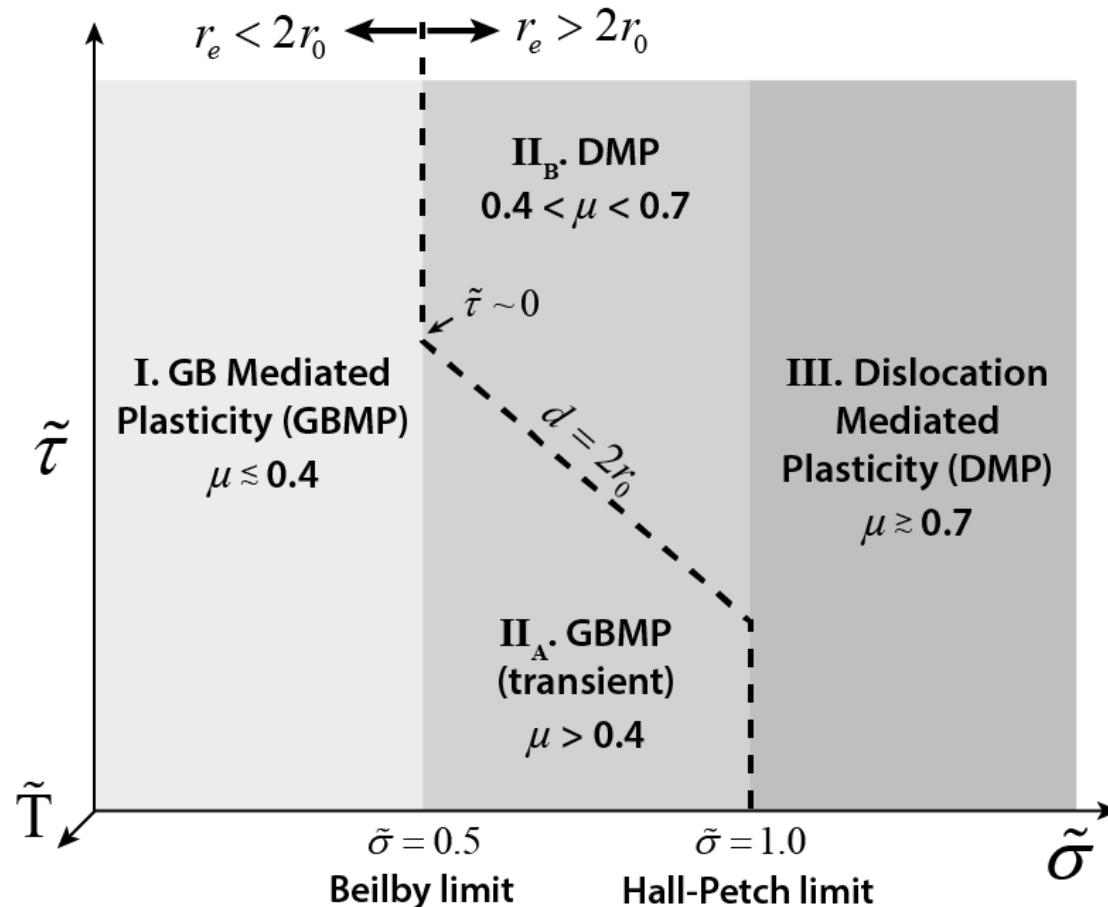
1. grain size goes to splitting distance, $\rightarrow d$

2. nucleation stress goes as inverse grain size, $\tilde{\sigma} \propto \frac{1}{d}$

But this says nothing about evolution... coarse grain surface can be driven to NC

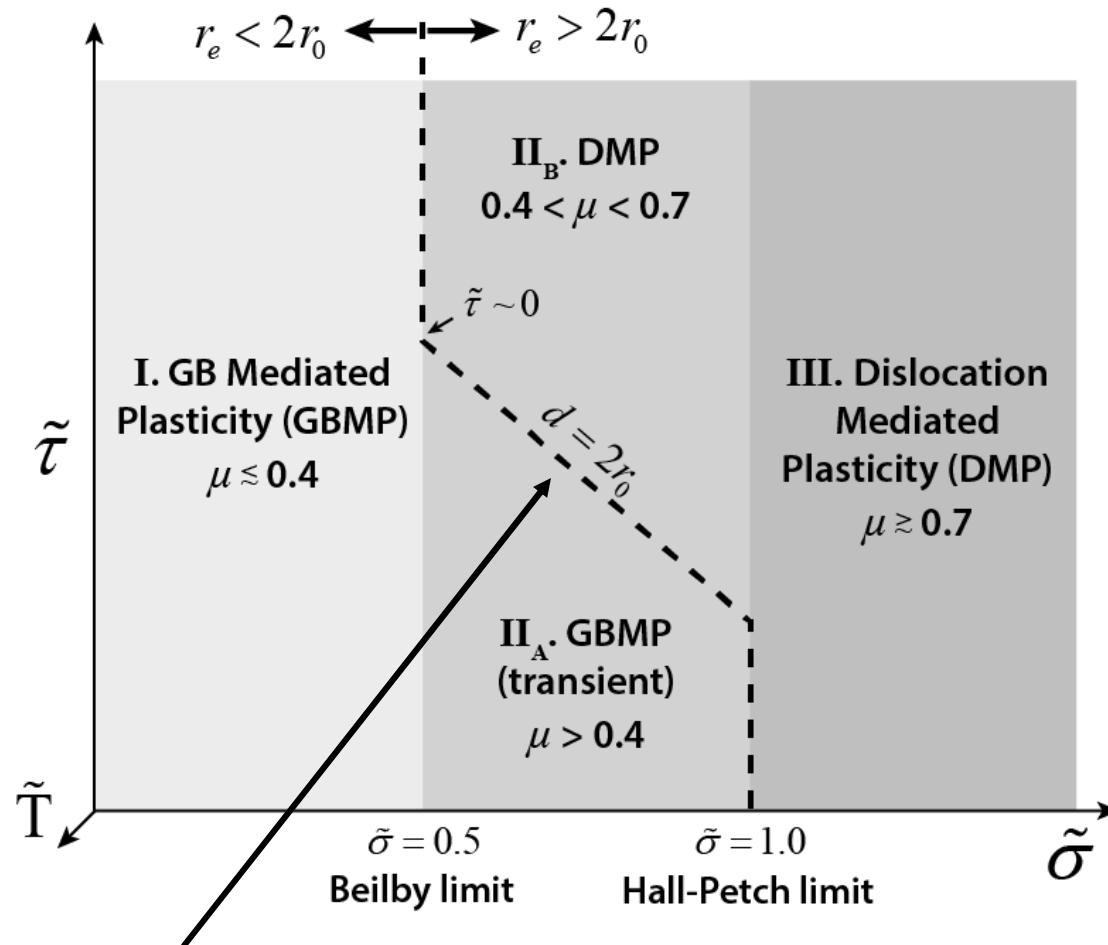


Returning to the microstructure-based friction regimes model...



We assume that wear events reset the surface relatively fast, where in the right conditions even coarse grained material is first **rapidly refined** then **gradually coarsened** via cyclic stress

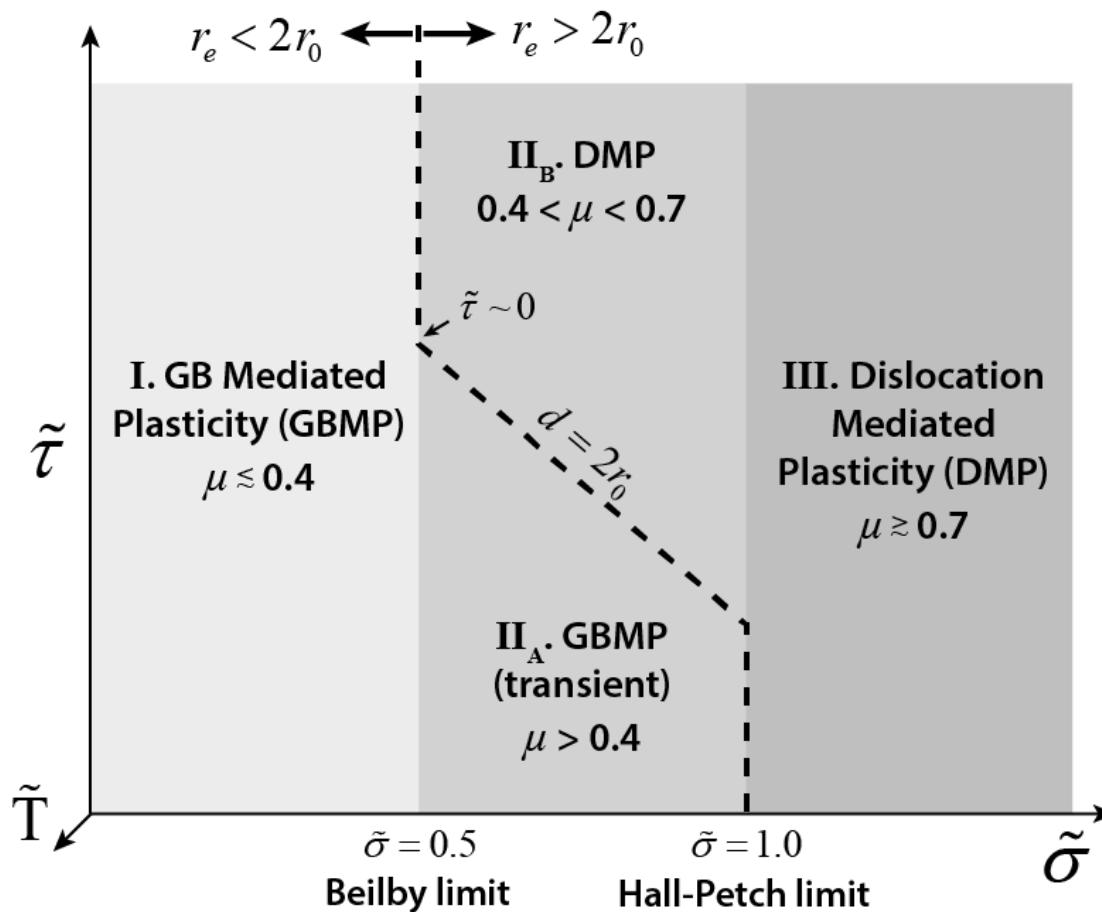
Returning to the microstructure-based friction regimes model...



