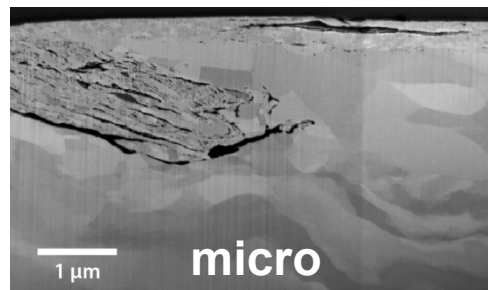
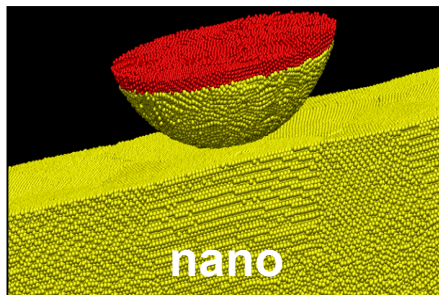


# Pushing the Performance Limits of Electrical Contact Materials *Connecting Nano to Macro*

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*

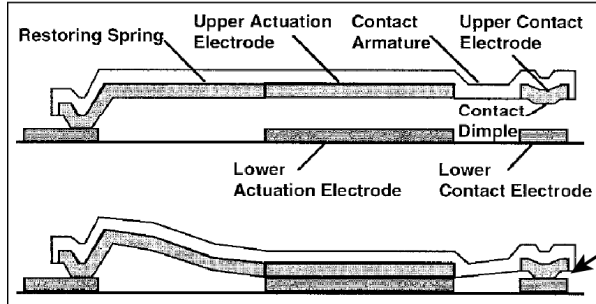


Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

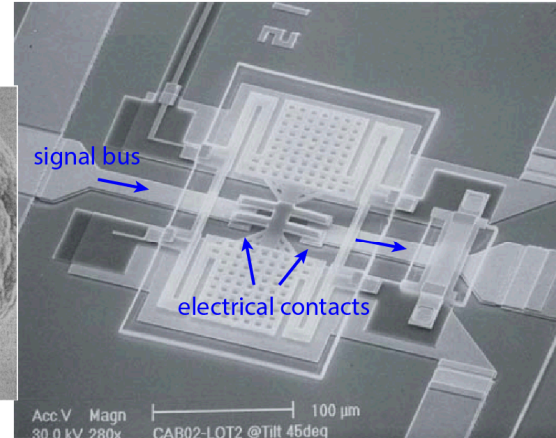
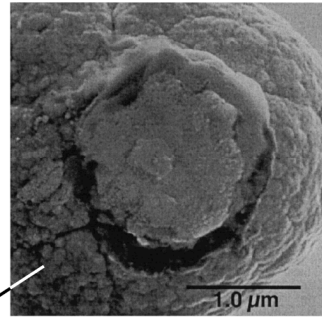
# Metals are widely used tribological materials – electrical contacts

## RF Micro Electromechanical Systems (MEMS)

switching GHz signals



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



Source: Rockwell Scientific metal-metal switch

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



## Aerospace and Energy



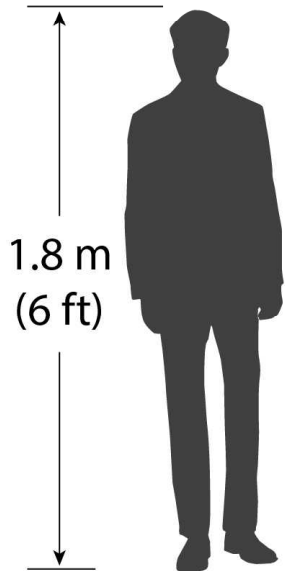
Source: Honeybee Robotics (<http://www.honeybeerobotics.com/portfolio/rolling-contact-connector/>)

# 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)...

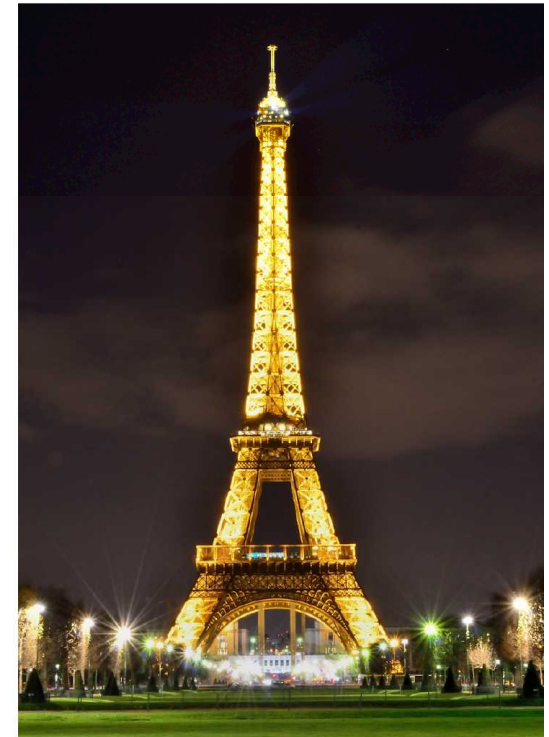
2.6 m (8.5 ft) wide



**Approximately  
US\$13.7 BILLION  
spent in 2010 alone on  
raw material**

\*2.6 m (8.5 ft) deep

... or enough to clad the surface of the Eiffel Tower with 70  $\mu\text{m}$  of pure gold *every year*

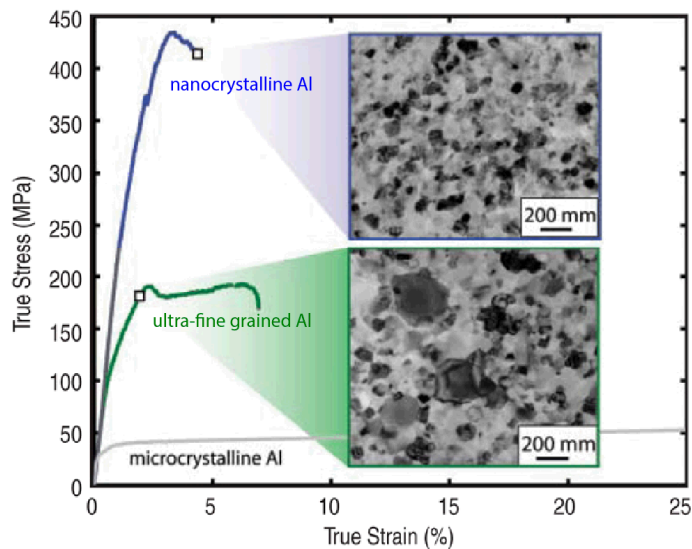


Reference: Gold Survey, Gold Fields Mineral Services Ltd., 2010

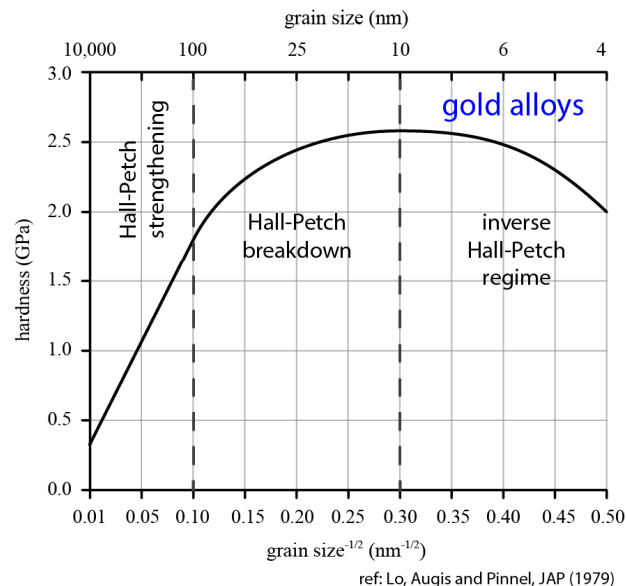


# Engineering advantages of nanocrystalline (NC) alloys and metal-matrix composites

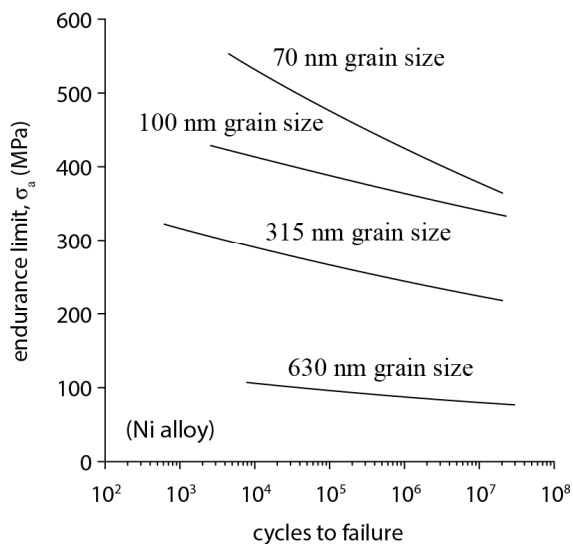
higher yield strength



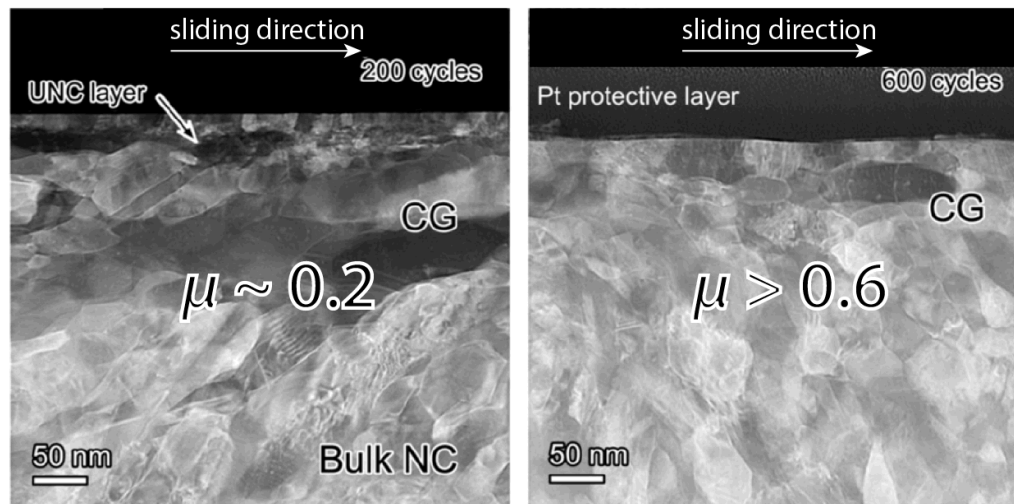
higher hardness



higher fatigue strength (endurance limit)



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

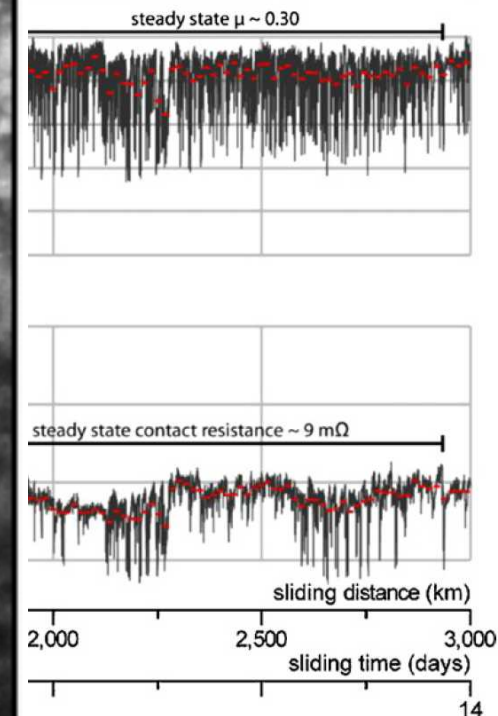
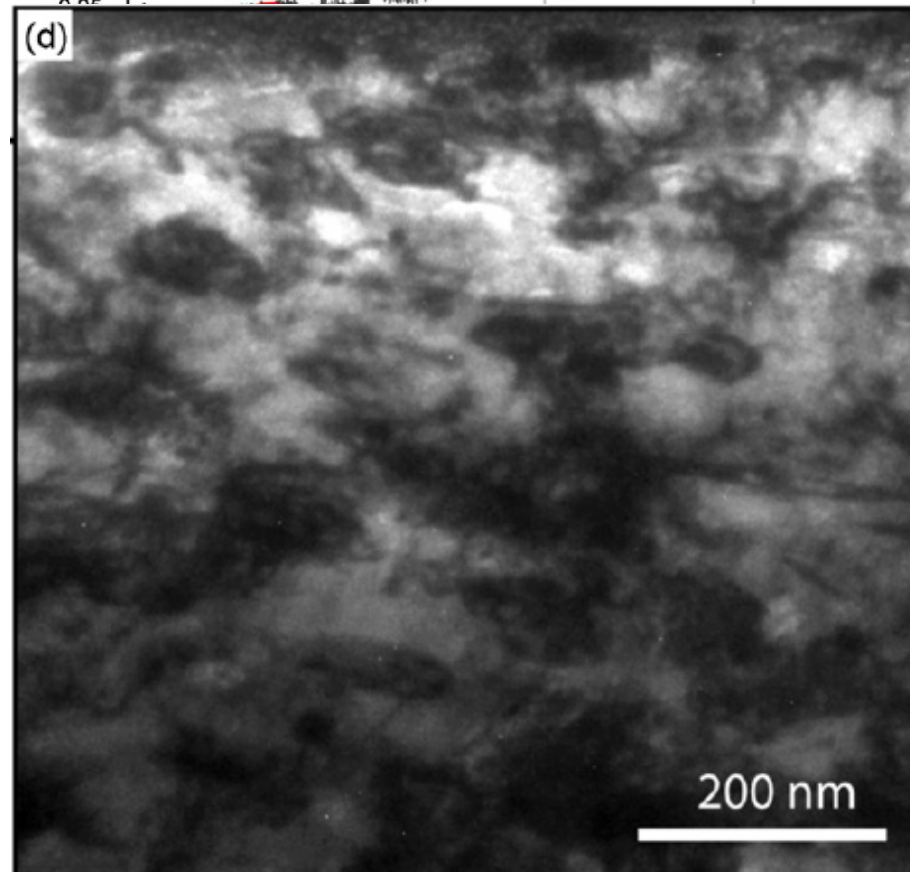
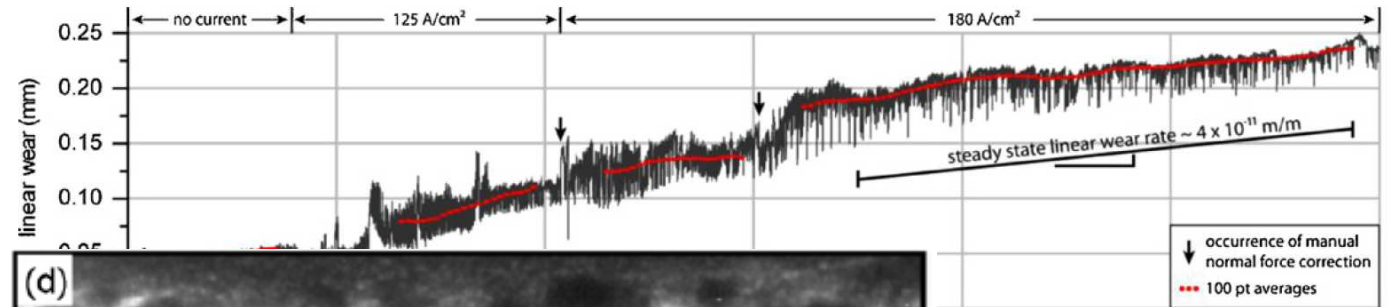
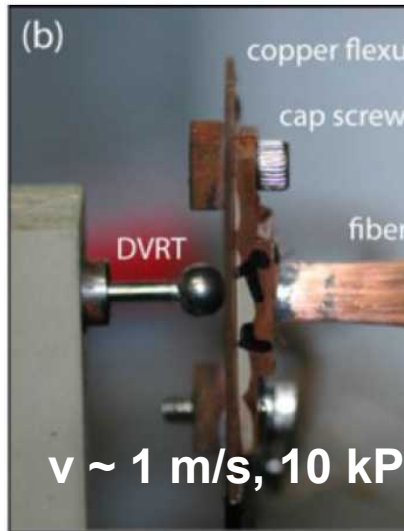


steady-state cross-sections of wear tracks



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

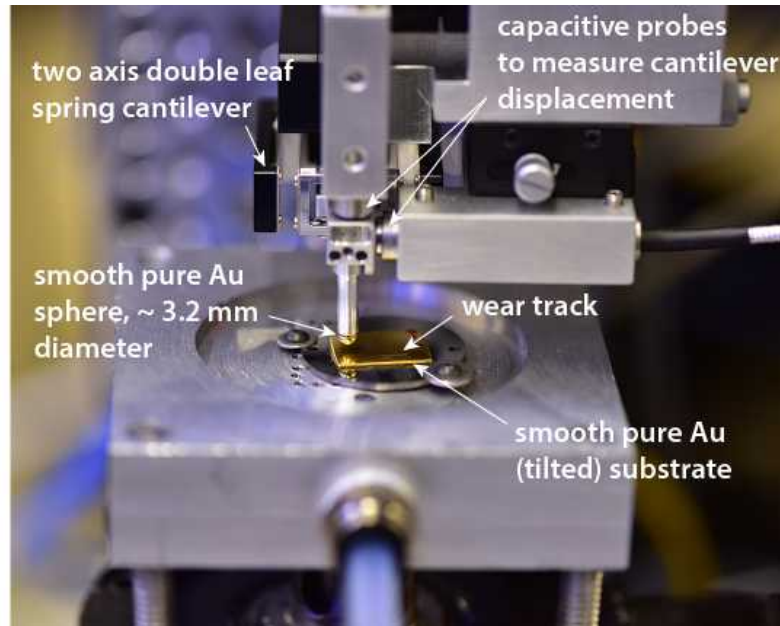
wear rate of  $\sim 1$  nm per kilometer  
 $\mu_{ss} \sim 0.3$



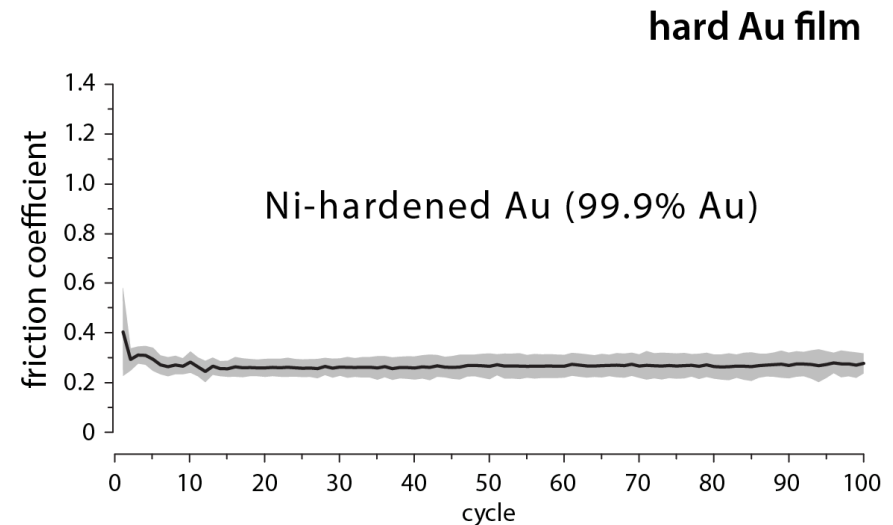
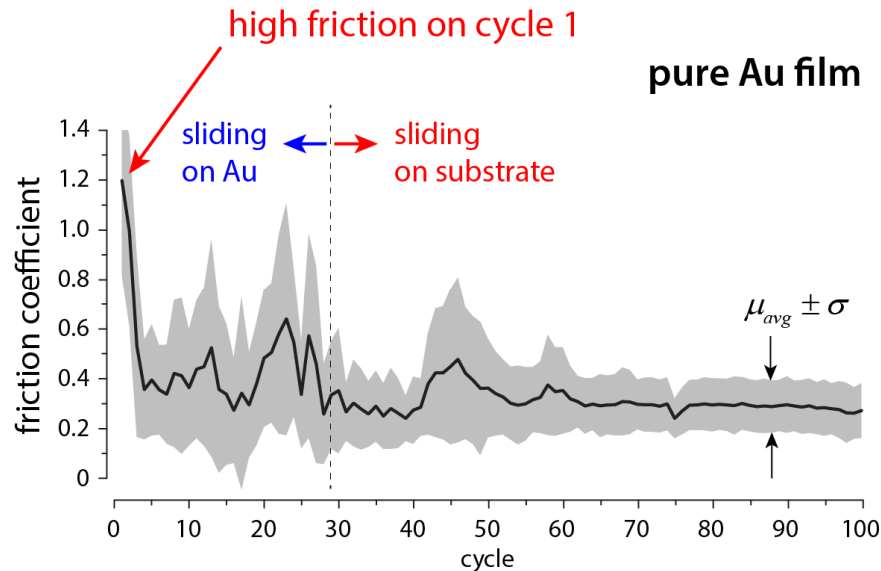
Low friction  
associated with  
nanocrystalline  
surface for a Cu-C  
system

ref: Argibay et al., Wear 2010

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

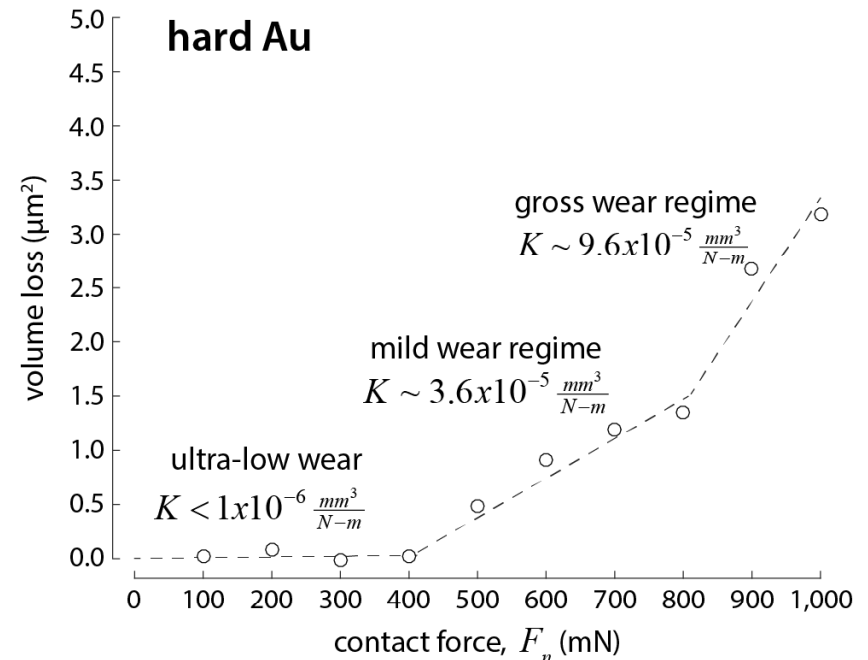
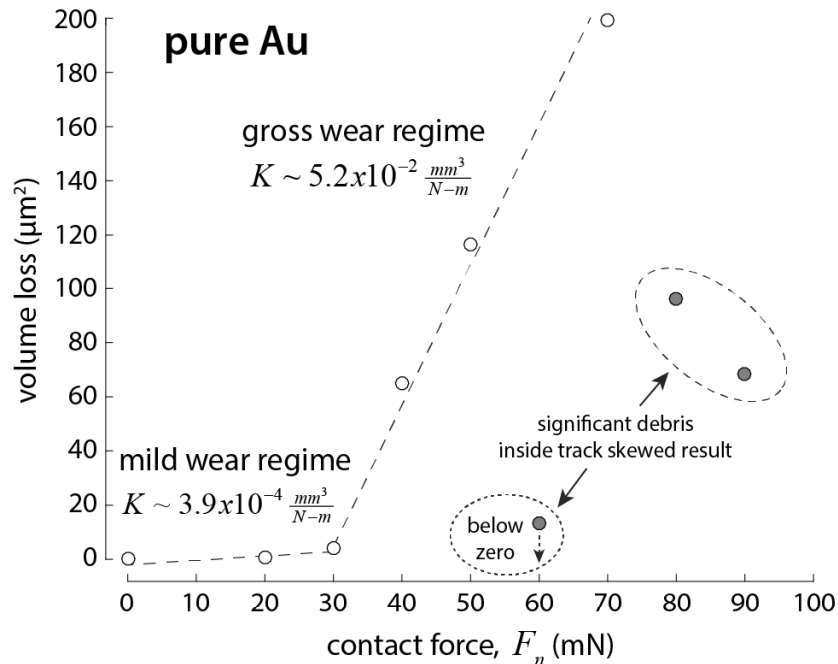


normal force = 100 mN  
ball radius = 1.6 mm  
speed = 1 mm/s



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

Note x- and y-axis scale difference!



