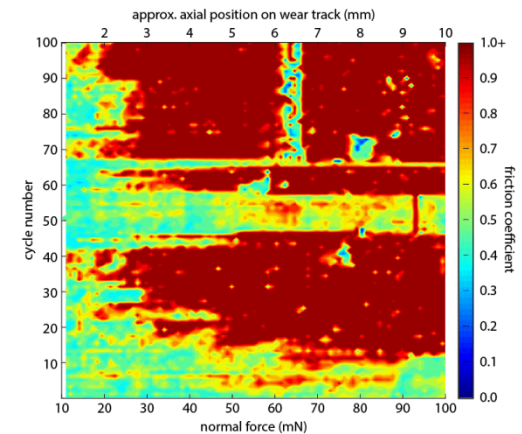
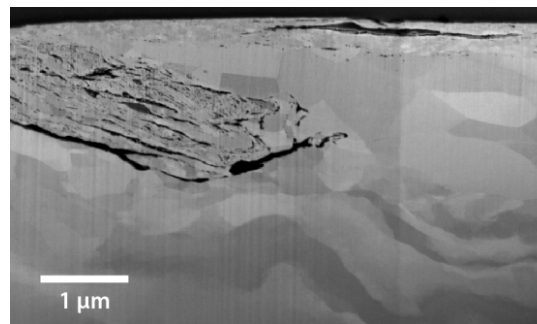
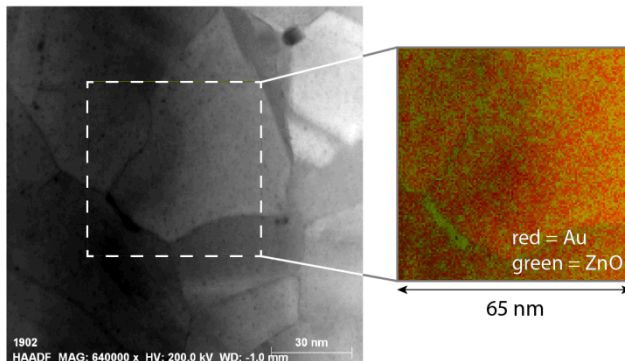


# Correlating Surface Microstructure Evolution to Regimes of Friction in Metals

Nicolas Argibay<sup>1</sup>, Michael E. Chandross<sup>1</sup>, Shengfeng Cheng<sup>2</sup>  
 Paul G. Kotula<sup>1</sup>, Joseph R. Michael<sup>1</sup>, Somuri V. Prasad<sup>1</sup>

<sup>1</sup> *Materials Science and Engineering Center  
 Sandia National Laboratories  
 Albuquerque NM USA*

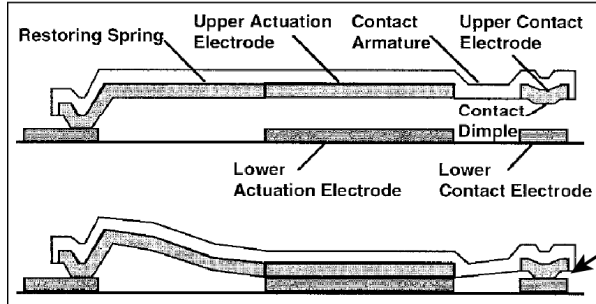
<sup>2</sup> *Department of Physics  
 Virginia Polytechnic  
 Blacksburg, VA*



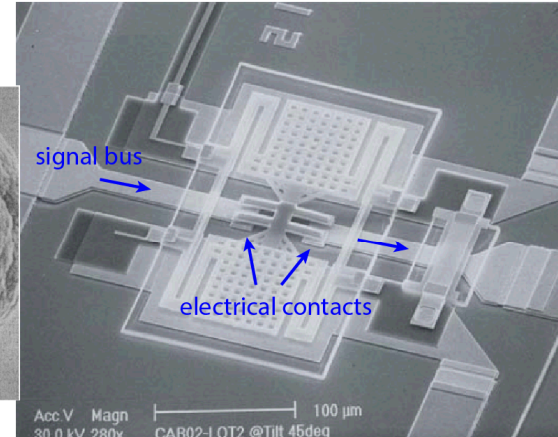
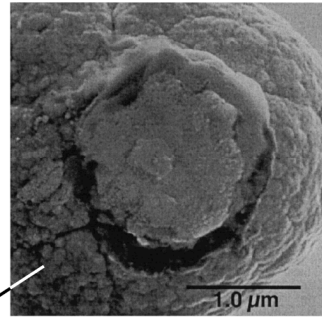
# Metals are widely used tribological materials – particularly, electrical contacts

## RF Micro Electromechanical Systems (MEMS)

switching GHz signals



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

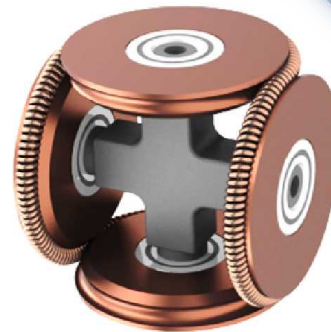


Source: Rockwell Scientific metal-metal switch

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



## Aerospace and Energy



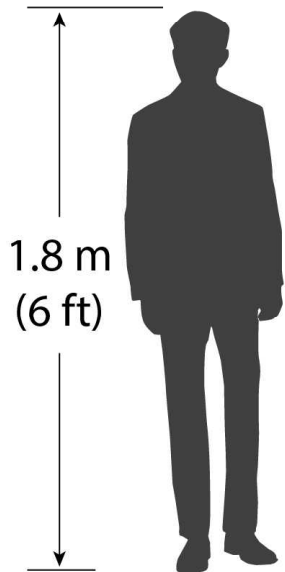
Source: Honeybee Robotics (<http://www.honeybeerobotics.com/portfolio/rolling-contact-connector/>)

# 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)...

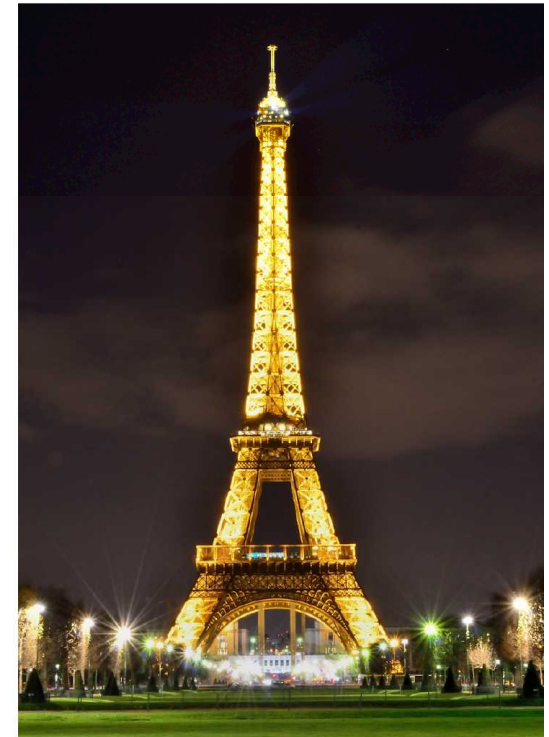
2.6 m (8.5 ft) wide



**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*

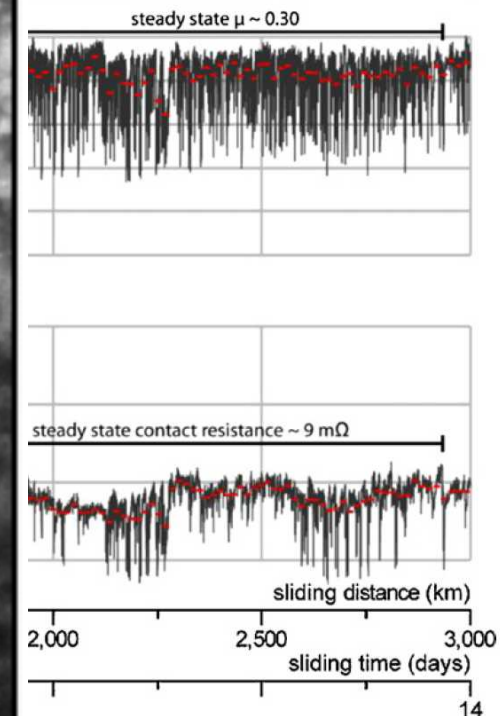
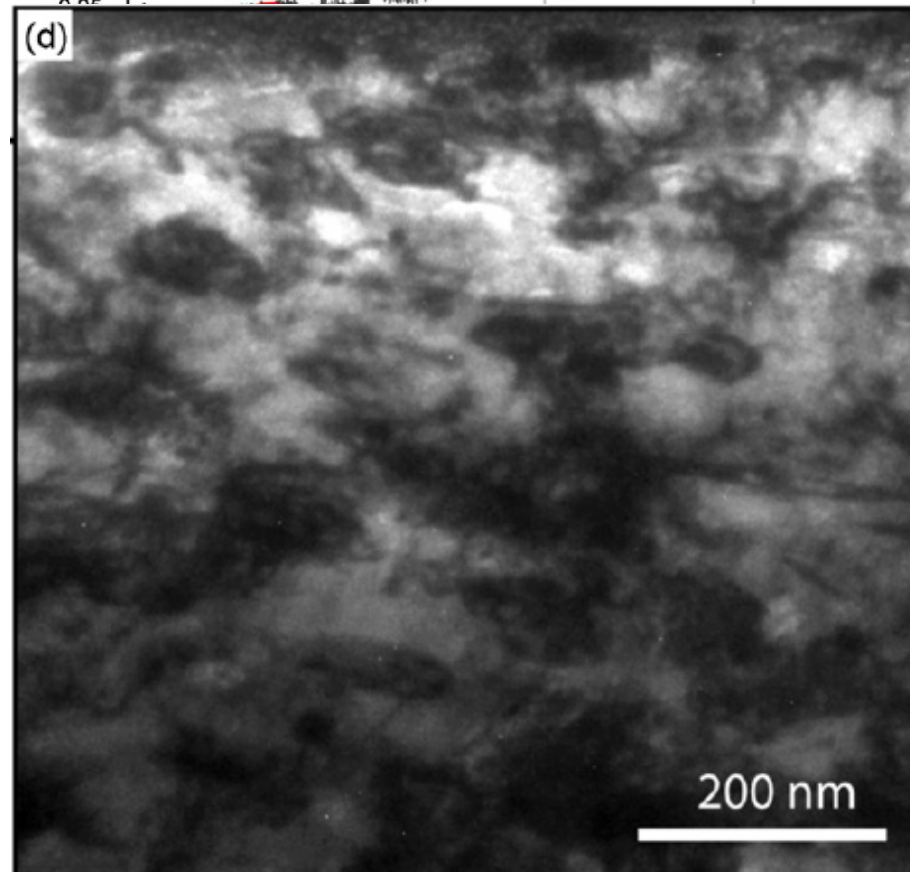
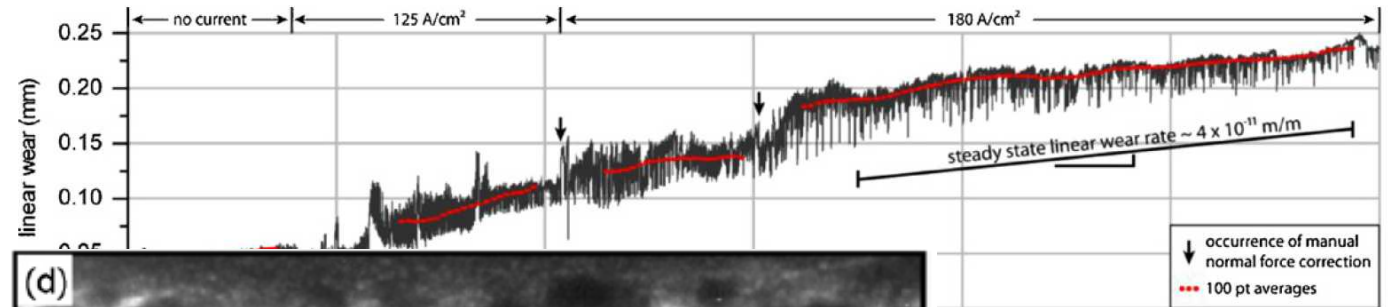
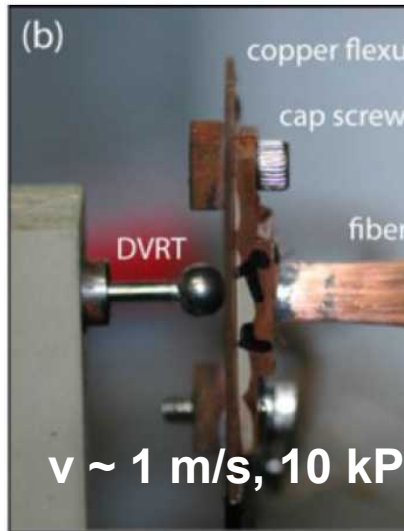


Reference: Gold Survey, Gold Fields Mineral Services Ltd., 2010



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

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



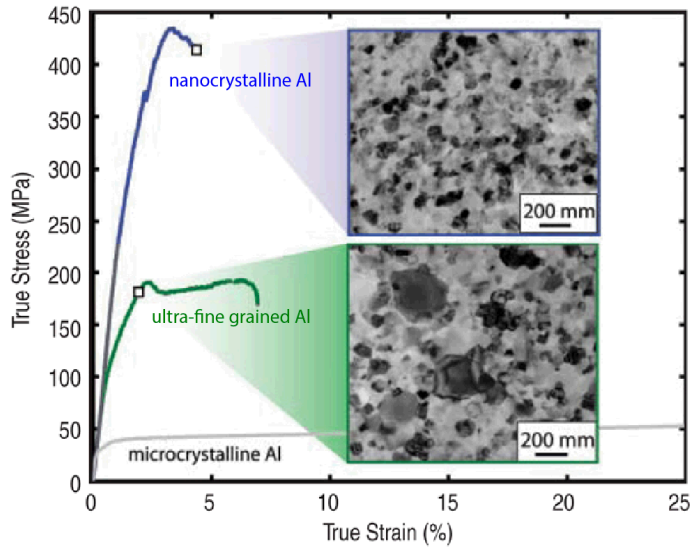
Low friction  
associated with  
nanocrystalline  
surface for a Cu-C  
system

ref: Argibay et al., Wear 2010

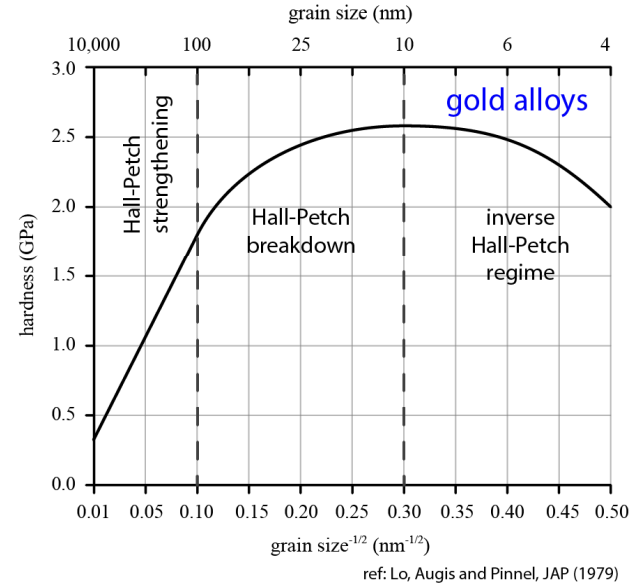


# Engineering advantages of NC metals, alloys and metal-matrix composites

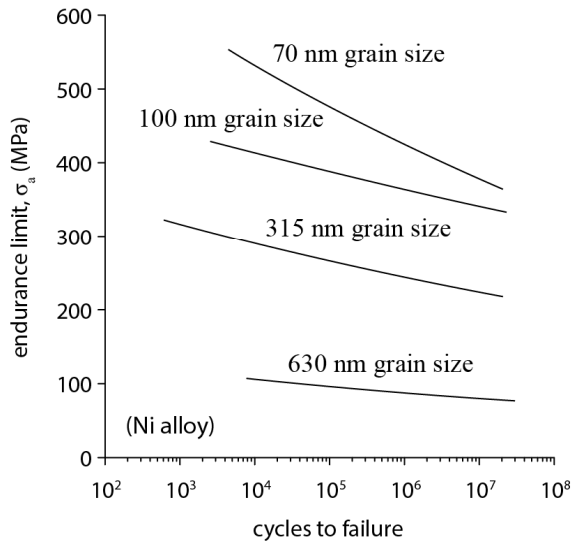
## higher yield strength



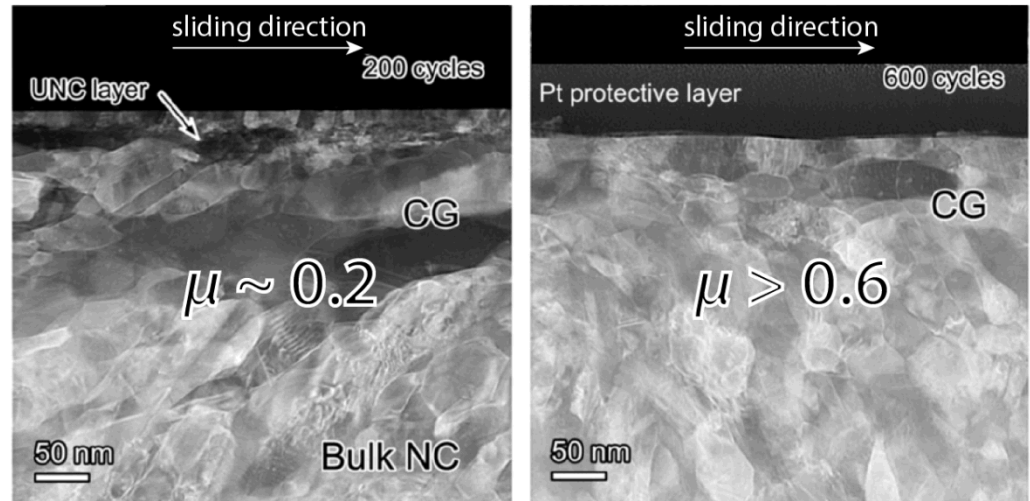
## higher hardness



## higher fatigue strength (endurance limit)

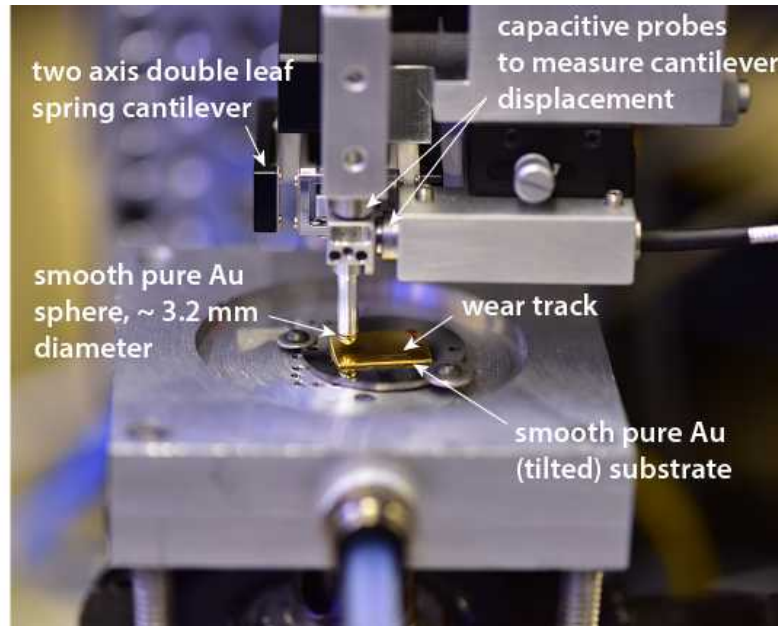


## lower friction and wear rates -- *but why?*

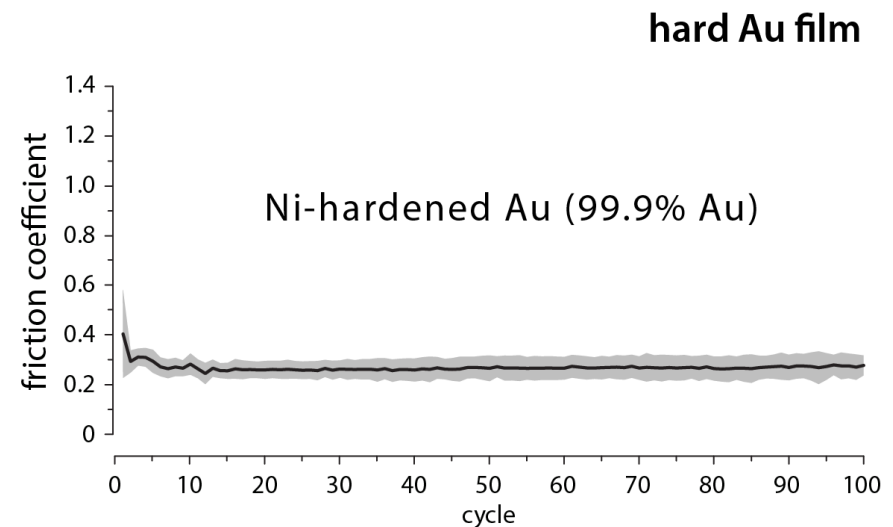
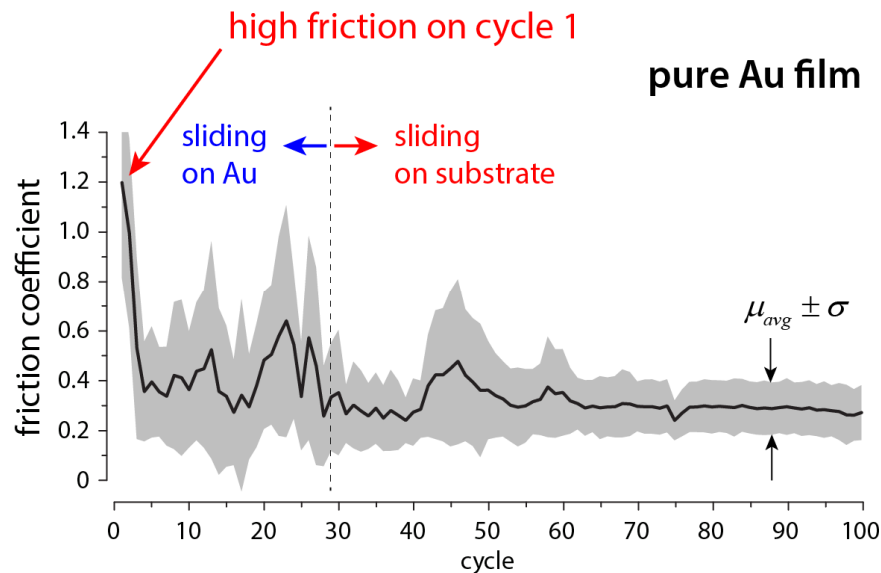