Then contact time until high friction is governed by stress- and temperature-dependent grain boundary speed:

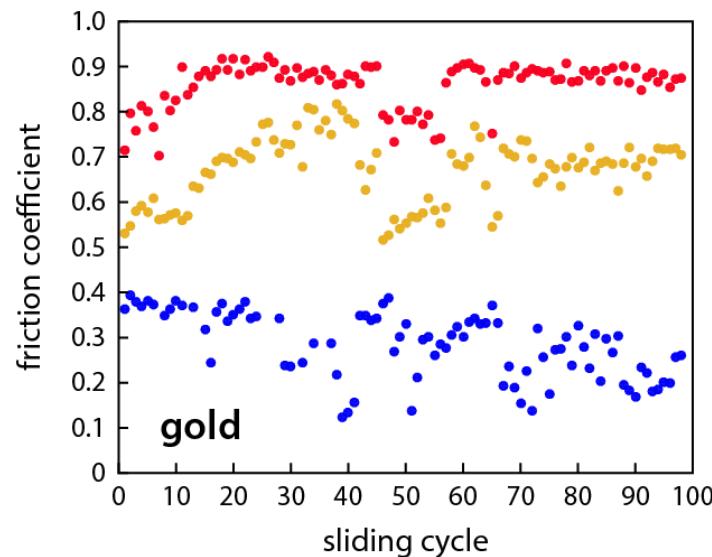
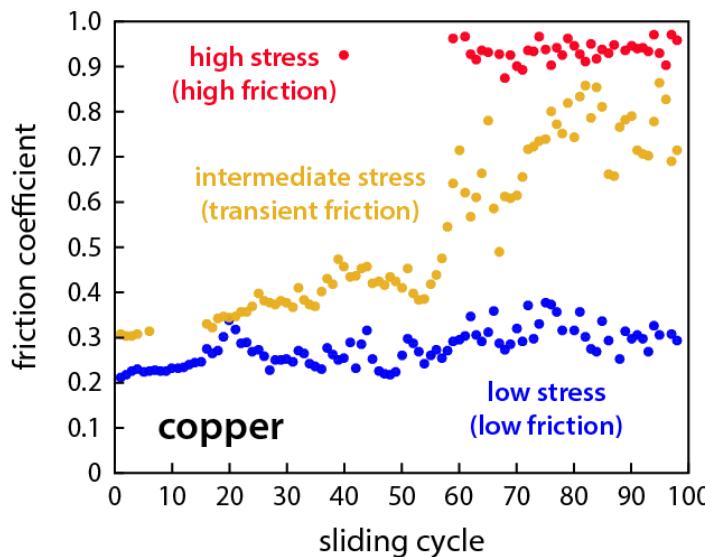
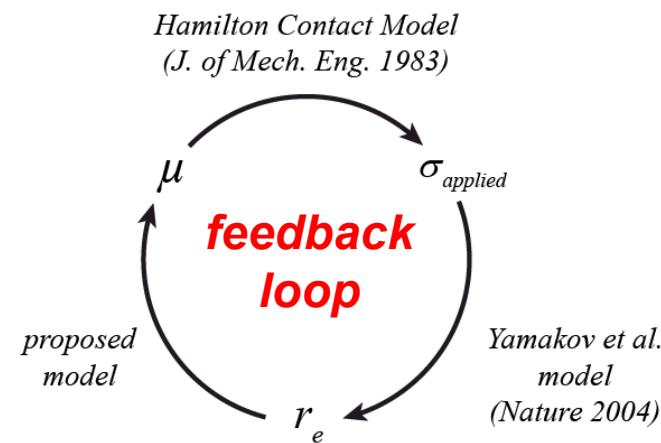
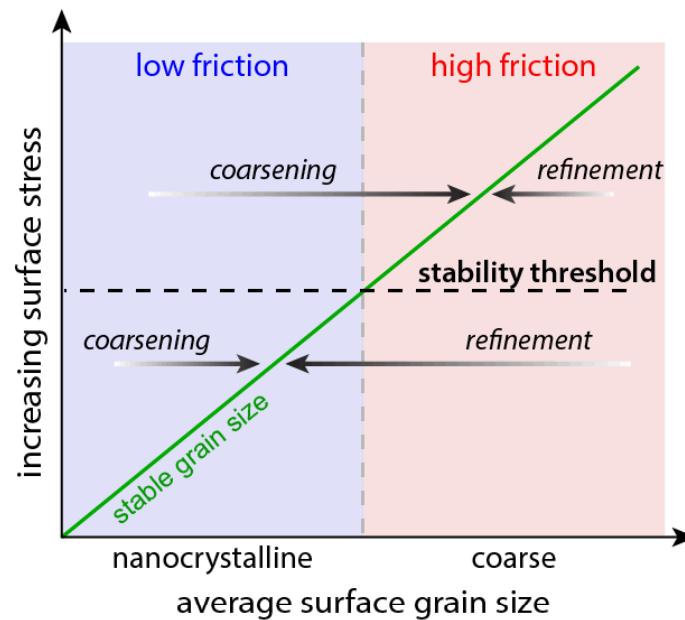
$$v_{gb} = \frac{4\gamma_{gb}}{d} M_0 \exp\left[\frac{-Q}{kT}\right] \exp\left[\frac{(\sigma - \frac{1}{2}\sigma_\infty)V^*(d)}{kT}\right]$$

What about boundary lubrication of metal contacts (e.g. graphite, DLC, MoS₂)?

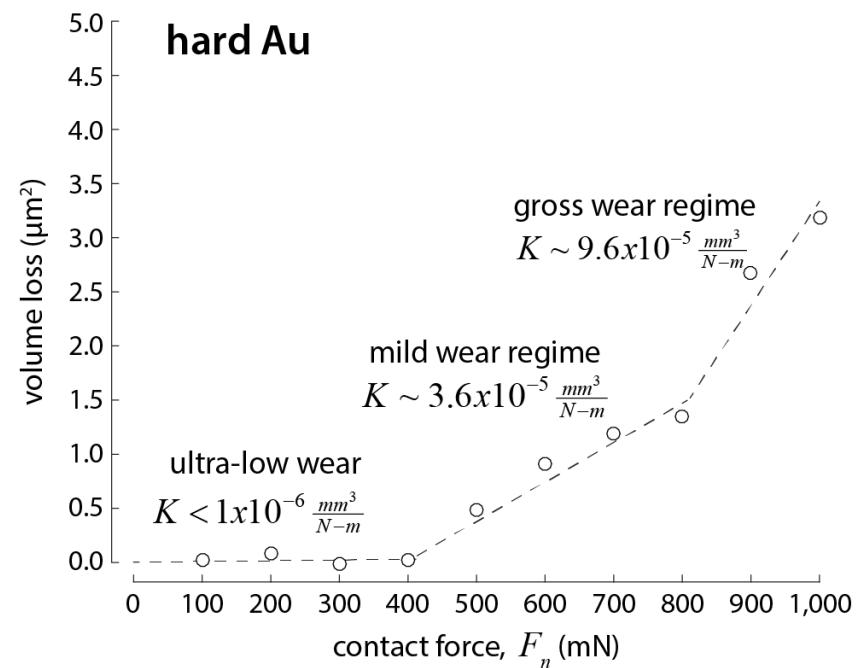
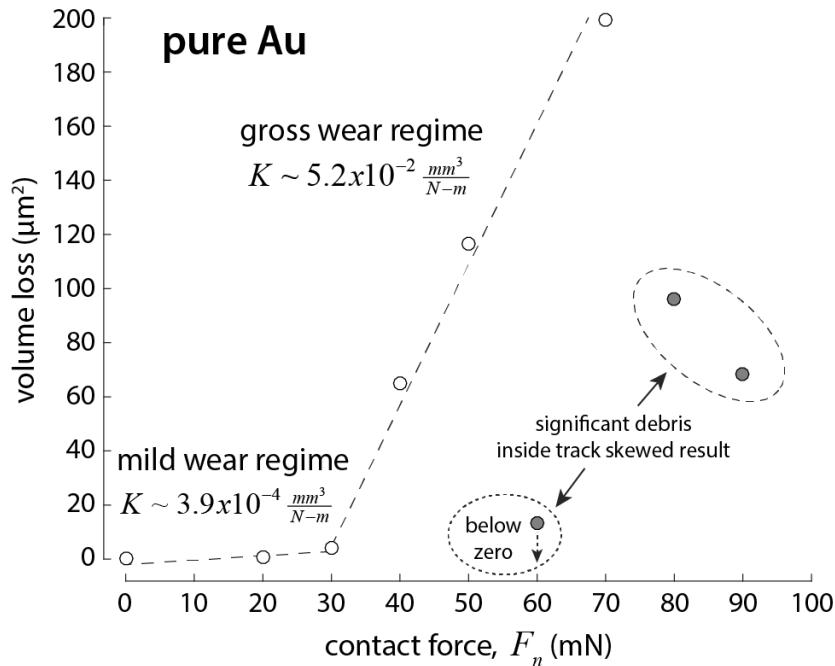


Boundary lubrication (e.g. graphite, MoS₂, engine oil) mitigates commensurate contact – thus it is possible to achieve low friction at higher normal force

Ok, that was a lot of information. Big picture is...