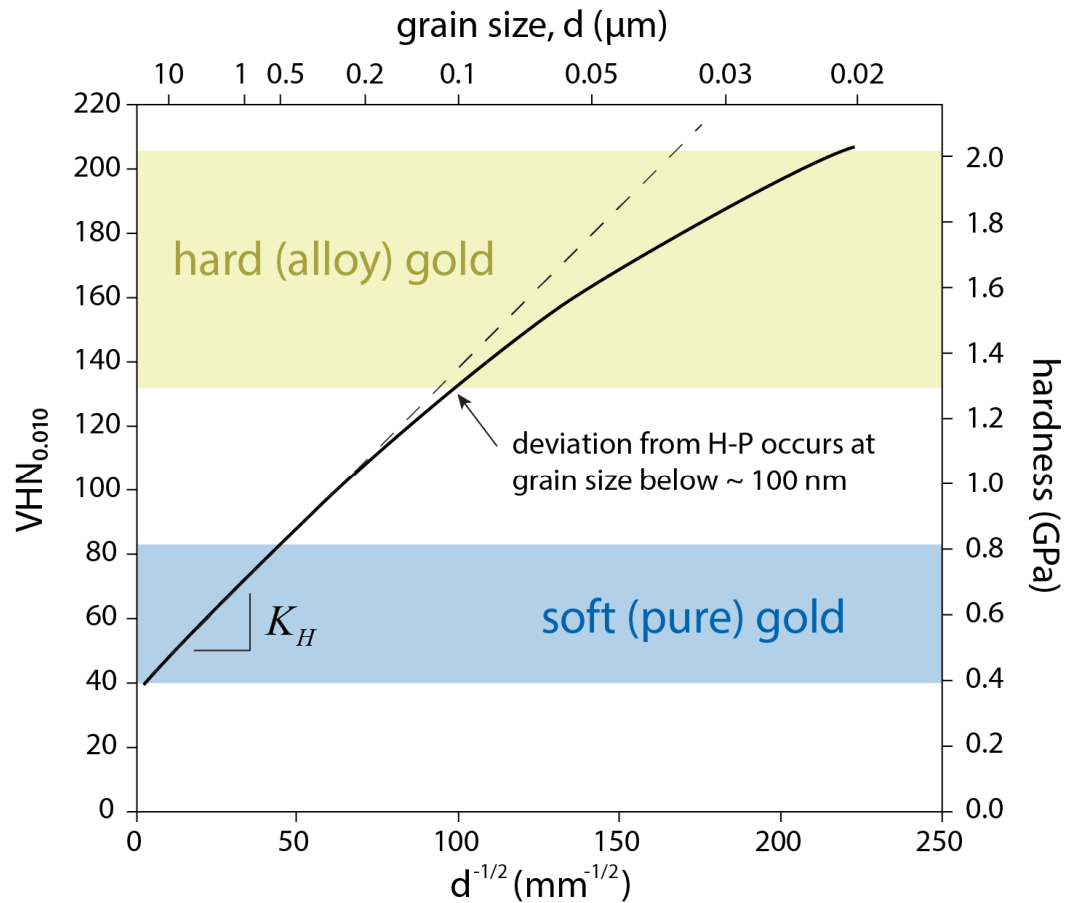
> 10,000x wear rate reduction with addition of 0.1% Ni

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 $\mu$ at higher stresses

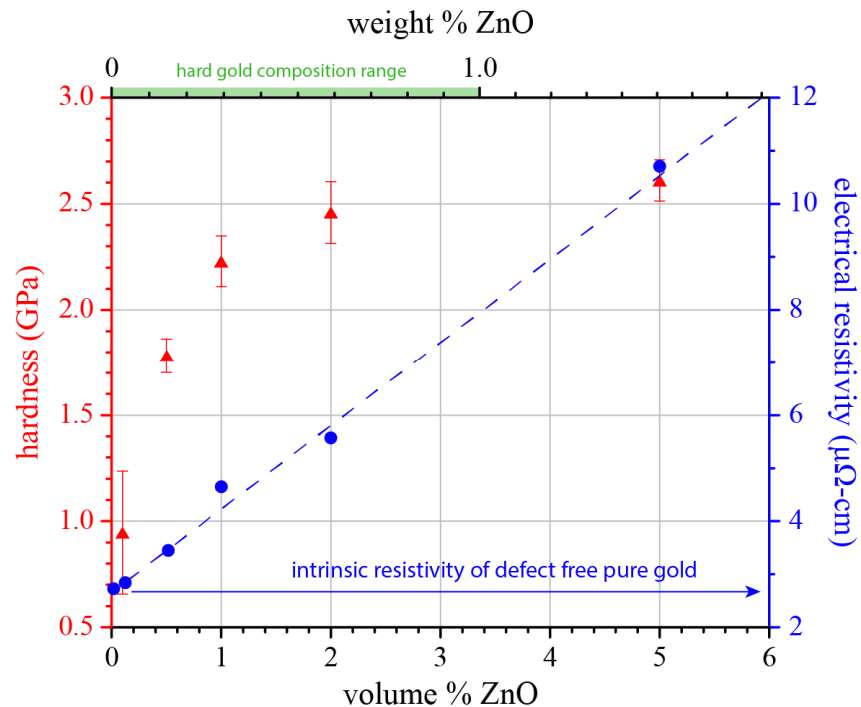
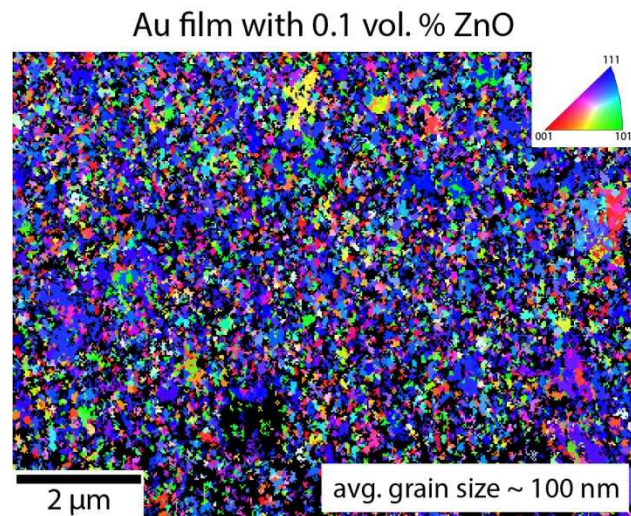
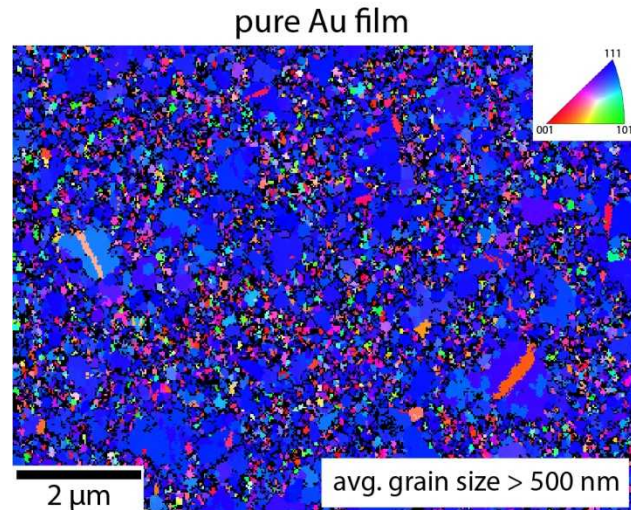


Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

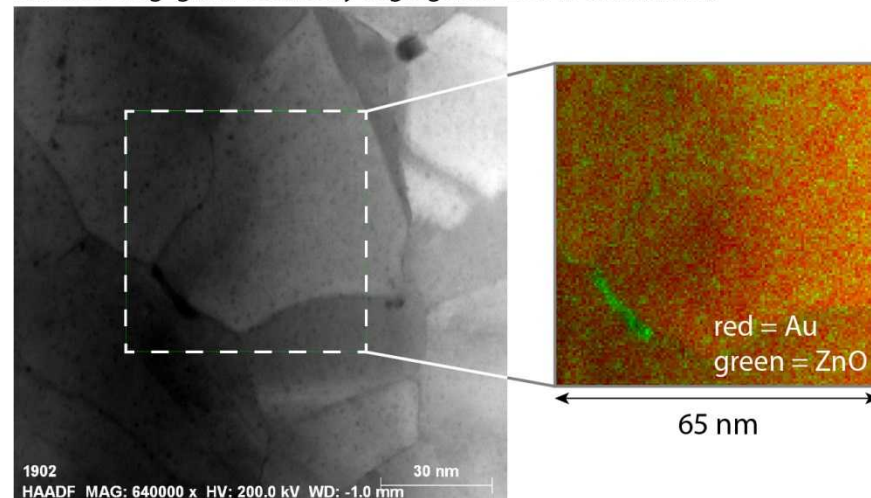
# Stable NC grain size can be also achieved by adding **non-metal species**!

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

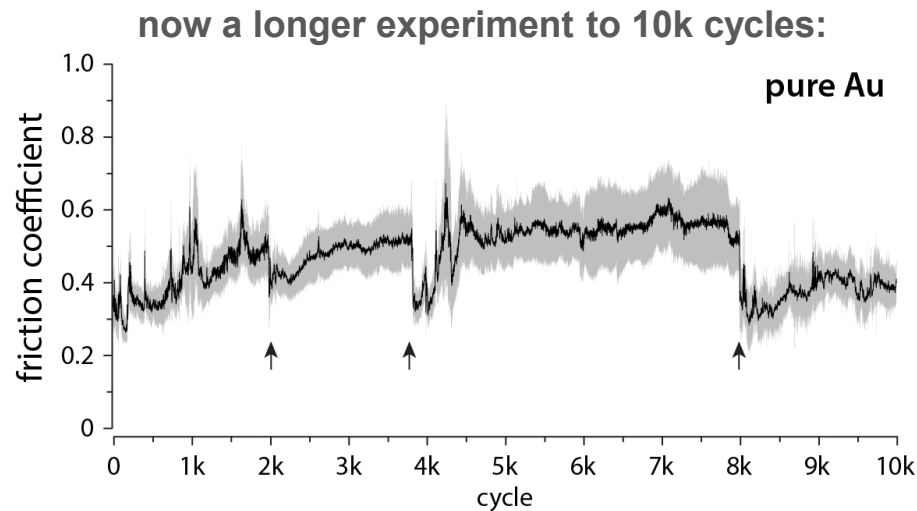
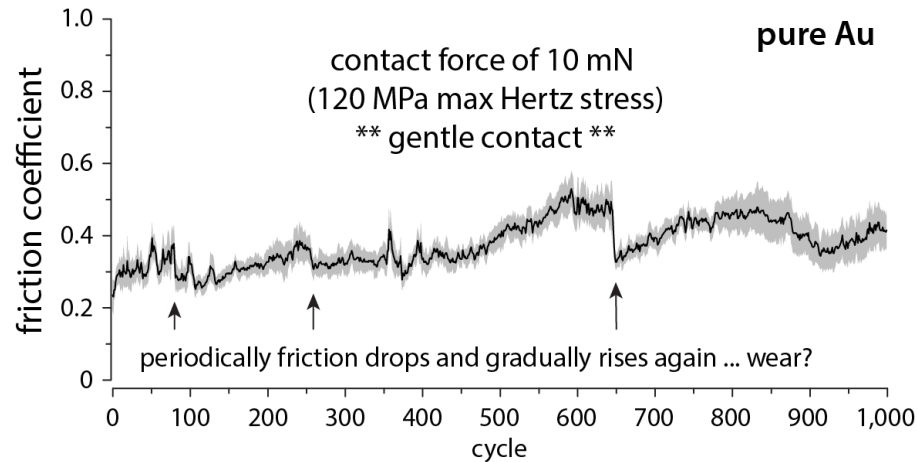
Surface-normal (planar) EBSD maps of e-beam deposited films:



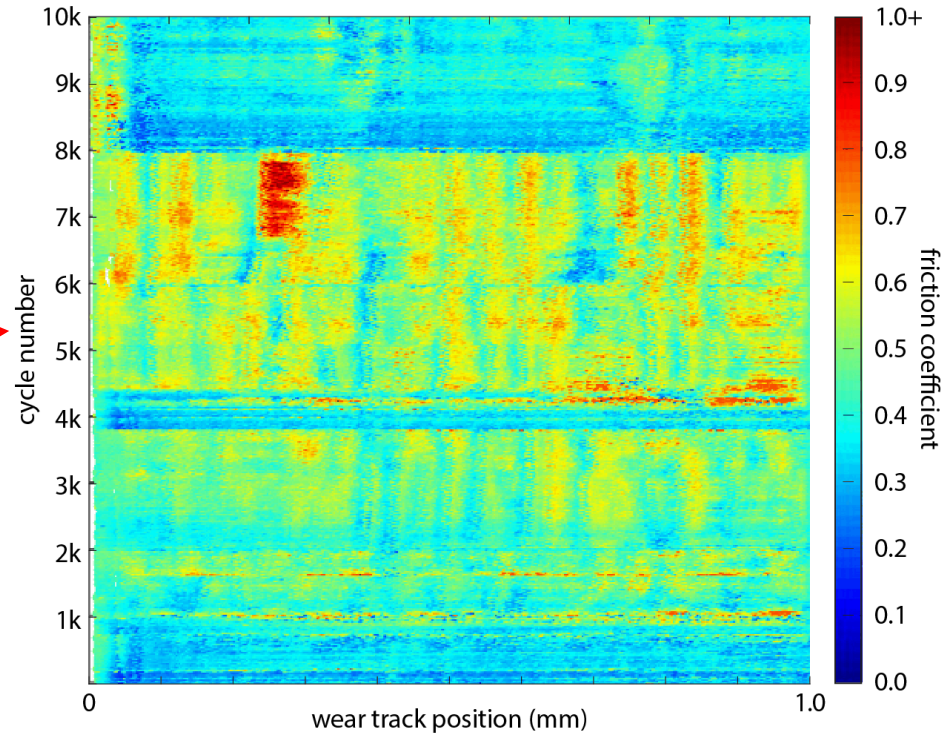
Cross-sectional composition map of a Au- 5 vol. % ZnO film showing grain boundary segregated ZnO in a Au matrix



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



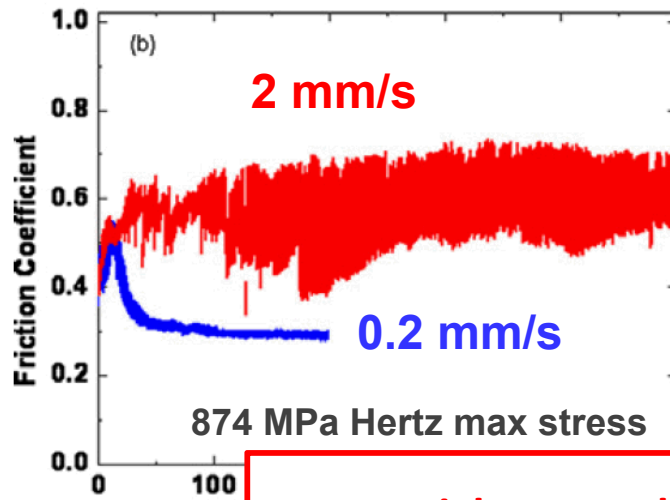
### Friction Mapping Reveals More



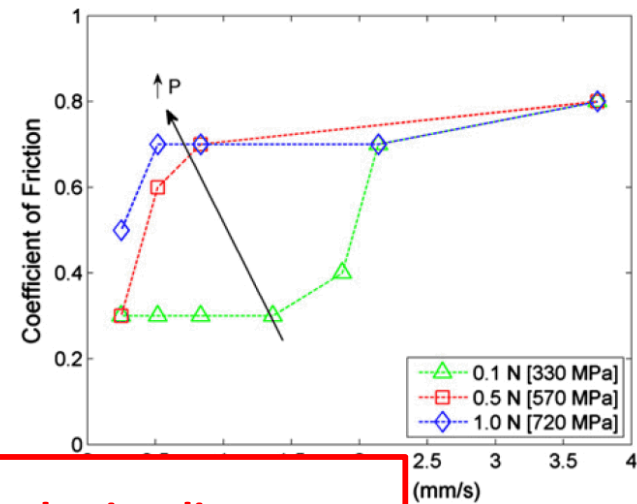


# Evidence of threshold stress and speed for low friction to prevail

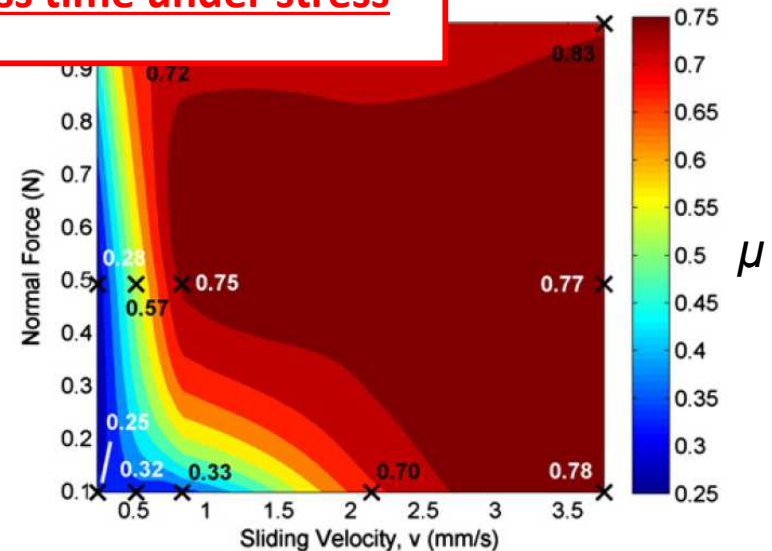
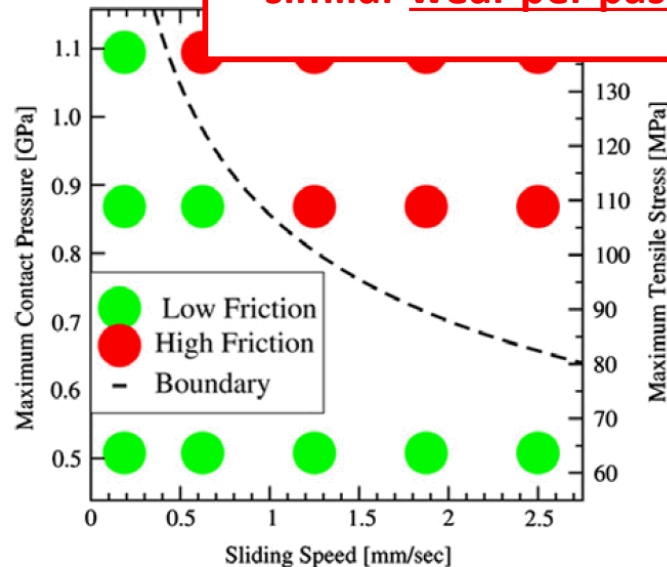
pure Ni data from S. V. Prasad et al., Scripta Mat. (2011)



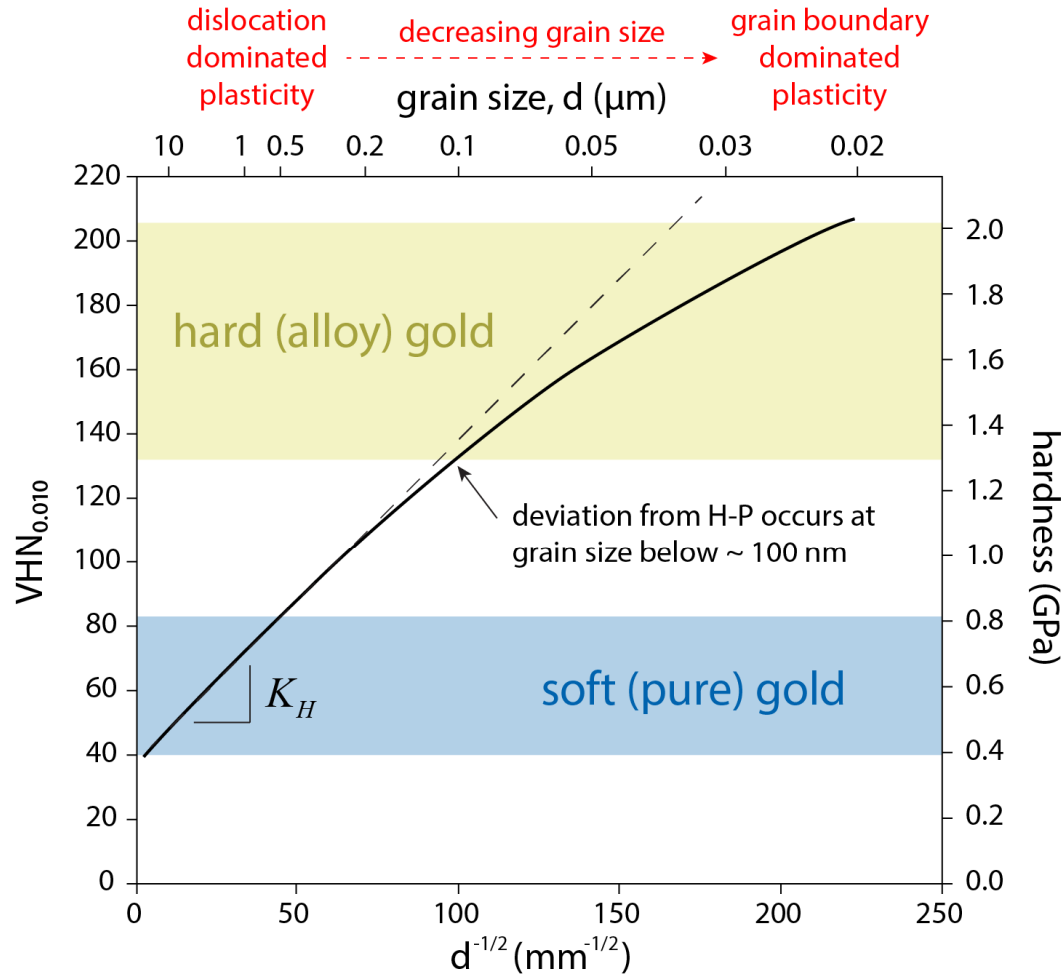
Ni-Fe data from H.A. Padilla et al., Wear (2013)