steady-state cross-sections of wear tracks

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

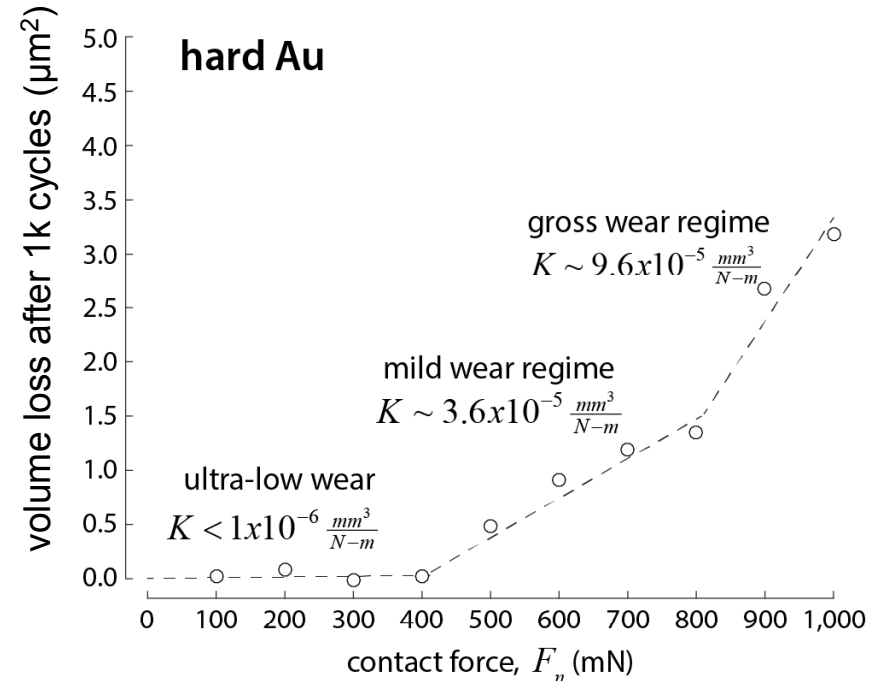
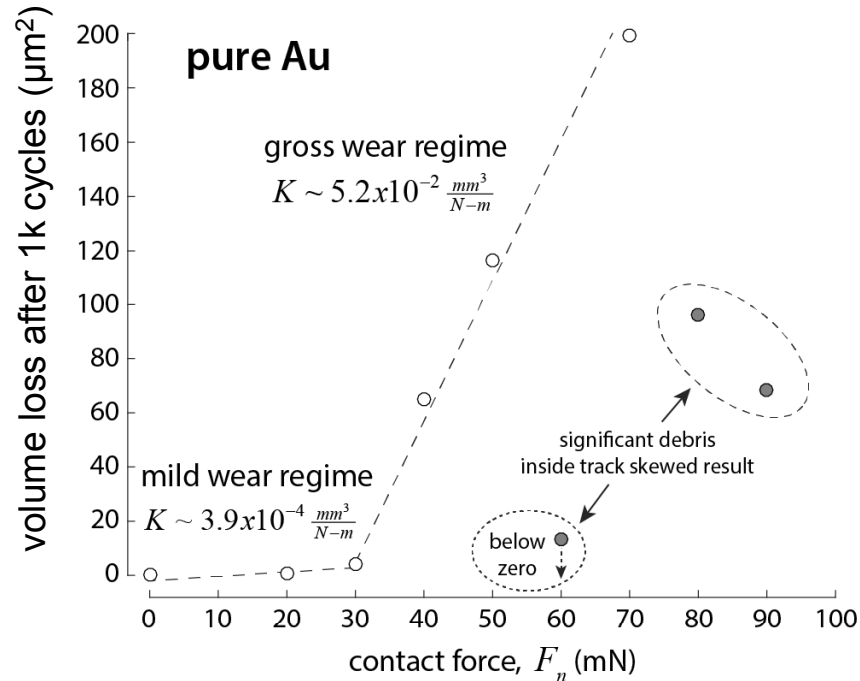


normal force = 100 mN  
ball radius = 1.6 mm  
speed = 1 mm/s



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

Note x- and y-axis scale difference!



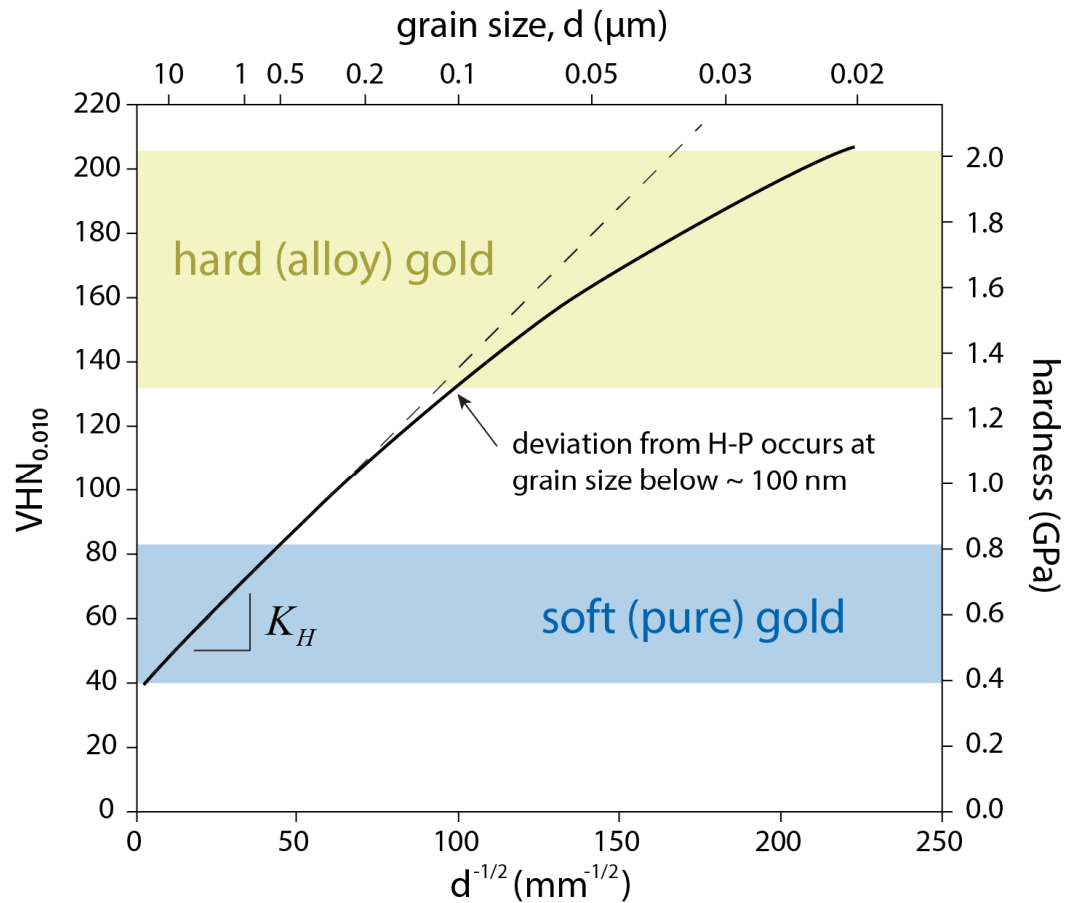
> 10,000x wear rate reduction with addition of 0.1% Ni

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

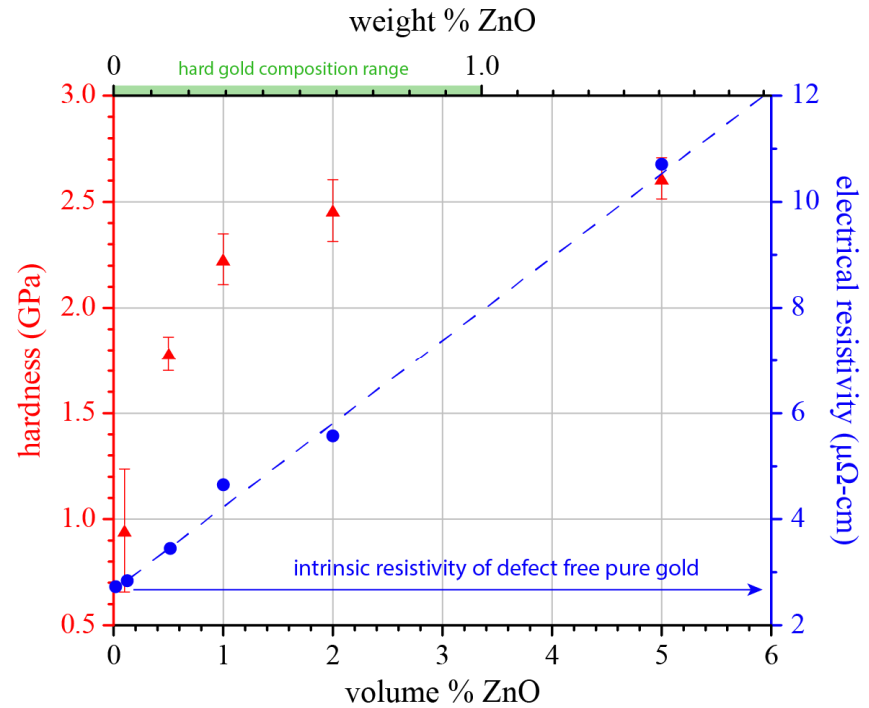
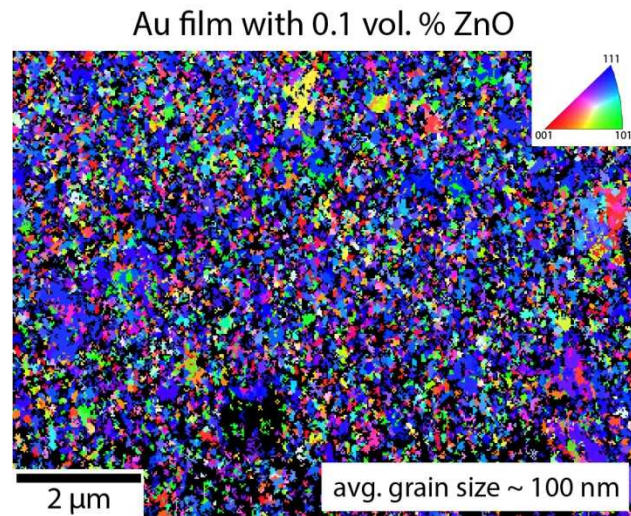
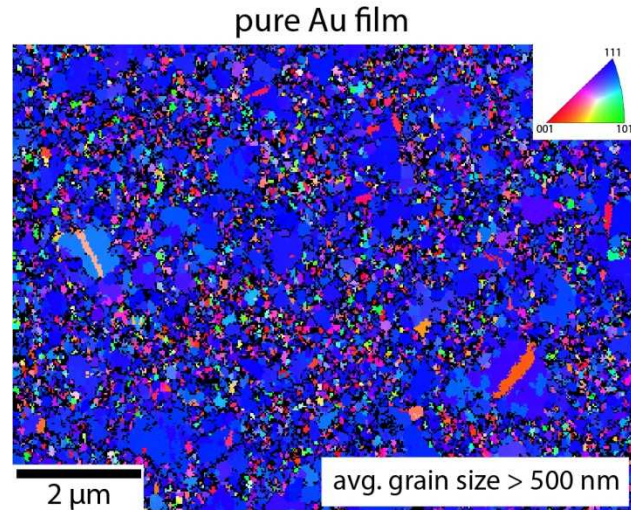


Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

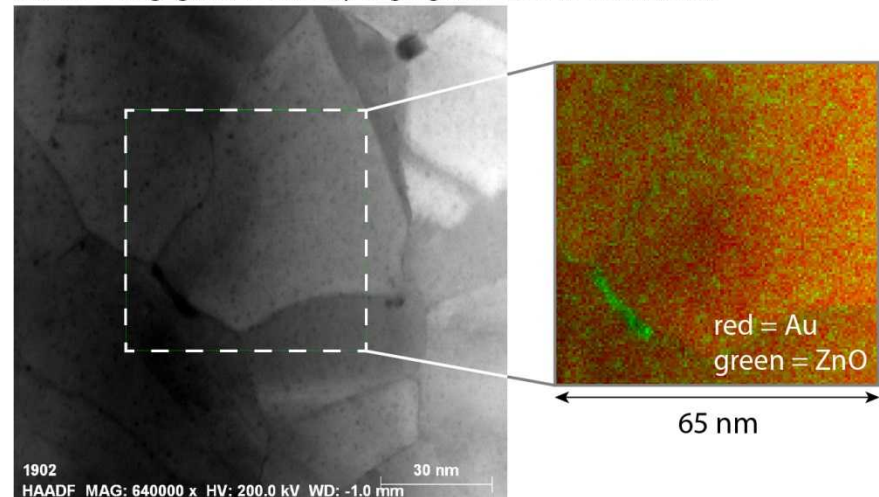
# Stable NC grain size can be achieved using non-metals

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

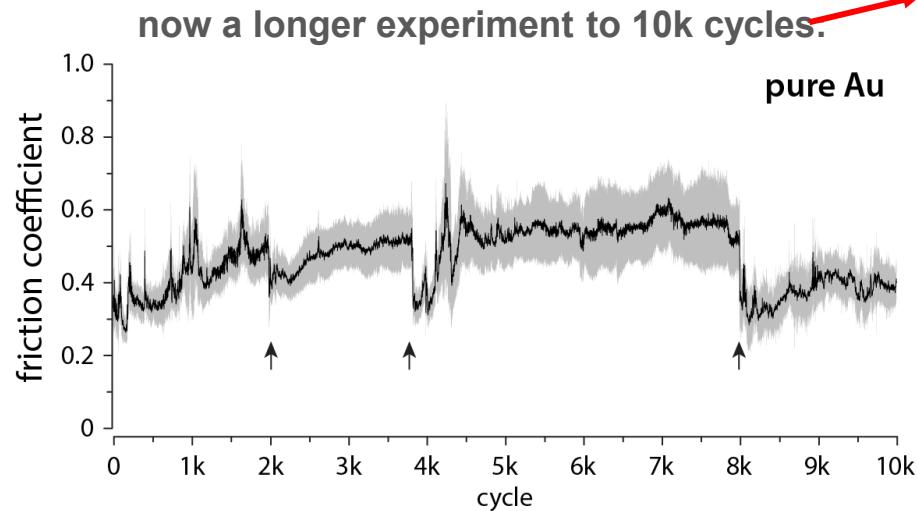
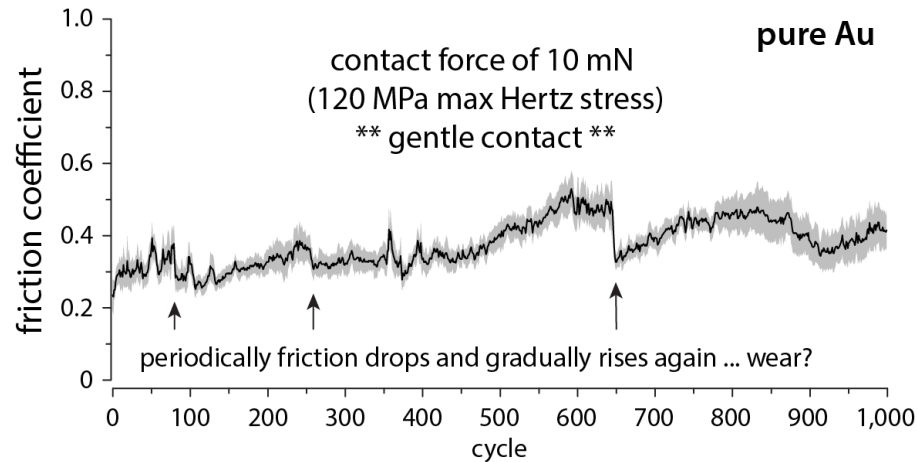
Surface-normal (planar) EBSD maps of e-beam deposited films:



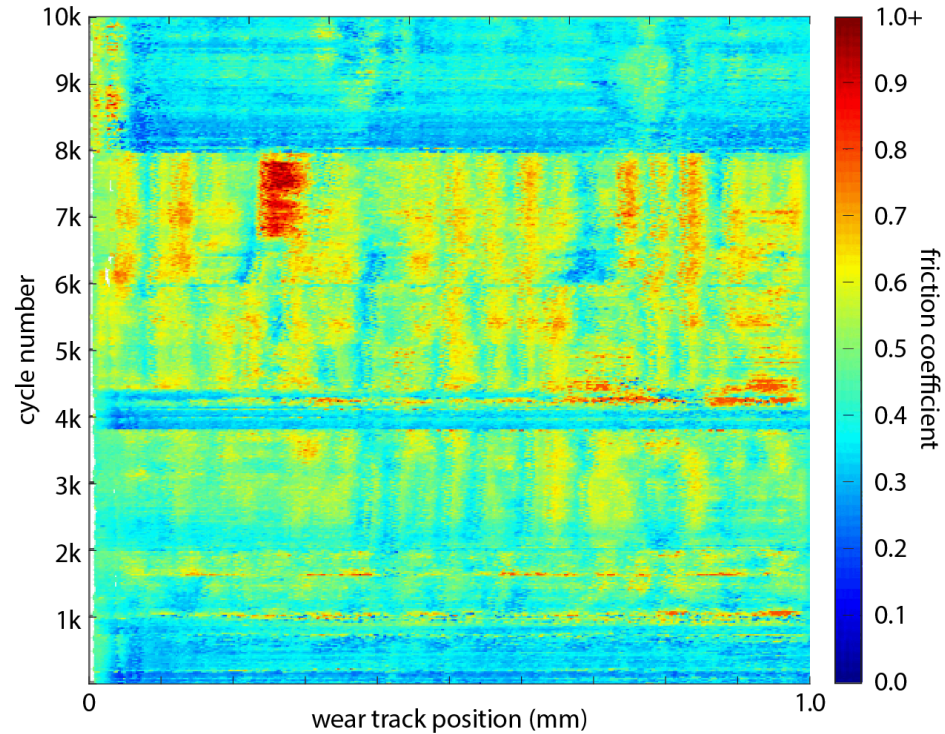
Cross-sectional composition map of a Au- 5 vol. % ZnO film showing grain boundary segregated ZnO in a Au matrix



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



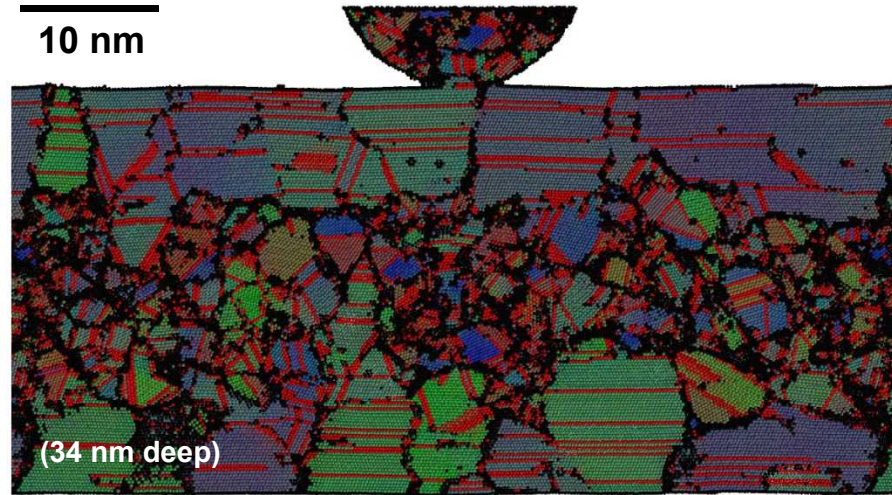
### Friction Mapping Reveals More





# What MD simulations reveal...

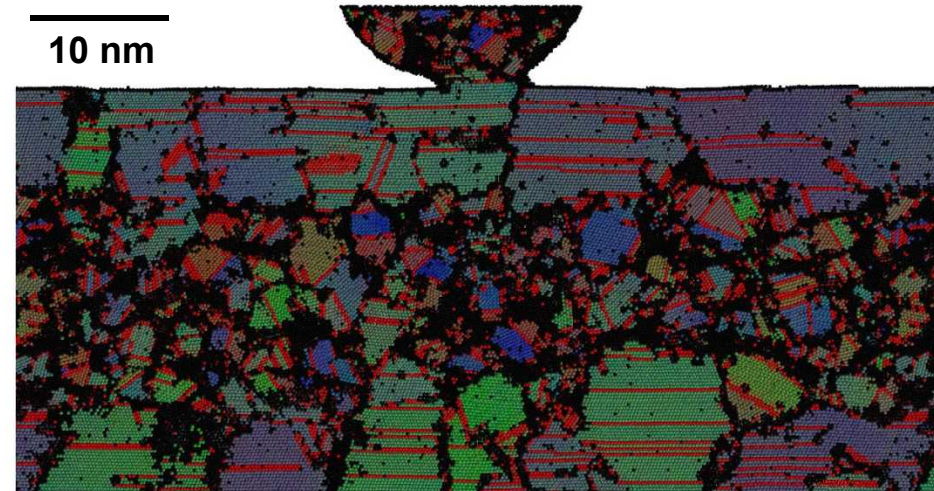
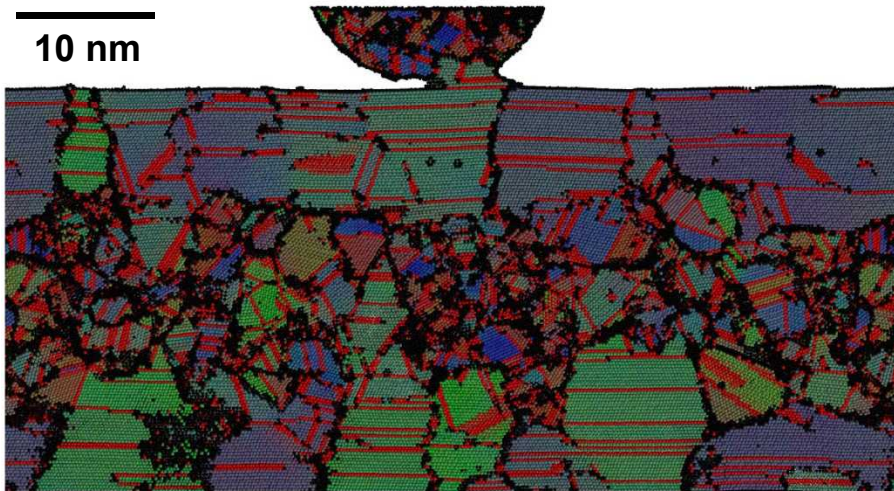
initial microstructure  
of Ag and Ag-Cu alloy  
(no sliding yet)