One more look at wear

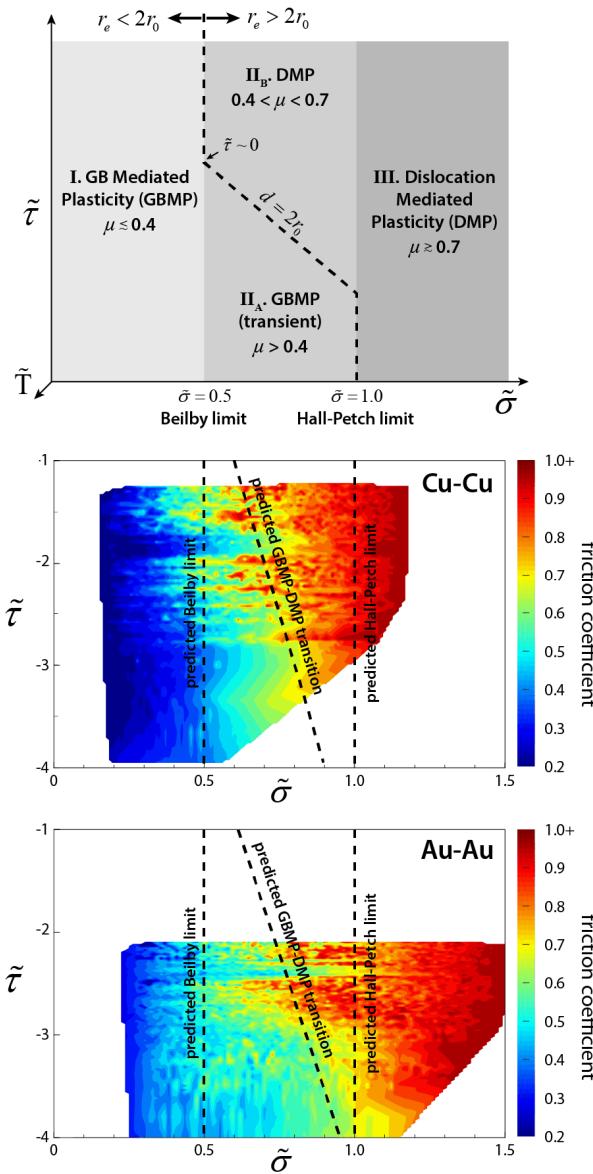


So...

friction regimes described by Hamilton (max surface stress)
wear regimes described by Holm (max bulk stress)

Only the beginning, much left to do... some exciting prospects below

- So far only applied to FCC metals. Apply to BCC metals, ionic solids -- ductility observed in nanoparticles of alumina
- Now exploring the temperature axis: optimizing high current density electrical sliding and rolling contacts
- Clearly there are other regimes and boundaries that have not been identified...
- Low friction regime is result of a competition between wear and stress-driven grain growth
- Can we **determine** stacking fault energy or grain boundary mobility for alloys?
- Can we model competing wear? ...difficult, but maybe



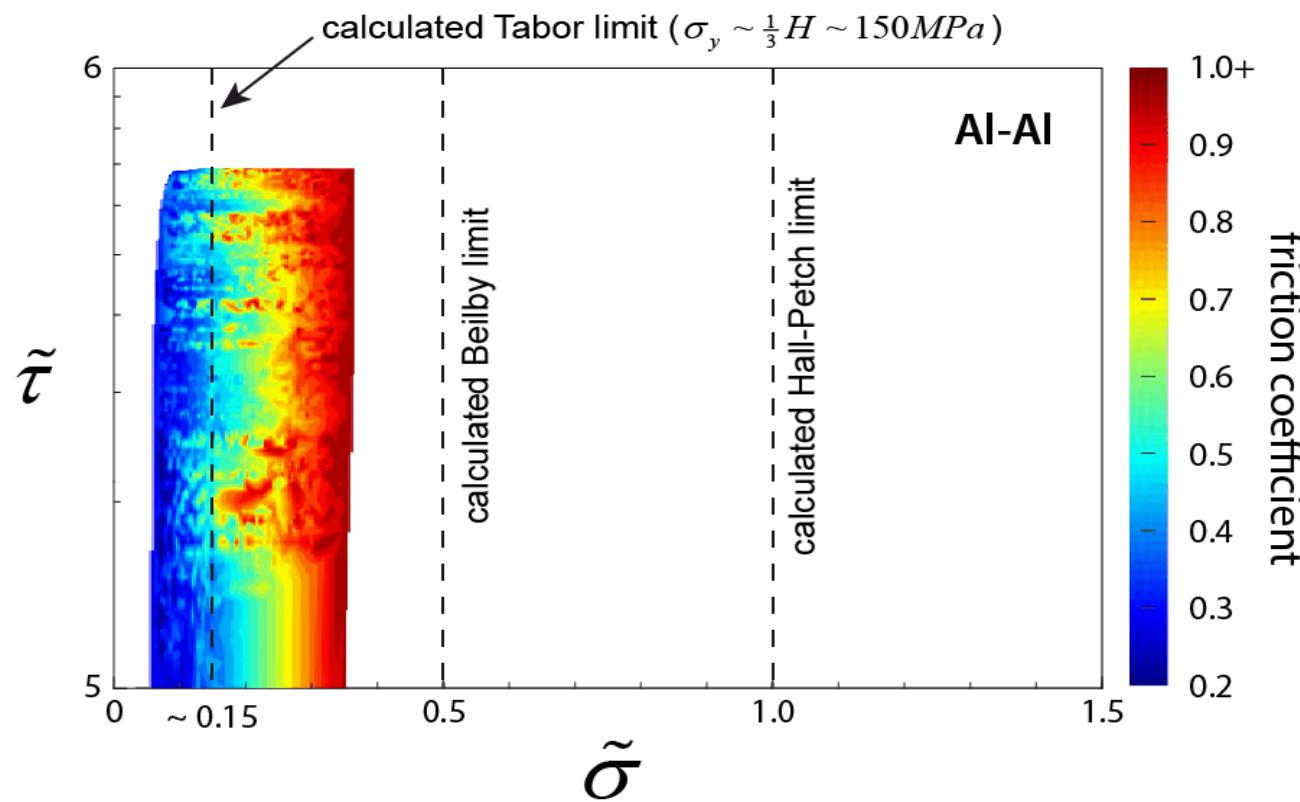
Appendix Slides

Material Properties and Calculated Parameters

property	material system				
	<i>Au</i>	<i>Cu</i>	<i>Al</i>	<i>Ni</i>	units
shear modulus, G	27	48	27	76	GPa
Poisson ratio, ν	0.44	0.36	0.35	0.31	-
lattice constant, a	4.08	3.61	4.05	3.52	Å
Burgers vector, b	2.88	2.55	2.86	2.49	Å
SFE, γ_{sf}	45	78	166	128	mJ/m ²
GBE, γ_{gb}	378	625	324		mJ/m ²
HAGB mobility, M_0	3.84×10^{-6}	30	2×10^{-2}		m/s-Pa
HAGB activation energy, Q	1.33	2.01	1.05		$\times 10^{-19}$ J
calculated parameters					
<i>equilibrium splitting distance, r_0</i>	8.7	5.9	2.0	2.8	nm
σ_∞	312	611	1,117	1,808	MPa
$\sigma(r = 2r_0)$	156	306	580	904	MPa



Aluminum and the Tabor limit



High stacking fault energy... BUT low strength!

Classical attempts to define wear & friction regimes were empirical/phenomenological

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VIEWPOINT SET No. 14

WEAR-MECHANISM MAPS

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(Revised October 16, 1989)

WEAR-MECHANISM MAPPING: THE APPROACH

Wear is the loss or transfer of material when contacting surfaces slide. In general, the wear rate W (defined here as the volume loss per unit area of surface per unit distance slid) depends on the bearing pressure F/A_n (where F is the load carried by the contact and A_n is its nominal area), on the sliding velocity, v , and on the material properties and geometry of the surface (Figure 1):

$$W = f(F/A_n, v, \text{Mat. Props., Geometry}) \quad (1)$$

But one such equation is not enough. There are many mechanisms of wear, each dependent in a different way on the variables. The dominant mechanism, at any given F and v , is the one leading to the fastest rate of wear. Table 1 lists some of the mechanisms encountered in wear studies of metals and of ceramics; it includes wear by melting, by chemical change induced by frictional heating, by low-temperature plasticity and by brittle fracture.

TABLE 1: MECHANISMS OF WEAR

METALS	CERAMICS
SEIZURE	SEIZURE (?)
MELT WEAR	MELT WEAR
SEVERE-OXIDATIONAL WEAR	THERMALLY-INDUCED STRUCTURE CHANGE
MILD-OXIDATIONAL WEAR	THERMAL CRACKING AND SPALLING
PLASTICITY-DOMINATED WEAR	BRITTLE SPALLING; INDENTATION CRACKING
ULTRA-MILD WEAR	

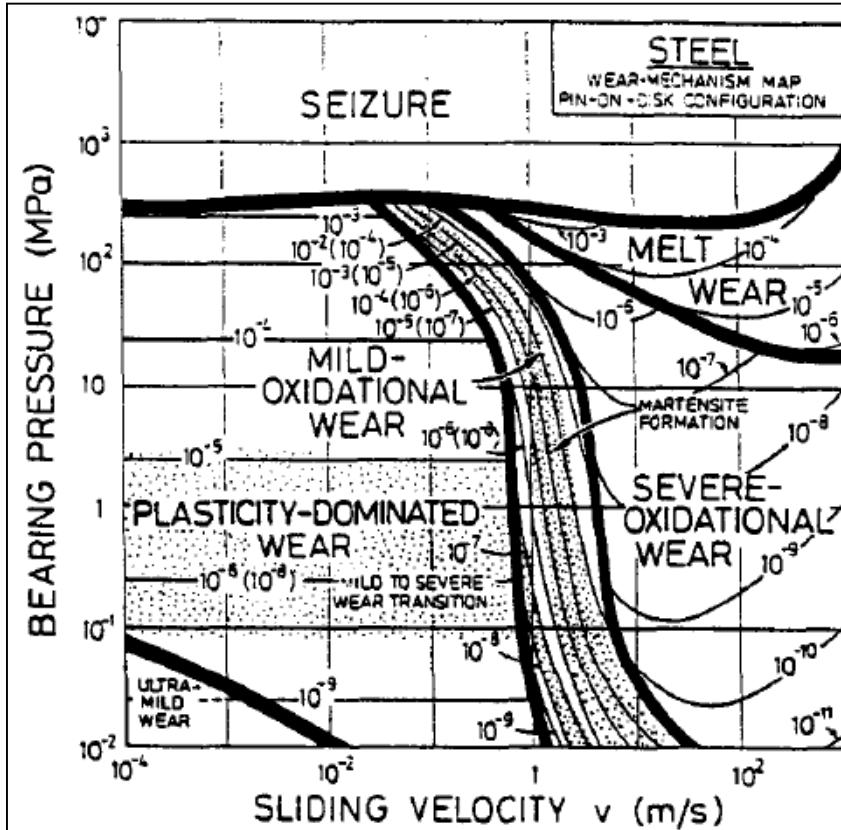
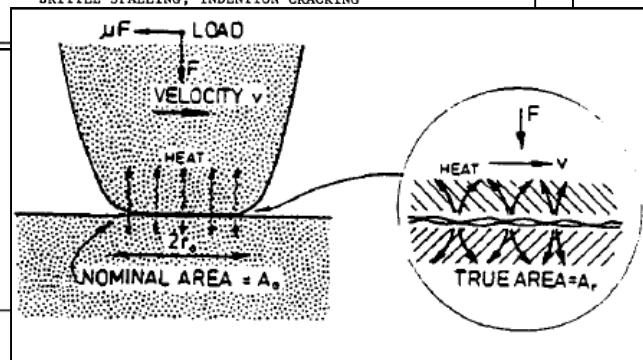
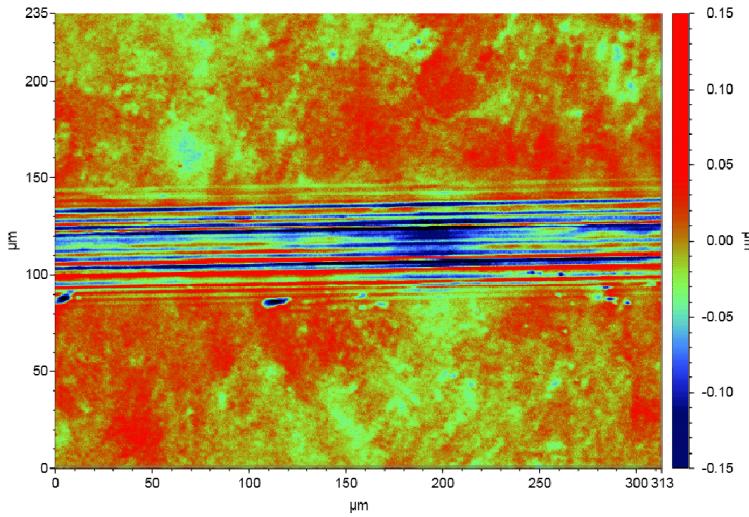