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



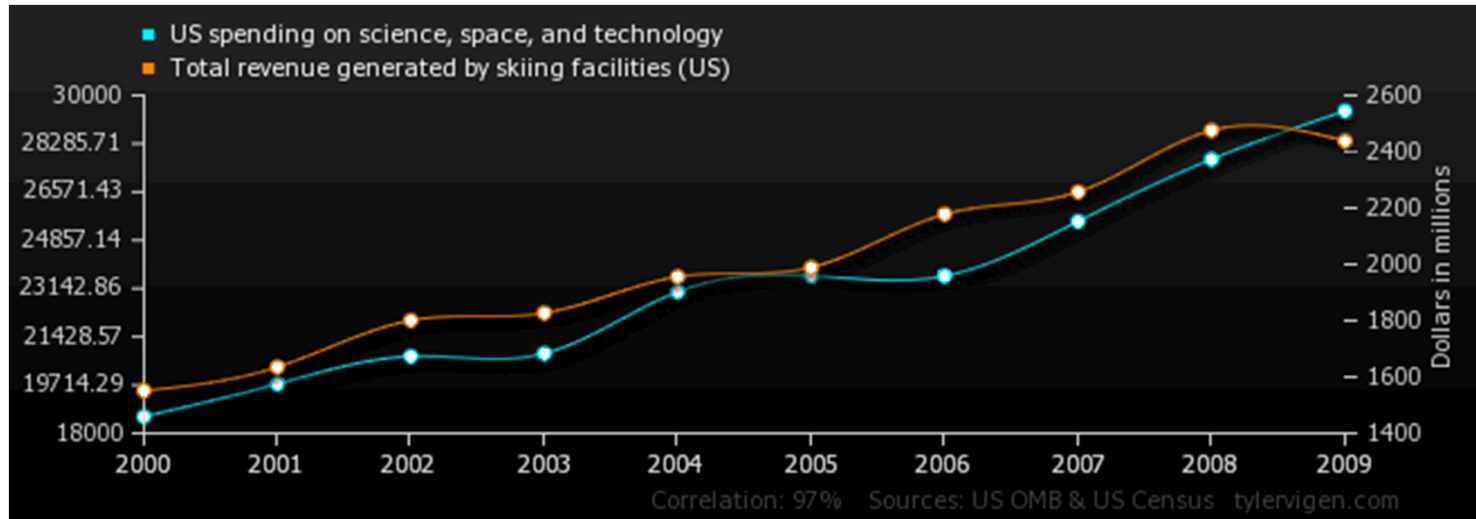
Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

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:

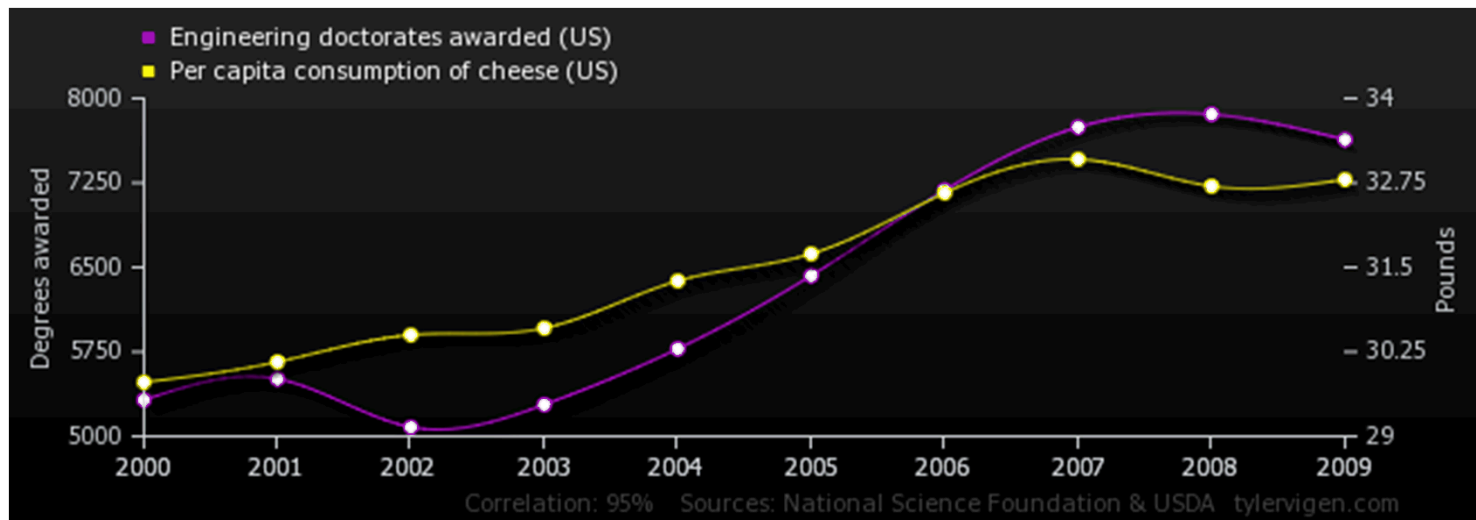
$$A_r \cong \frac{F_n}{H}$$

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

## Correlation is not causation...



$R \sim 0.97$



$R \sim 0.95$

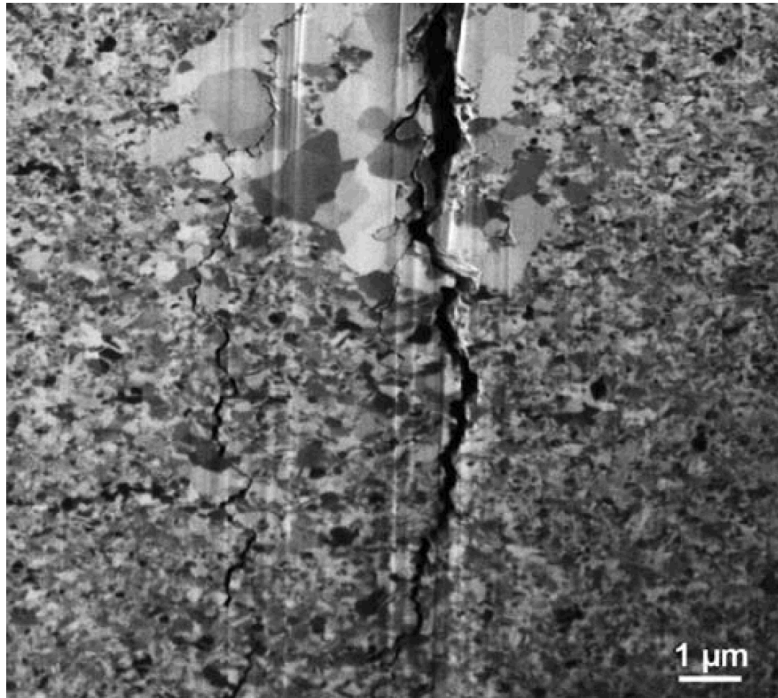
**hardness is not the answer  
(the answer seems to be grain boundary stability  
and grain size evolution)**



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

## stress-driven grain growth

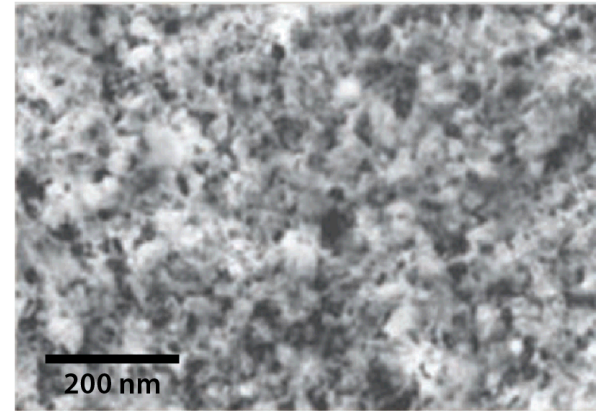
initially nanocrystalline Ni-Mn



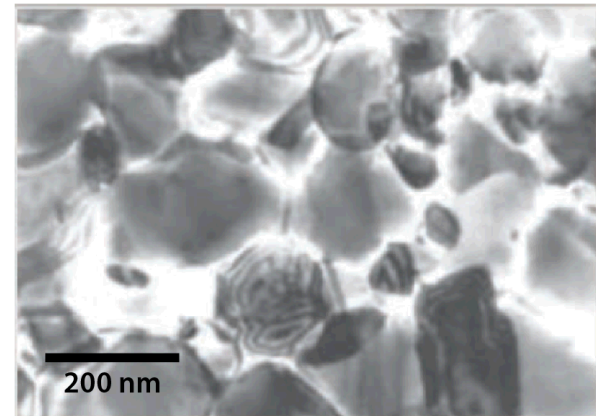
ref: Padilla & Boyce, *Exp. Mech.* (2010)

## 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**

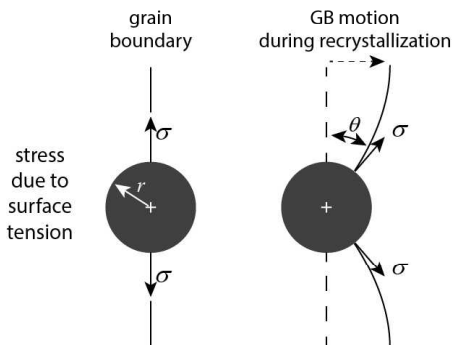
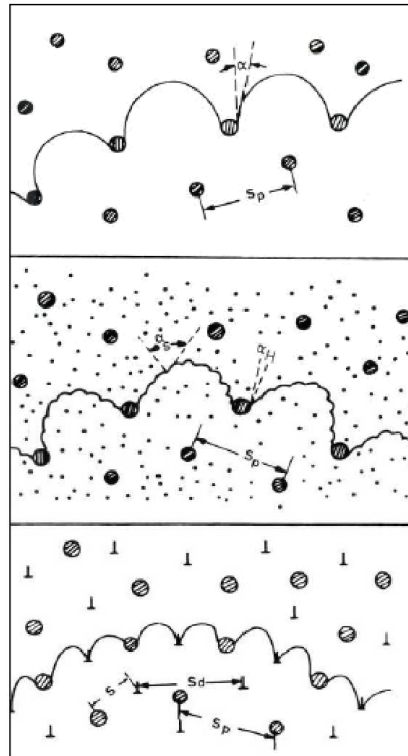
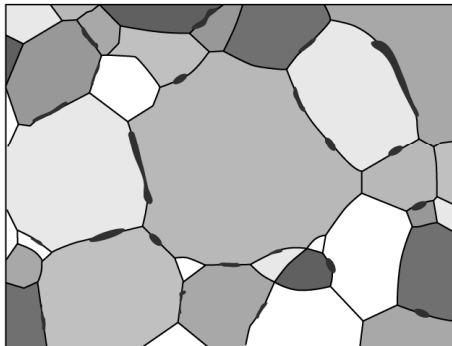
ref: Simoes et al., Nanotech. (2010)

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

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

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

$P$  = pressure on grain boundary

$\gamma_o$  = 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

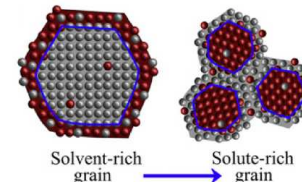
Regular Nanocrystalline Solution (RNS) Model:

ref: Chookajorn et al., Science, 2012

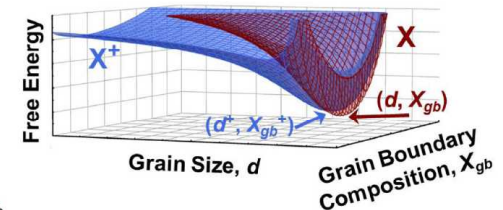
$$\Delta G^{\text{mix}} = (1 - f_{\text{gb}})\Delta G_c^{\text{mix}} + f_{\text{gb}}\Delta G_{\text{gb}}^{\text{mix}} + z\nu f_{\text{gb}}(X_{\text{gb}} - X_c) \left[ (2X_{\text{gb}} - 1)\omega_{\text{gb}} - \frac{1}{zt}(\Omega^B\gamma^B - \Omega^A\gamma^A) \right]$$

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

Grain structure model: segregated 2-phase metal system



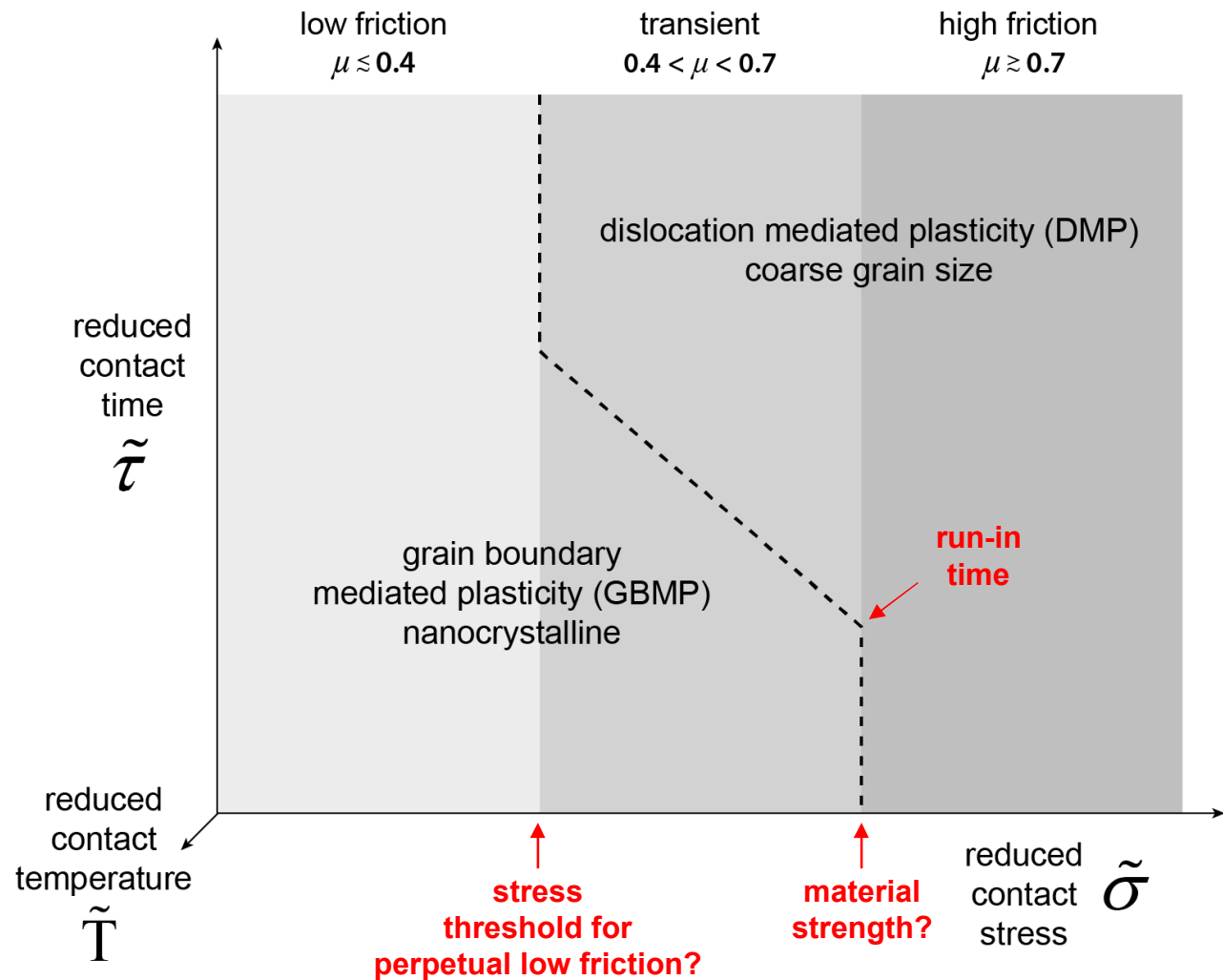
ref: Murdoch et al., Acta Mat. (2013)



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

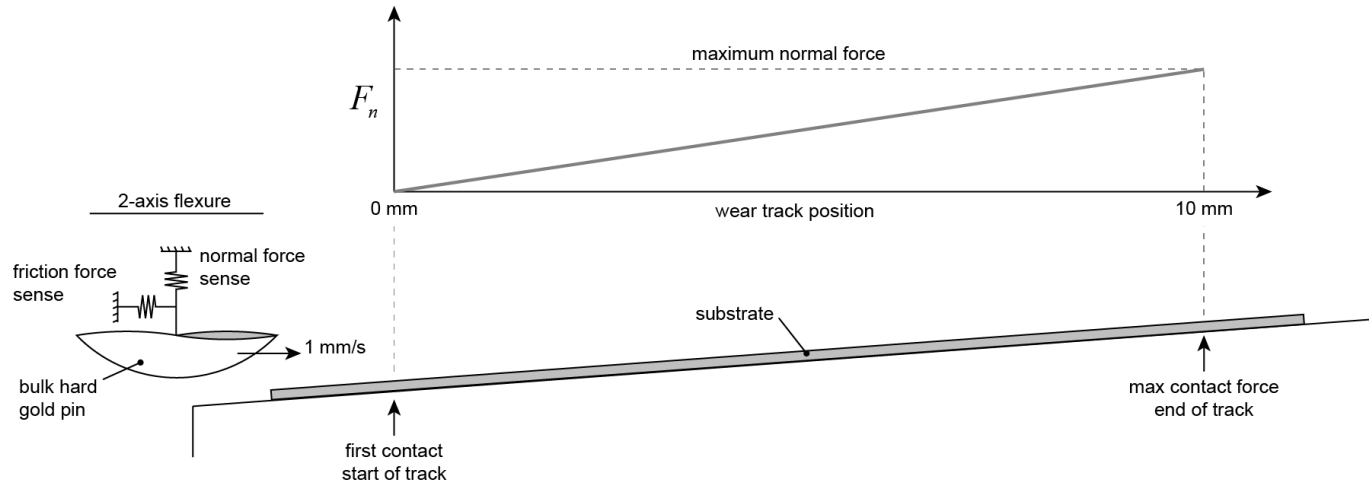
## What does a **microstructure-based friction regimes model** look like?

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**

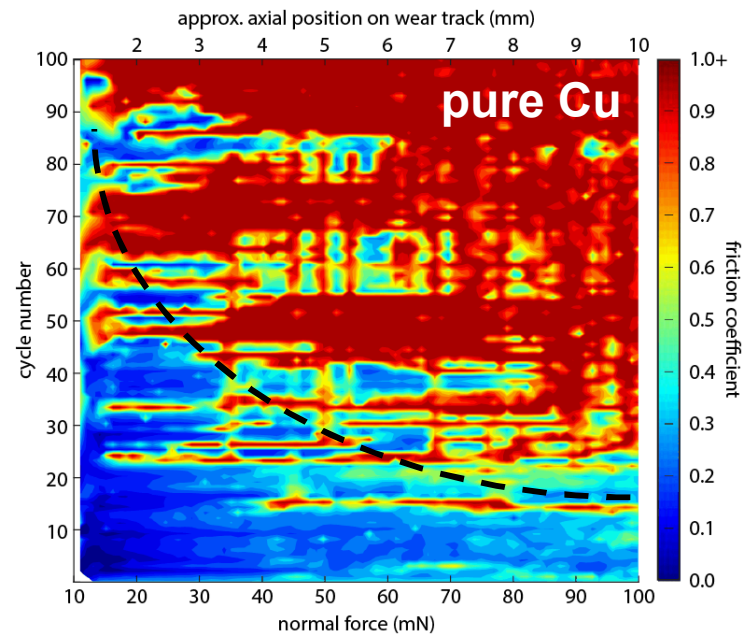
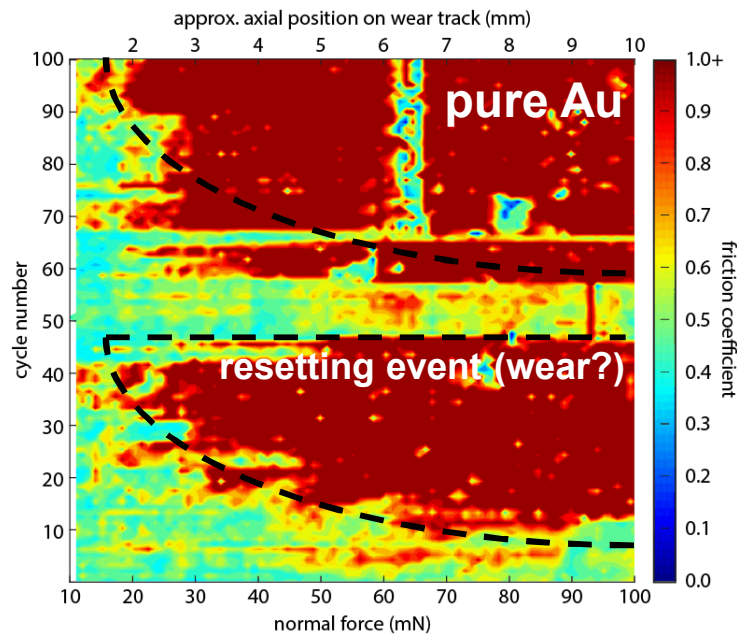




# Ramped contact force experiments and friction mapping reveals much



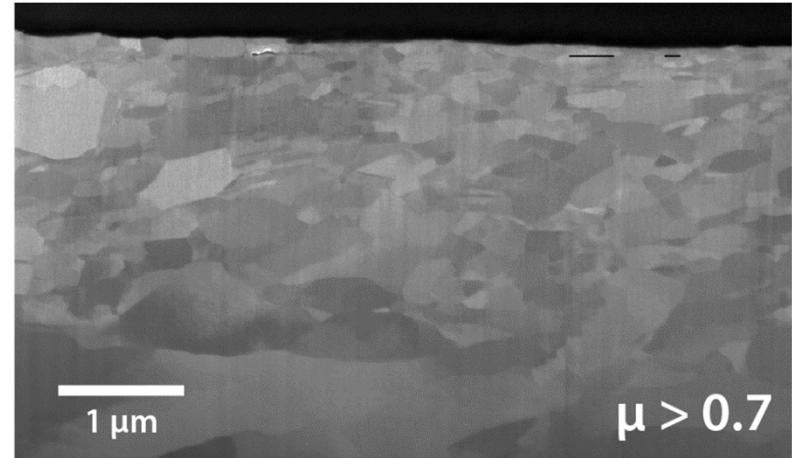
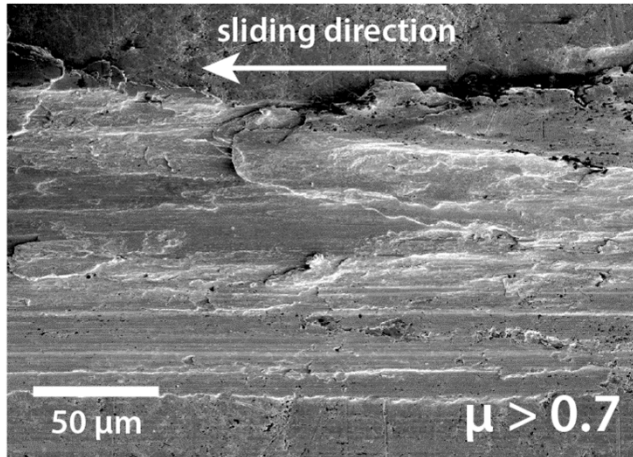
**Messy (tribology...), but there is stress dependent envelope!**