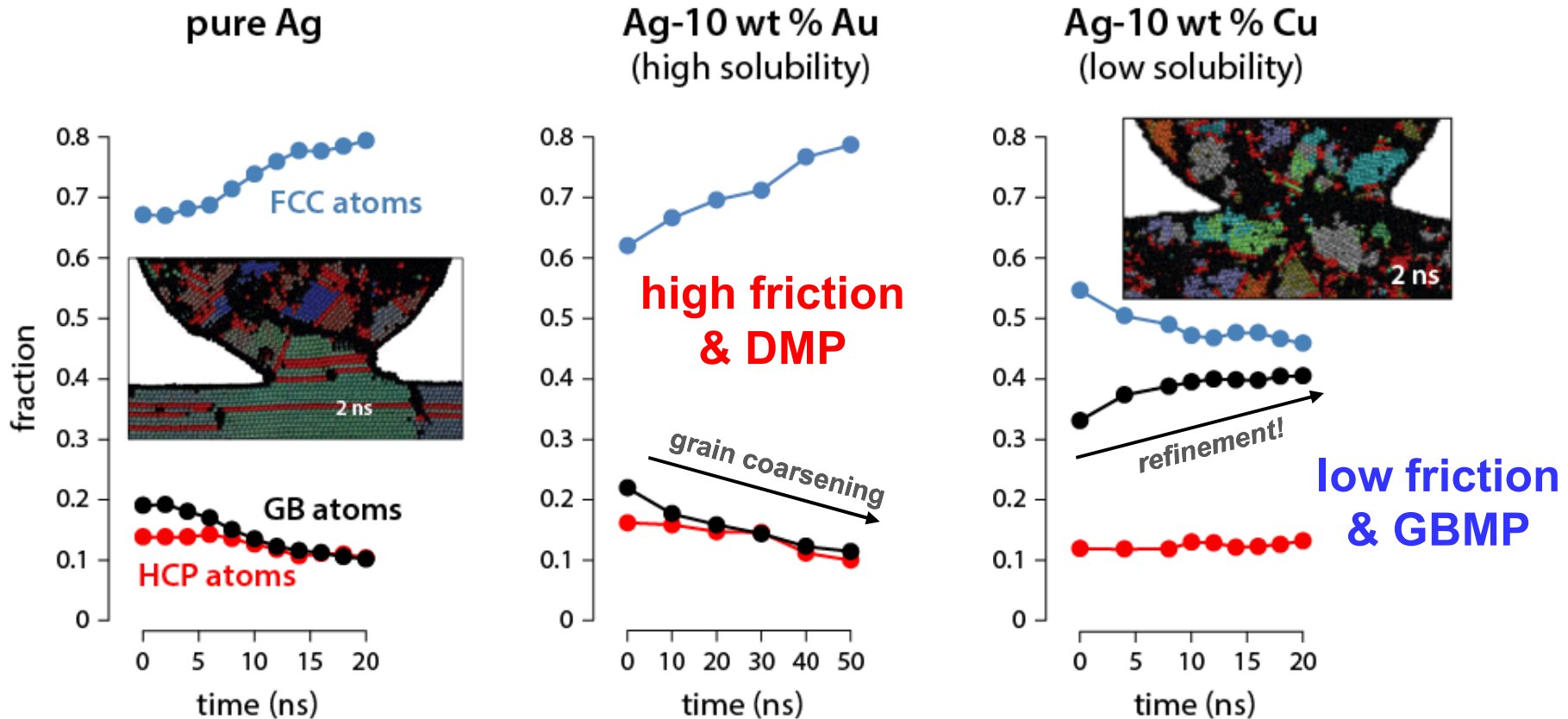
300 MPa contact stress  
300 K temperature  
2 m/s sliding speed

**pure Ag** after 4 nm of sliding

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

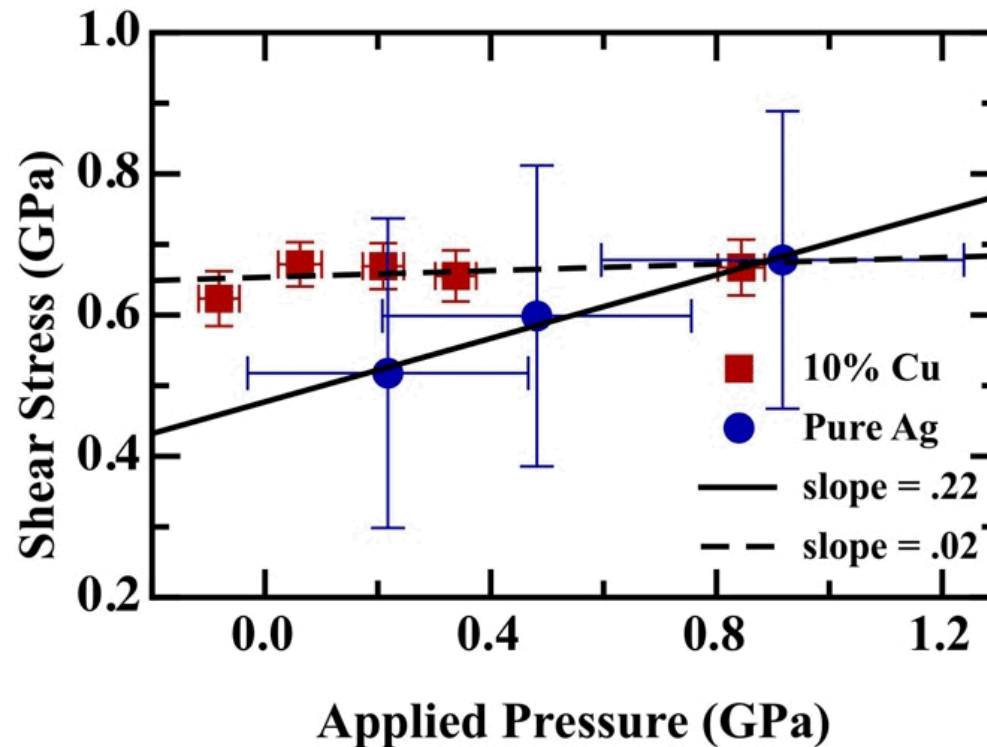


## Alloying changed **deformation mechanism**



- 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: stable GBs produce low friction at higher stress

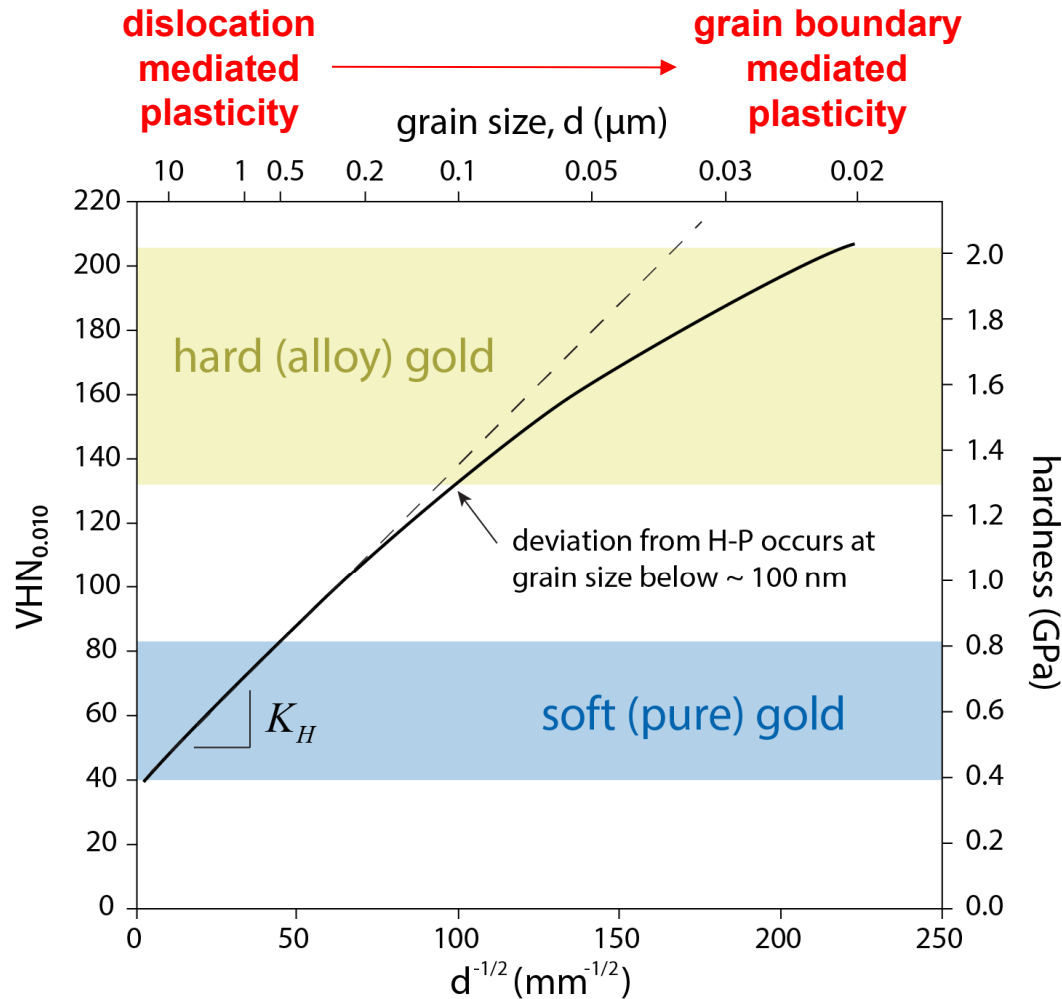
MD also showed that low solubility alloys **exhibit lower friction at equivalent stress**



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



# Why is hard better? Primarily due to grain size reduction & GB stabilization



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

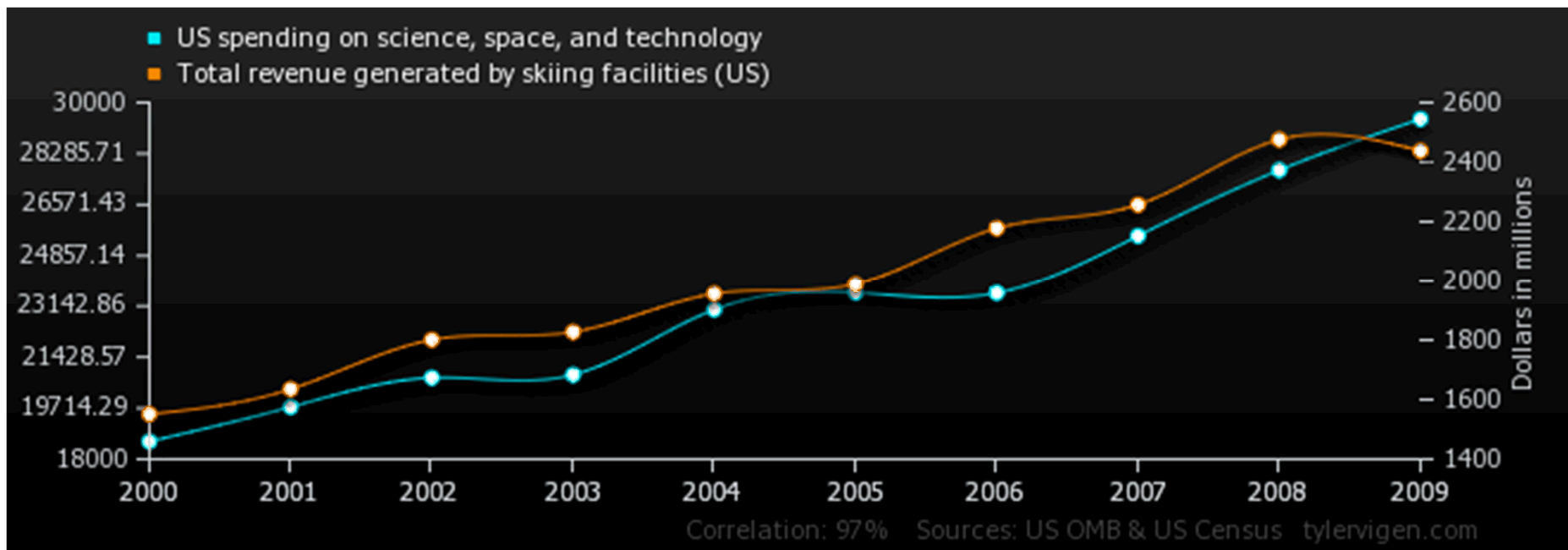
The widely held misconception that hardness increase is the source of low wear and friction is loosely attributed to the notion that real contact area drops with hardness:

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

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

In other words, correlation is not causation...

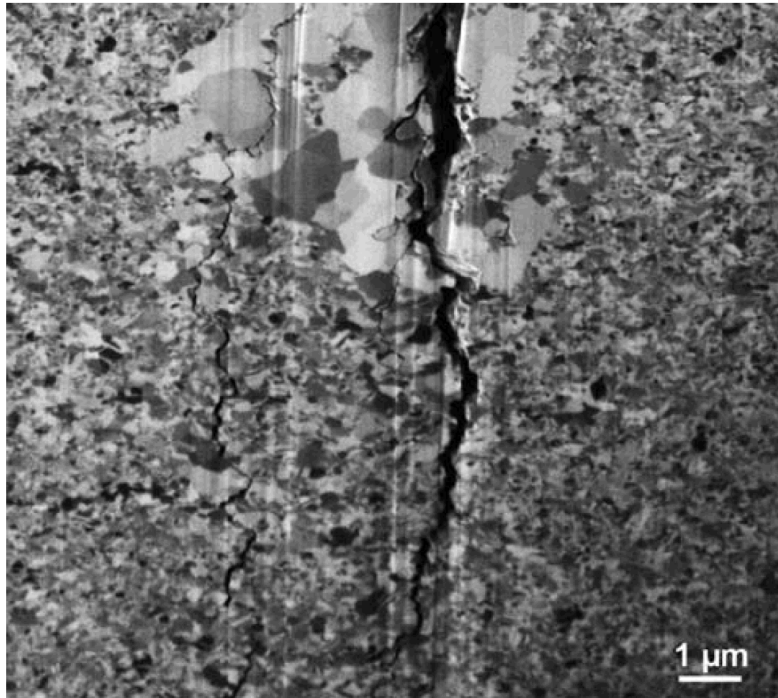
**Hardness is not the answer**  
***instead, imparting higher stability to GBs***  
***makes it easier to achieve GB-mediated plasticity***  
***at relatively higher applied stress***



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

## stress-driven grain growth

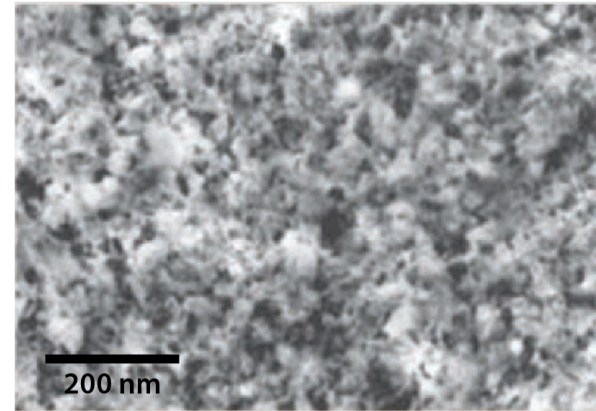
initially nanocrystalline Ni-Mn



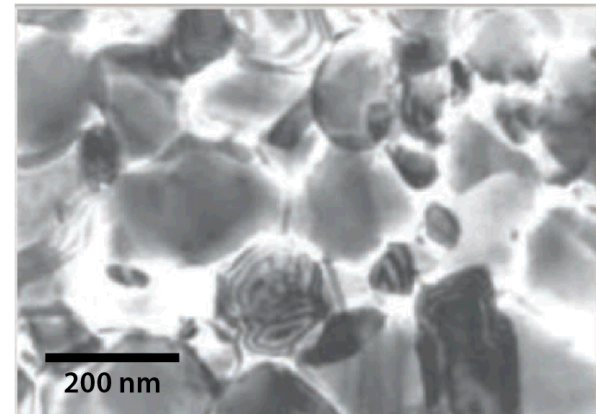
ref: Padilla & Boyce, *Exp. Mech.* (2010)

## 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**

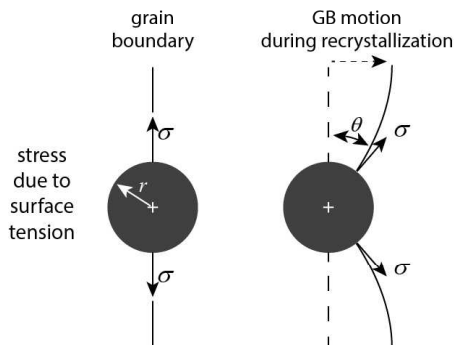
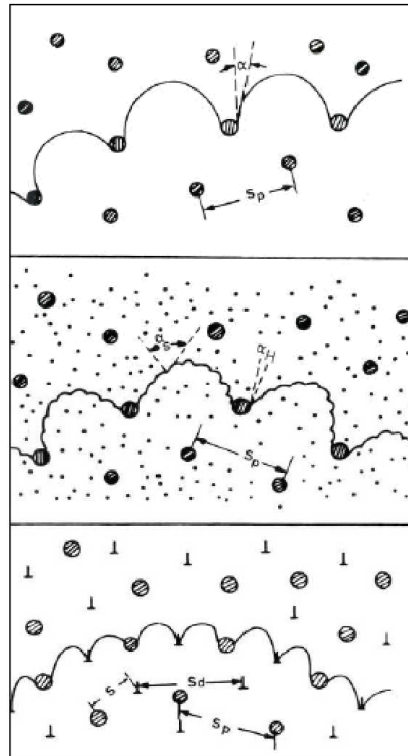
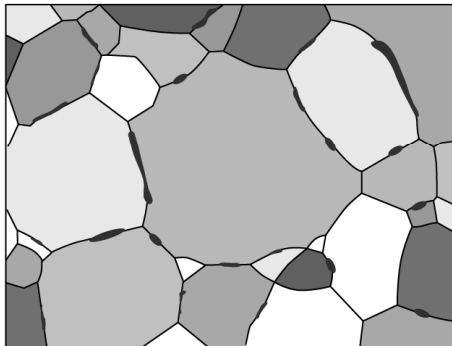
ref: Simoes et al., Nanotech. (2010)

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

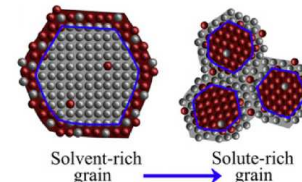
Regular Nanocrystalline Solution (RNS) Model:

ref: Chookajorn et al., Science, 2012

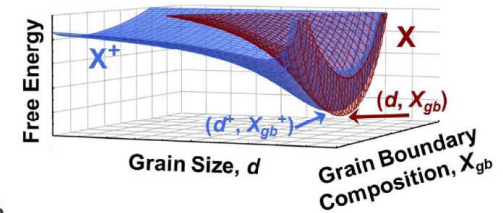
$$\Delta G^{\text{mix}} = (1 - f_{\text{gb}})\Delta G_c^{\text{mix}} + f_{\text{gb}}\Delta G_{\text{gb}}^{\text{mix}} + z\nu f_{\text{gb}}(X_{\text{gb}} - X_c) \left[ (2X_{\text{gb}} - 1)\omega_{\text{gb}} - \frac{1}{zt}(\Omega^B\gamma^B - \Omega^A\gamma^A) \right]$$

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

Grain structure model: segregated 2-phase metal system



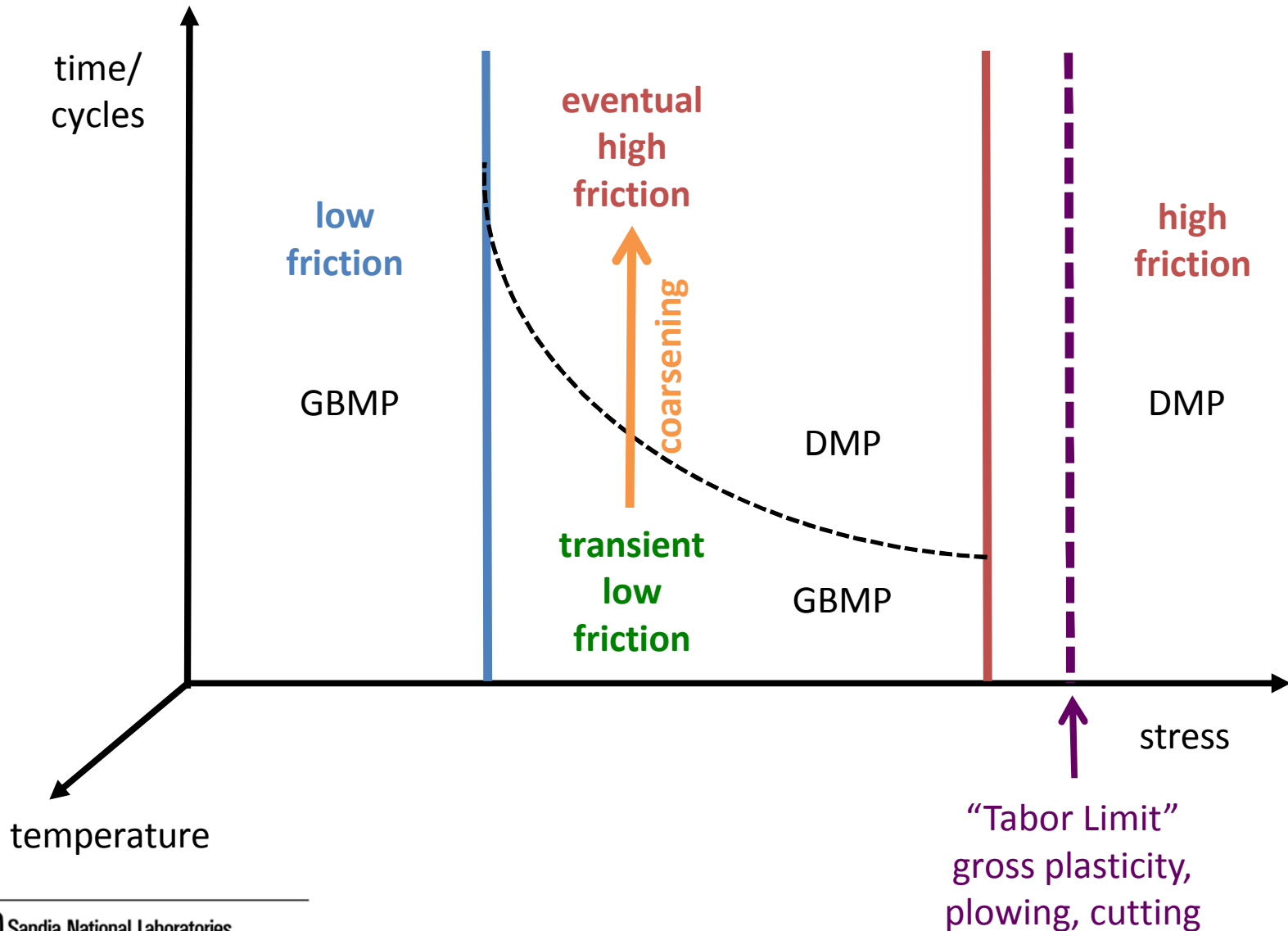
ref: Murdoch et al., Acta Mat. (2013)