Figure 3. A wear-mechanism map for low-carbon steel based on physical modelling calibrated to experiments. The shaded regions show transitions.

Wear analysis of pure and alloy gold surfaces along wear track for ramped force test

Wear tracks analyzed using a scanning white light interferometer, sample image shown below:



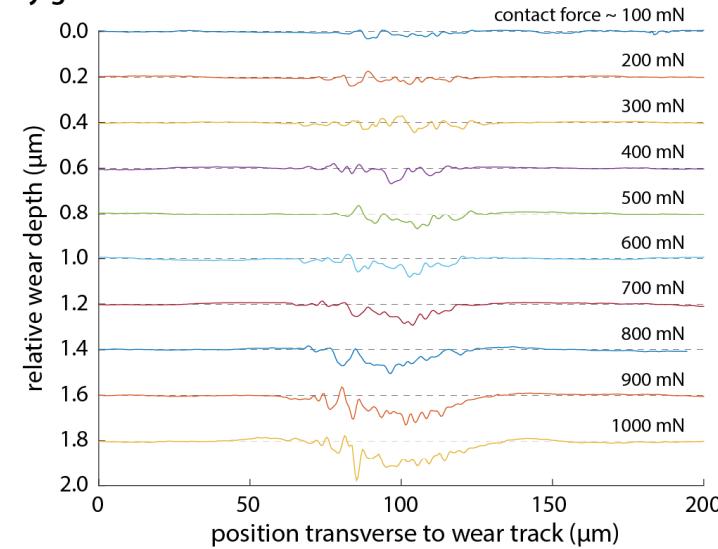
Images taken at 1 mm intervals along 10 mm long wear tracks

Each image then collapsed into a single line plot showing the average wear track cross-section (right images)

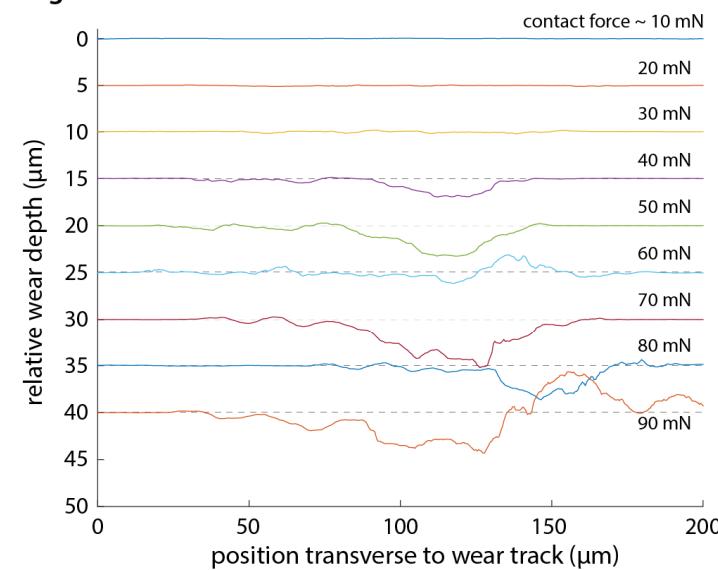
Wear at each interval calculated based on contact force average in this part of the track, number of cycles, and volume loss

Change in contact force along length of image (313 μm) was about +/- 3% of max load

alloy gold film surface evolution

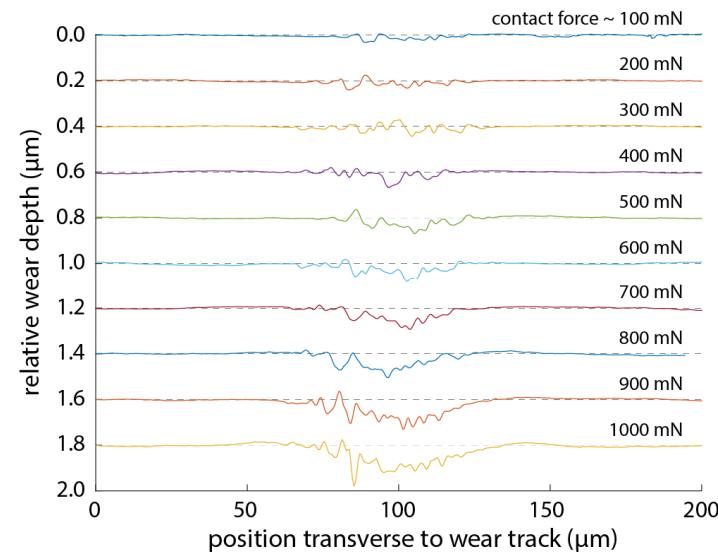
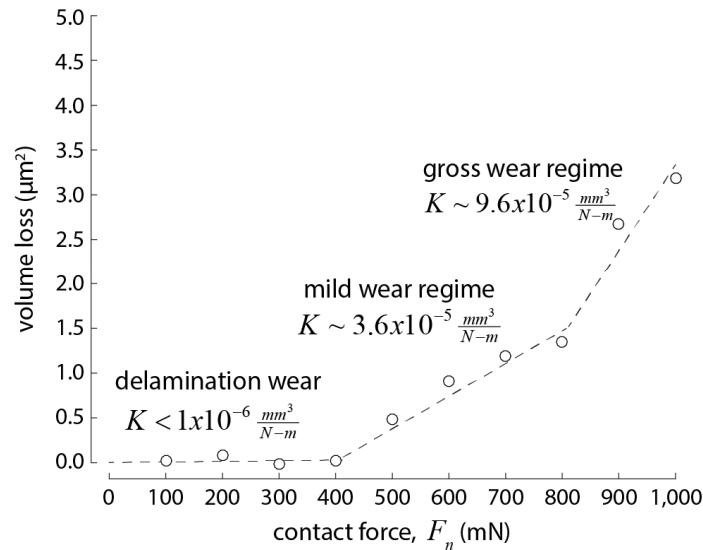


pure gold substrate surface evolution

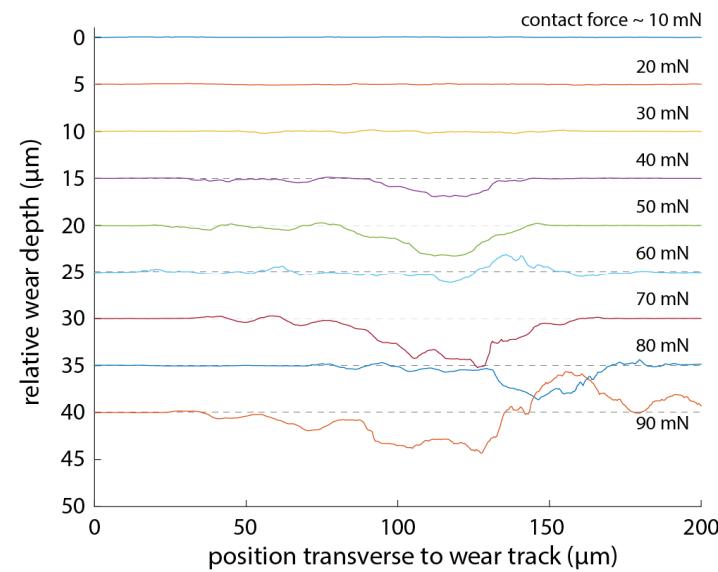
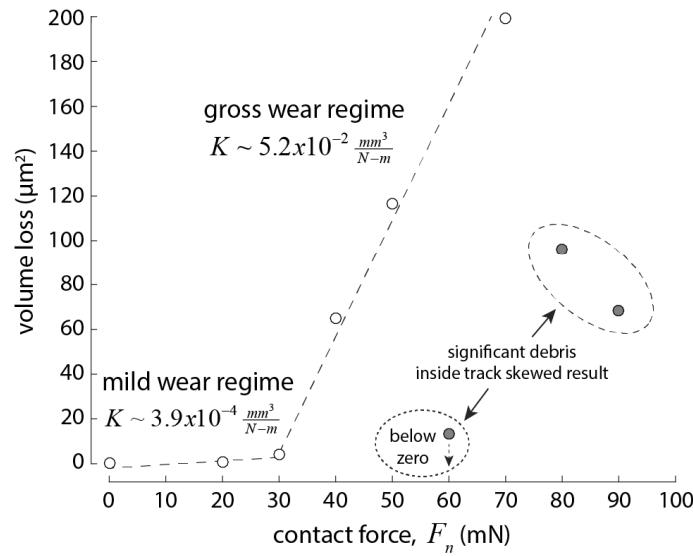