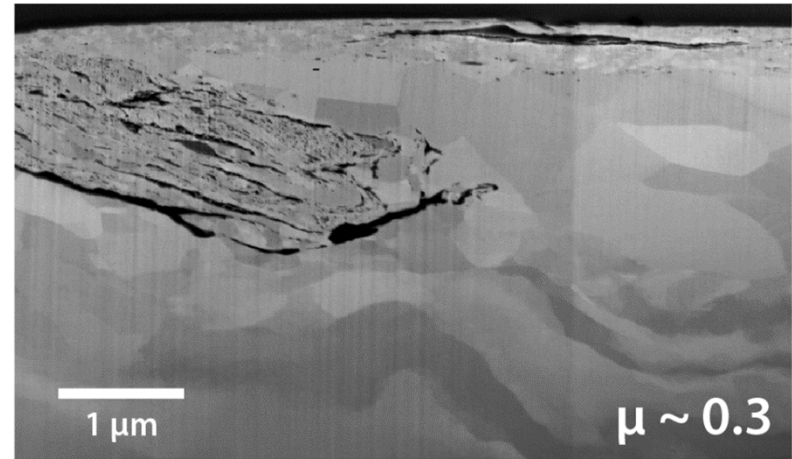
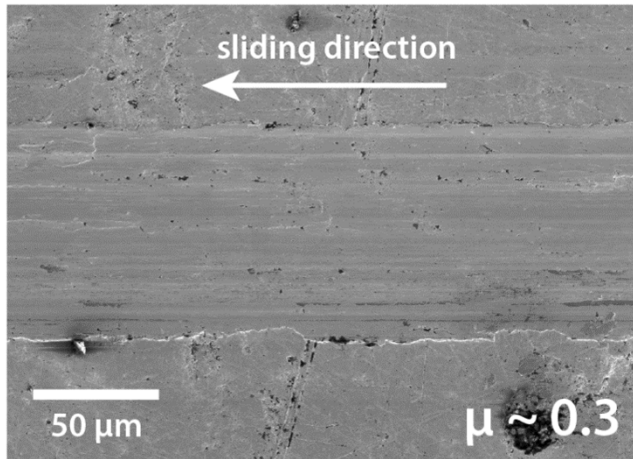
Again, low friction associated with nanocrystalline surface.. see shear banding too

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

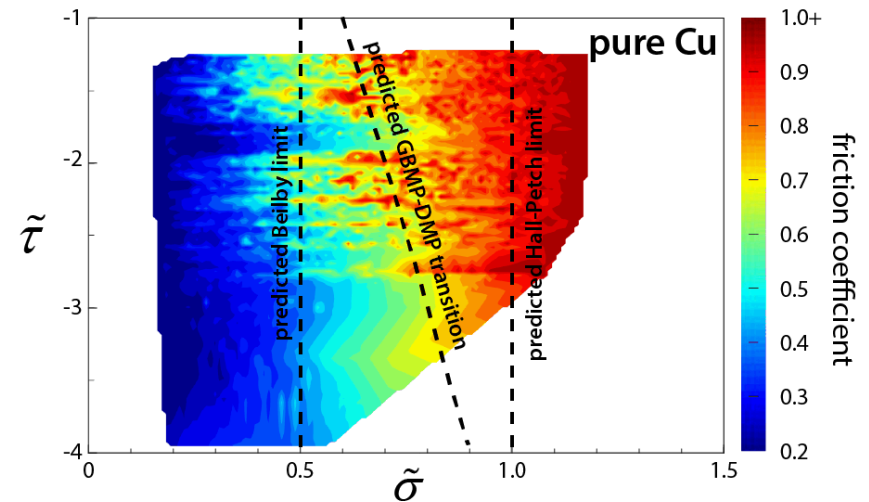
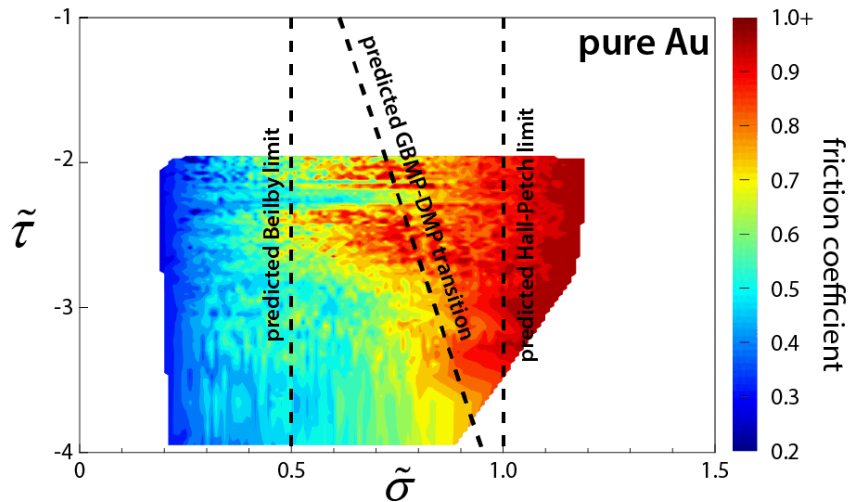
high  
friction



low  
friction

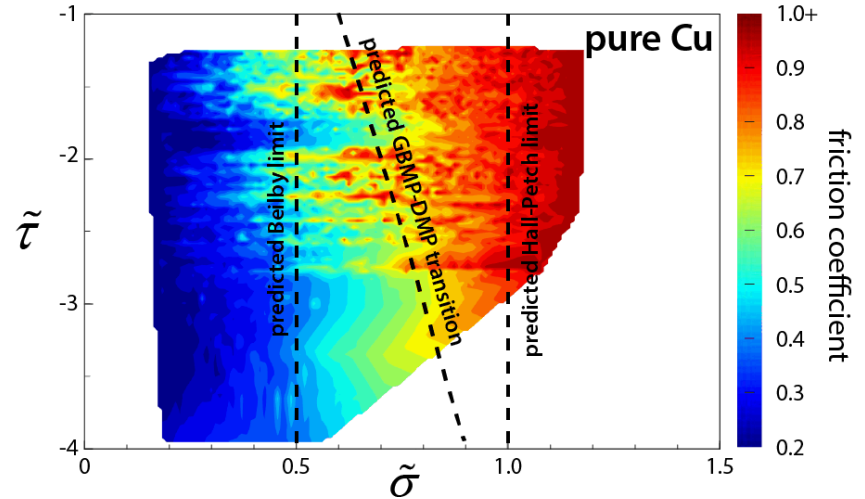
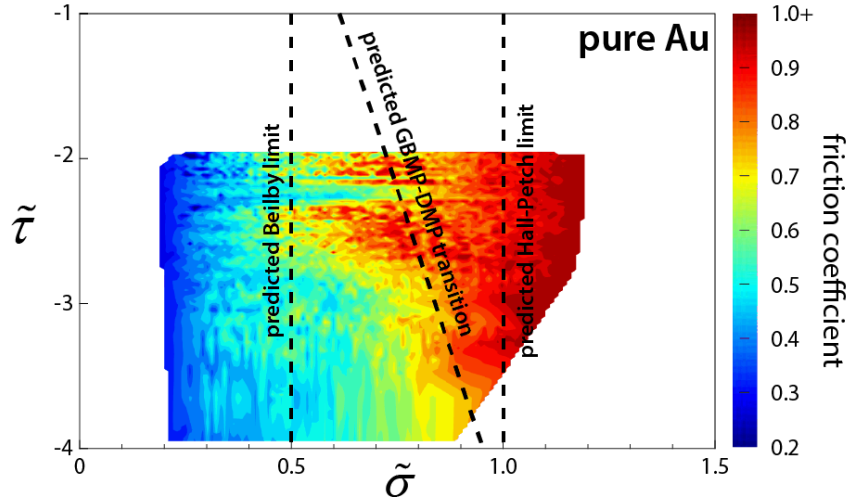


## The punchline first: this is what the reduced data looks like



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

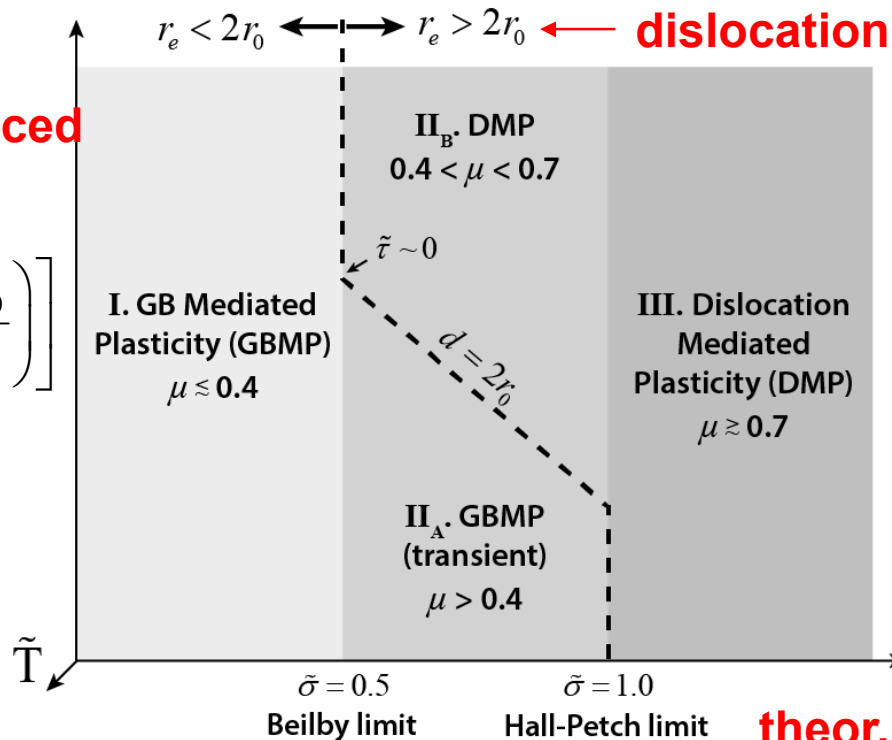
predicted!



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

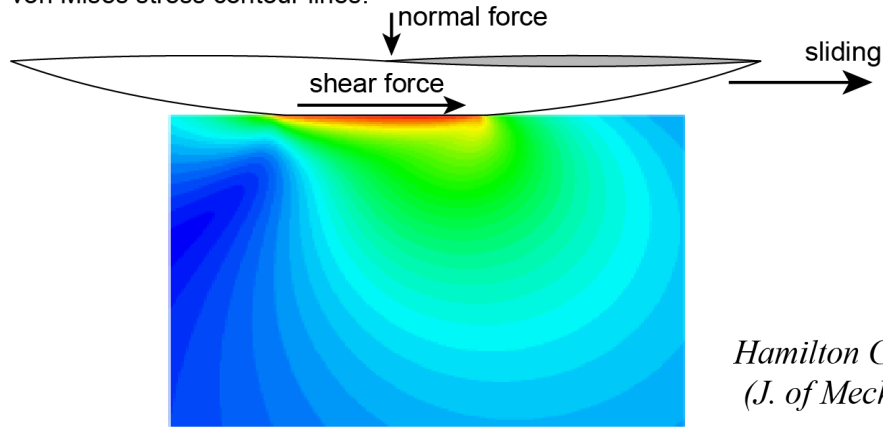
$$\tilde{\sigma} = \frac{\sigma_{surf,max}}{\sigma_{\infty}}$$

theor. strength  $\rightarrow \sigma_{\infty}$



# The connection between friction and microstructure evolution

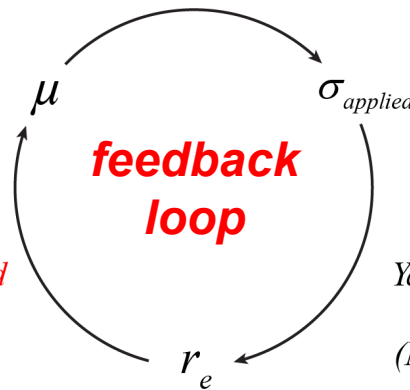
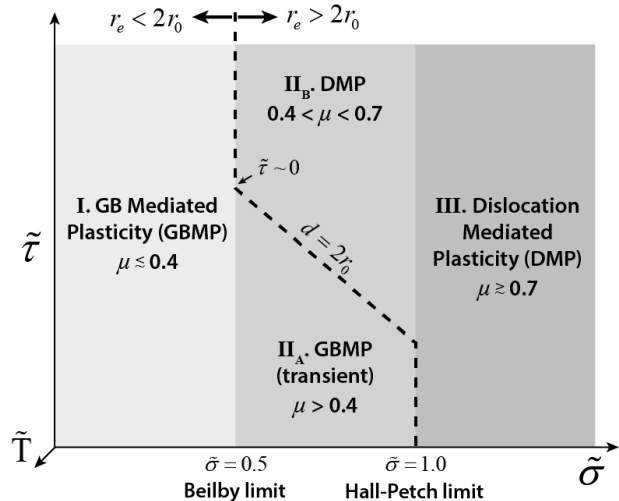
von Mises stress contour lines:



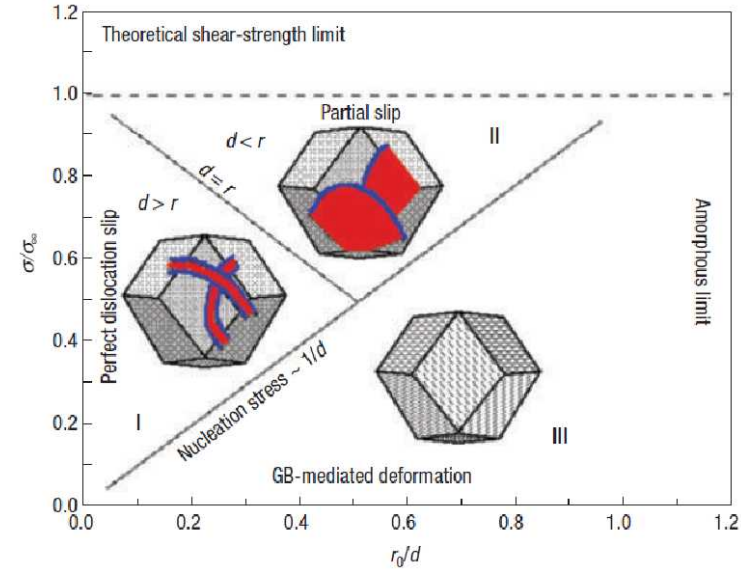
$$\sigma_{a,\max} = \frac{3F_n}{2\pi a^2} \left[ \frac{1-2\nu}{3} + \frac{(4+\nu)}{8} \pi\mu \right]$$

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

*proposed  
model*

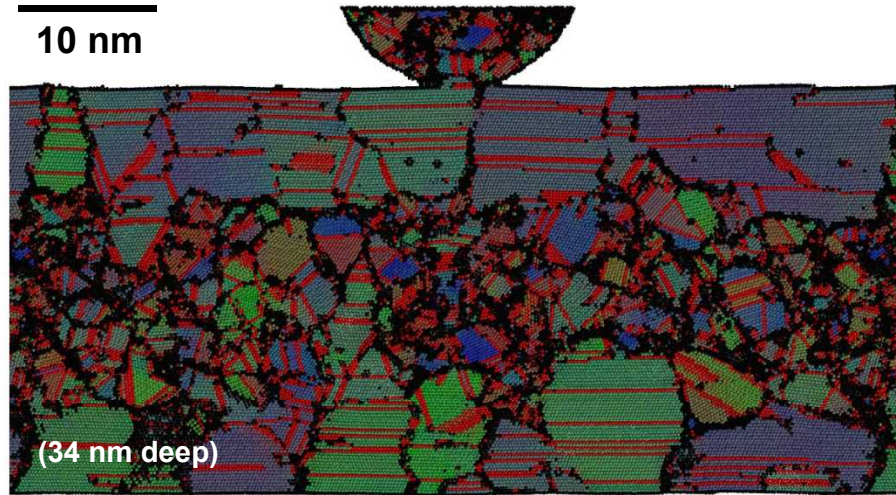


*Yamakov et al.  
model  
(Nature 2004)*



# What did we learn from MD simulations...

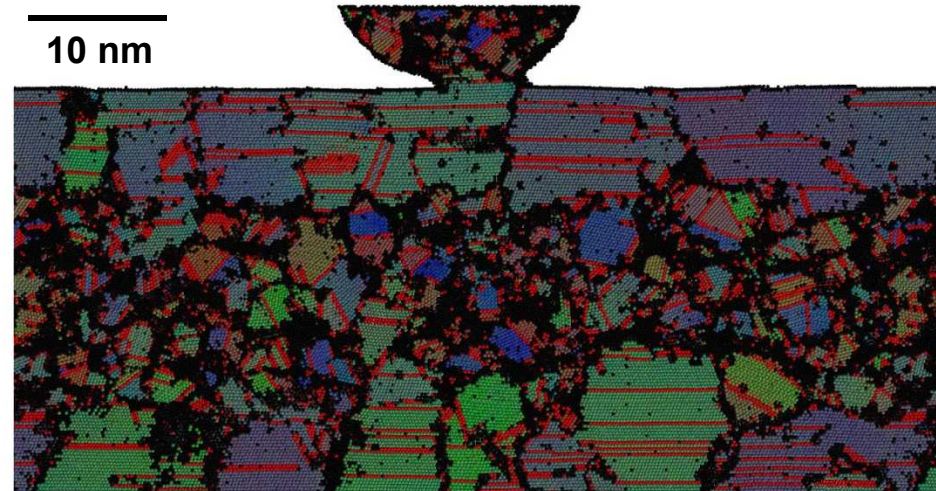
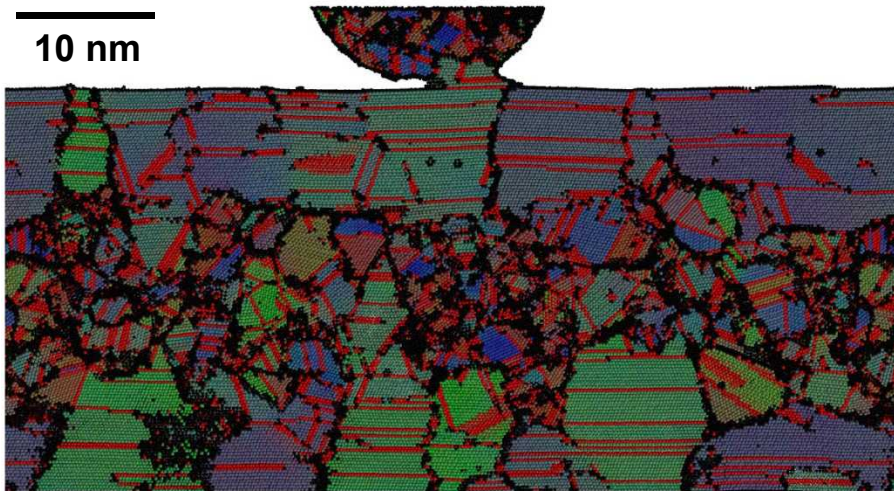
initial microstructure  
of Ag and Ag-Cu alloy  
(no sliding yet)

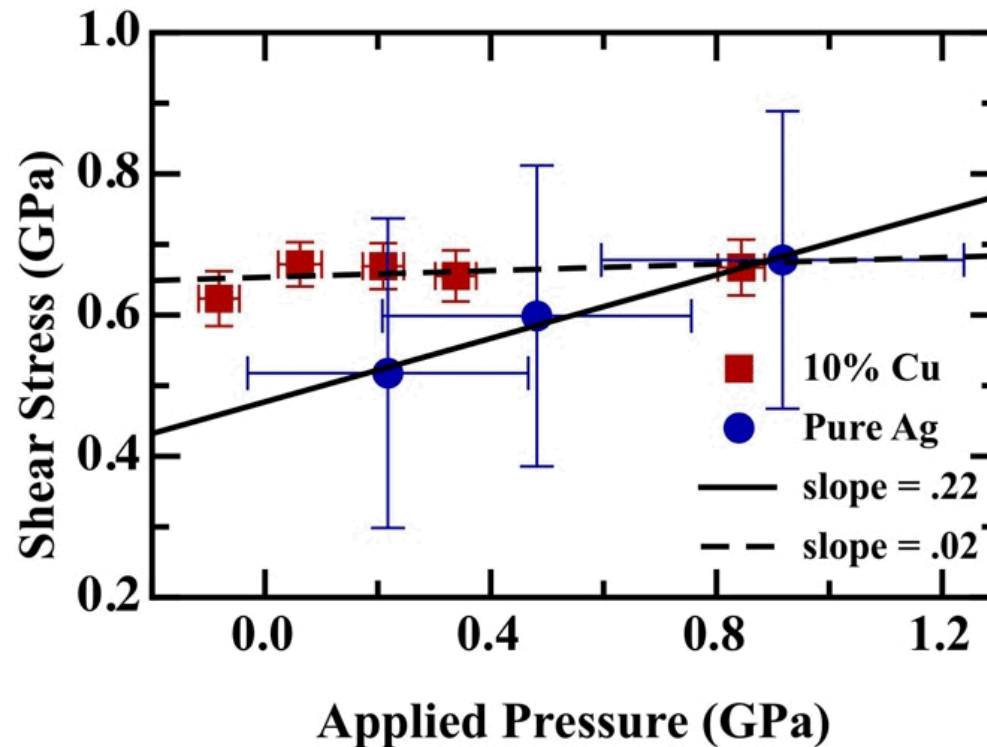


300 MPa contact stress  
300 K temperature  
2 m/s sliding speed

pure Ag after 4 nm of sliding

Ag-10% Cu alloy after 4 nm of sliding

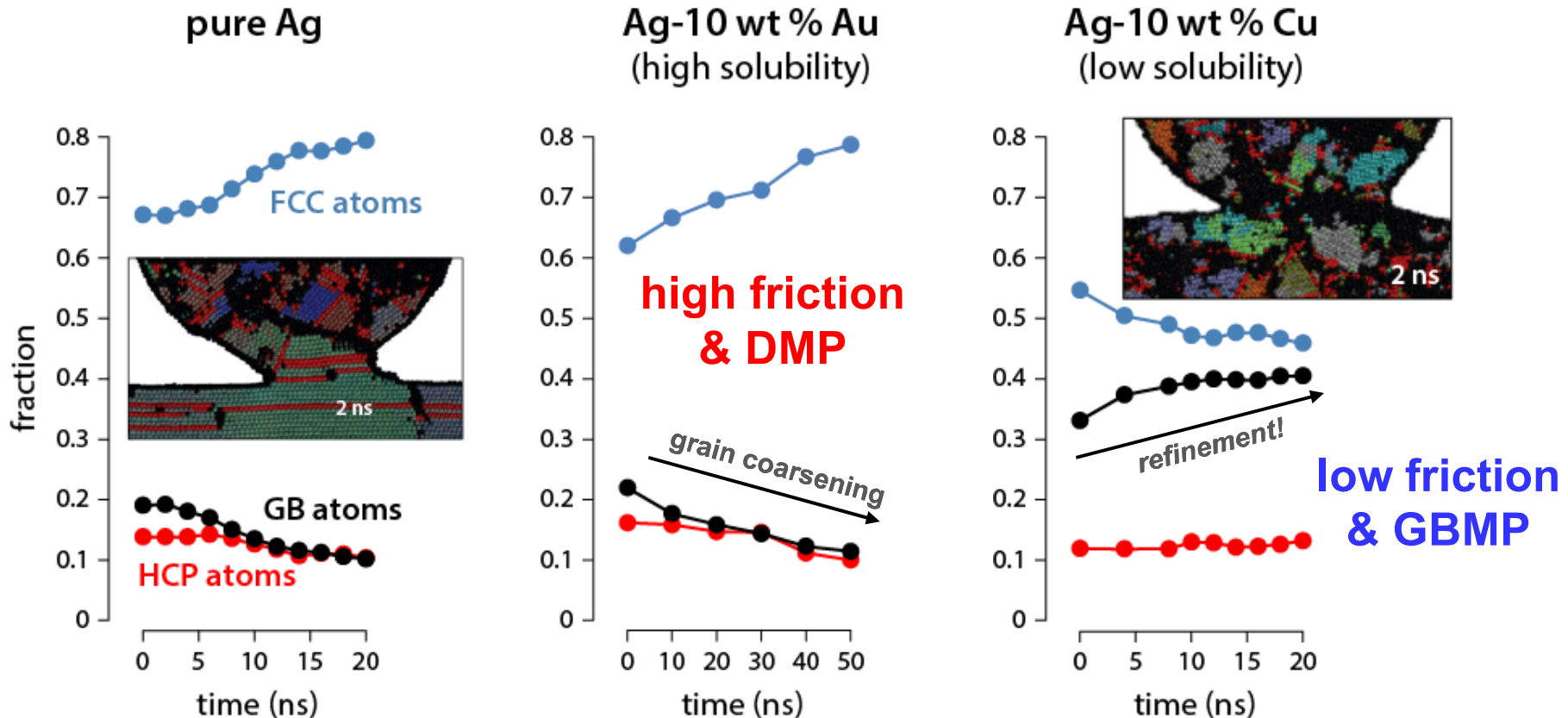




- AgCu is similar to hard gold (AuNi, AuCo...)
- Friction coefficient is the slope of line
- Change in shear accommodation changes the friction