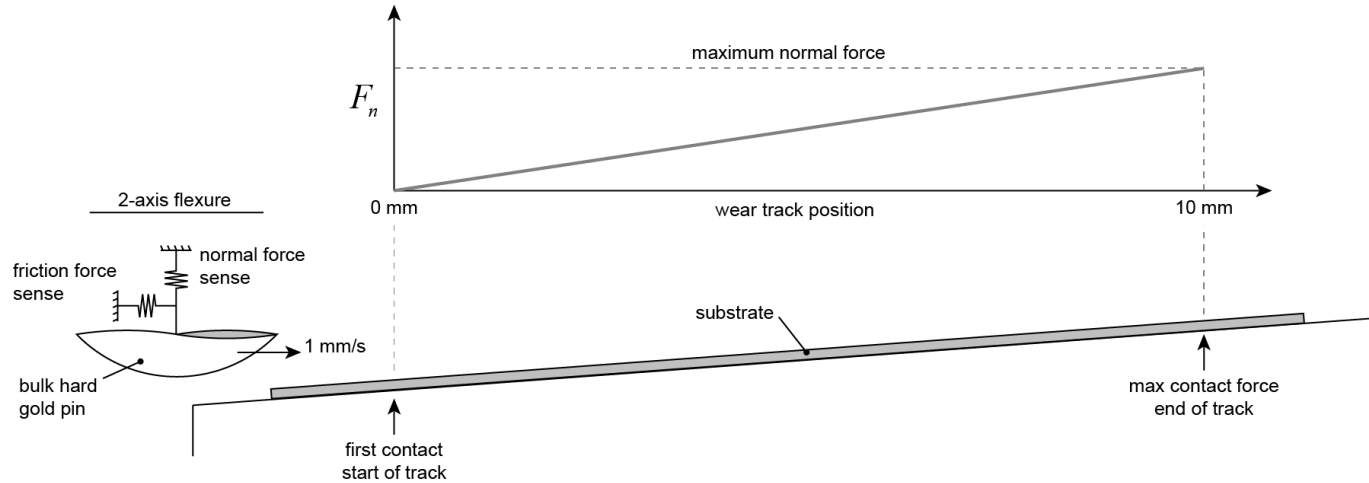
ref: Murdoch et al., Acta Mat. (2013)

# Conceptual friction map

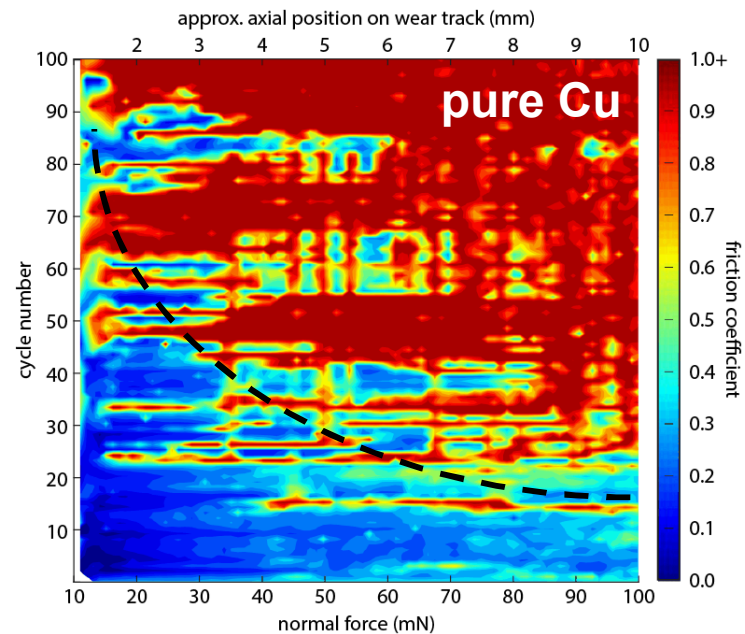
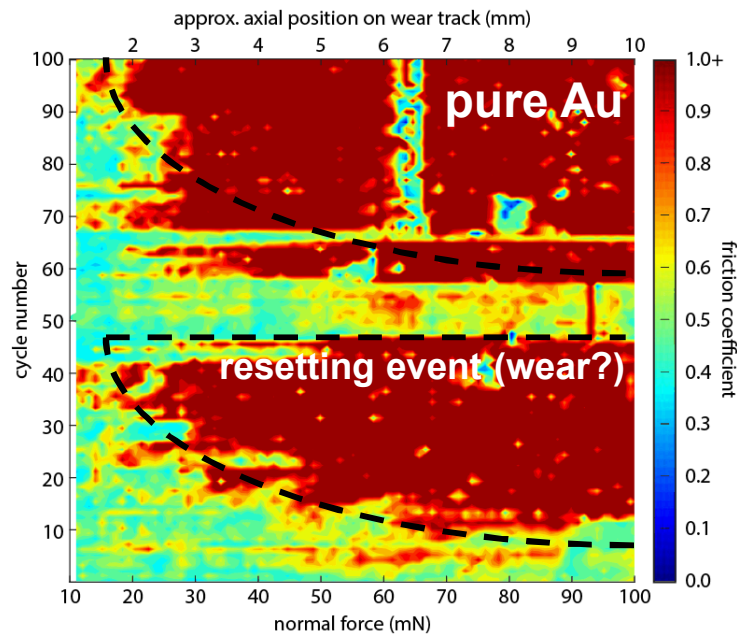
- Friction regimes boundaries based on stress thresholds
- Time evolution only at intermediate stresses



# Ramped contact force experiments and friction mapping reveals much!



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

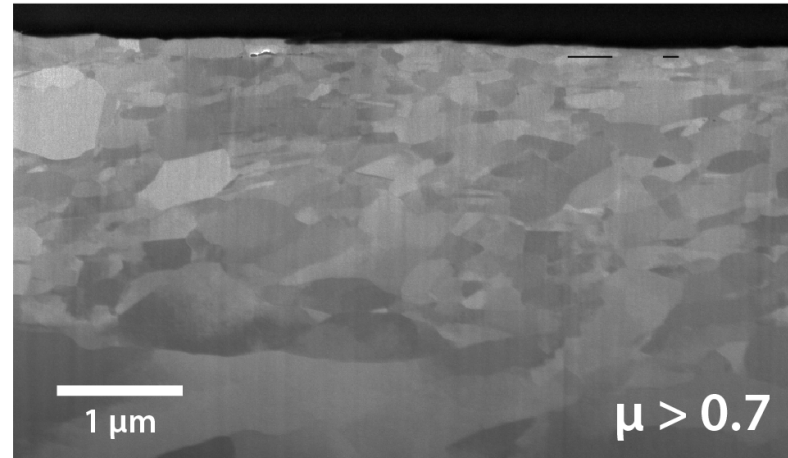
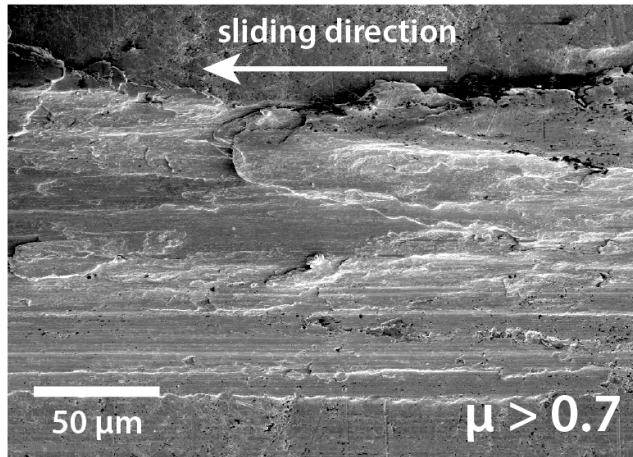




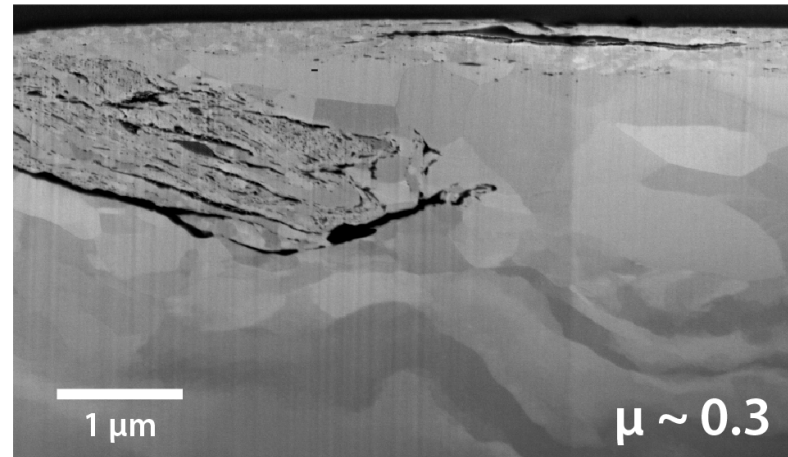
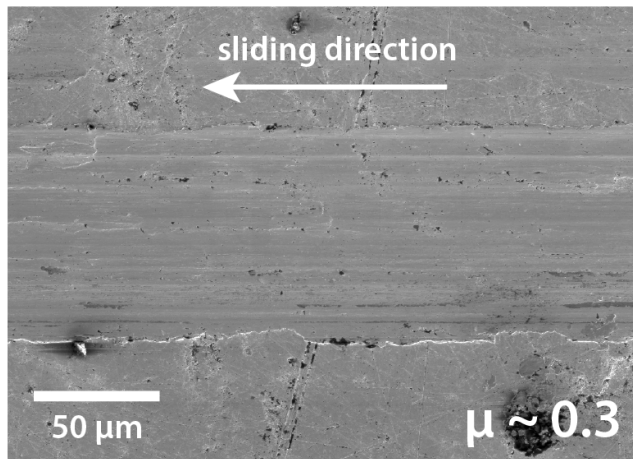
Again, low friction associated with nanocrystalline surface.. see shear banding too

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

high  
friction

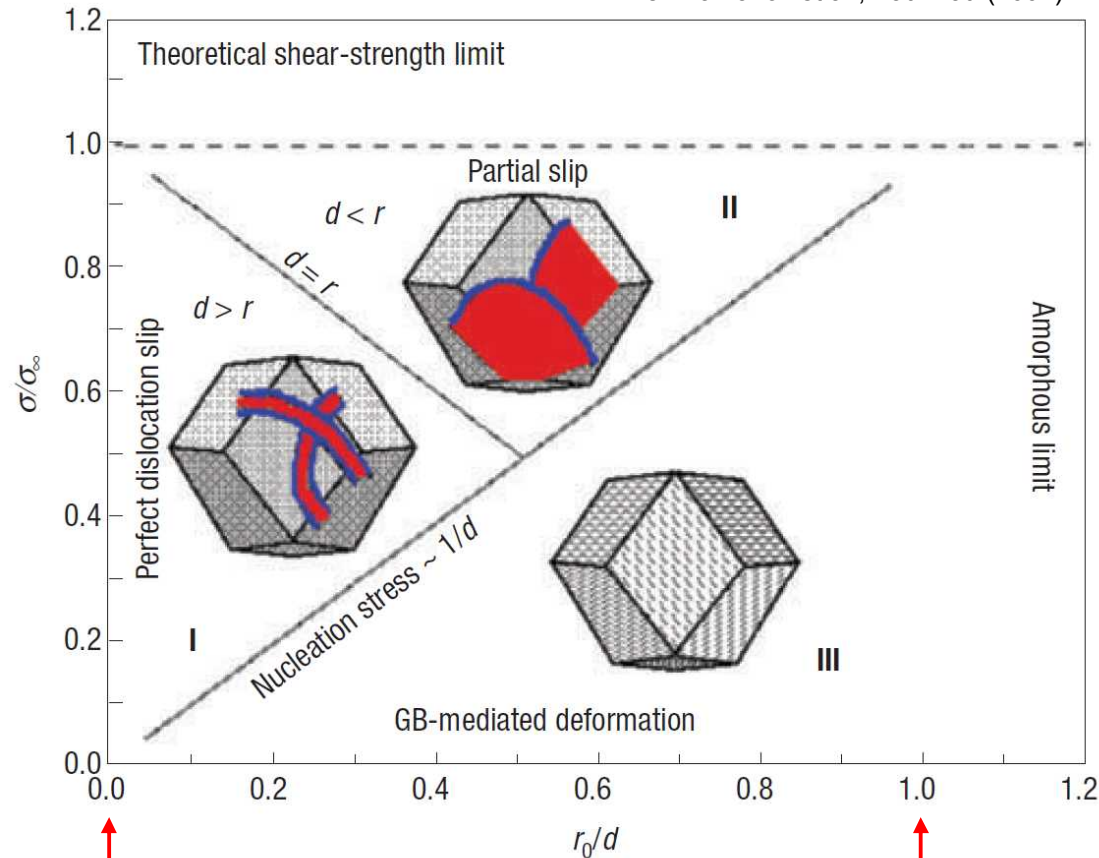


low  
friction



# What parameter can we use to make **predictions** about stress boundaries?

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:**

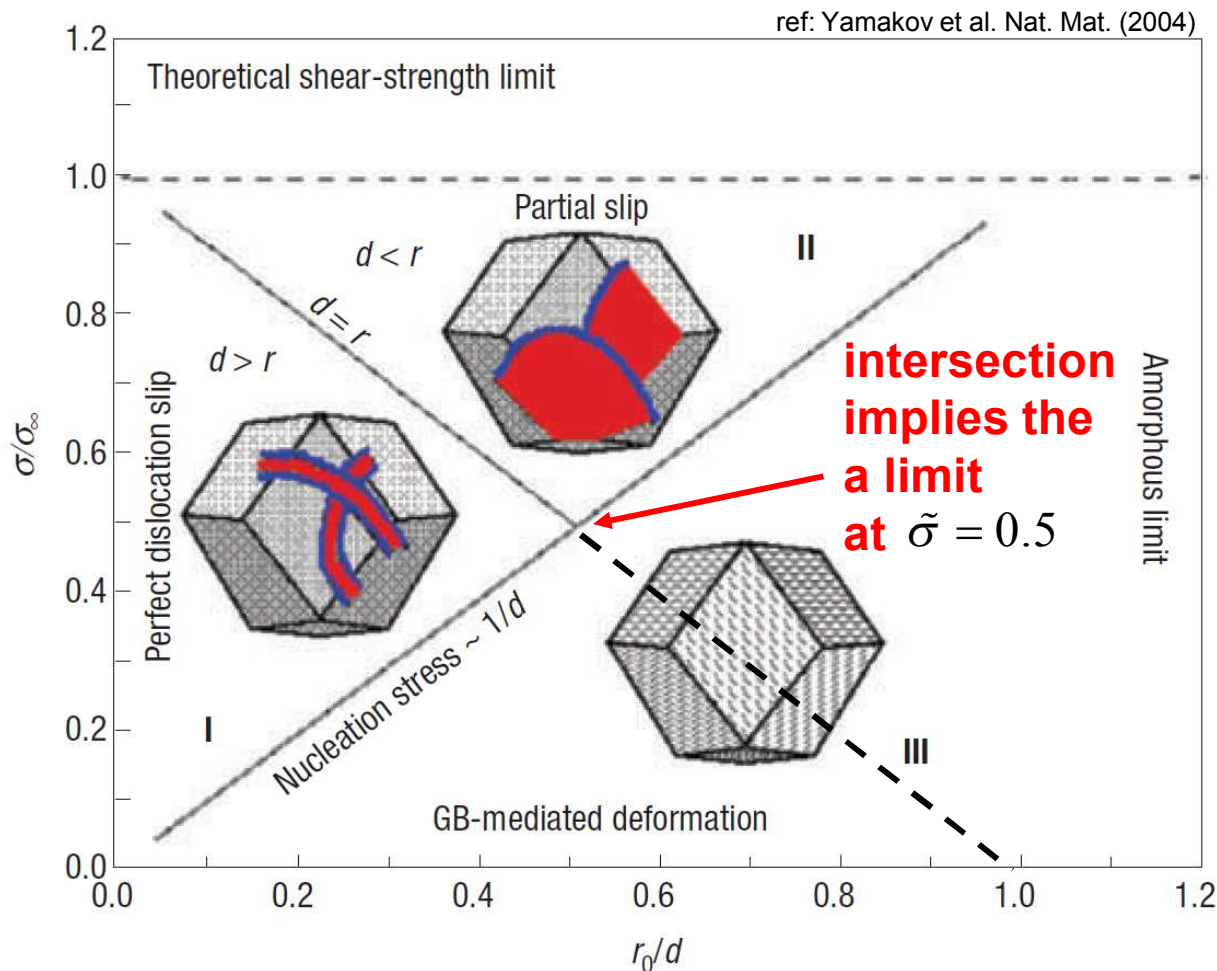
$$r_e = \frac{r_0}{1 - \sigma_a / \sigma_\infty}$$

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

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

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

# Defining the Beilby limit: applied stress below which GBMP always dominates

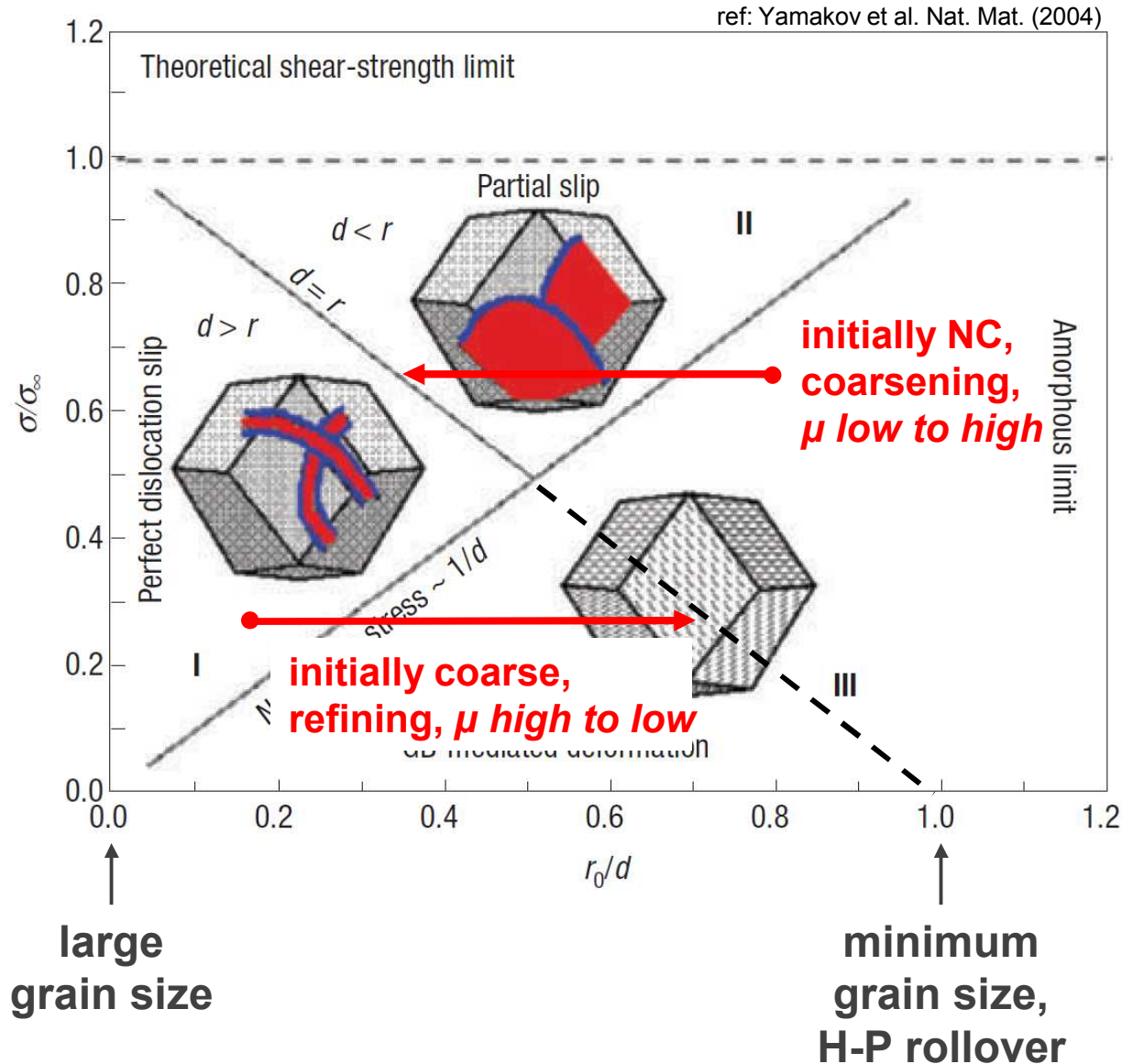


## Assumptions:

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

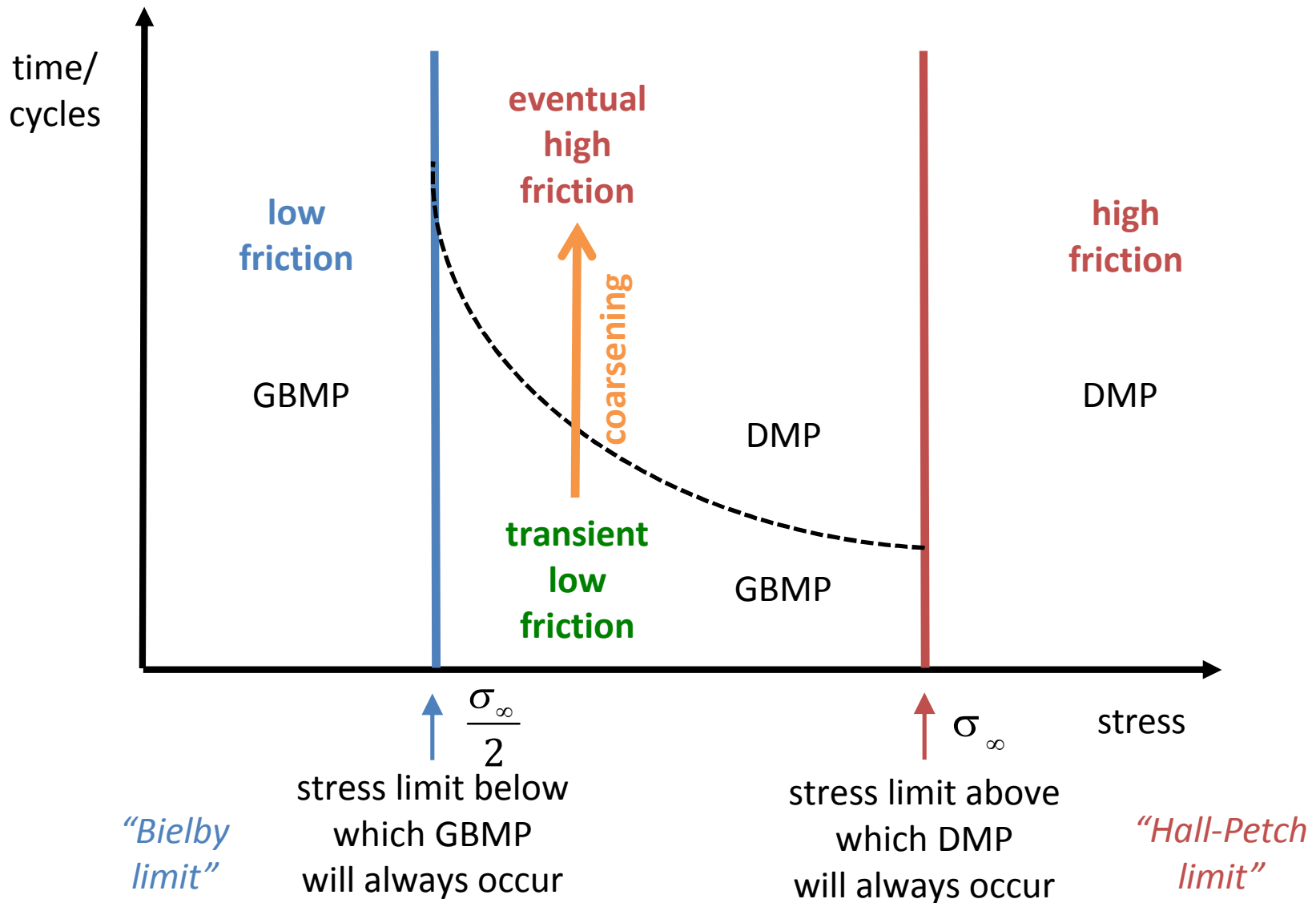
$$\tilde{\sigma} \propto \frac{1}{d}$$

# What about evolution? ... coarse grained surface can be driven to NC





## Two limits defined



**Defined by materials parameters only!**

## What about grain size evolution in the transient regime?

---

$$v_{gb} = \frac{2\gamma_{GB}}{d} M_0 e^{(-Q/kT)}$$

$\gamma_{GB}$  = grain boundary energy       $M_0$  = grain boundary mobility  
 $d$  = grain diameter       $Q$  = activation energy