Observed three wear regimes

alloy gold film surface evolution



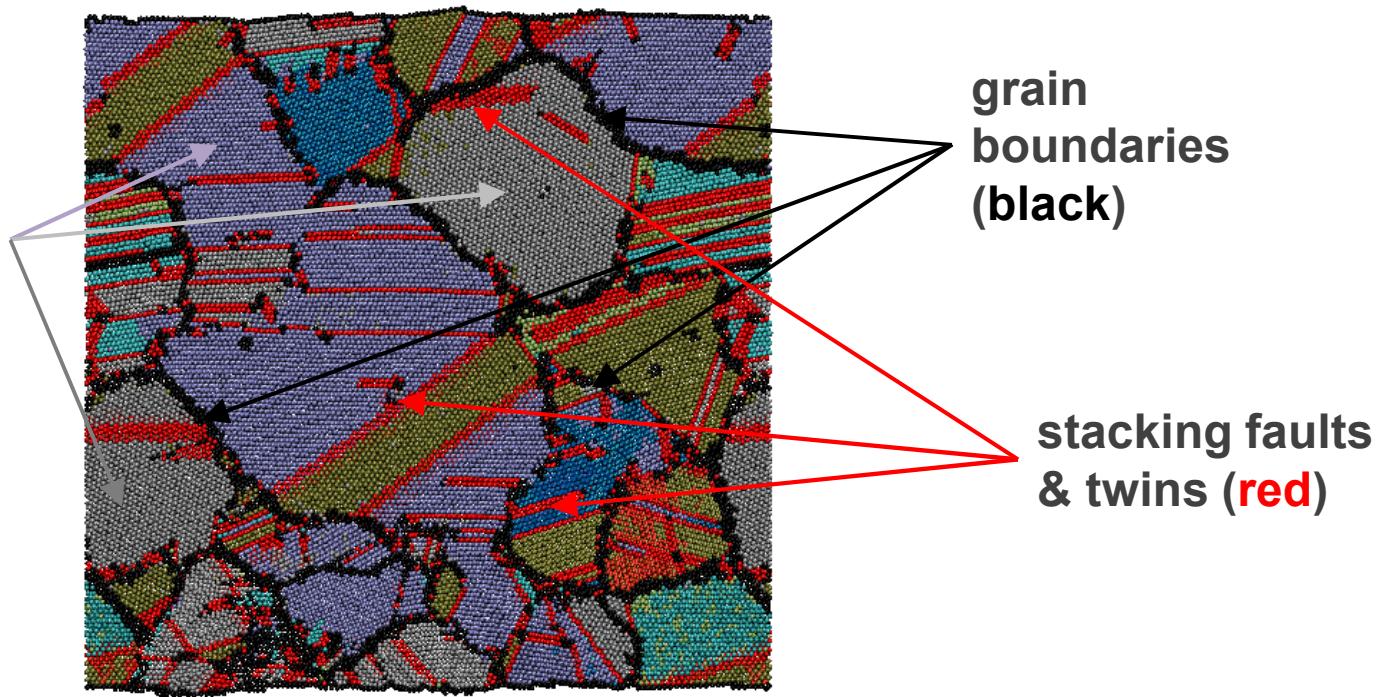
pure gold substrate surface evolution



MD Simulations: how to interpret the following images...

Cross-sectional slices of a 3D space filled with atoms

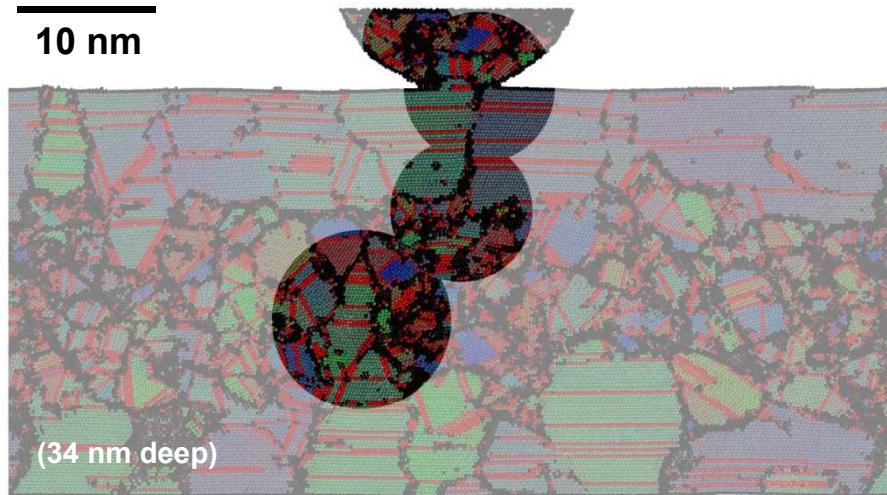
grains/crystallites
(color according
to
orientation/Euler
angle)



- Locally FCC atoms colored according to Euler angle
- Locally HCP atoms colored red – twins & stacking faults
- Otherwise colored black – grain boundaries

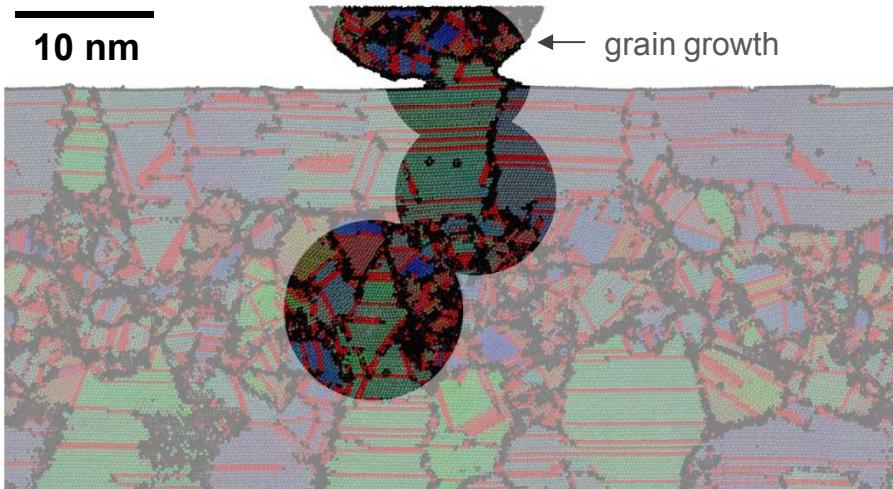
Comparison between pure and alloyed Ag grain evolution: **stabilization thru alloying**

initial microstructure
of Ag and Ag-Cu alloy
(no sliding yet)