## Alloying also impacts **microstructural evolution**

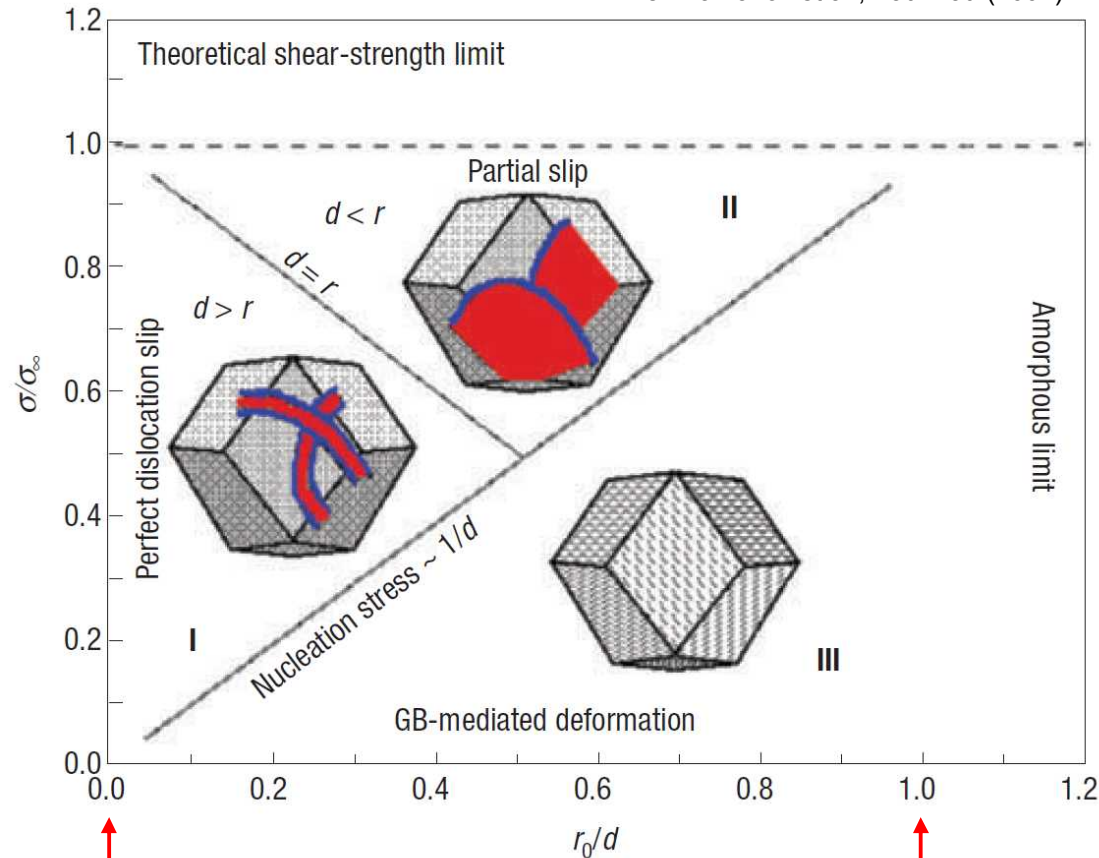


- Experiments: alloying reduces grain size and stabilizes grain boundaries
- Simulations: alloying mitigates stress-driven grain growth at interface and promotes defect (primarily GB) mediated plasticity
- Connection: stabilizing grain boundaries reduces friction



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

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



↑  
grain size  
goes to  
single crystal

←  
increasing  
grain size

↑  
minimum  
attainable  
grain size  
(peak H-P)

**Equilibrium (zero stress) dislocation splitting distance:**

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

**Stress-dependent splitting distance:**

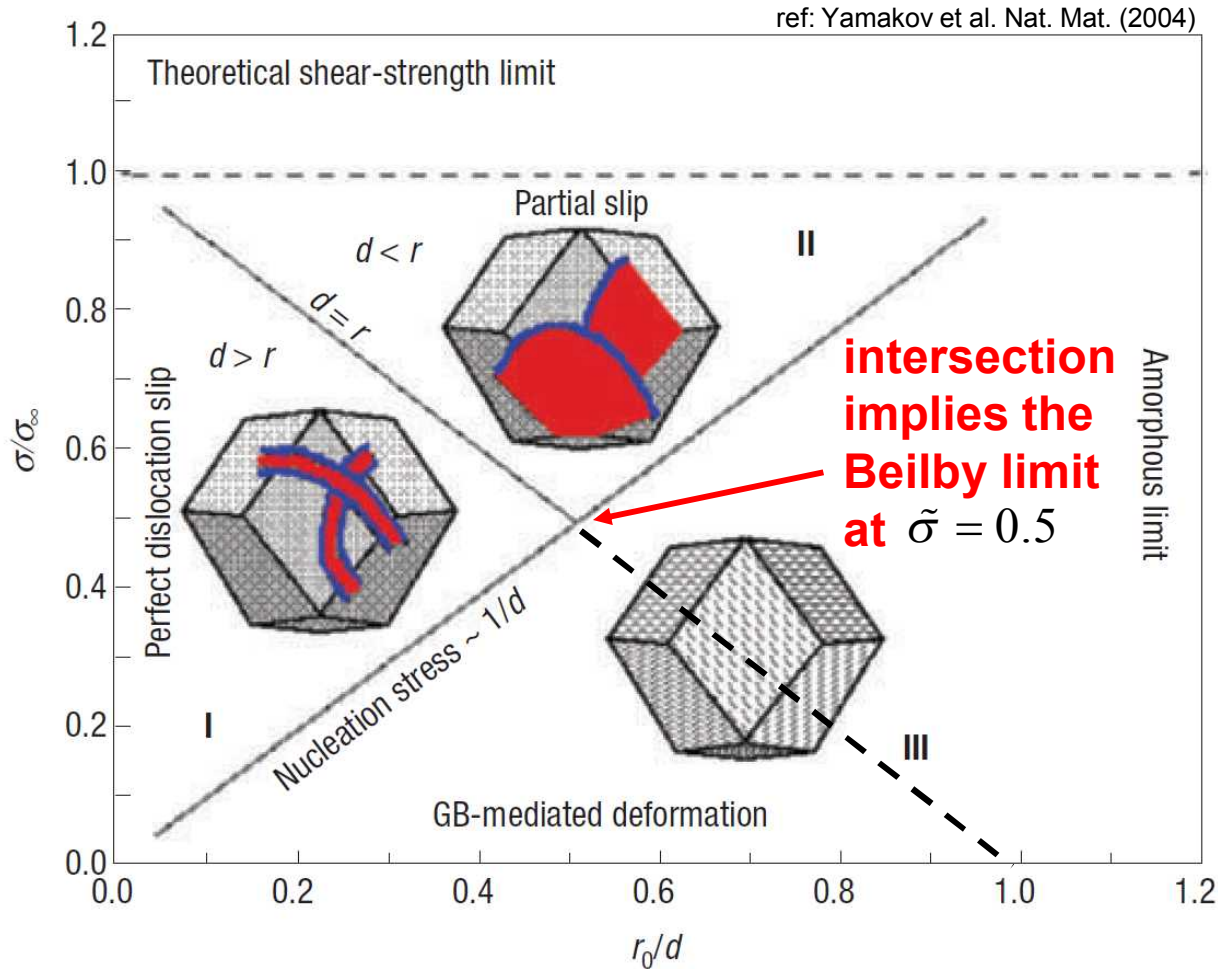
$$r_e = \frac{r_0}{1 - \sigma_a / \sigma_\infty}$$

**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

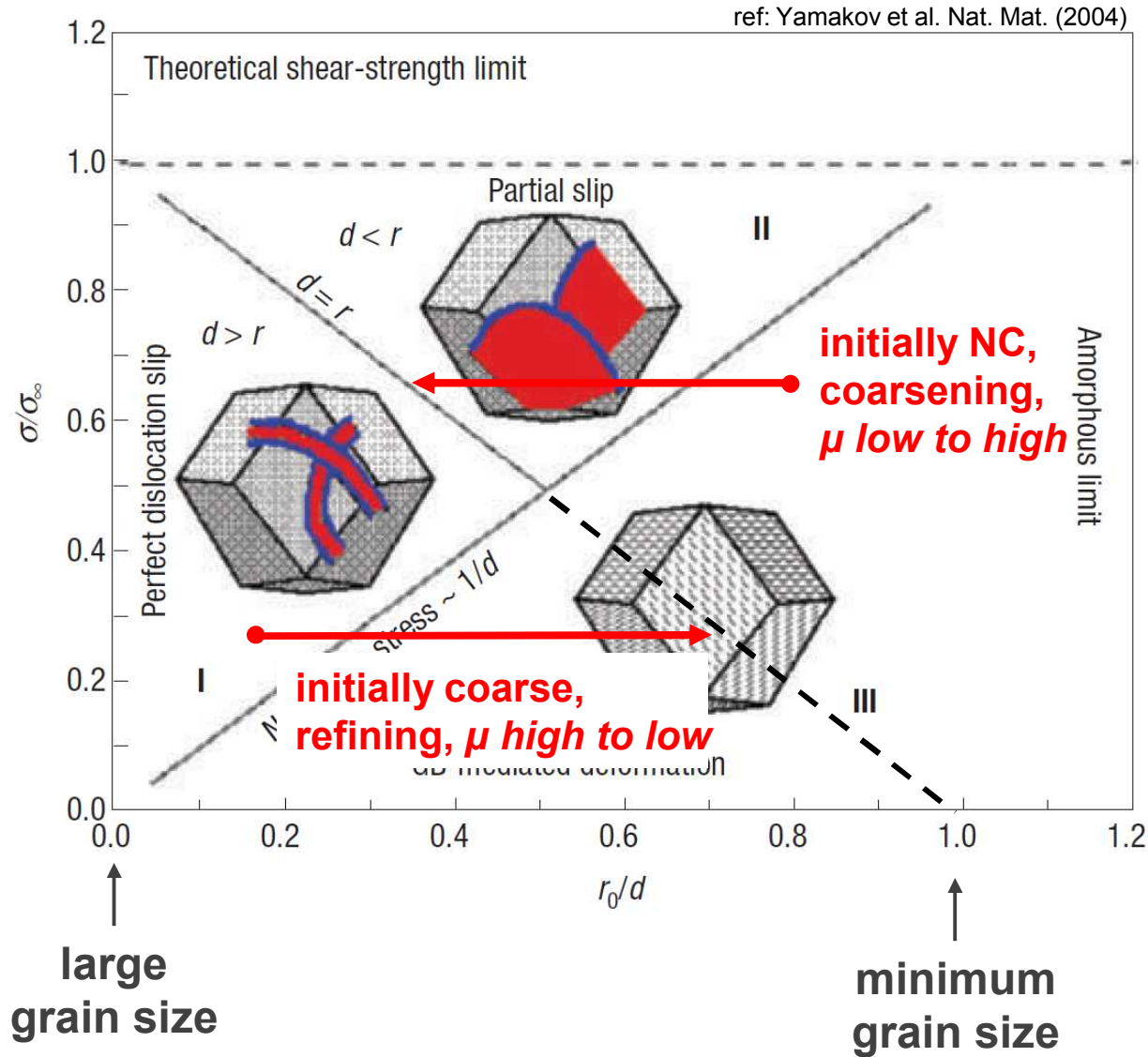


## Assumptions:

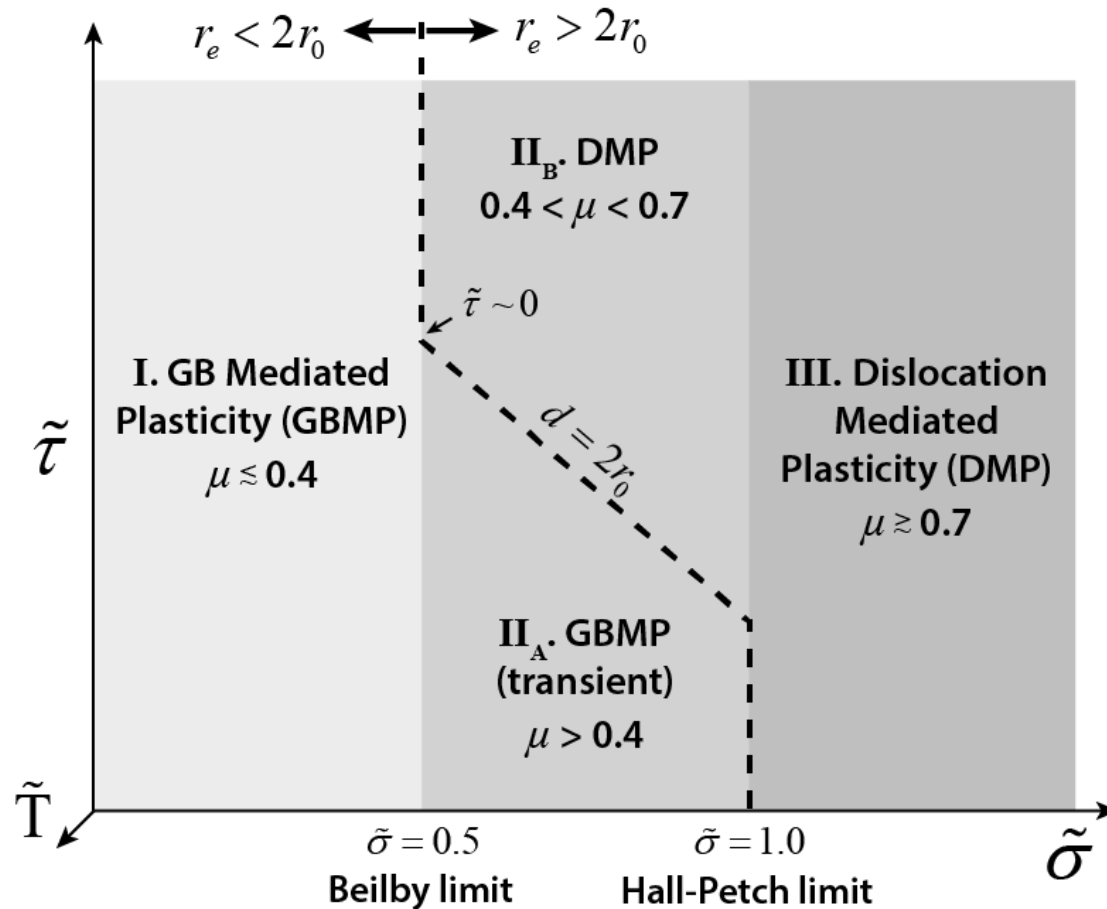
1. grain size goes to splitting distance,  $\rightarrow d$
2. nucleation stress goes as inverse grain size,

$$\tilde{\sigma} \propto \frac{1}{d}$$

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



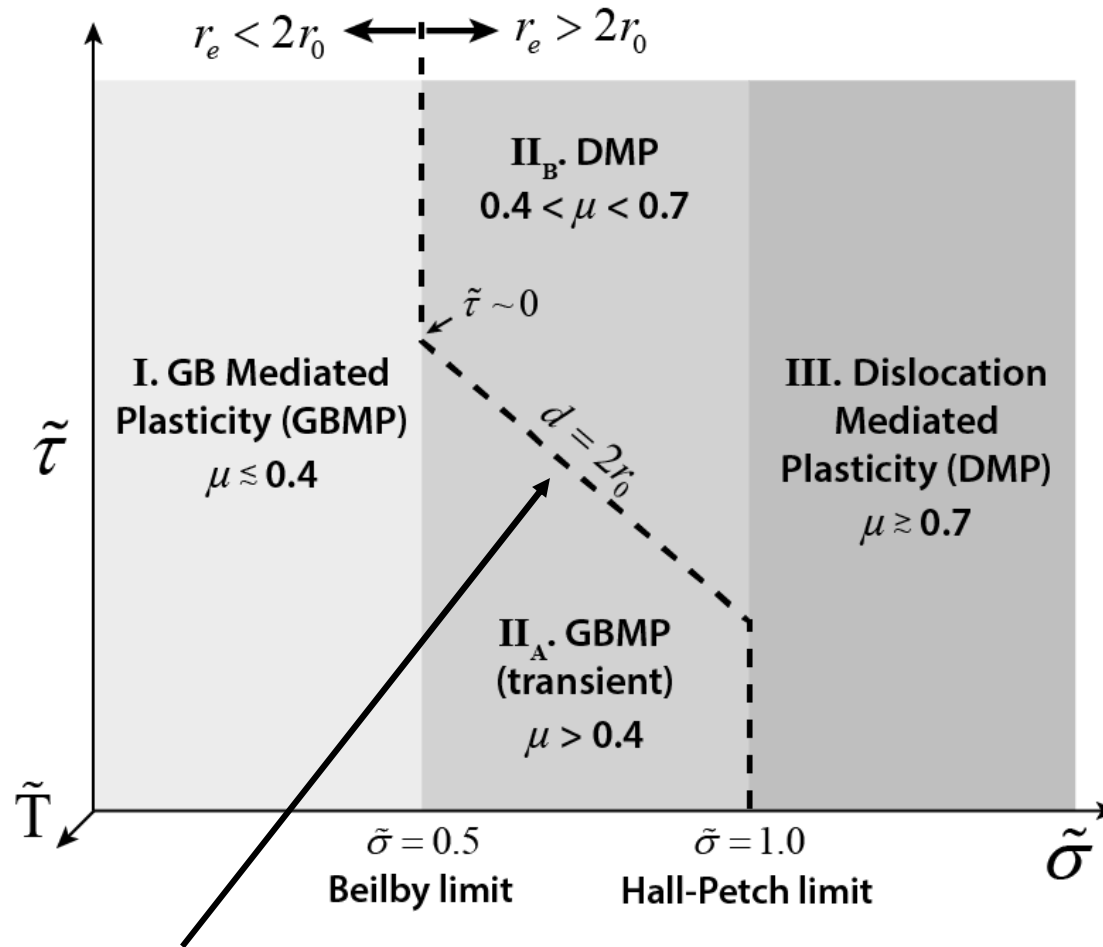
## Returning to the microstructure-based friction regimes model...



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



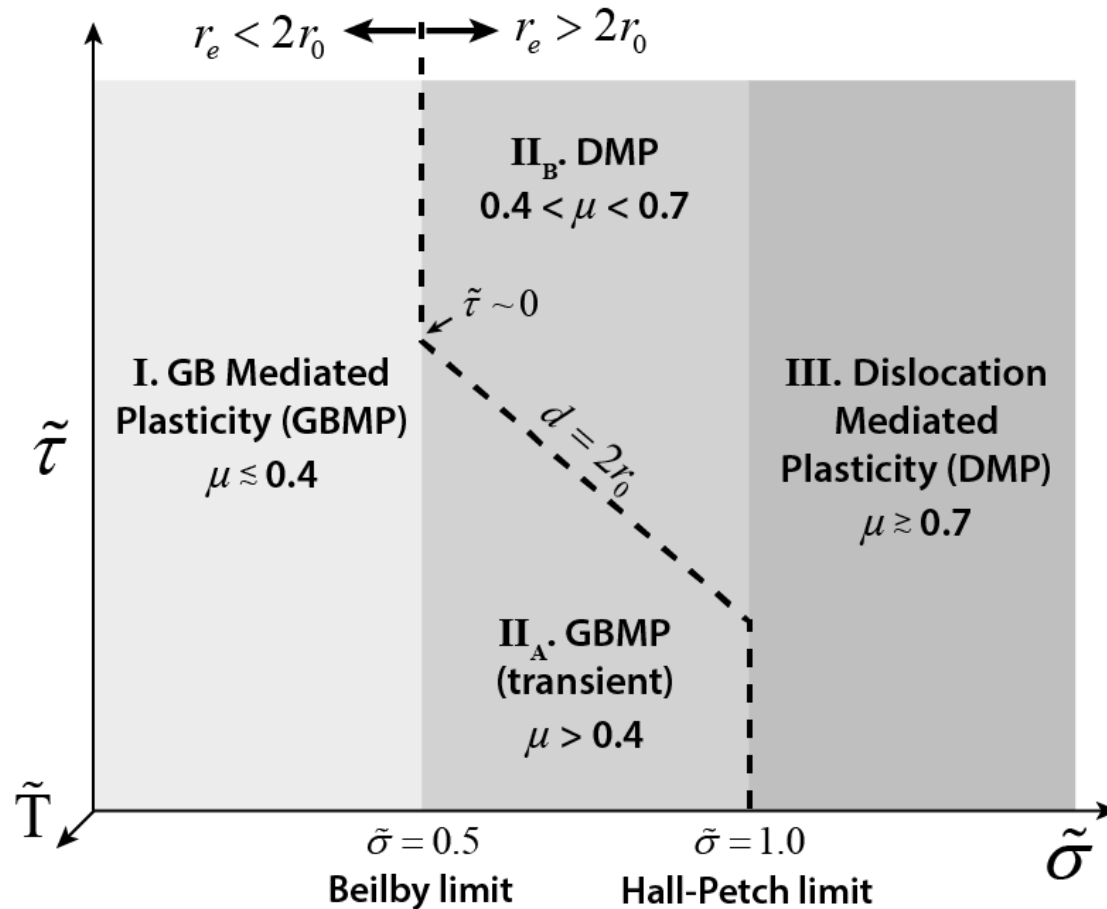
## Returning to the microstructure-based friction regimes model...