- Classical grain growth equation

*Defined by materials parameters only!*

## What about grain size evolution?

---

$$v_{gb} = \frac{2\gamma_{GB}}{d} M_0 e^{(-Q/kT)} e^{[(\sigma - \sigma_{\infty}/2)V^*/kT]}$$

$\gamma_{GB}$  = grain boundary energy

$M_0$  = grain boundary mobility

$d$  = grain diameter

$Q$  = activation energy

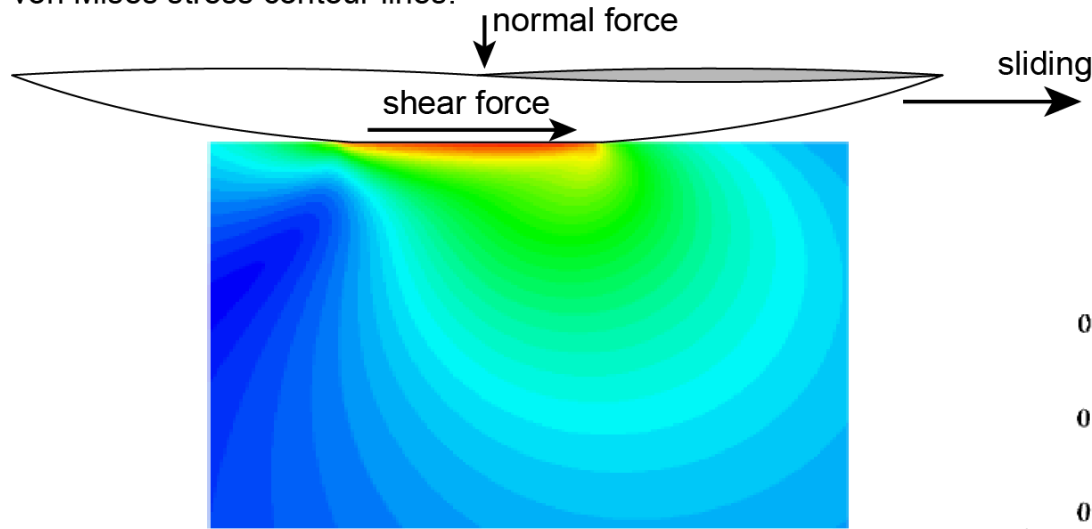
$V^*$  = activation volume  $\simeq 10b^3$

- Classical grain growth equation
- Extra term depends on applied stress
- Assume initial cycle heavily refines surface to  $r_0$
- Use this to see how long it takes to evolve grains to  $2r_0$

***Defined by materials parameters only!***

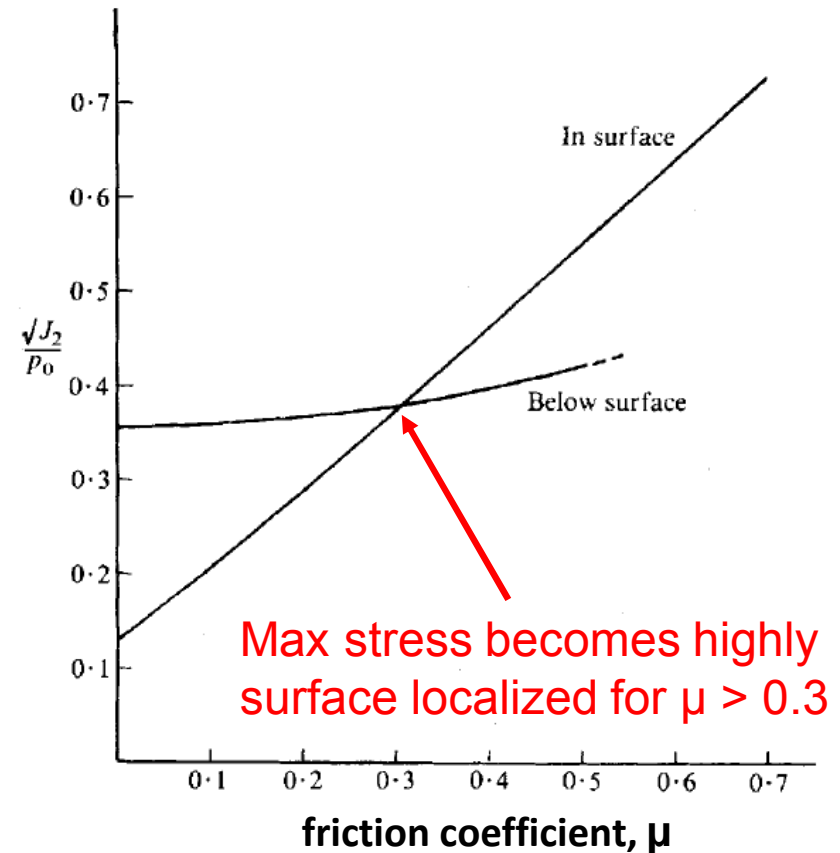
# Finally, applied stress? Hamilton model -> max surface von Mises stress

von Mises stress contour lines:



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

- G. Hamilton, *Proc. Inst. of Mech. Eng. C*, 1983
- Like Hertz, but with friction
- Uses Hertz solution for contact radius



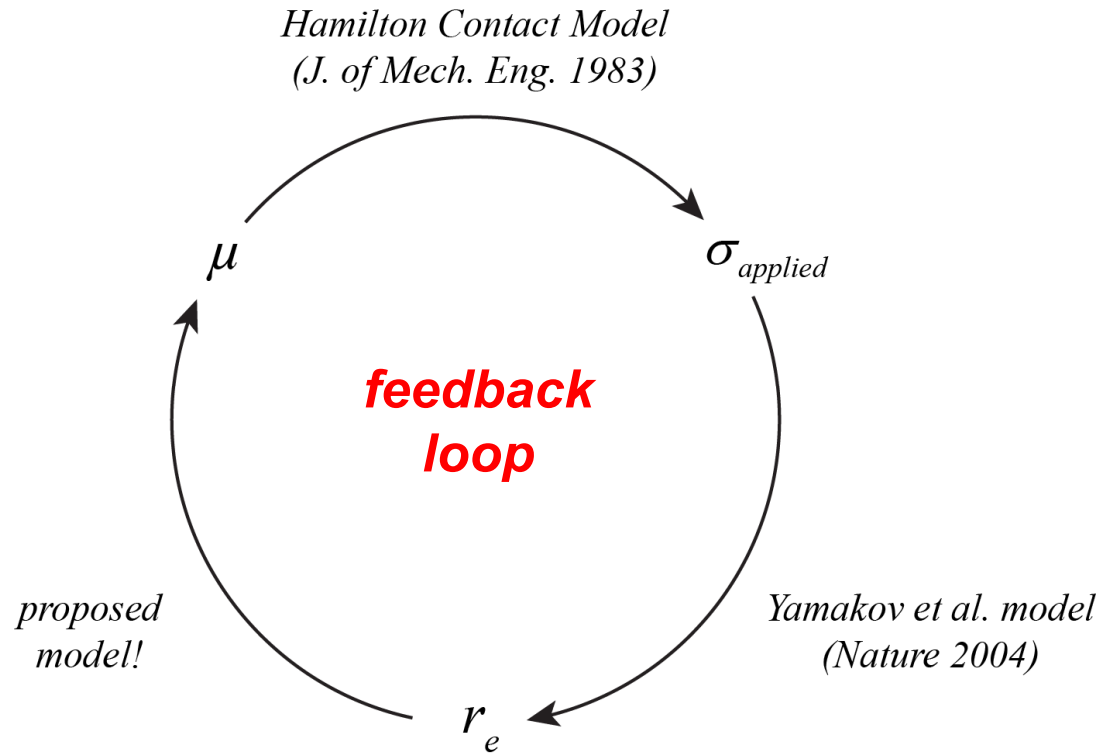


**reduced stress:**  $\tilde{\sigma} = \frac{\sigma_{surf, max}}{\sigma_{\infty}}$

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

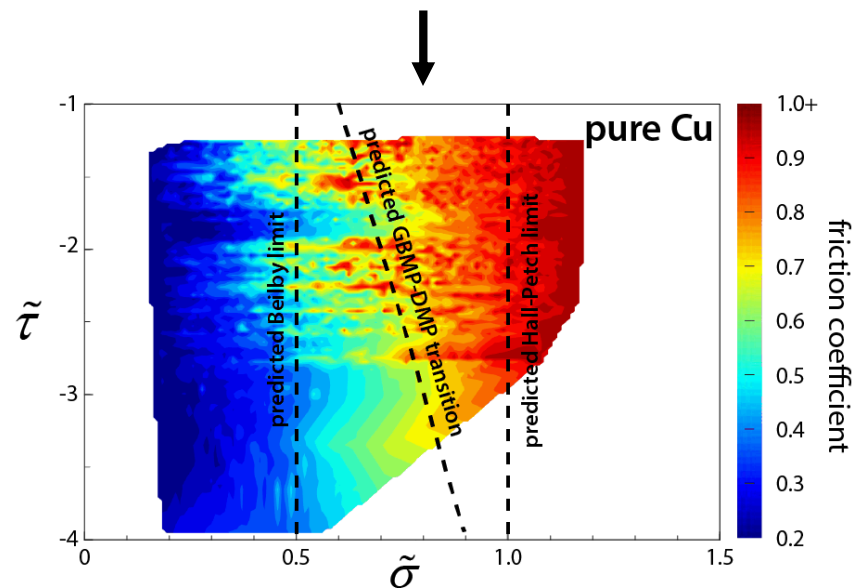
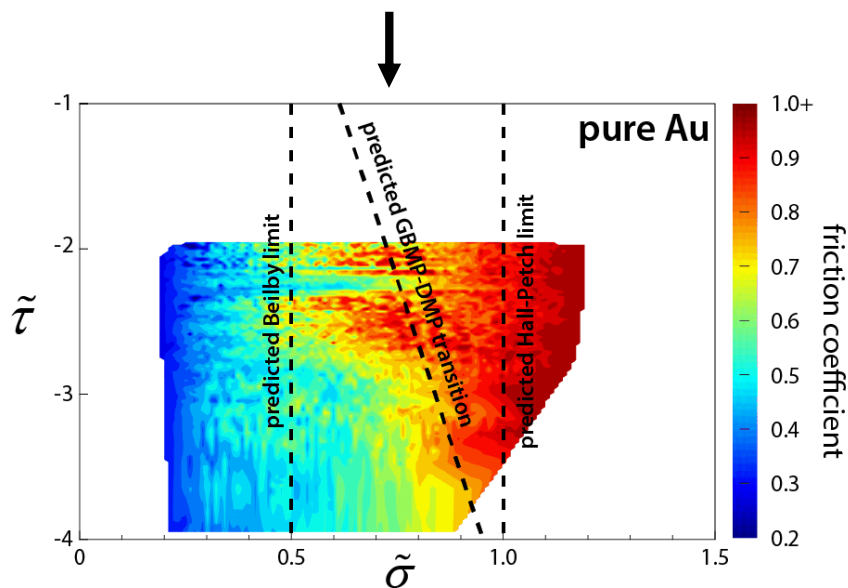
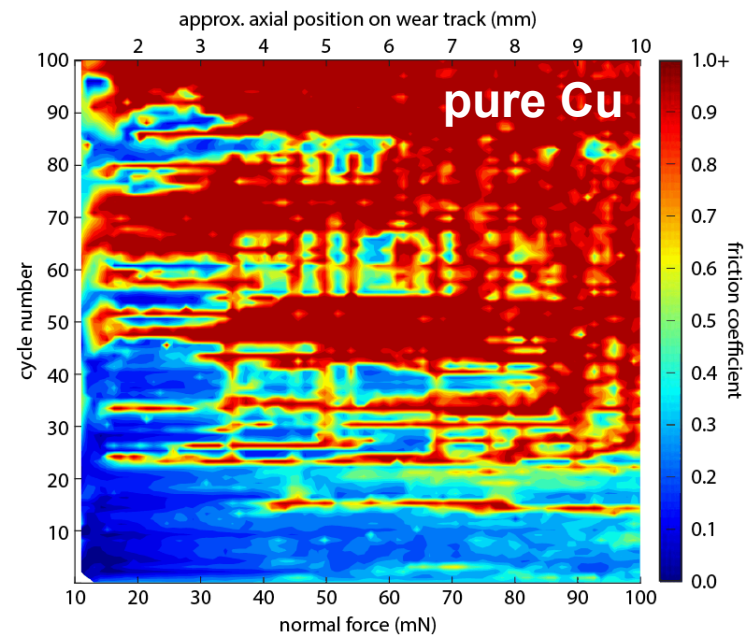
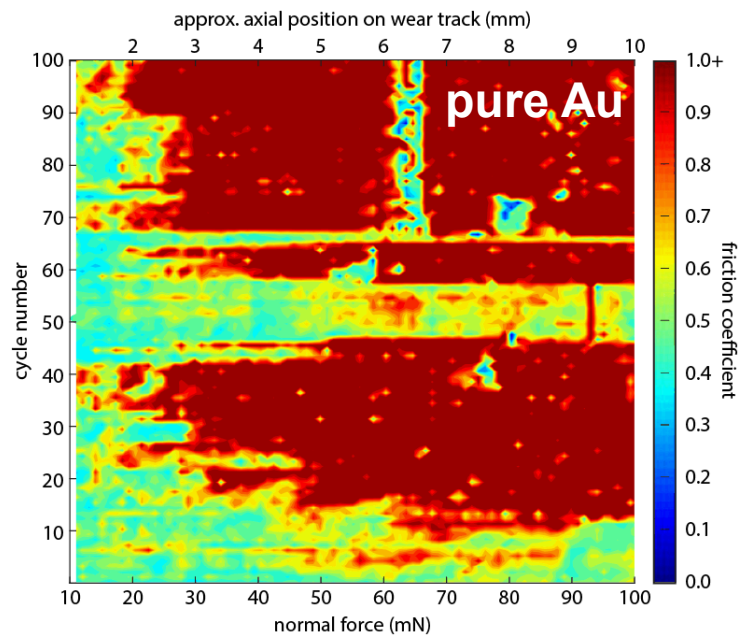
- Normalize stress by a fundamental stress
- Normalize time by the fundamental “grain boundary time”
- Plot semilog

# Can Now Complete the Circle

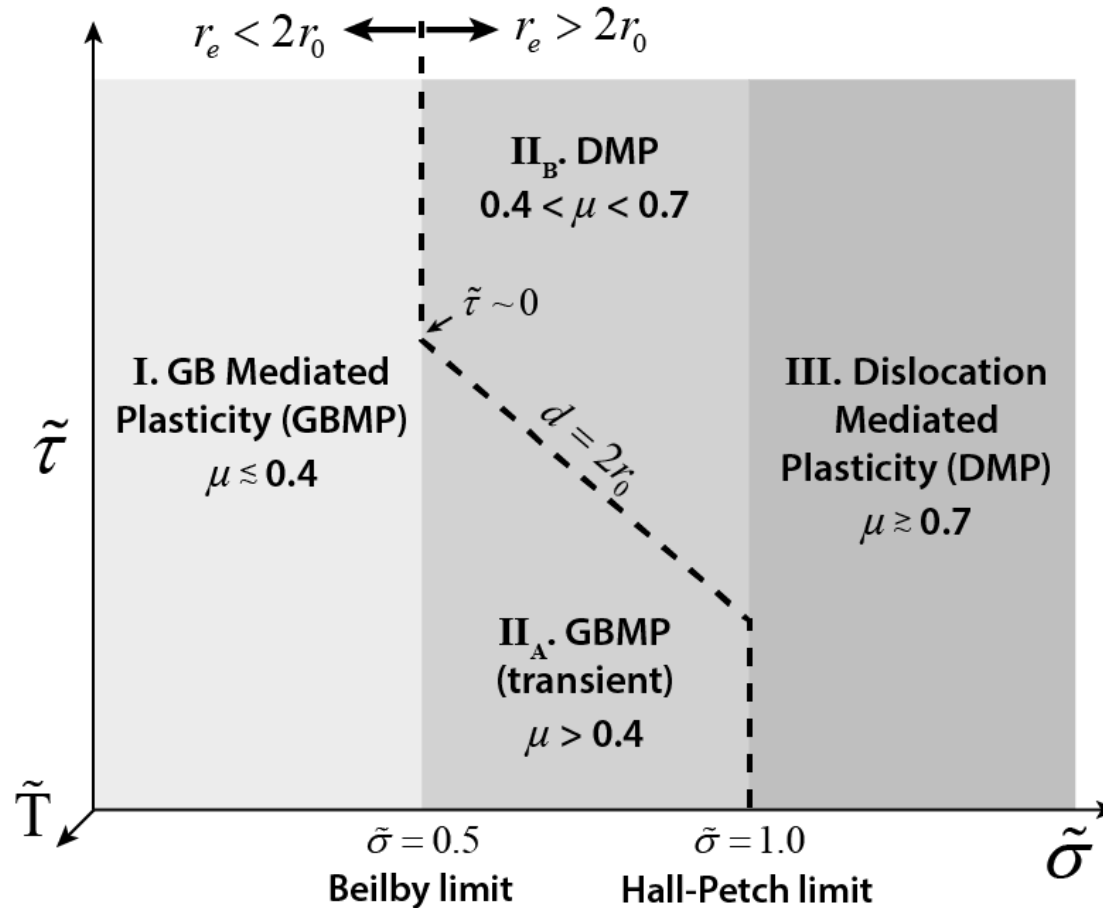


- Numerical correlation between applied stress, grain size and friction coefficient.
- All based on materials parameters.

# Apply reduction to ramped friction data...



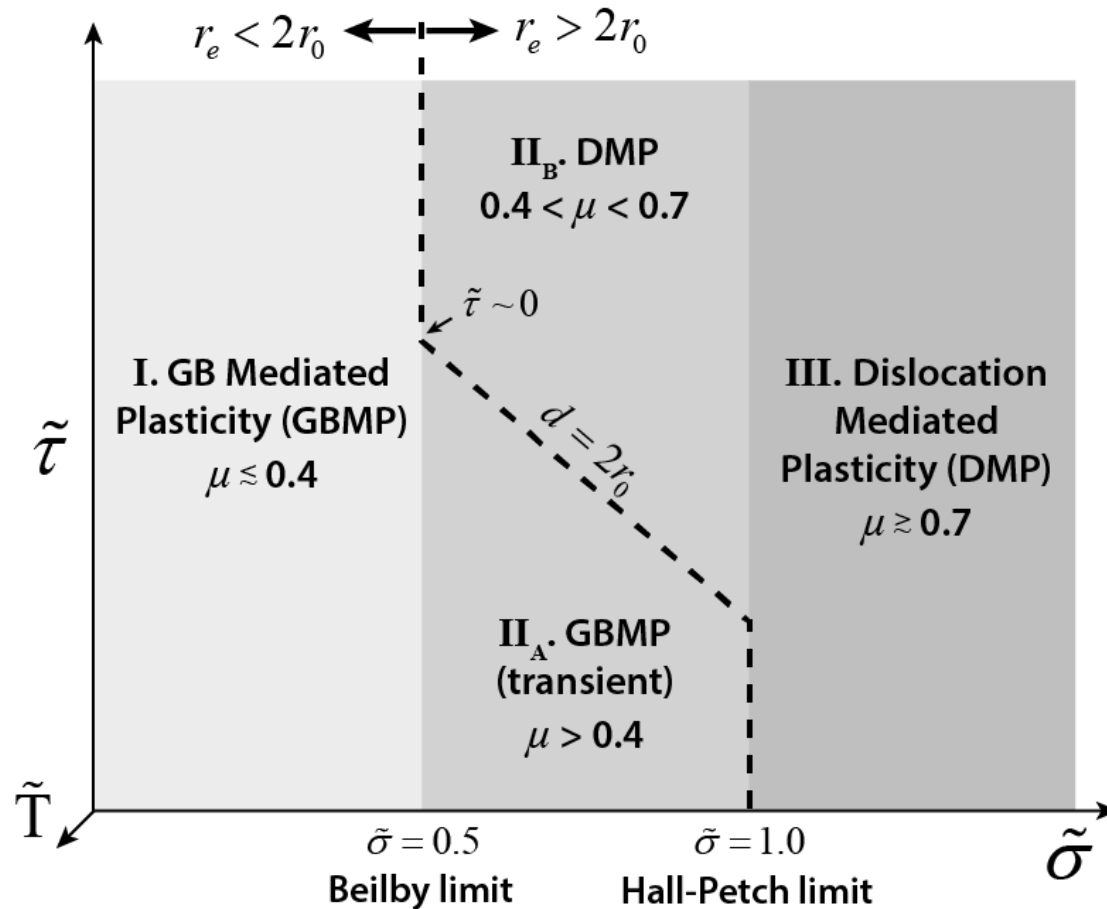
## Returning to the microstructure-based friction regimes model...