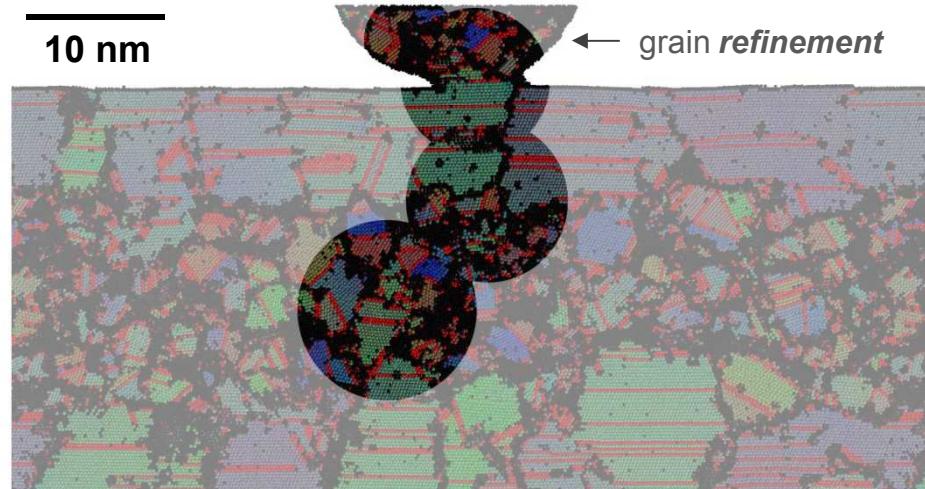


300 MPa contact stress
300 K temperature
2 m/s sliding speed

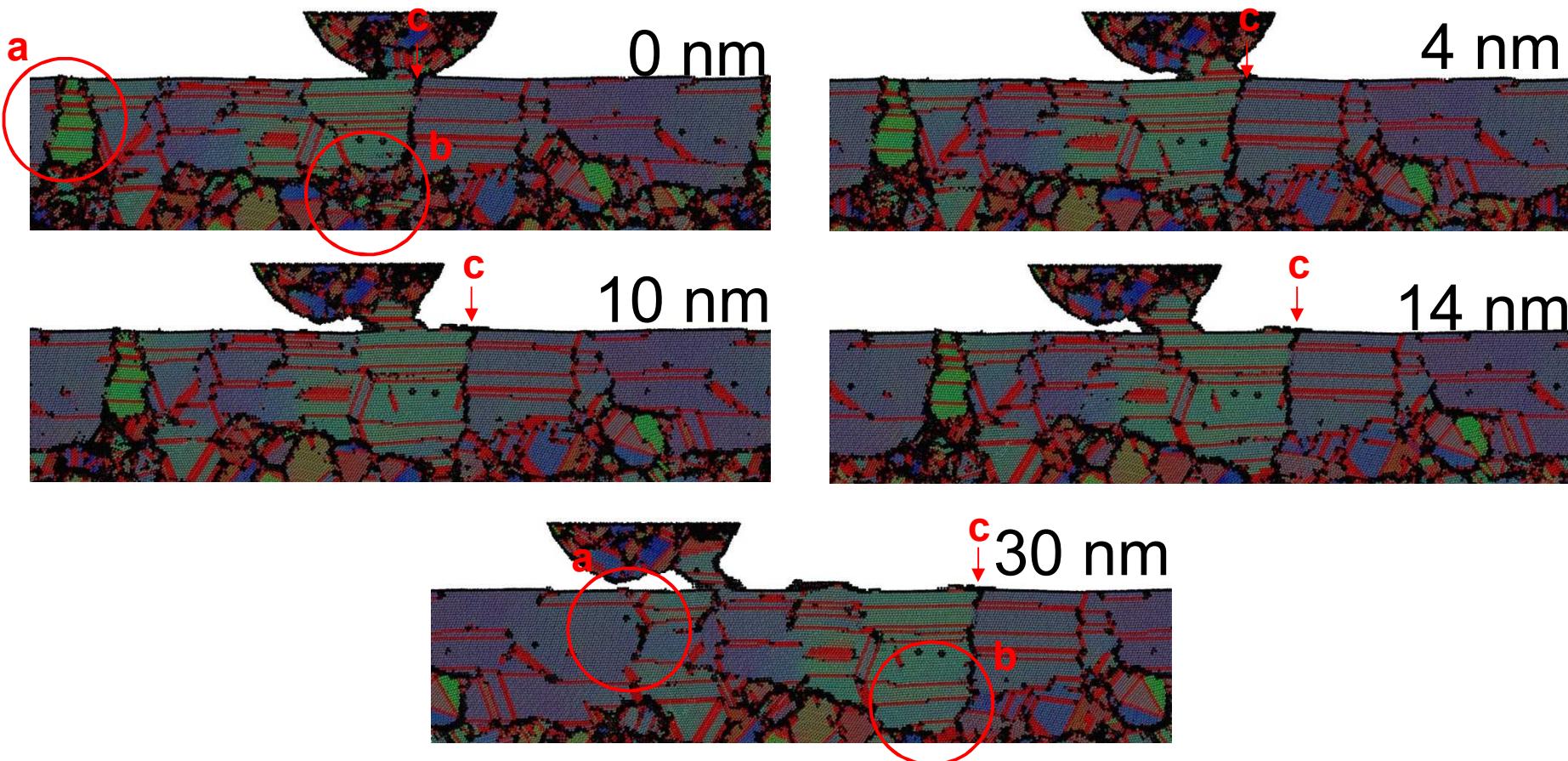
pure Ag after 4 nm of sliding



Ag-10% Cu alloy after 4 nm of sliding

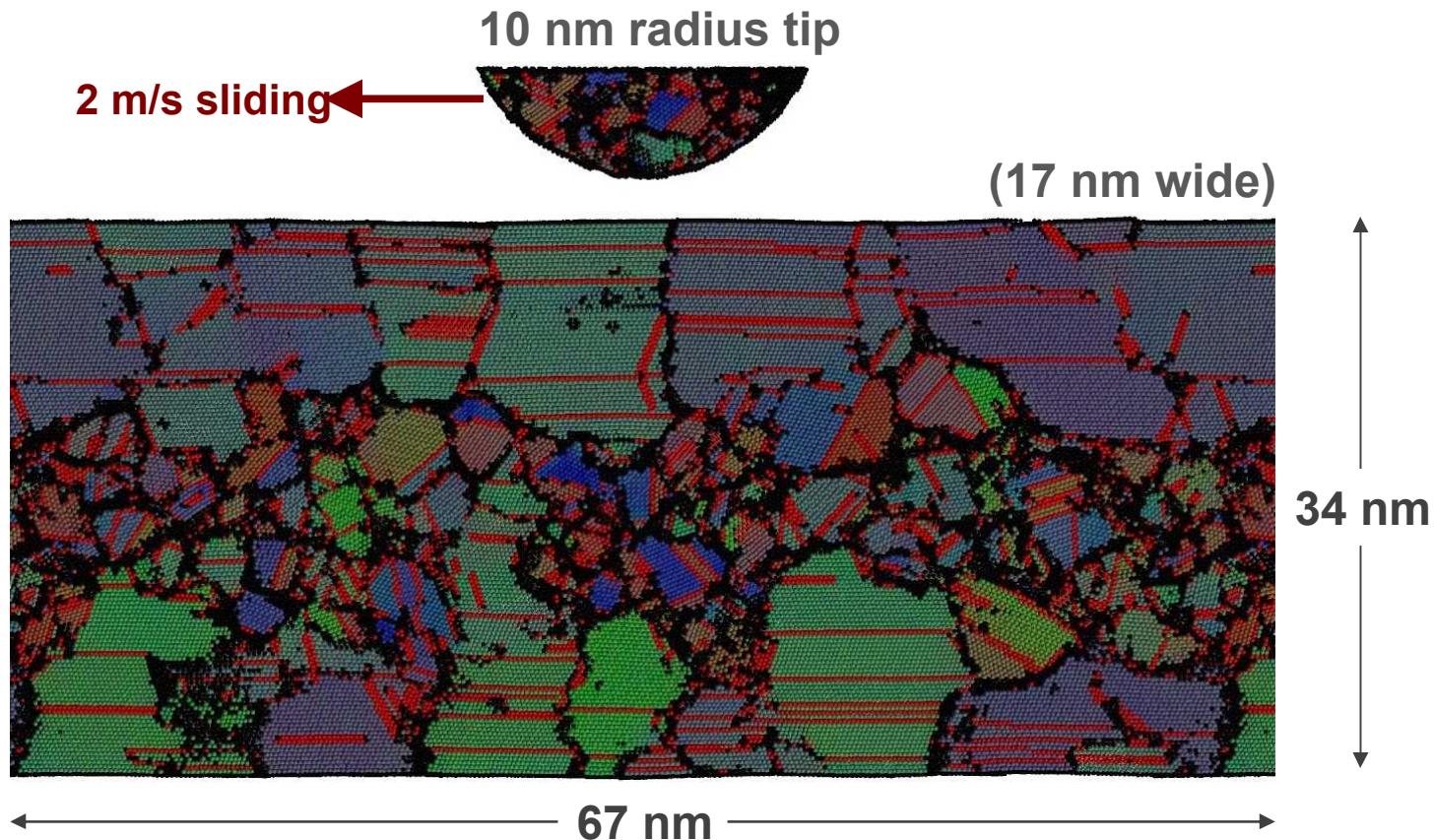


Another look, now at **pure Au** tip/slab contact evolution over a longer sliding time



- Initially distinct grains
- After shear (**adhesive** load), coalescence – now a mode II crack
- Single grain forms across interface – stress induced grain growth