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

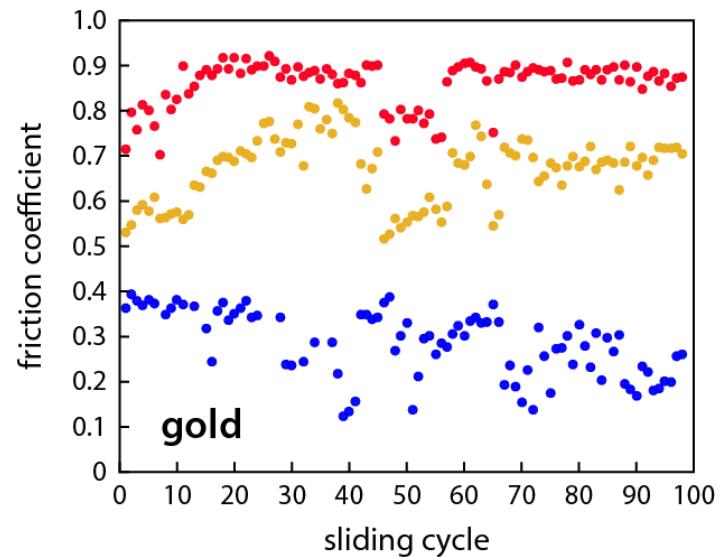
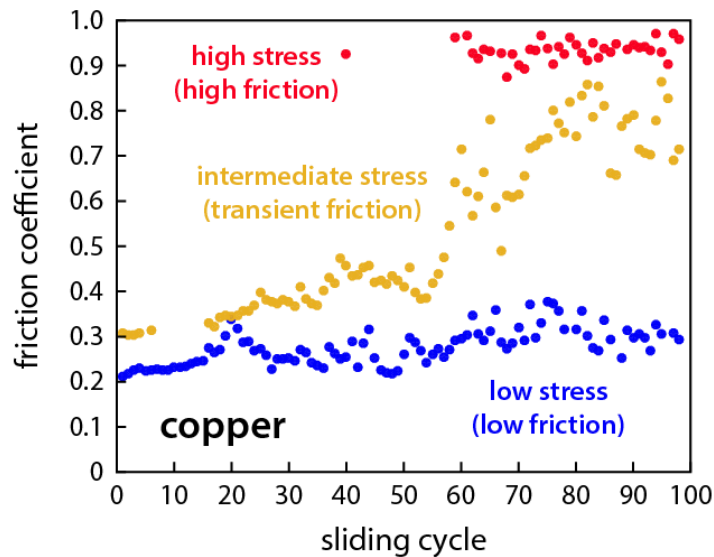
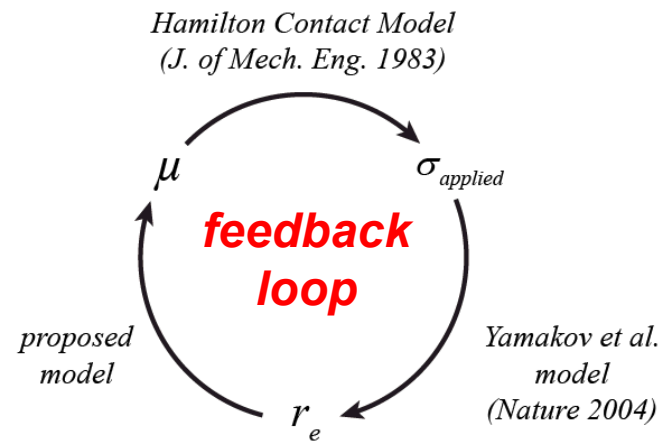
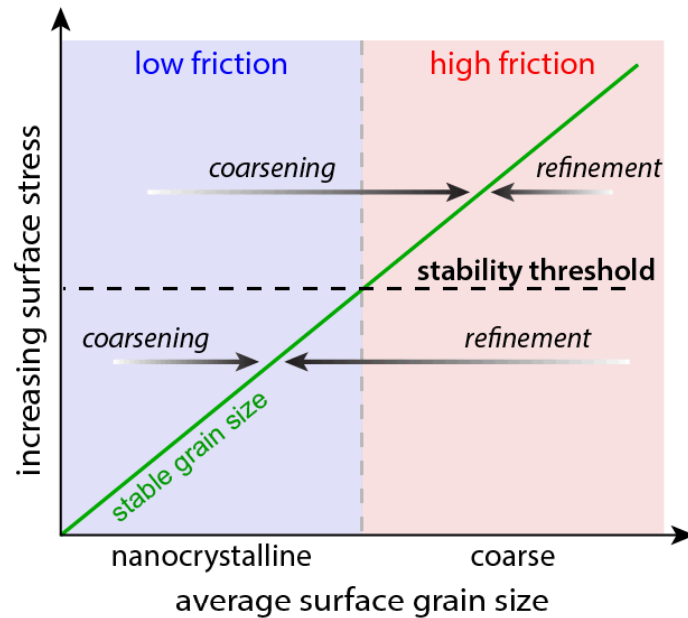
$$v_{gb} = \frac{4\gamma_{gb}}{d} M_0 \exp\left[\frac{-Q}{kT}\right] \exp\left[\frac{(\sigma - \frac{1}{2}\sigma_\infty)V^*(d)}{kT}\right]$$

## What about boundary lubrication of metal contacts (e.g. graphite, DLC, MoS<sub>2</sub>)?

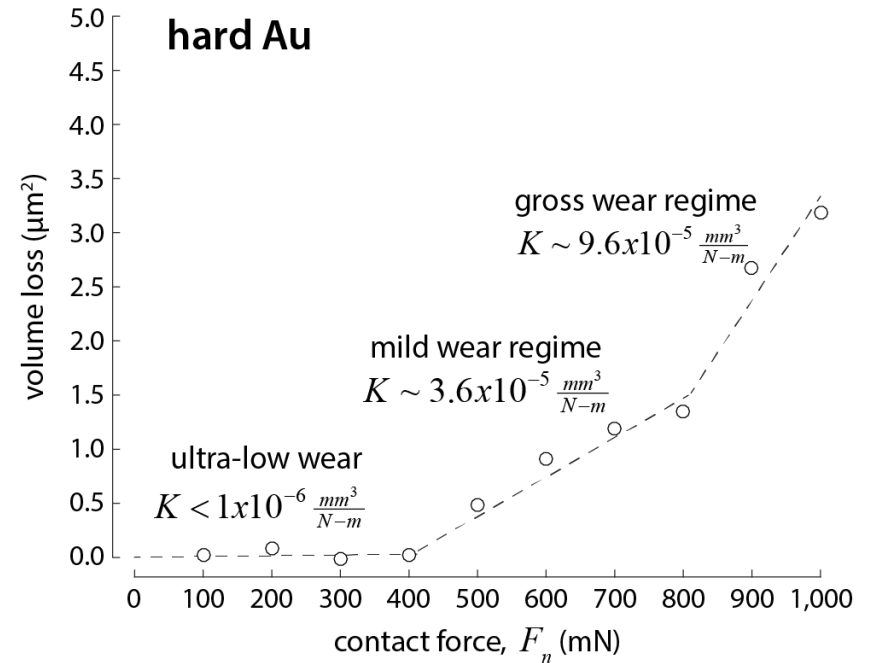
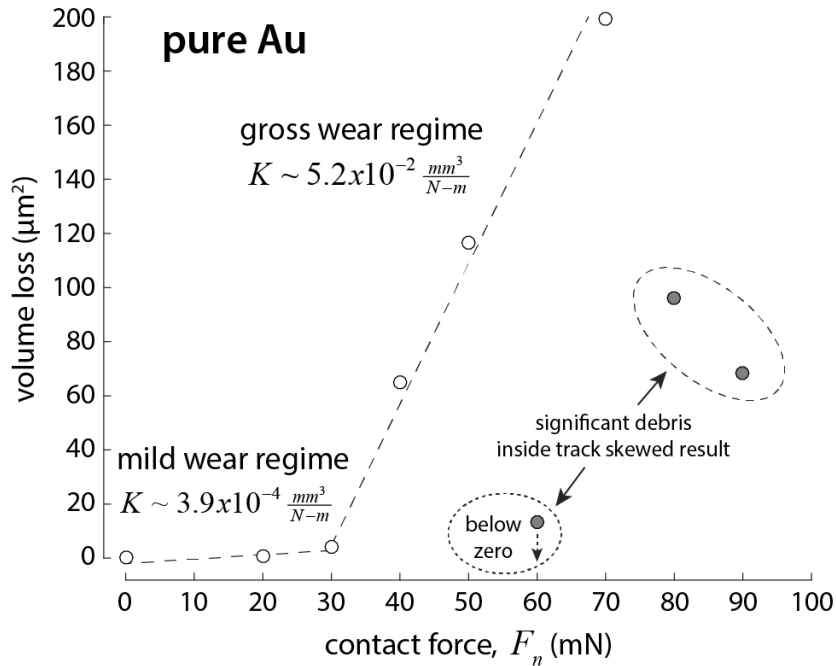


**Boundary lubrication (e.g. graphite, MoS<sub>2</sub>, engine oil) mitigates commensurate contact – thus it is possible to achieve low friction at higher normal force**

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



# One more look at wear



So...

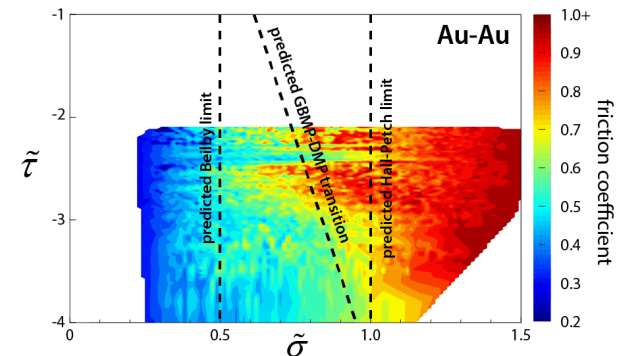
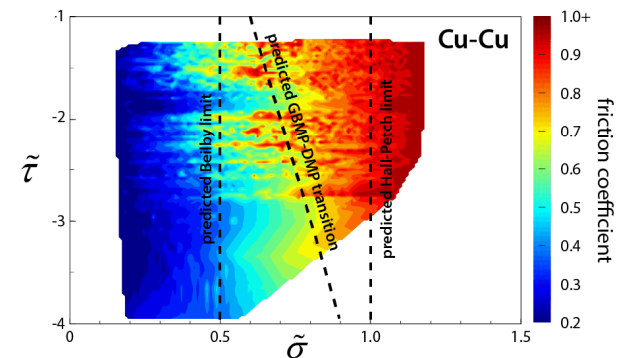
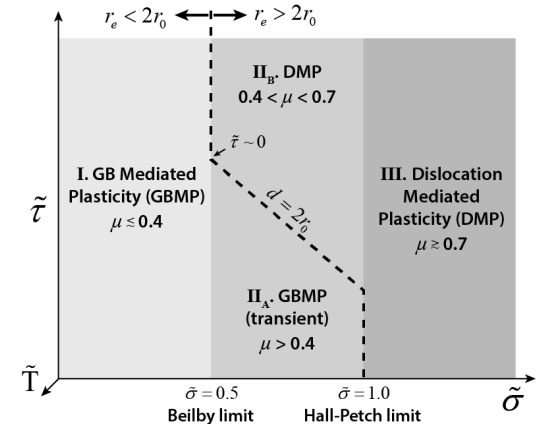
**friction** regimes described by **Hamilton** (max surface stress)

**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

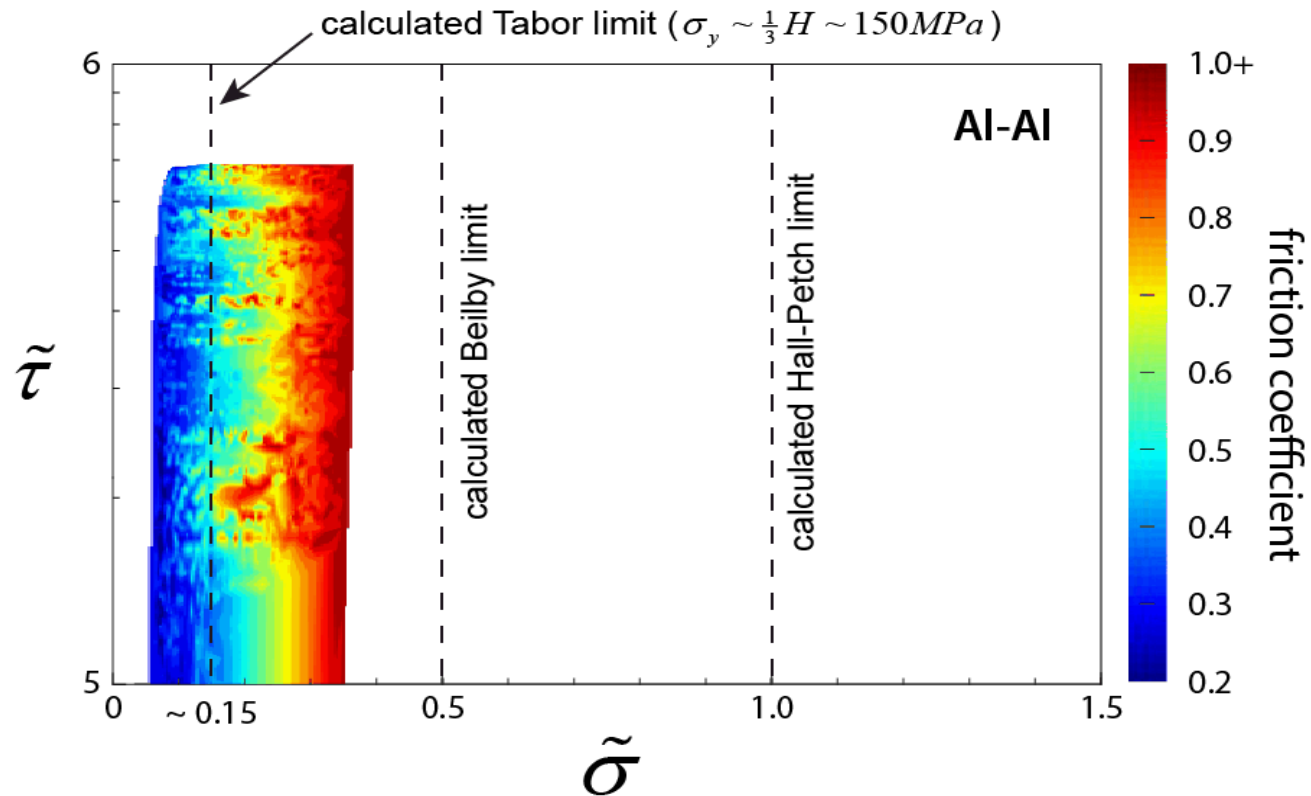


# Appendix Slides

# Material Properties and Calculated Parameters

property	material system				
	<i>Au</i>	<i>Cu</i>	<i>Al</i>	<i>Ni</i>	<i>units</i>
shear modulus, $G$	27	48	27	76	GPa
Poisson ratio, $\nu$	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, $\gamma_{sf}$	45	78	166	128	mJ/m <sup>2</sup>
GBE, $\gamma_{gb}$	378	625	324		mJ/m <sup>2</sup>
HAGB mobility, $M_0$	$3.84 \times 10^{-6}$	30	$2 \times 10^{-2}$		m/s-Pa
HAGB activation energy, $Q$	1.33	2.01	1.05		$\times 10^{-19}$ J
calculated parameters					
equilibrium splitting distance, $r_0$	8.7	5.9	2.0	2.8	nm
$\sigma_\infty$	312	611	1,117	1,808	MPa
$\sigma(r = 2r_0)$	156	306	580	904	MPa





**High stacking fault energy... BUT low strength!**



# Classical attempts to define wear & friction regimes were

## empirical/phenomenological

Scripta METALLURGICA  
et MATERIALIA

Vol. 24, pp. 805-810, 1990  
Printed in the U.S.A.

Pergamon Press plc  
All rights reserved

VIEWPOINT SET No. 14

### WEAR-MECHANISM MAPS

M. F. Ashby\* and S. C. Lim†,

\*Engineering Department, Cambridge University, Cambridge CB2 1PZ, UK.  
†National University of Singapore, Kent Ridge Road, Singapore 0511.

(Received August 15, 1989)  
(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):

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

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	

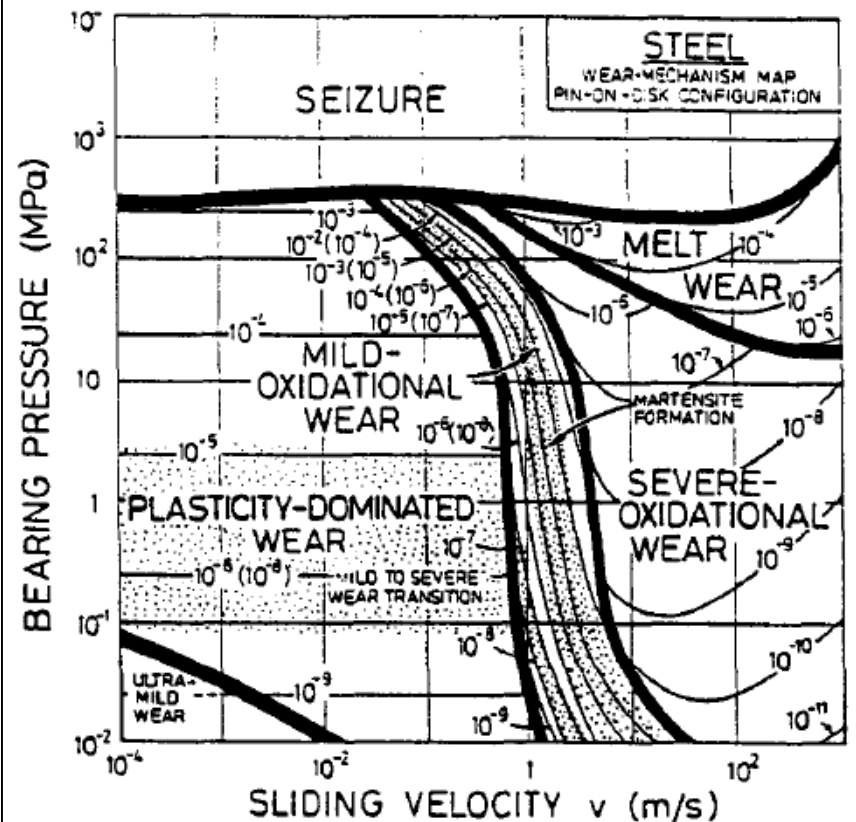
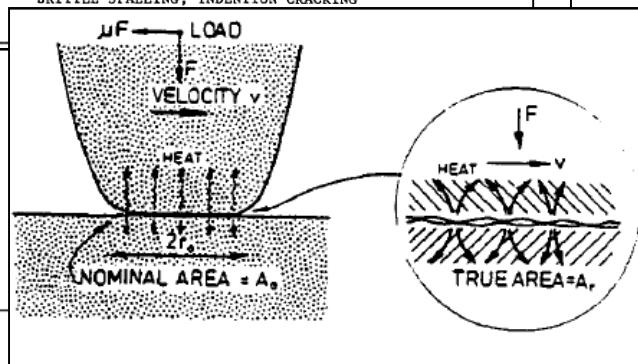
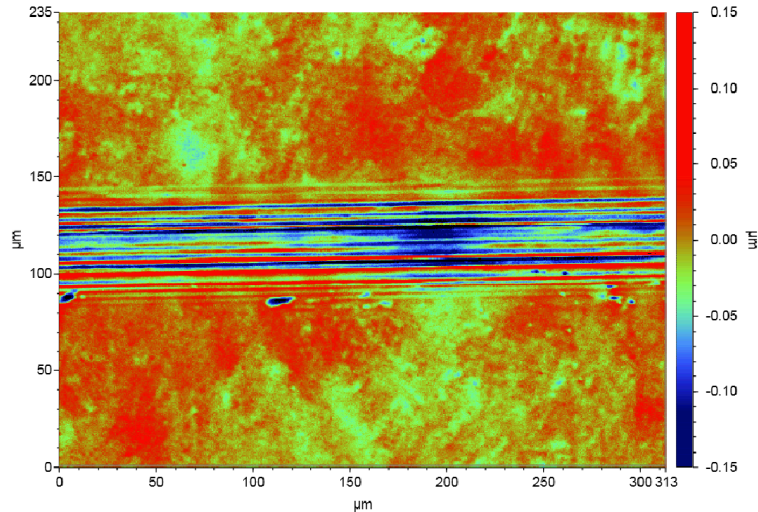


Figure 3. A wear-mechanism map for low-carbon steel based on physical modelling calibrated to experiments. The shaded regions show transitions.