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

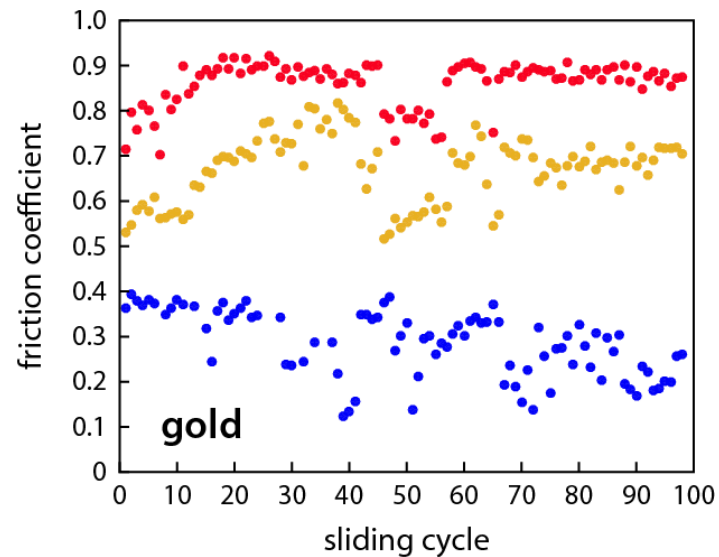
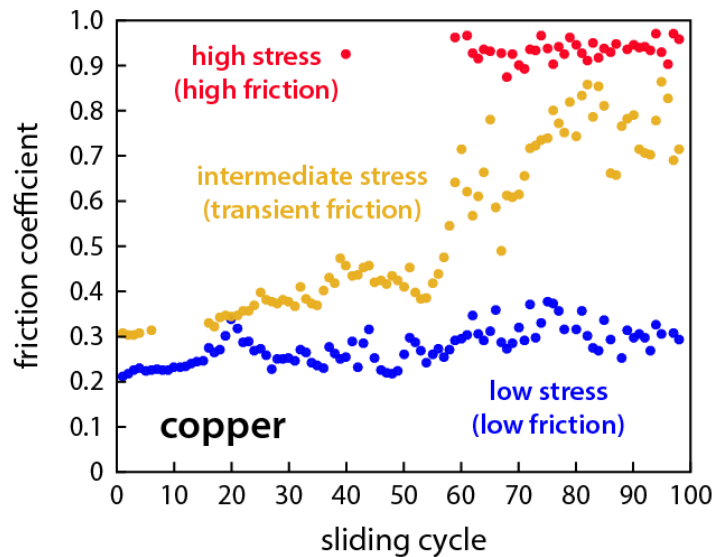
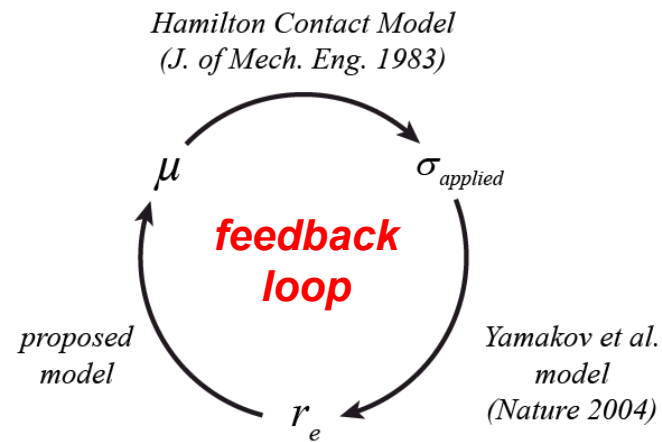
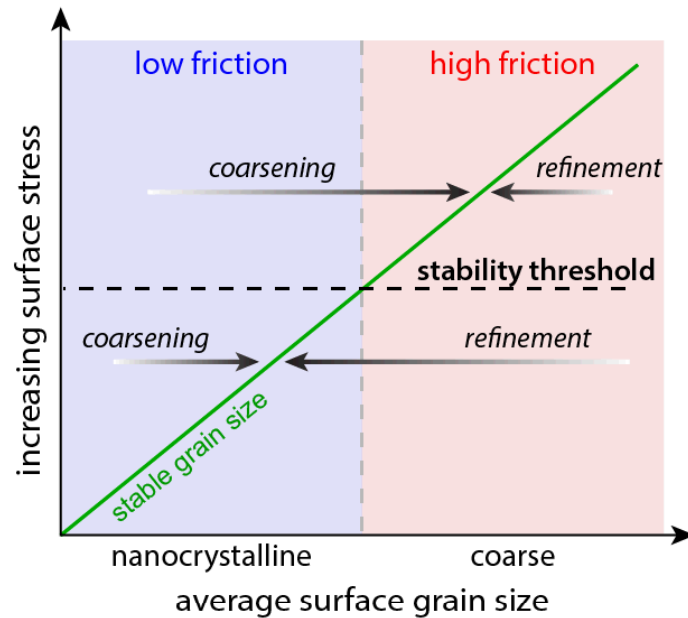


## What about boundary lubrication of metal contacts (e.g. graphite, DLC, MoS<sub>2</sub>)?



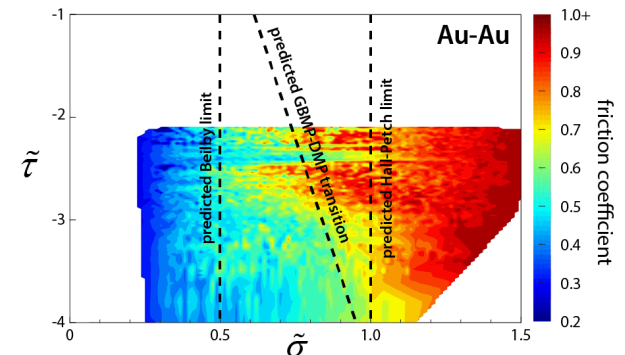
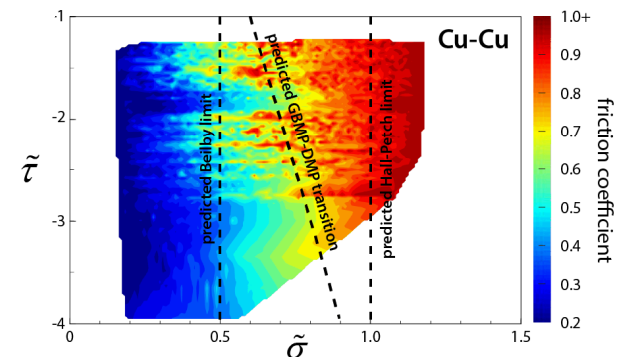
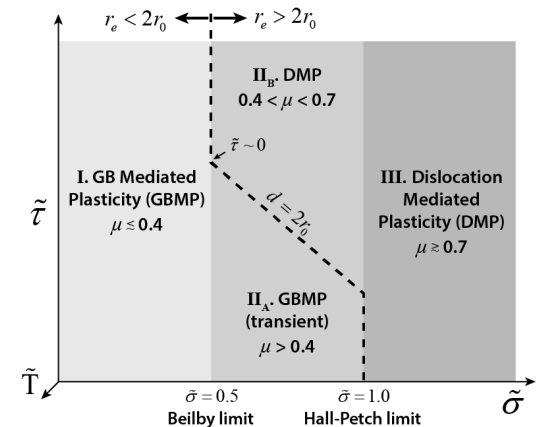
**Boundary lubrication (e.g. graphite, MoS<sub>2</sub>, engine oil) mitigates commensurate contact – thus it is possible to achieve low friction at higher normal force**

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



# Only the beginning, much left to do...

- 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



# Classical attempts to define wear & friction regimes were

## empirical/phenomenological

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et MATERIALIA

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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	

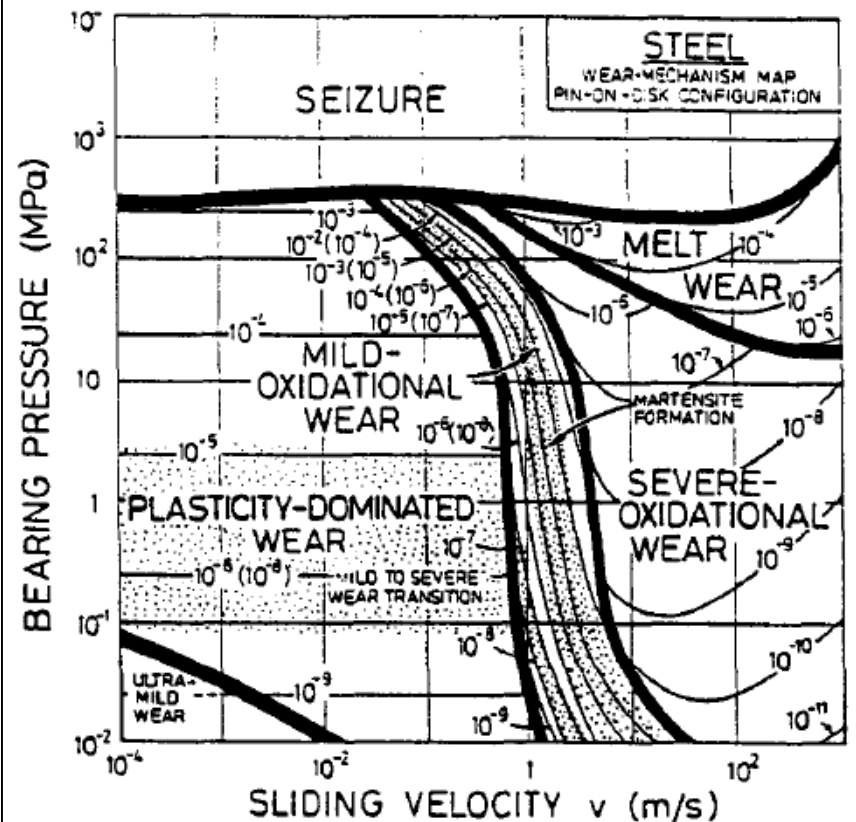
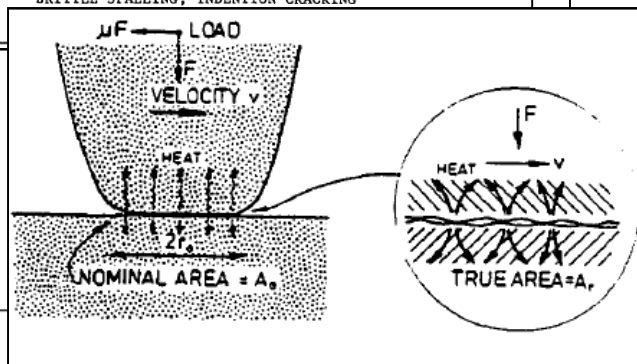
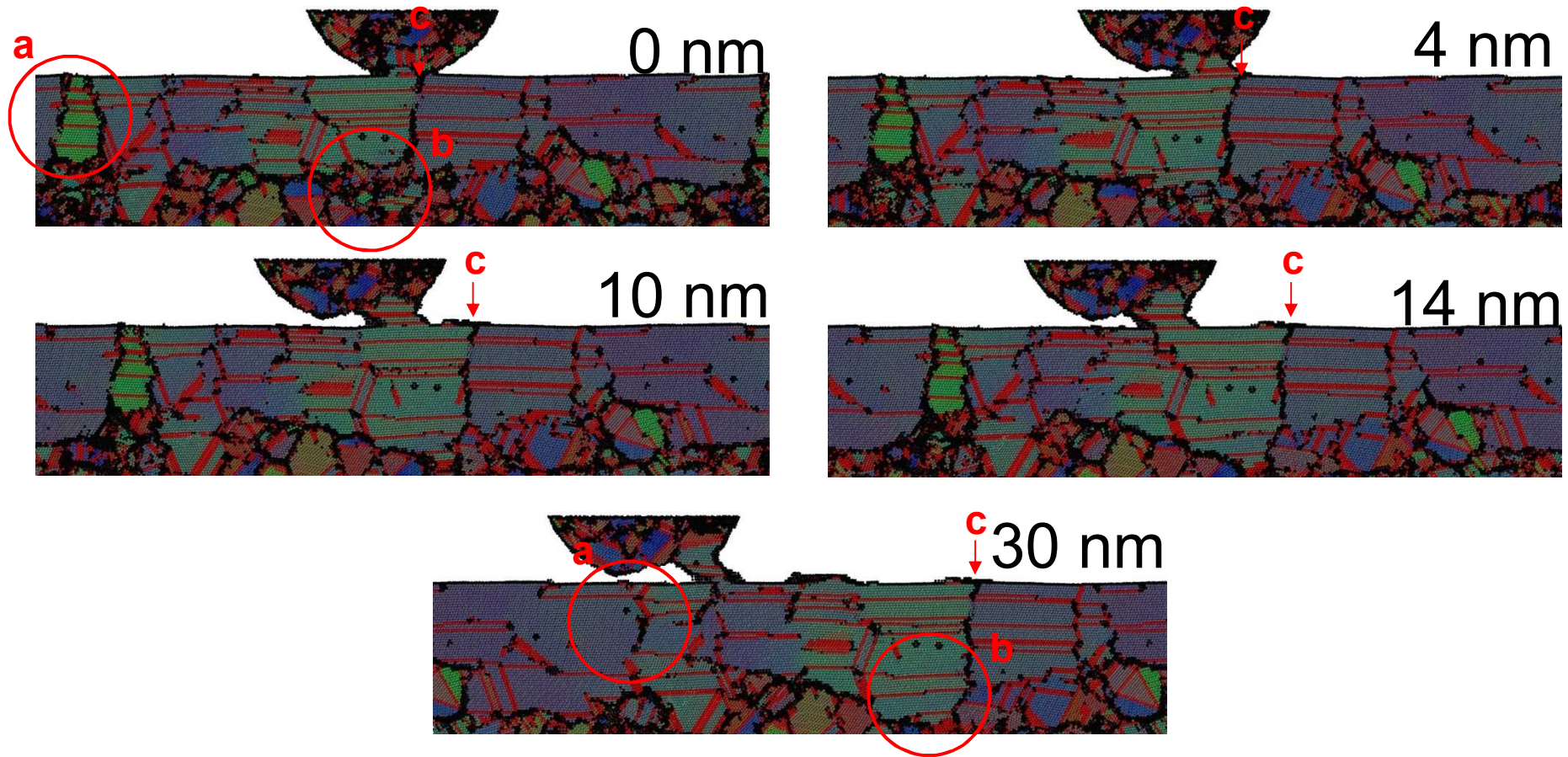


Figure 3. A wear-mechanism map for low-carbon steel based on physical modelling calibrated to experiments. The shaded regions show transitions.

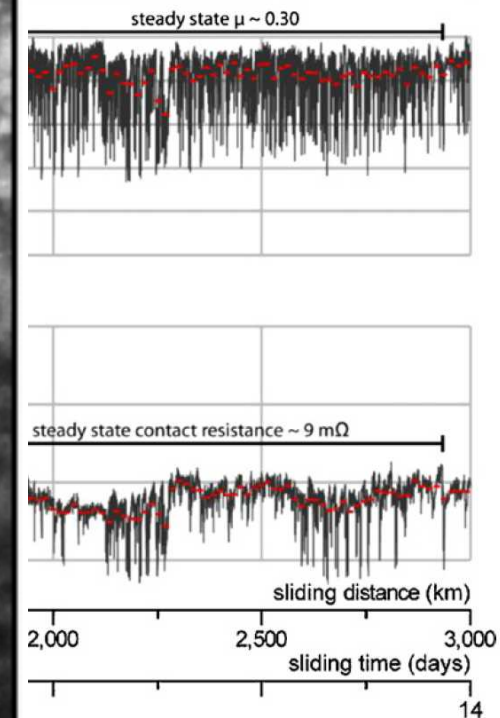
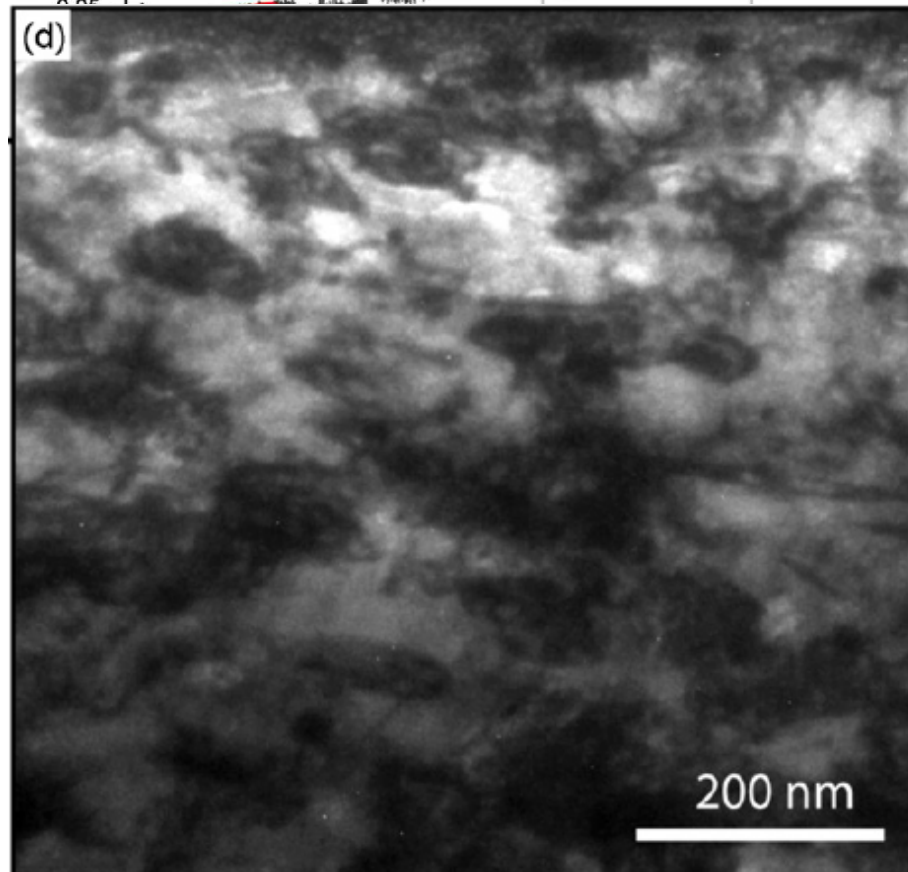
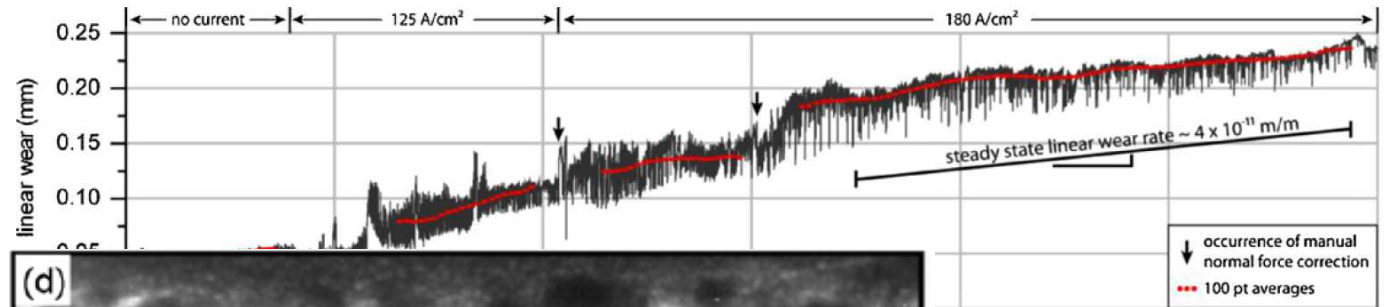
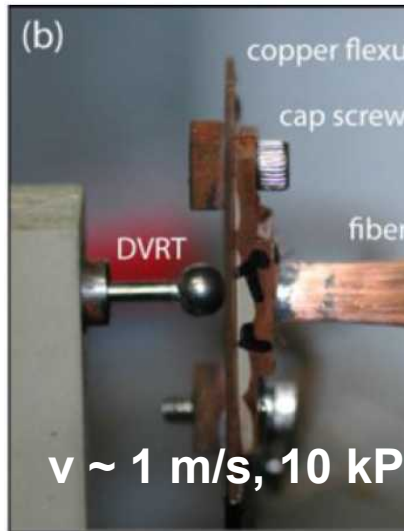
Another look, now at **pure Au** tip/slab contact evolution over a longer sliding time