Tip based friction simulations : this is what the initial condition looks like

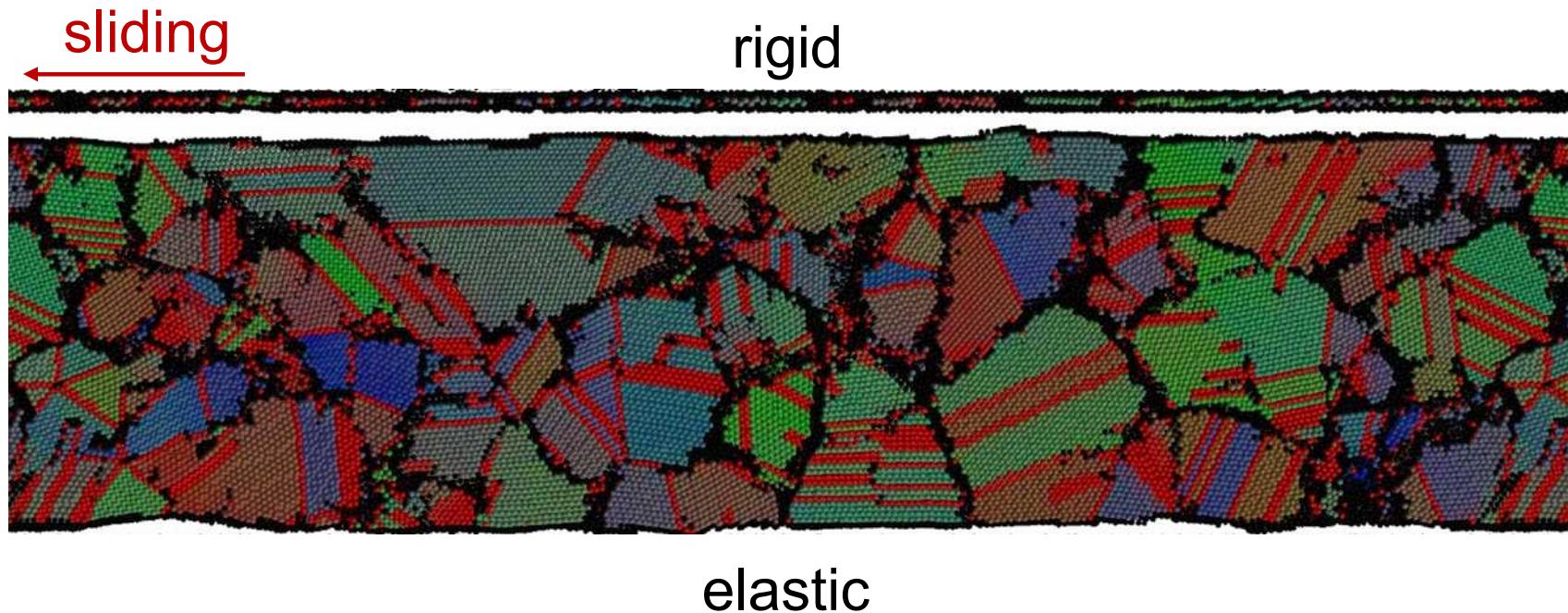


Substrate: nanocrystalline Ag

Constraint 1: constant velocity

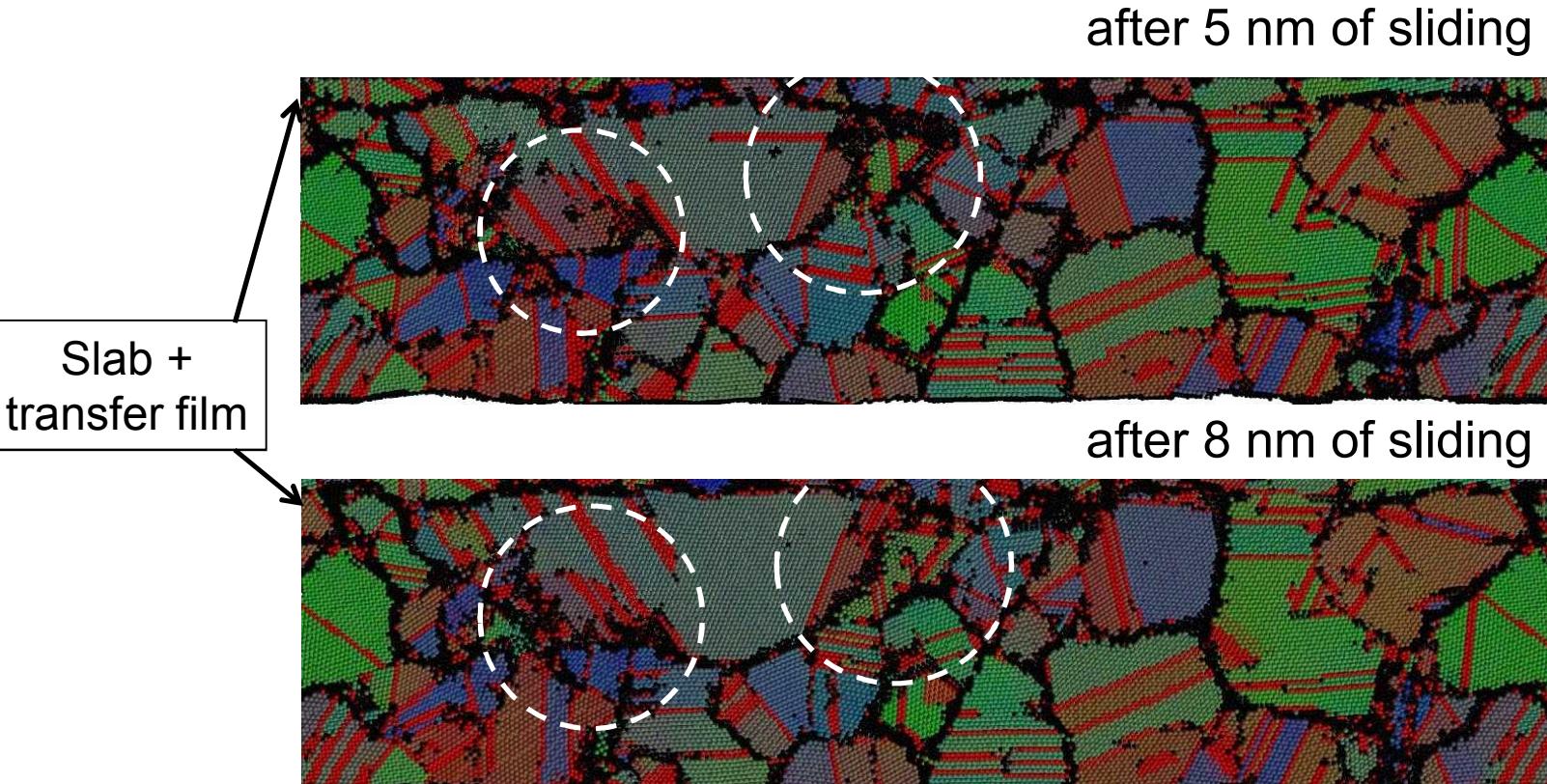
Constraint 2: constant separation **or** normal force

Slab-on-slab sliding contact simulations remove wear, enable friction quantification



- Rigid slabs suppress grain growth
- No plowing is possible/reduced contact stress

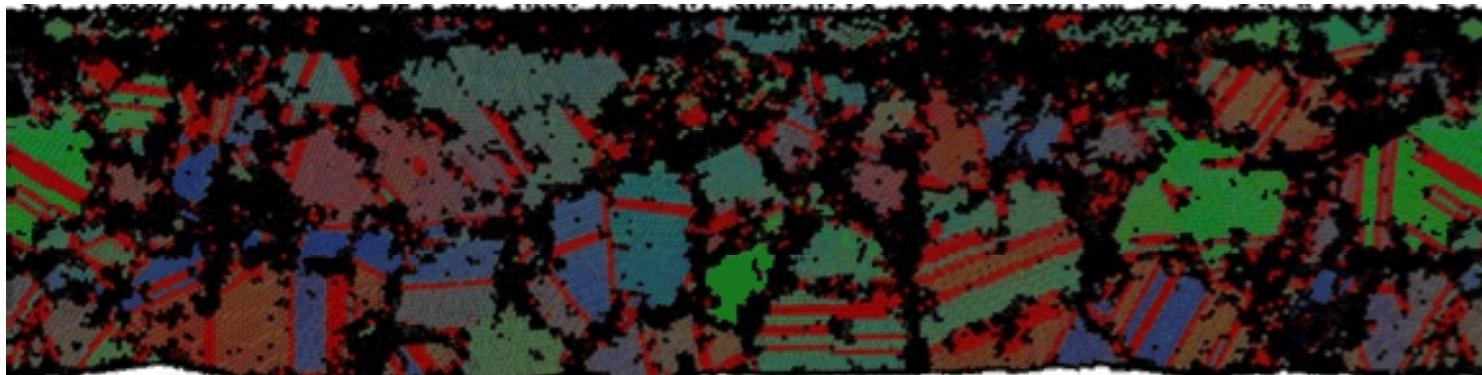
Sliding of pure Ag slabs



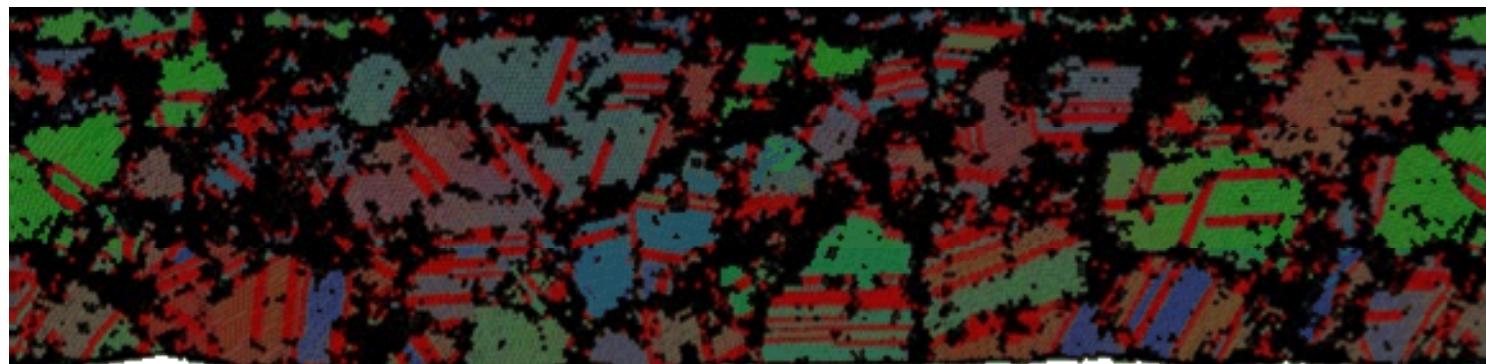
- Slight grain growth, forms transfer film
- Slides along transfer film grain boundaries or nearby stacking faults depending on availability

Sliding of Ag alloy (10% Cu) contact

after 6 nm of sliding



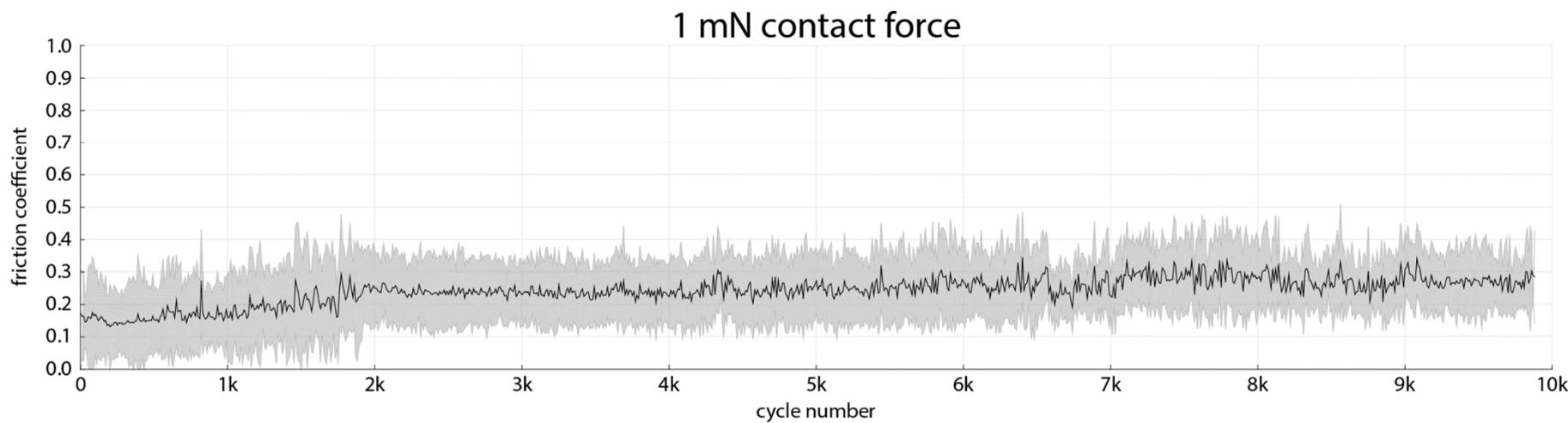
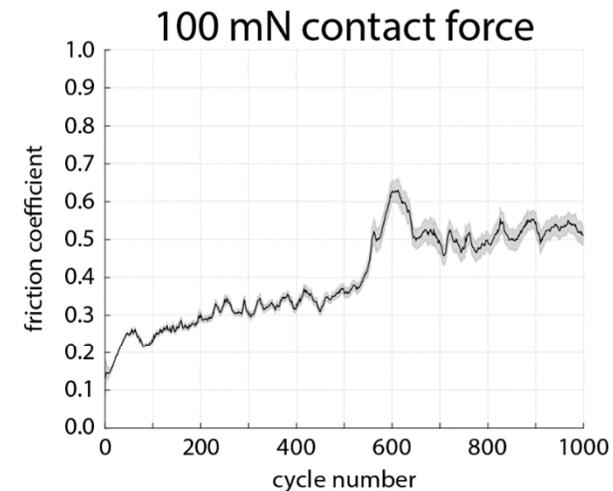
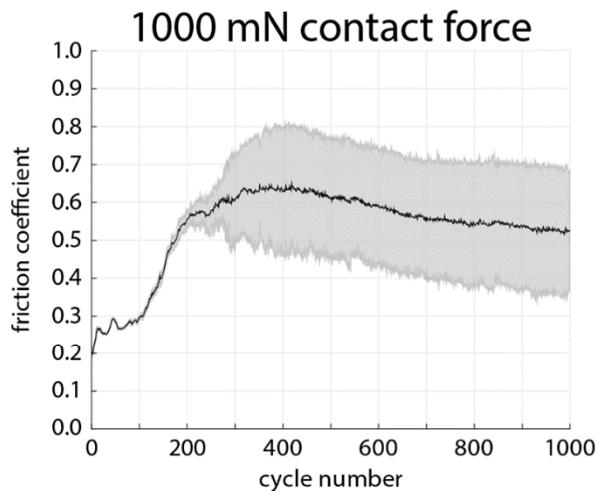
after 16 nm of sliding



- Alloy slides at transfer film boundary, but **also throughout substrate**
- The pure Ag slabs on previous slide started with the exact same microstructure (lots of coarsening on the pure Ag slabs simulation!)