# 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:



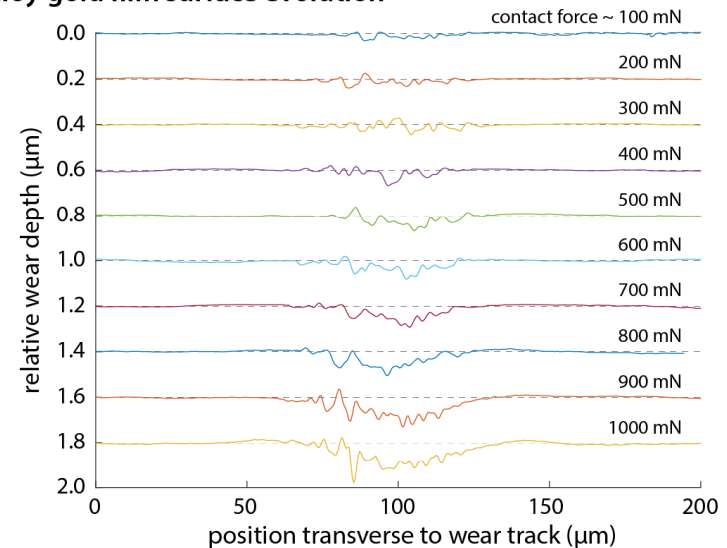
Images taken at 1 mm intervals along 10 mm long wear tracks

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

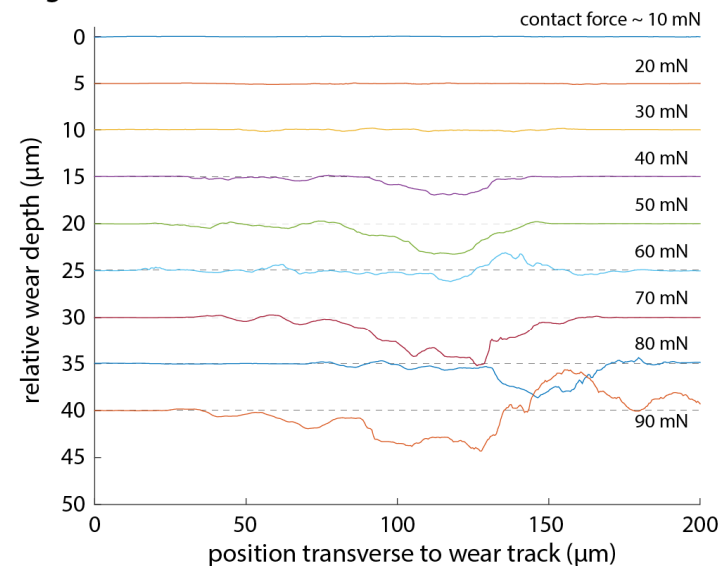
Wear at each interval calculated based on contact force average in this part of the track, number of cycles, and volume loss

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

## alloy gold film surface evolution

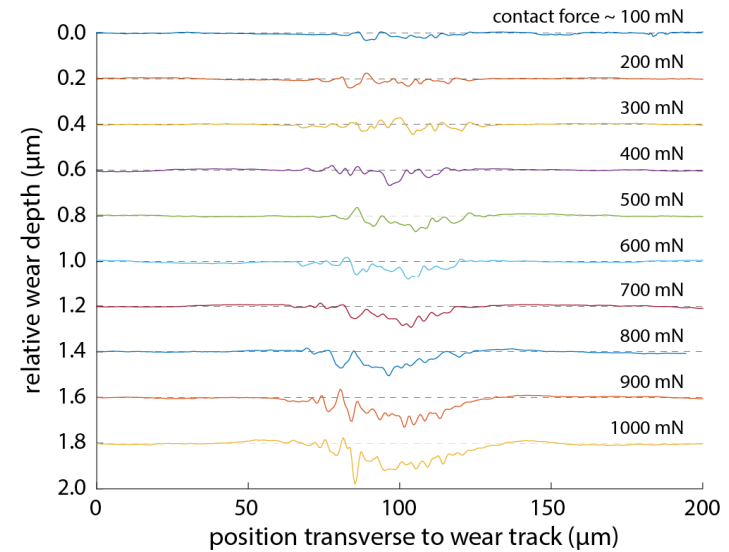
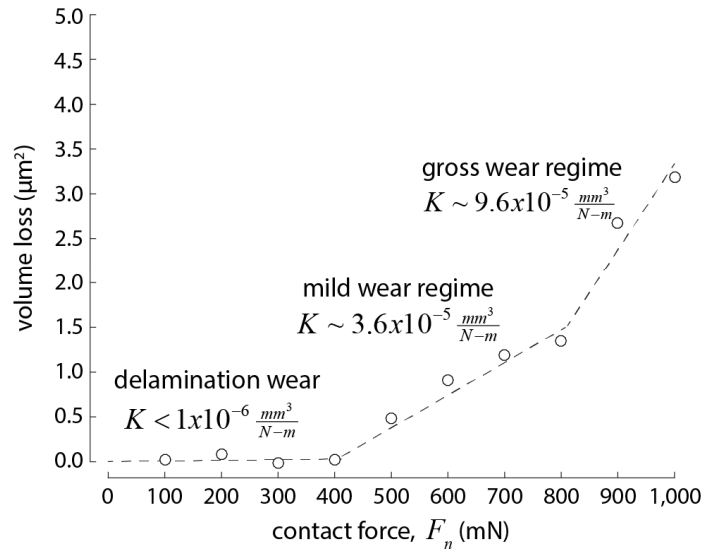


## pure gold substrate surface evolution

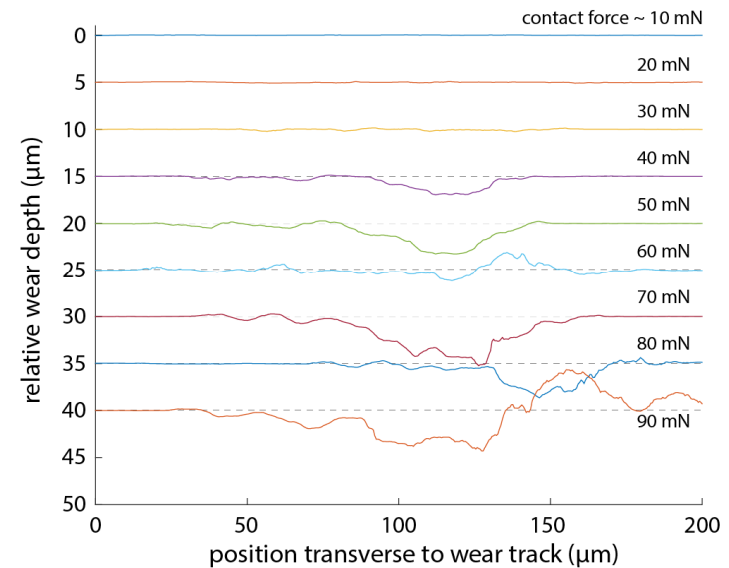
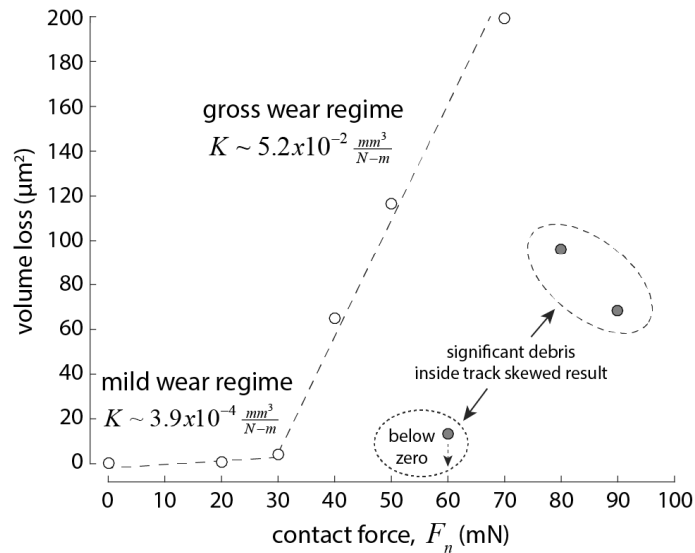


# Observed three wear regimes

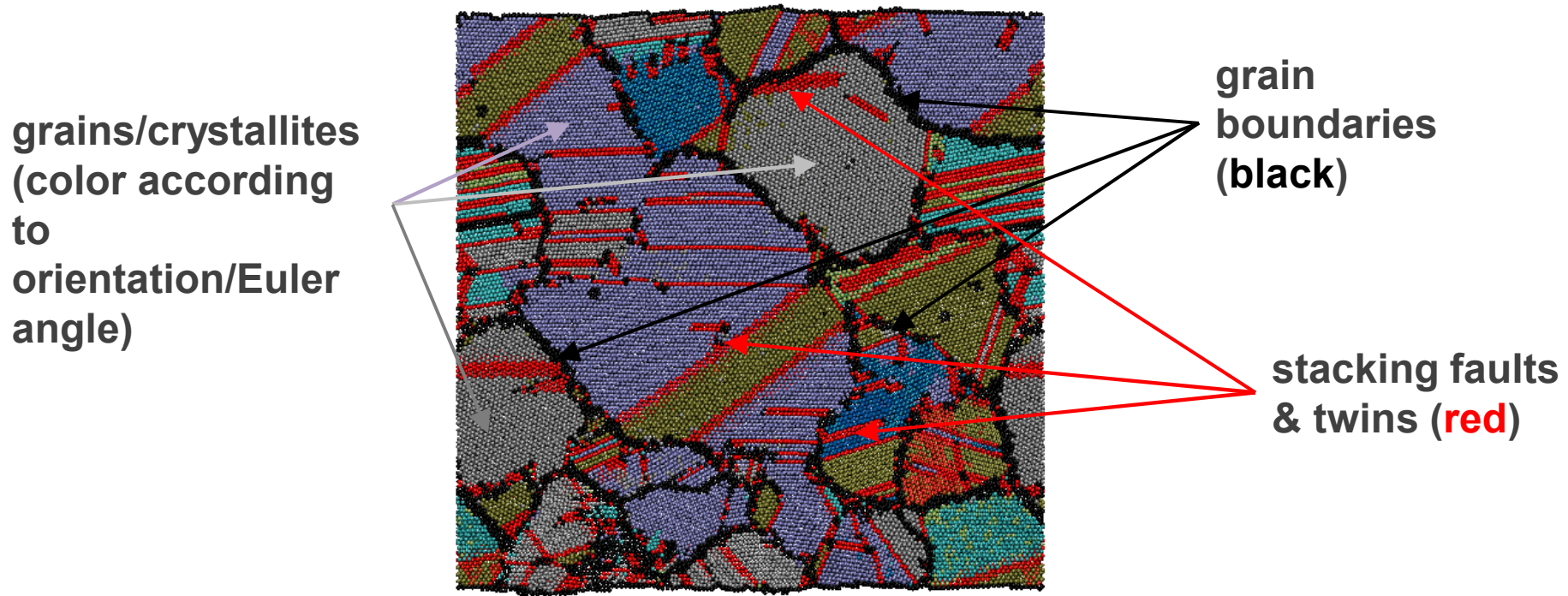
## alloy gold film surface evolution



## pure gold substrate surface evolution



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

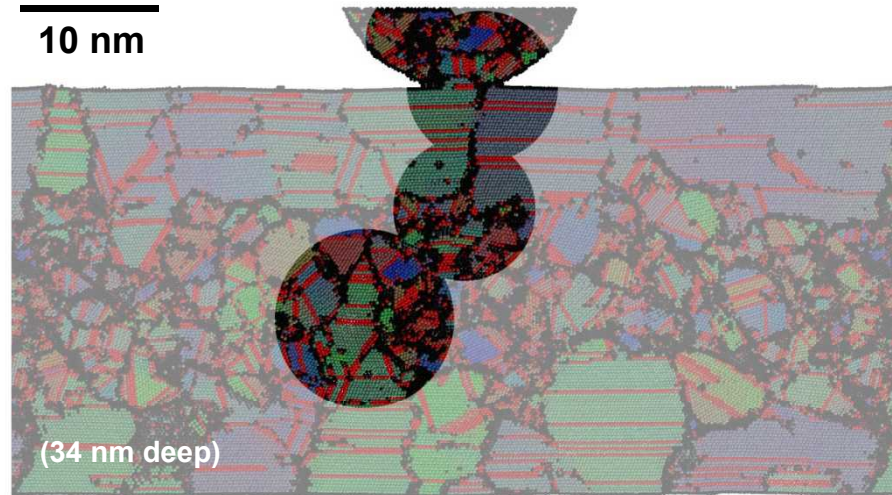


- Locally FCC atoms colored according to Euler angle
- Locally HCP atoms colored red – twins & stacking faults
- Otherwise colored black – grain boundaries



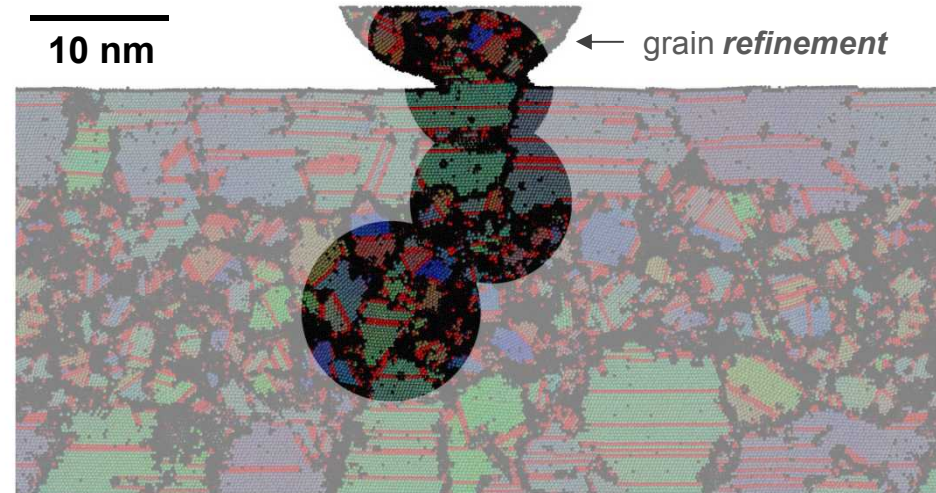
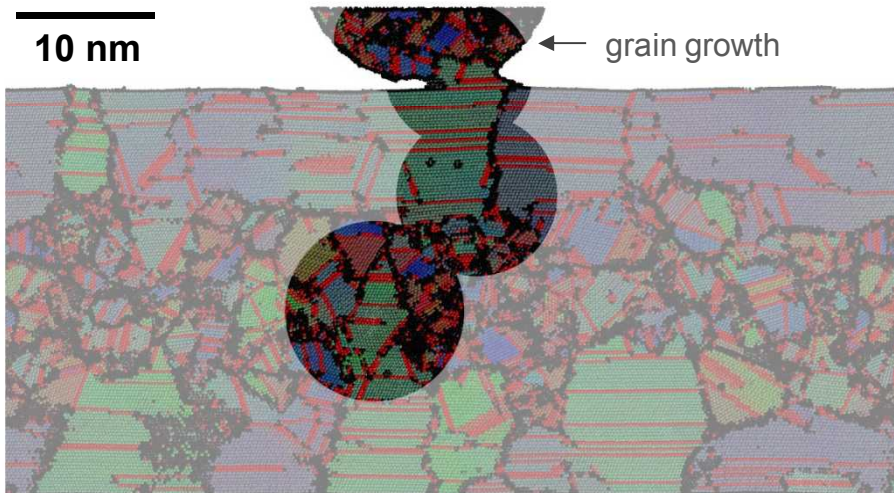
# Comparison between pure and alloyed Ag grain evolution: **stabilization thru alloying**