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

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

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



Again, low friction associated with nanocrystalline surface for a Cu-C system

# Classical attempts to define wear & friction regimes were

## empirical/phenomenological

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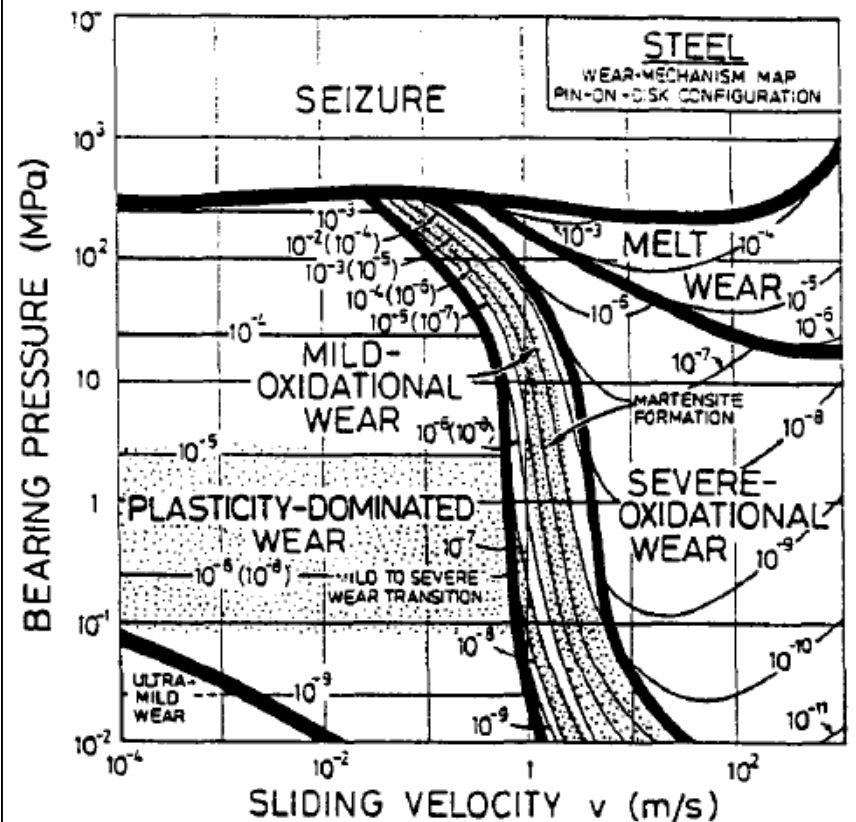
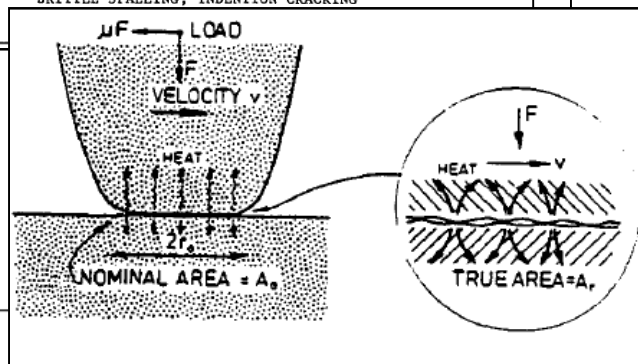
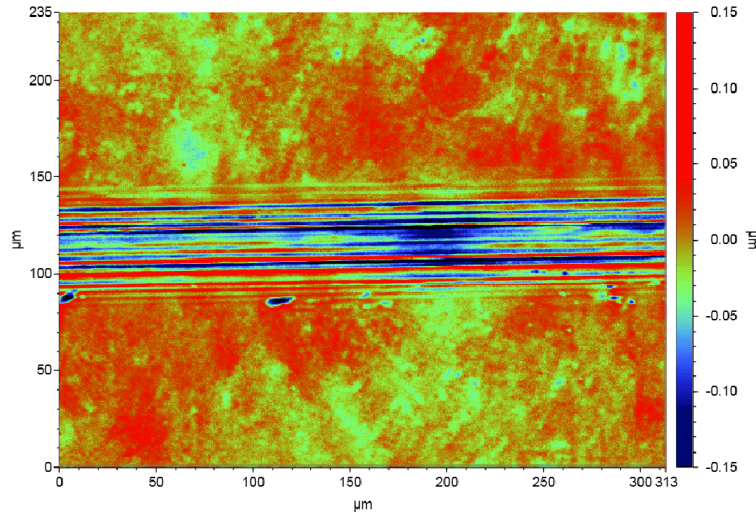


Figure 3. A wear-mechanism map for low-carbon steel based on physical modelling calibrated to experiments. The shaded regions show transitions.



# 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:



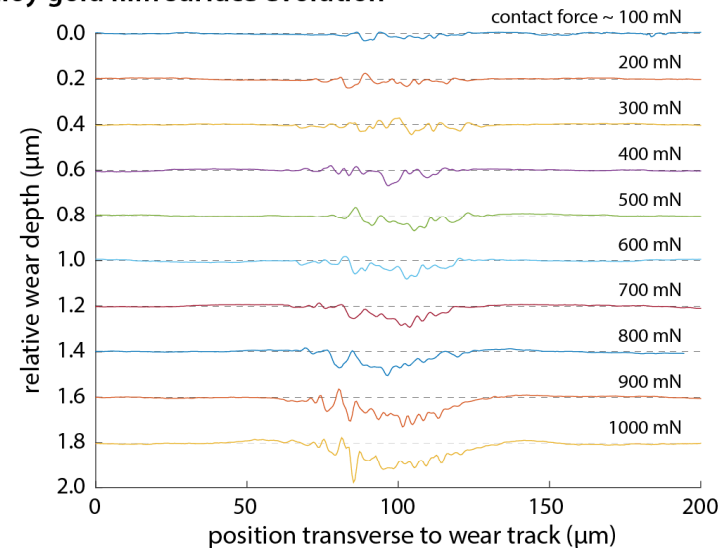
Images taken at 1 mm intervals along 10 mm long wear tracks

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

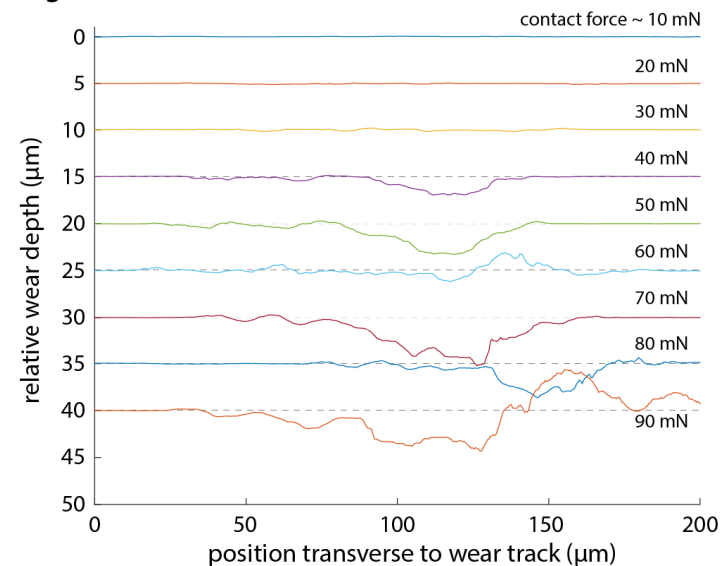
Wear at each interval calculated based on contact force average in this part of the track, number of cycles, and volume loss

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

## alloy gold film surface evolution

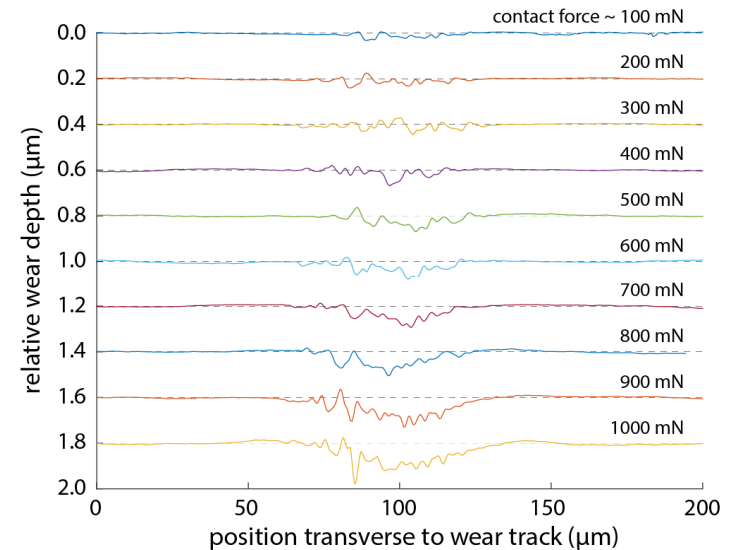
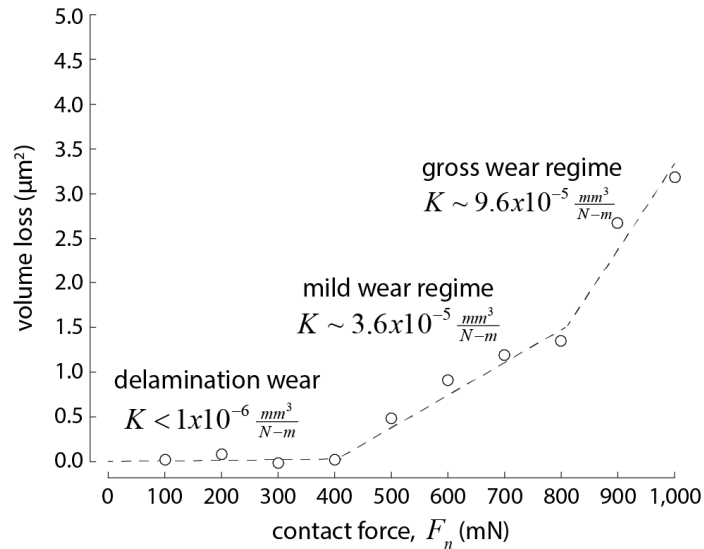


## pure gold substrate surface evolution

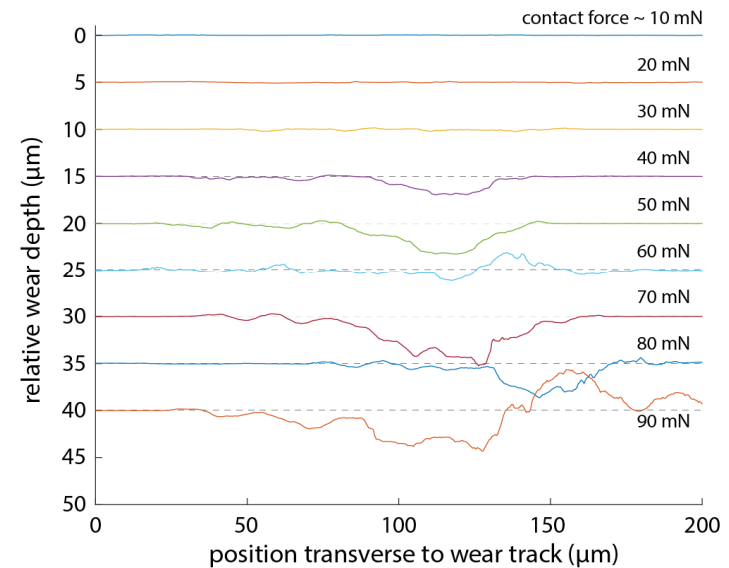
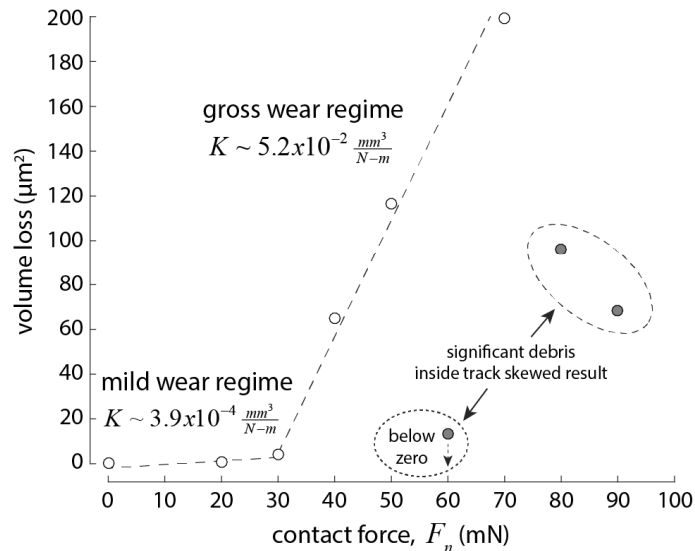


# Observed three wear regimes

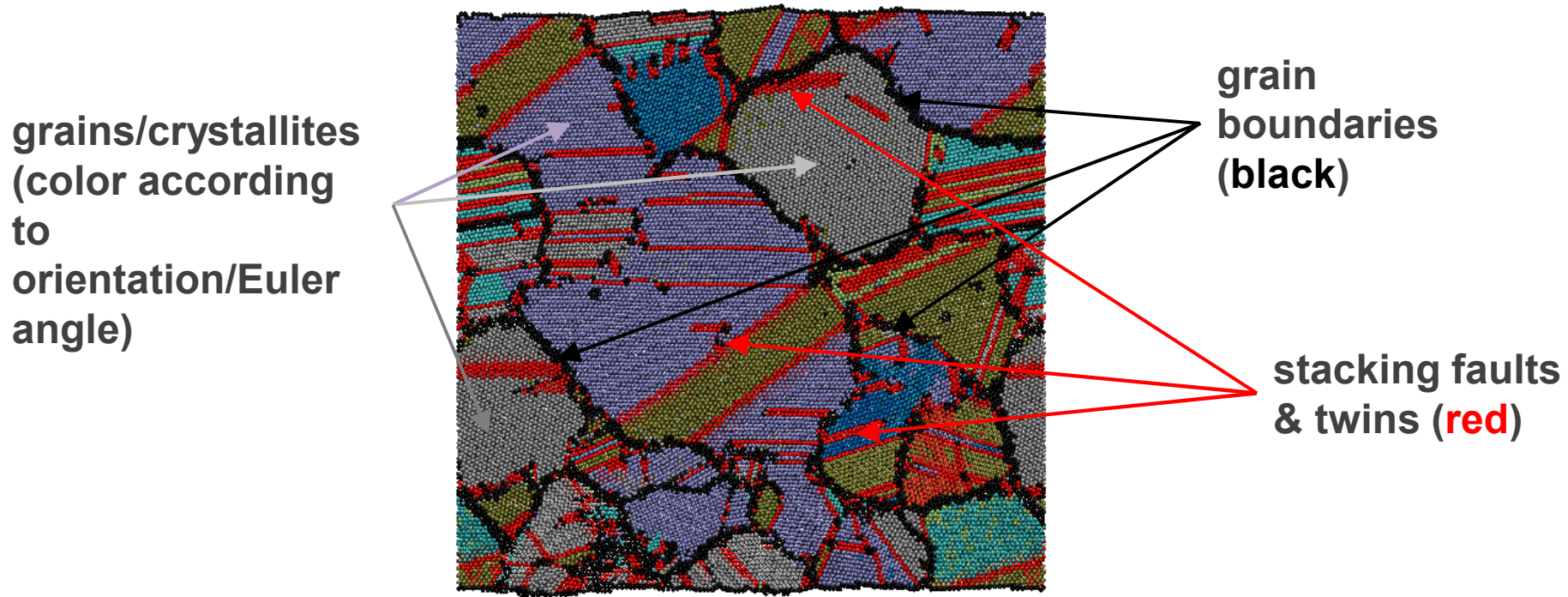
## alloy gold film surface evolution



## pure gold substrate surface evolution



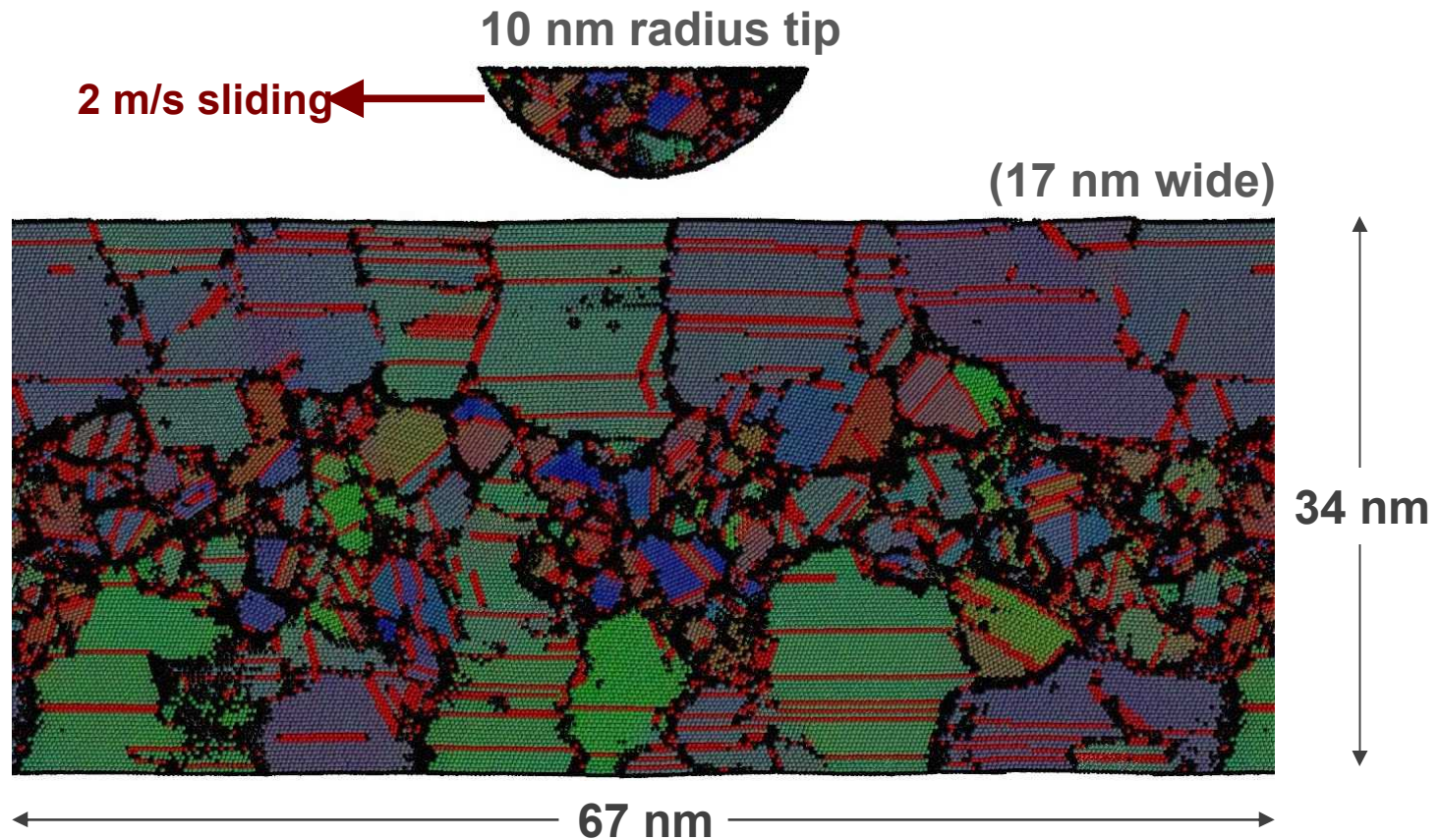
### Cross-sectional slices of a 3D space filled with atoms



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



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



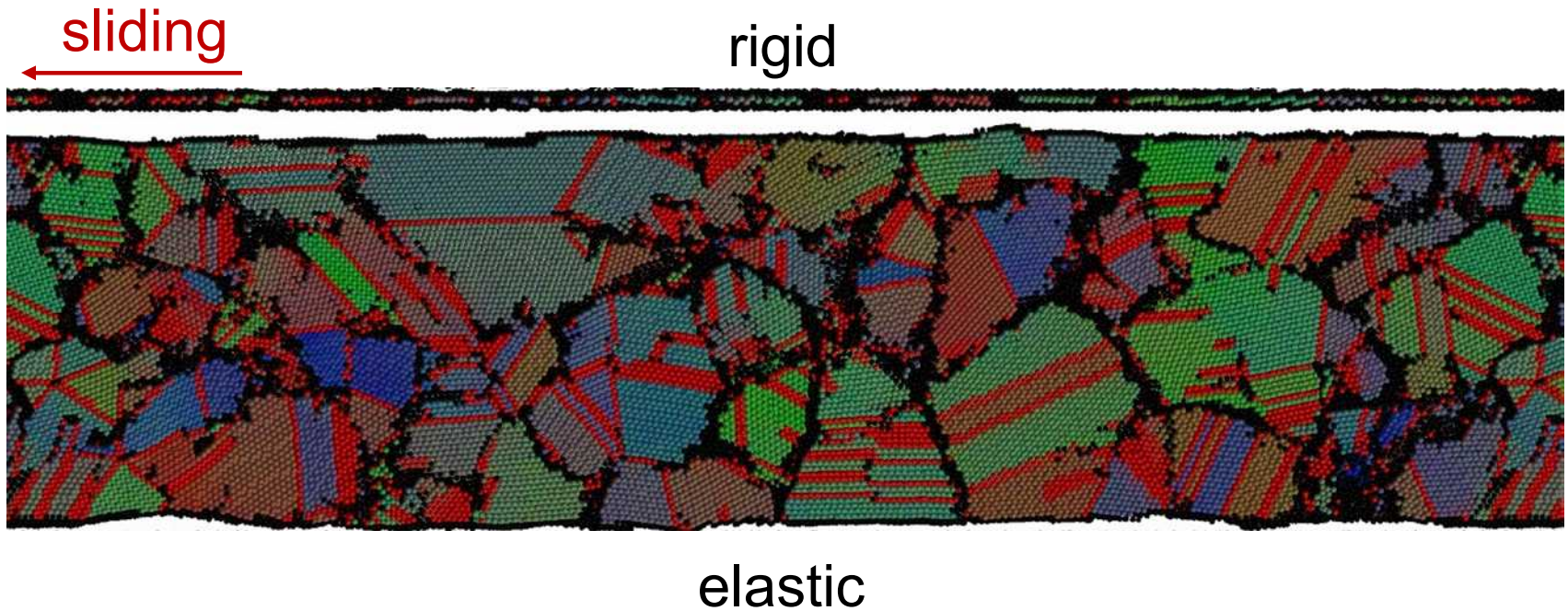
Substrate: nanocrystalline Ag

Constraint 1: constant velocity

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

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

---

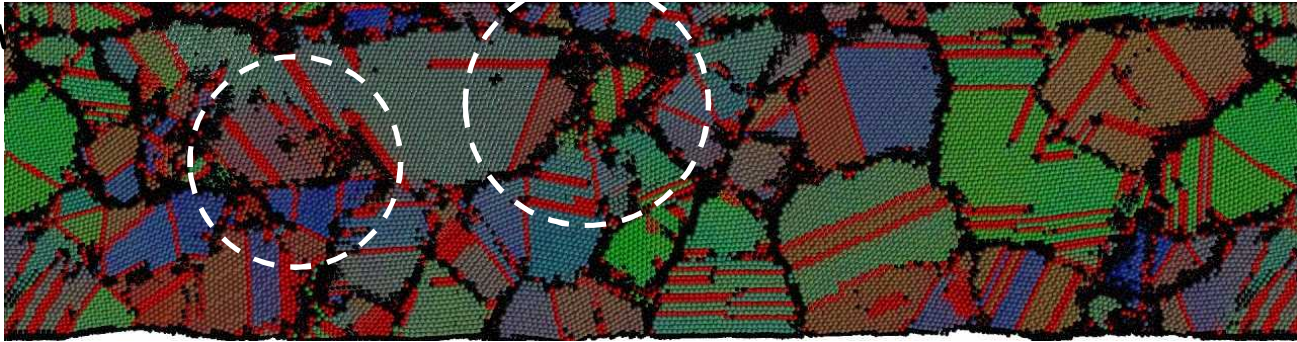


- Rigid slabs suppress grain growth
- No plowing is possible/reduced contact stress