Three regimes observed for 60Ni-40W at.% vs sapphire in oxidizing environment

1 mm/s sliding speed
three contact forces used
bidirectional sliding
2mm long track
sapphire ball 1.6 mm diameter
sliding in lab air



FIB-TEM wear track cross-section of 1 mN normal force / 10k cycle test

off-track reference

UNC Ni-40%W
(XRD \sim 5 nm grains)

brass substrate

200 nm

1.5 μ m

1 mN, 10k cycles track

no apparent change
in grain size
($\mu \sim 0.3$, steady-state)

200 nm

FIB-TEM wear track cross-section of 100 mN normal force / 1k cycle test

off-track reference

UNC Ni-40%W
(XRD \sim 5 nm grains)

200 nm

brass substrate

1.5 μ m

100 mN, 1k cycles track

no apparent change
in grain size
($\mu \sim 0.5$, transient)

FIB-TEM wear track cross-section of 100 mN normal force / 1k cycle test

off-track reference

UNC Ni-40%W
(XRD \sim 5 nm grains)

200 nm

brass substrate

1.5 μ m

100 mN, 1k cycles track

mixed UNC metal/oxide

refined near surface Ni-W

FIB-TEM wear track cross-section of 1000 mN normal force / 1k cycle test

off-track reference

UNC Ni-40%W
(XRD \sim 5 nm grains)

brass substrate

200 nm

1.5 μ m

1N, 1k cycles track

significant coarsening
into the film!
($\mu \sim 0.5 \pm 0.2$, steady-state)

200 nm

Disruptive breakthrough in 2012: *intrinsic thermal stability* possible with NC alloys!

Regular Nanocrystalline Solution (RNS) model

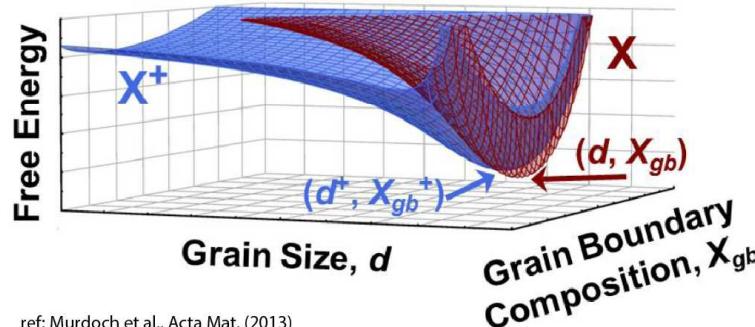
ref: Chookajorn et al., Science, 2012

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

change in Gibbs free energy is positive, but local minimas exist!

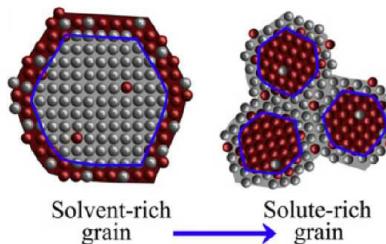
Implications:
Will not drive toward fine grain size, but will remain there

Two examples of predicted nanocrystalline intrinsic stability for global solute concentrations (X and X^+) for a W-based binary alloy:

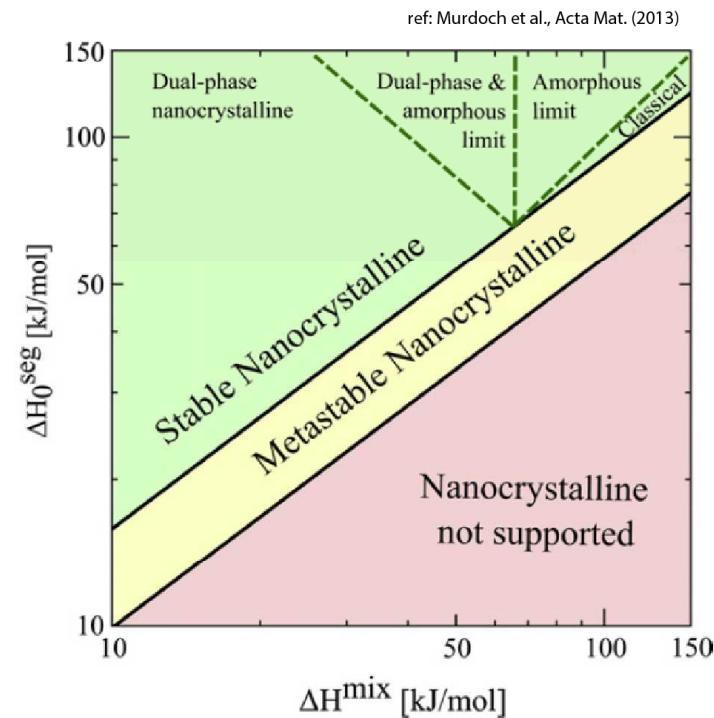


ref: Murdoch et al., Acta Mat. (2013)

Grain structure model: segregated 2-phase metal system:



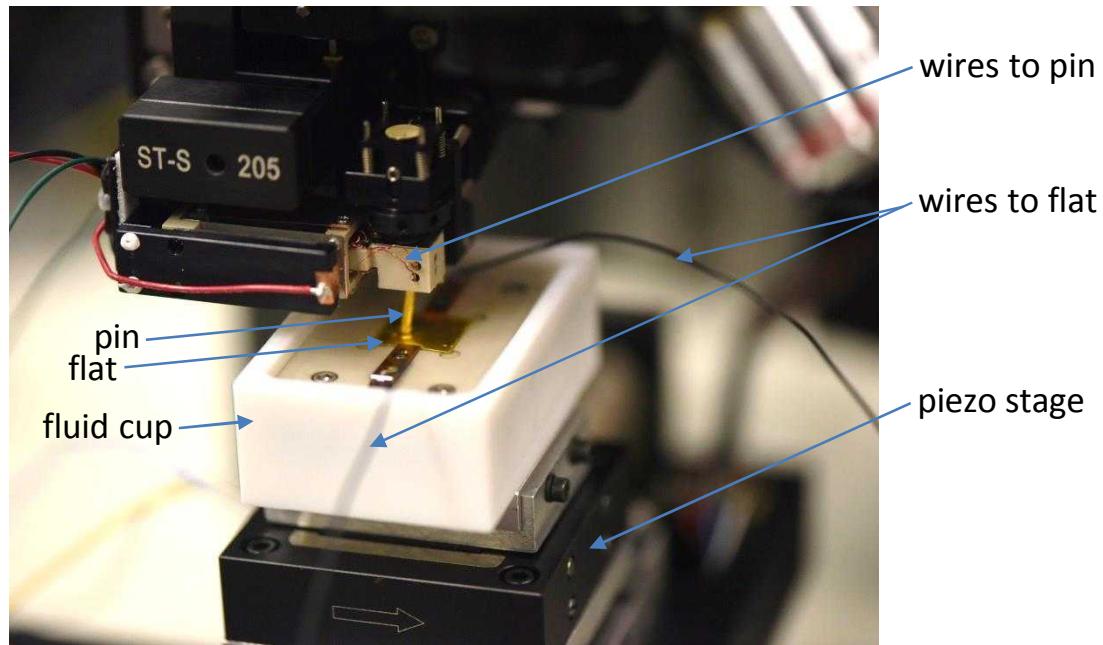
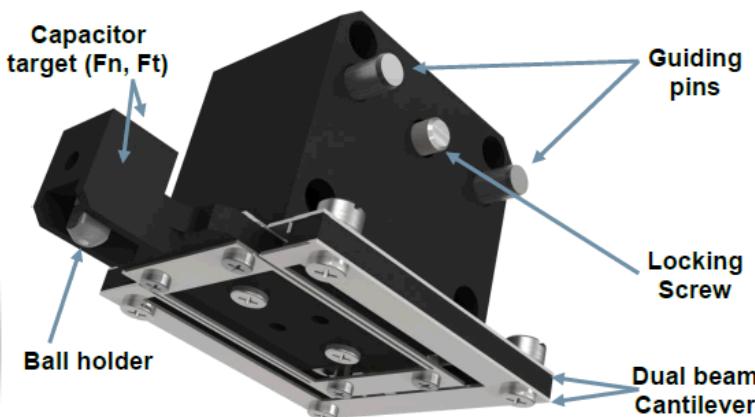
ref: Murdoch et al., Acta Mat. (2013)



$$\Delta H_o^{\text{seg}} = z \left(\omega_c - \frac{\omega_{\text{gb}}}{2} \right) \quad \Delta H^{\text{mix}} = z \omega_c X (1 - X)$$

General condition for stability: $\Delta H_o^{\text{seg}} > \Delta H^{\text{mix}}$

Modified CSM Nanotribometer – friction and wear testing platform



CSM nanotribometer modified for 4-wire ECR measurement

- DC power supply
- nano-ohm meter

Test parameters:

- $F_n = 100 \mu\text{N}$ to 1000 mN
- pin radius = 1.6 mm
- track length = 0.1 to 10 mm
- $v = 0.01$ to 10 mm/s