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



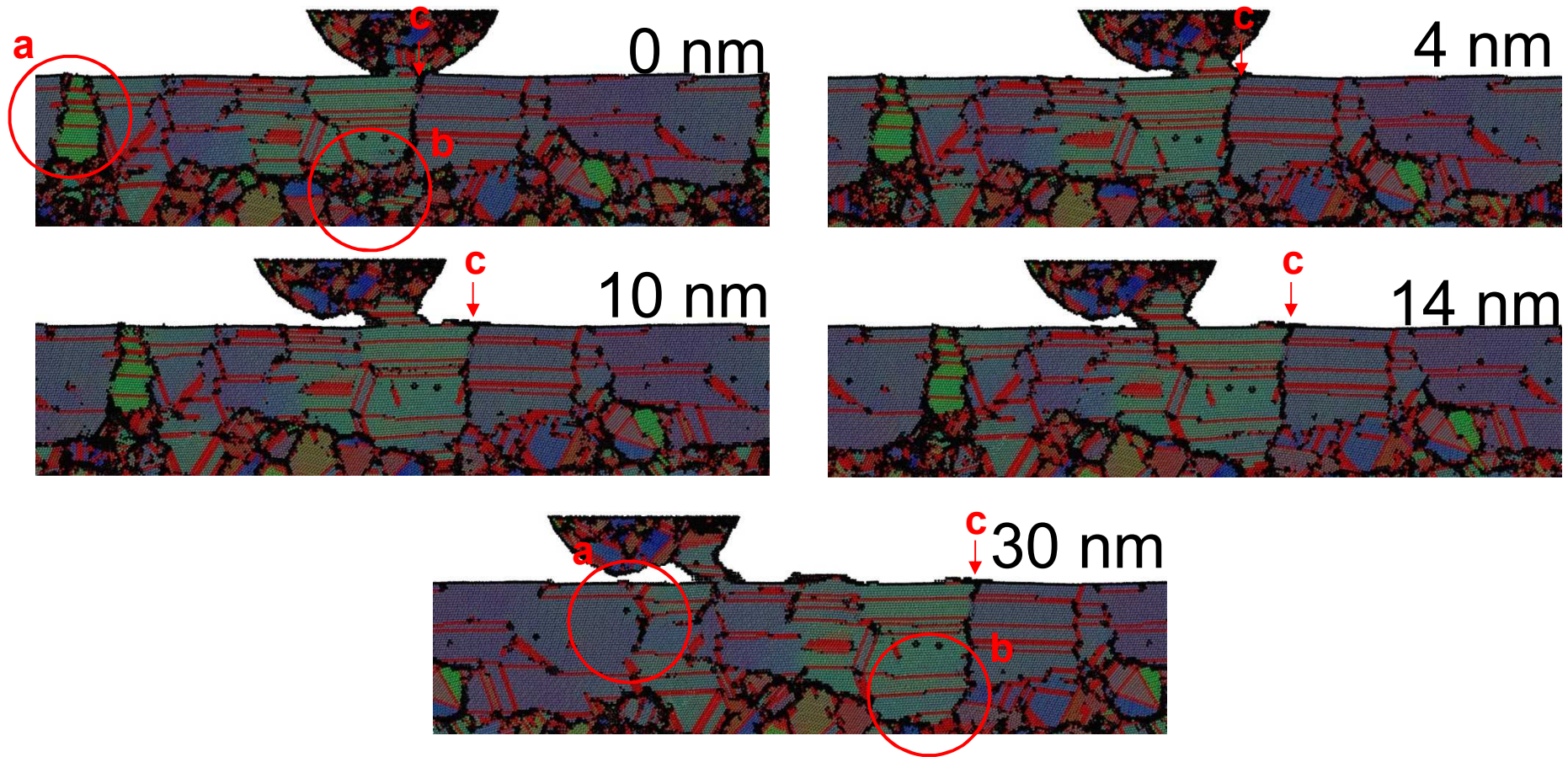
**pure Ag** after 4 nm of sliding

**Ag-10% Cu alloy** after 4 nm of sliding



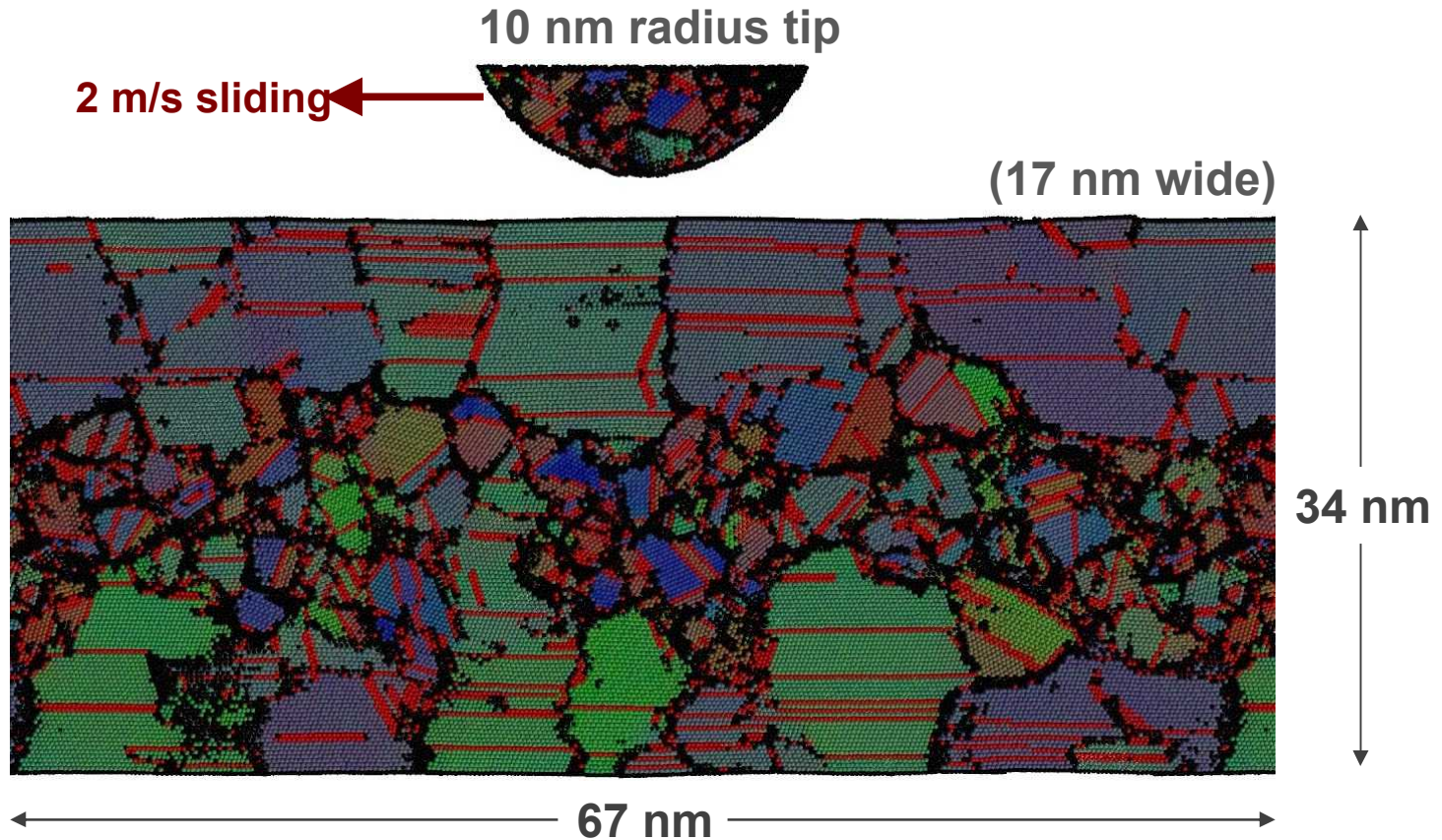


## Another look, now at **pure Au** tip/slab contact evolution over a longer sliding time



- 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

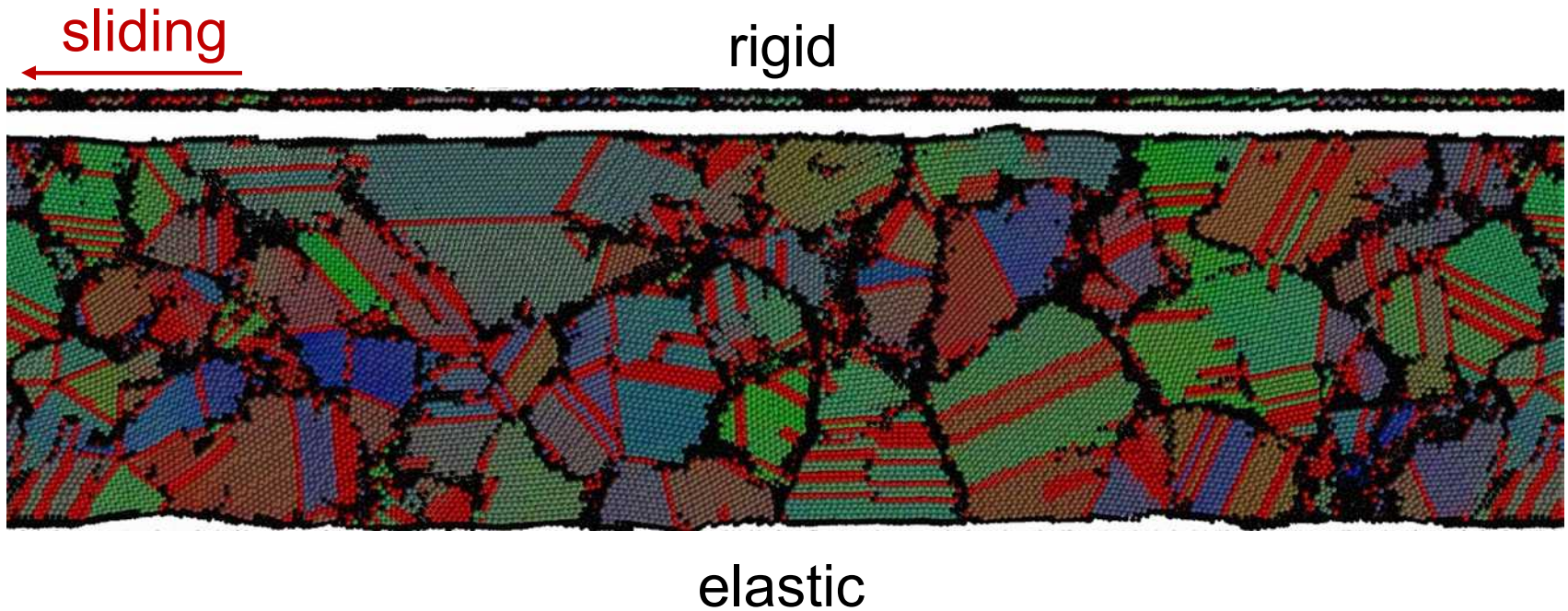
Constraint 1: constant velocity

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



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

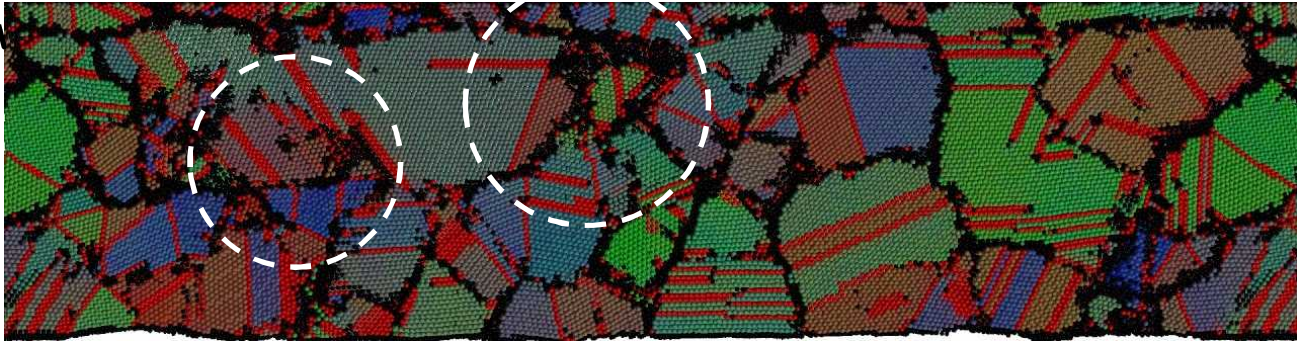
---



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

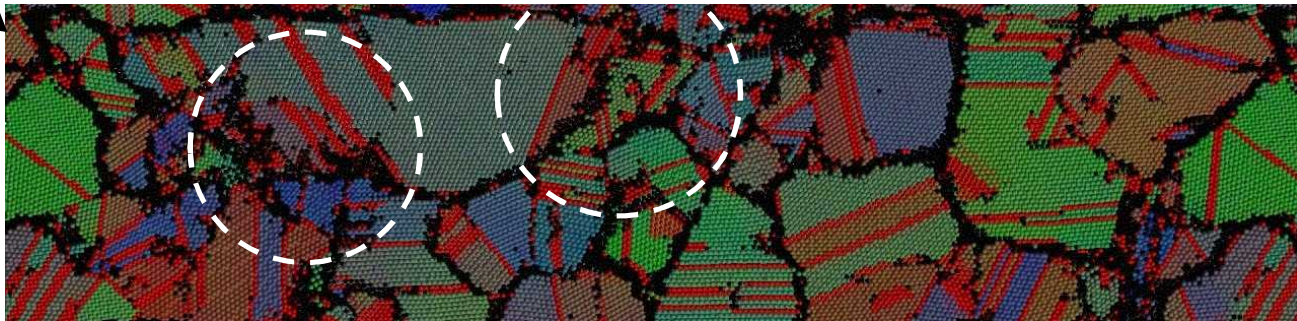
## Sliding of pure Ag slabs

after 5 nm of sliding



Slab +  
transfer film

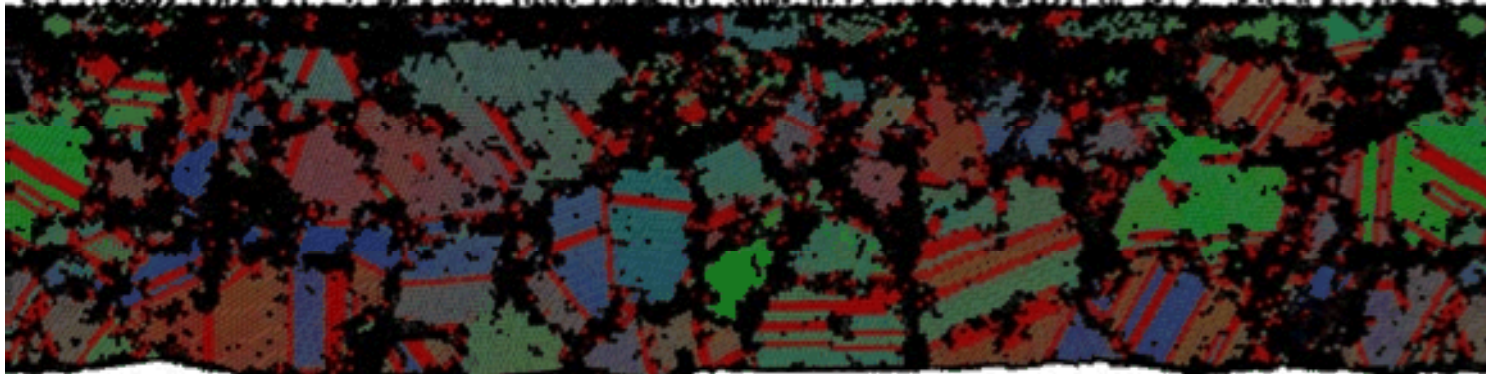
after 8 nm of sliding



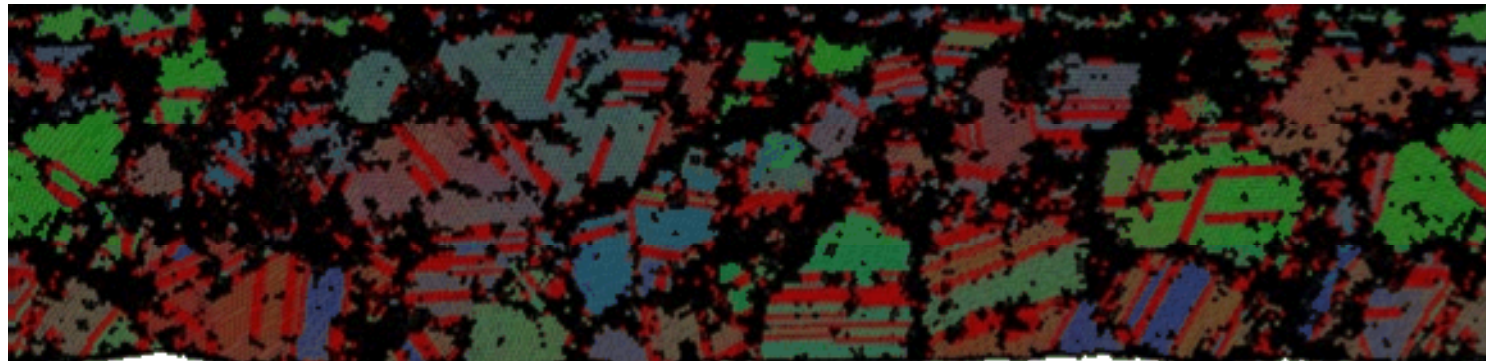
- Slight grain growth, forms transfer film
- Slides along transfer film grain boundaries or nearby stacking faults depending on availability



after 6 nm of sliding



after 16 nm of sliding

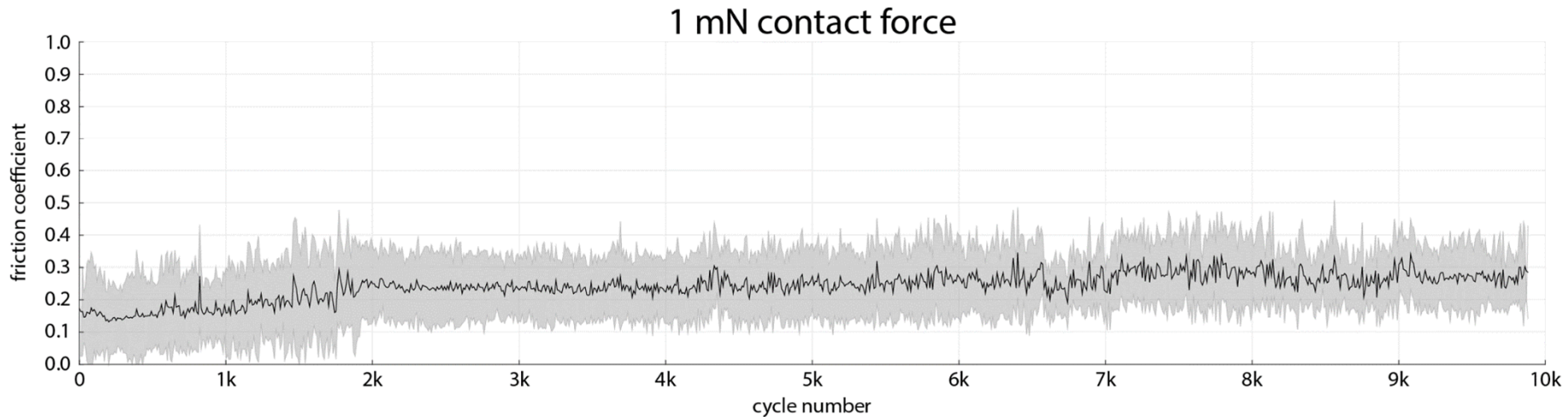
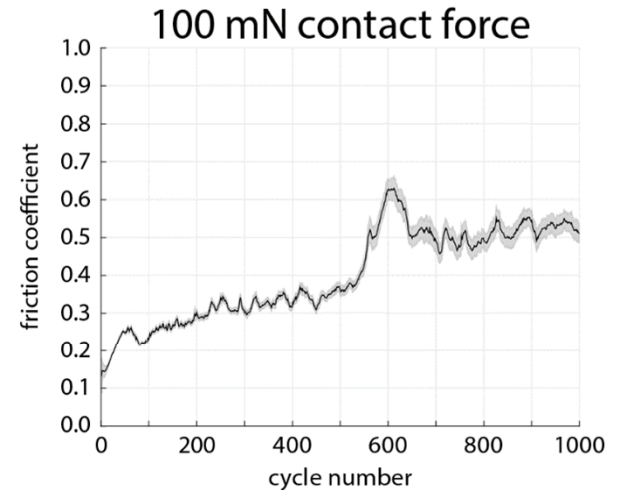
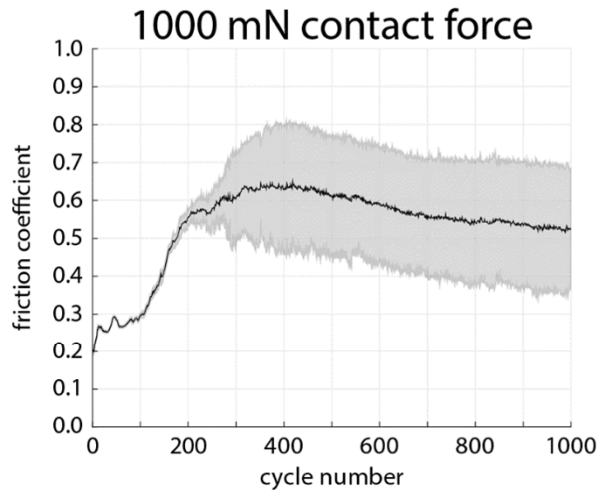


- Alloy slides at transfer film boundary, but **also throughout substrate**
- The pure Ag slabs on previous slide started with the exact same microstructure (lots of coarsening on the pure Ag slabs simulation!)



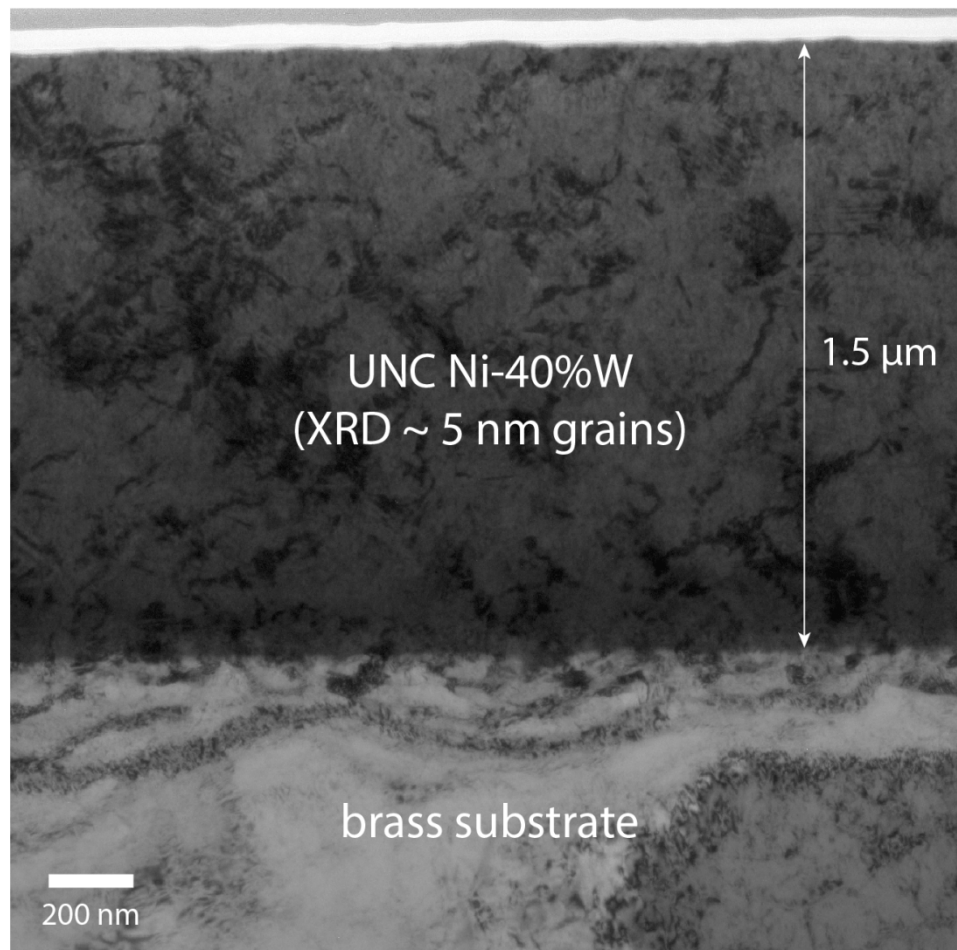
# Three regimes observed for 60Ni-40W at.% vs sapphire in oxidizing environment

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



1 mN, 10k cycles track



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

off-track reference

100 mN, 1k cycles track

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

1.5  $\mu\text{m}$

brass substrate

200 nm

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

100 mN, 1k cycles track

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

1.5  $\mu\text{m}$

brass substrate

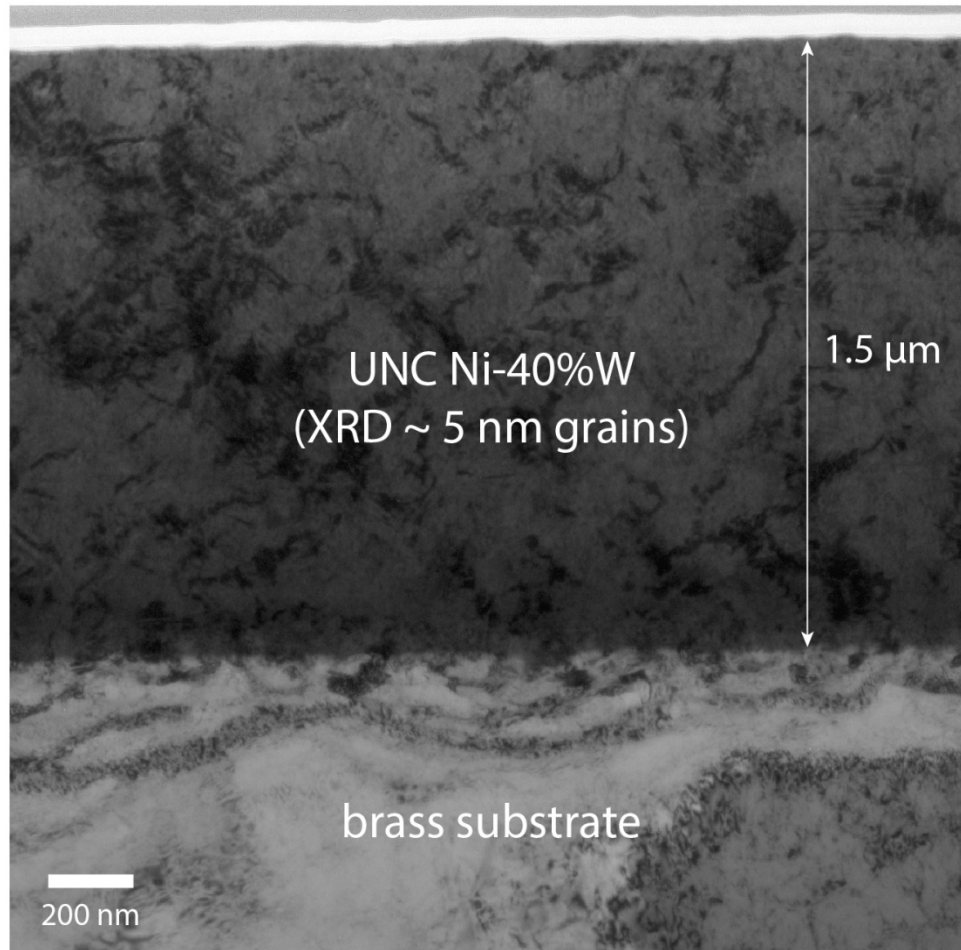
200 nm

mixed UNC metal/oxide

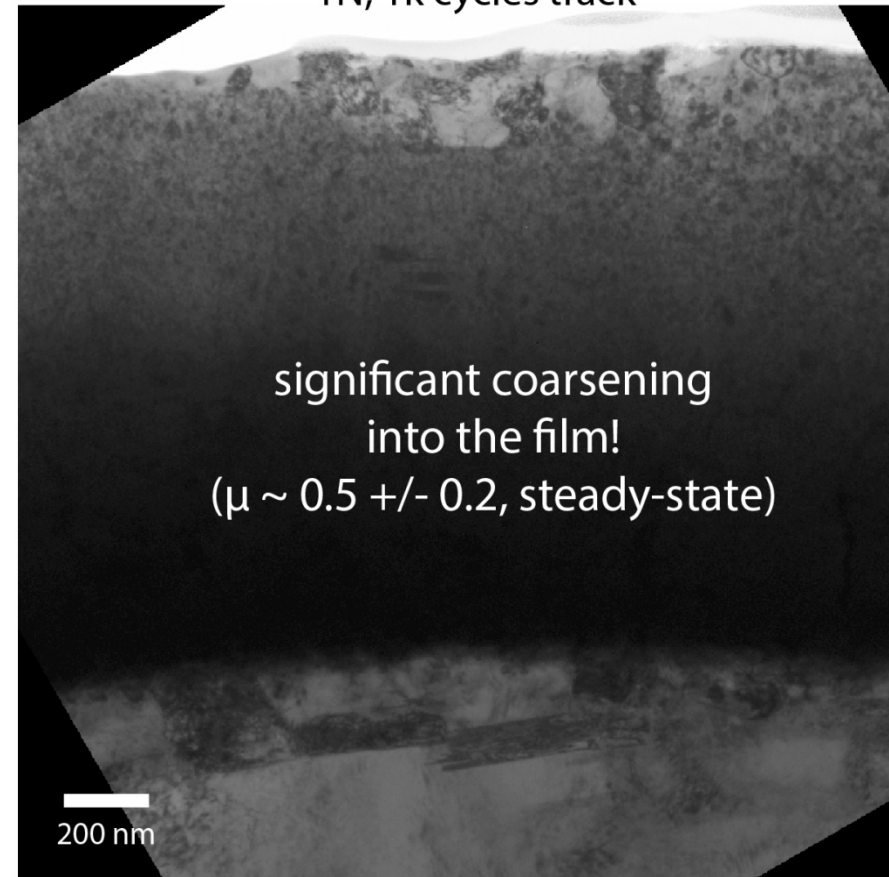
refined near surface Ni-W

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

off-track reference



1N, 1k cycles track





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

## Regular Nanocrystalline Solution (RNS) model

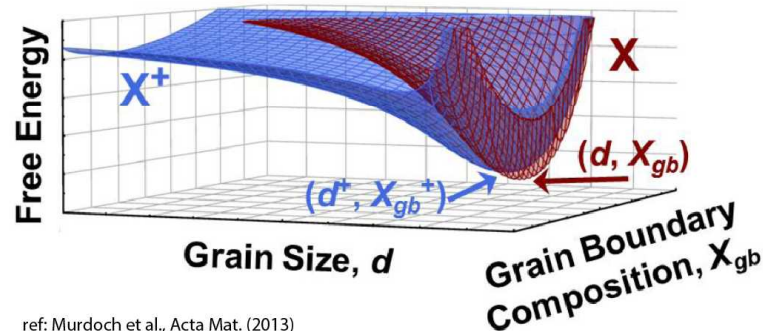
ref: Chookajorn et al., Science, 2012

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

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

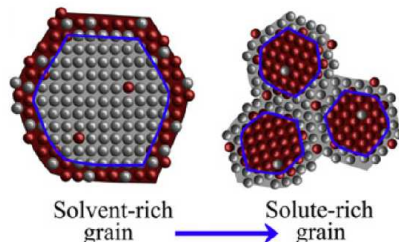
Implications:  
Will not drive toward fine grain size, but will remain there

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

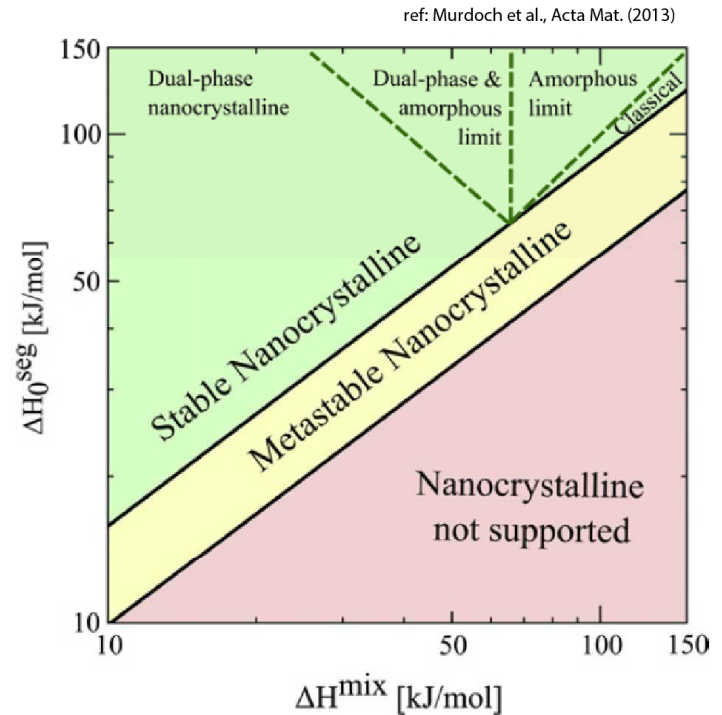


ref: Murdoch et al., Acta Mat. (2013)

Grain structure model: segregated 2-phase metal system:



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

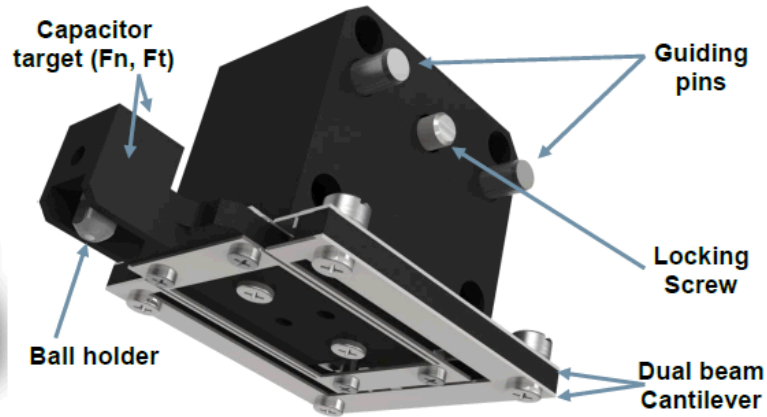


ref: Murdoch et al., Acta Mat. (2013)

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

**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