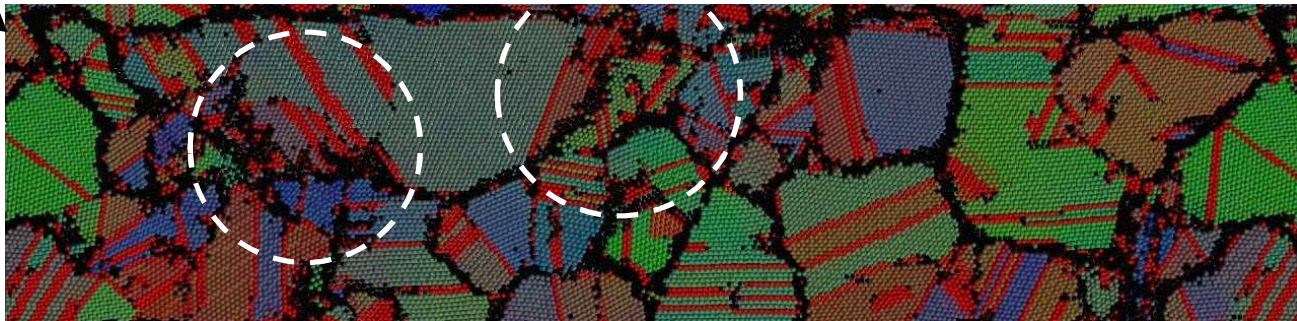
## Sliding of pure Ag slabs

after 5 nm of sliding



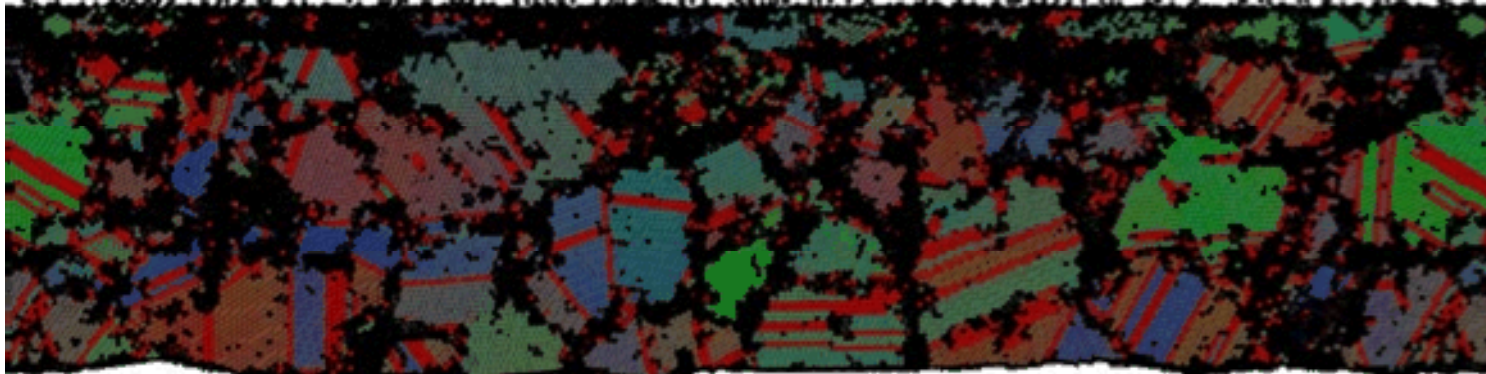
Slab +  
transfer film

after 8 nm of sliding

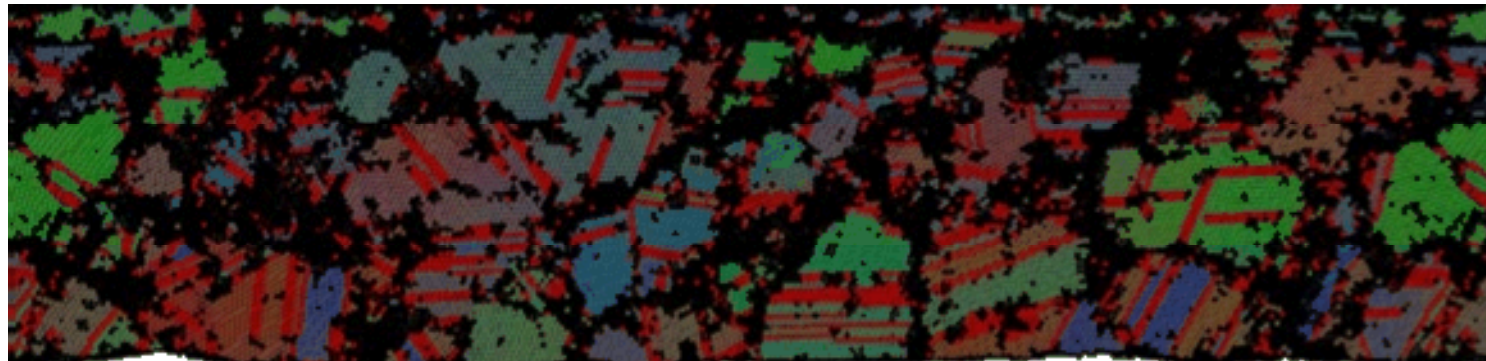


- Slight grain growth, forms transfer film
- Slides along transfer film grain boundaries or nearby stacking faults depending on availability

after 6 nm of sliding



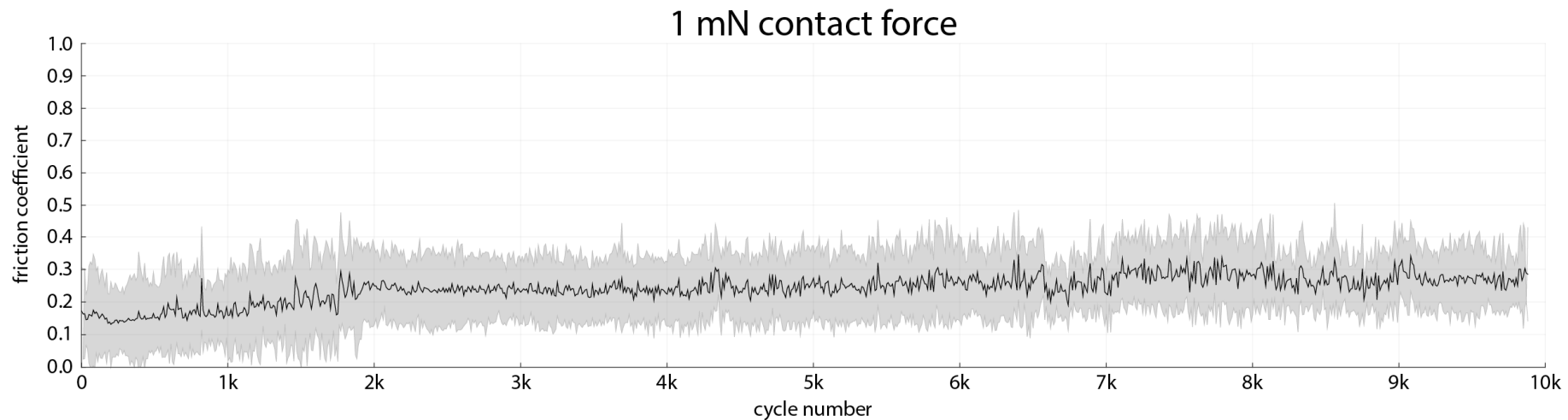
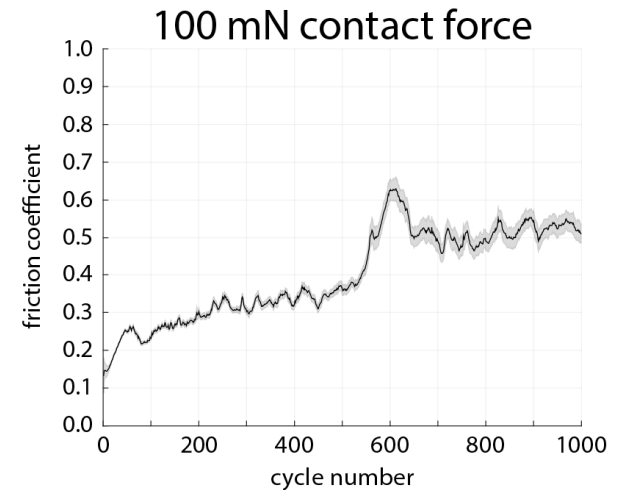
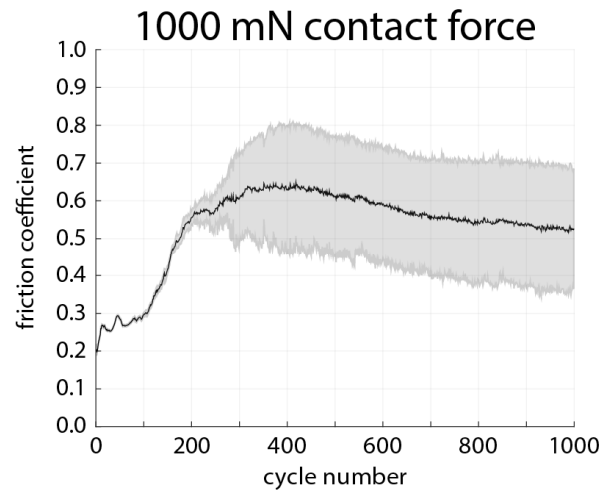
after 16 nm of sliding



- 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

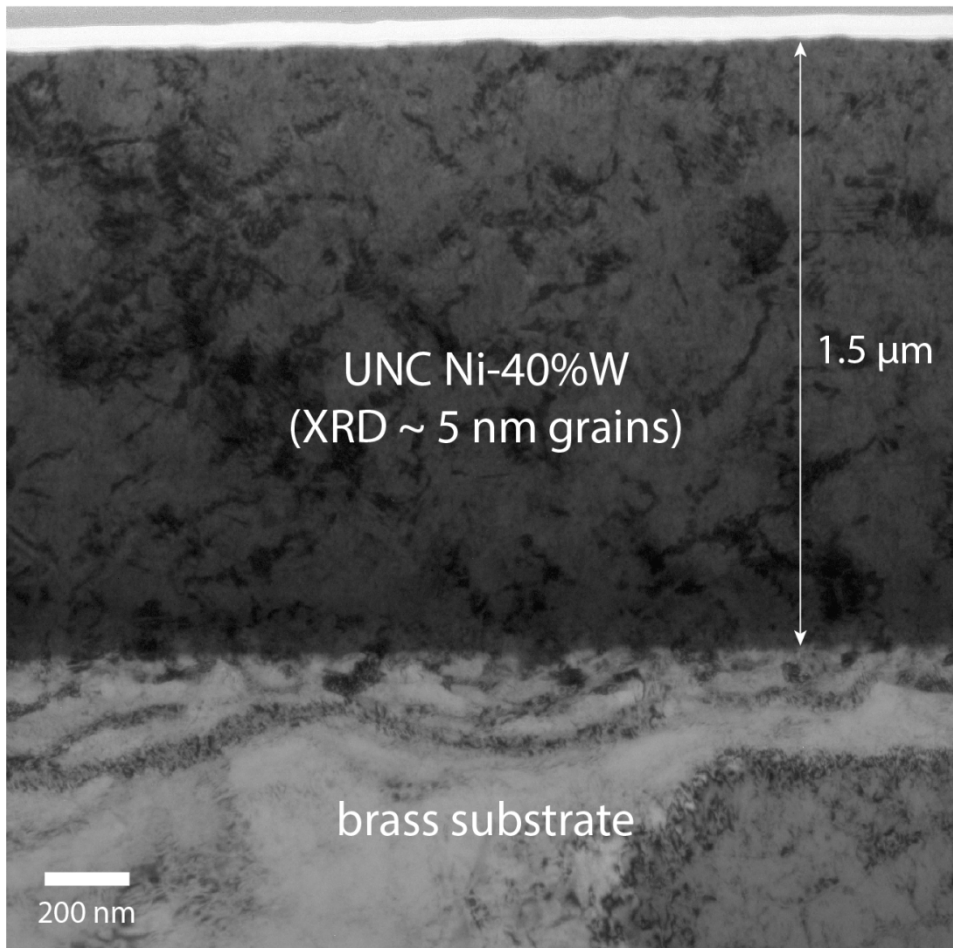
1 mm/s sliding speed  
three contact forces used  
bidirectional sliding  
2mm long track  
sapphire ball 1.6 mm diameter  
sliding in lab air





# 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

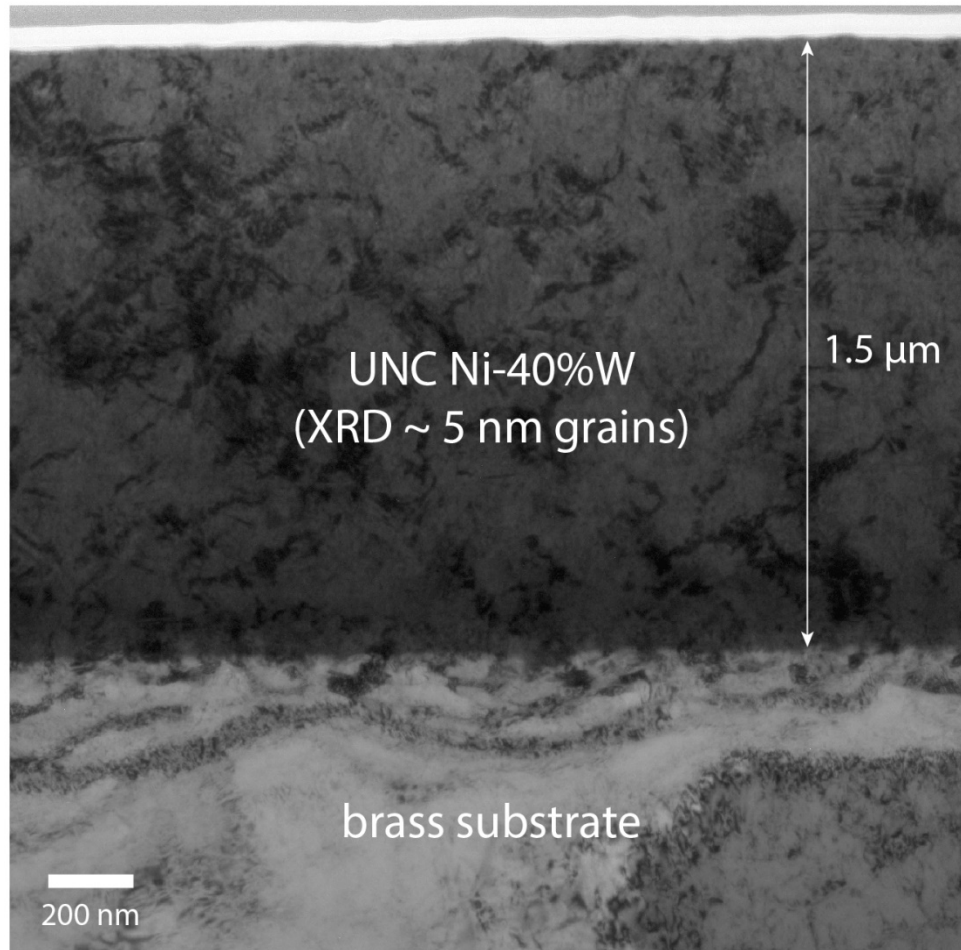
200 nm

mixed UNC metal/oxide

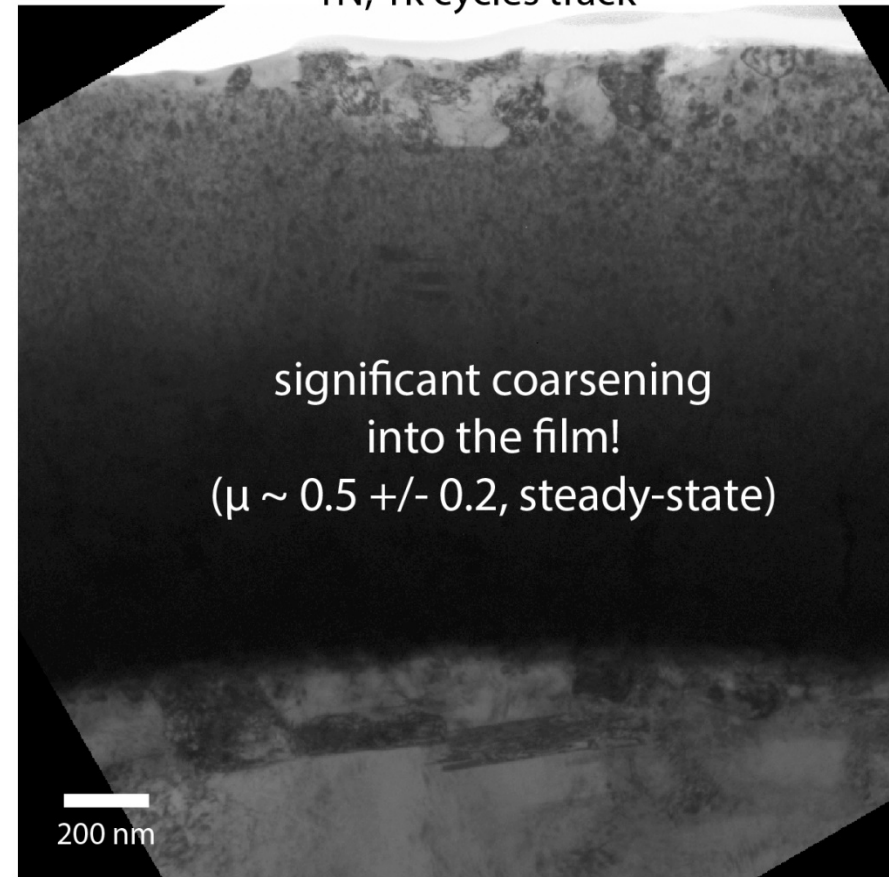
refined near surface Ni-W

# 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

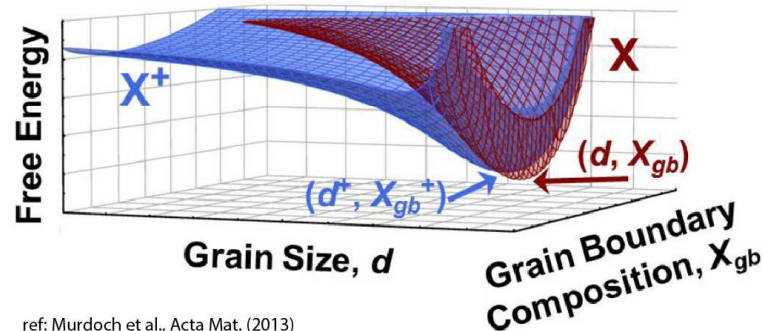
ref: Chookajorn et al., Science, 2012

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

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

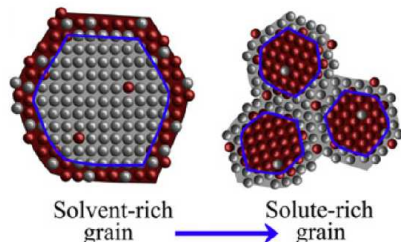
Implications:  
Will not drive toward fine grain size, but will remain there

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

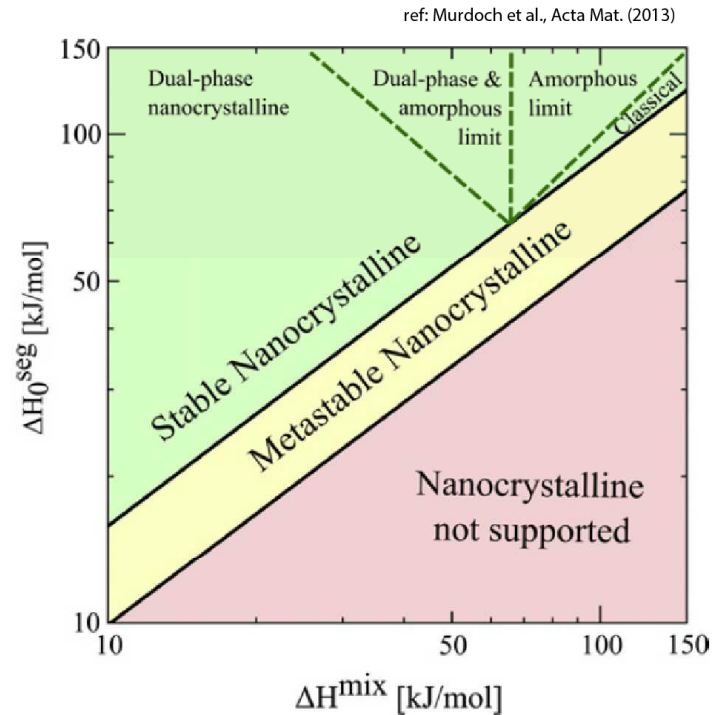


ref: Murdoch et al., Acta Mat. (2013)

Grain structure model: segregated 2-phase metal system:



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

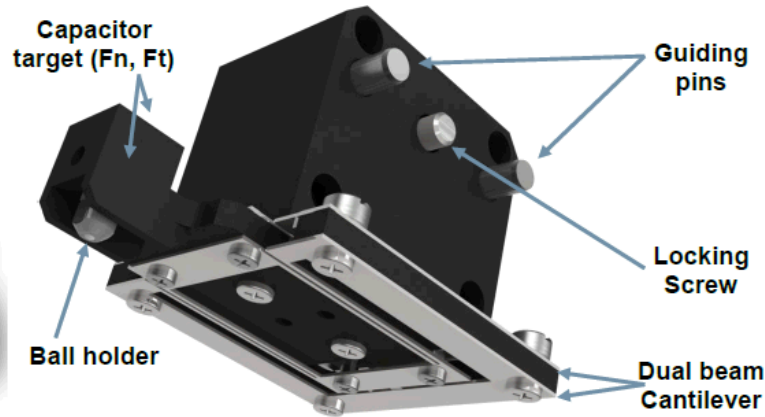


ref: Murdoch et al., Acta Mat. (2013)

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

**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

