SAND2015-3366C

Exploring the mechanical and thermal stability of nanocrystalline metal composite and alloy thin films

Nicolas Argibay[1], Michael E. Chandross[1], Shengfeng Cheng[2]
Michael T. Dugger[1], Brad L. Boyce[1], S. V. Prasad[1], Blythe G. Clark[1]
Brendan L. Nation[1], Jon-Erik Mogonye[1]

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

[2] *Department of Phyiscs*
Virginia Tech
Blacksburg VA USA

Sandia National Laboratories

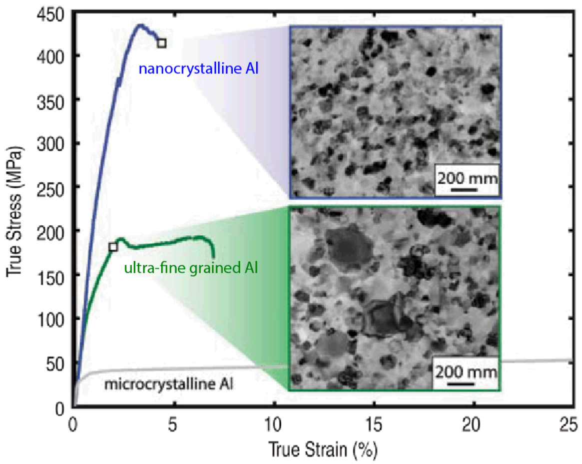
NNSA National Nuclear Security Administration

U.S. DEPARTMENT OF ENERGY

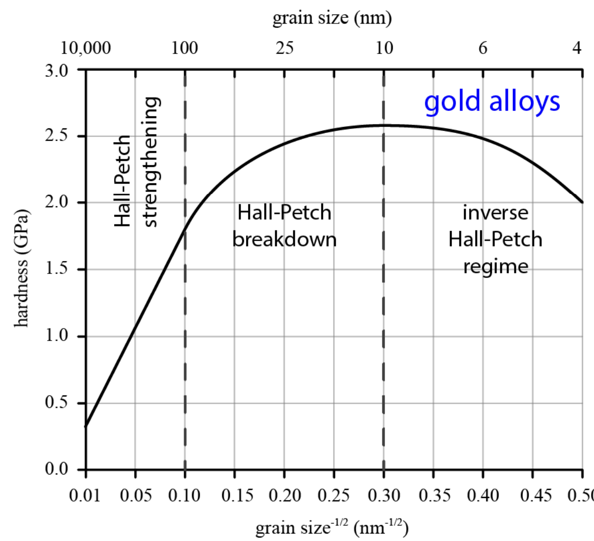
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

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

higher yield strength

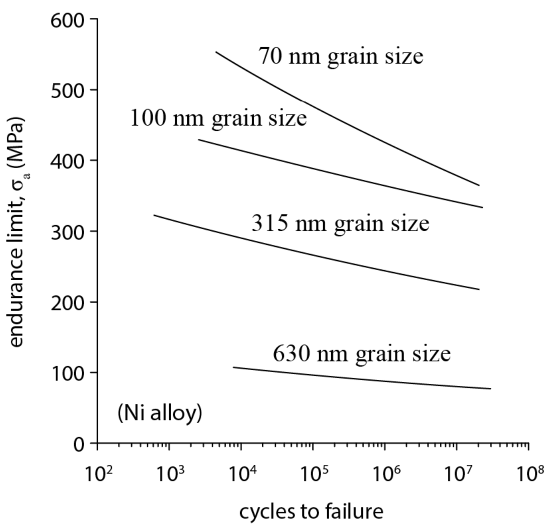


higher hardness



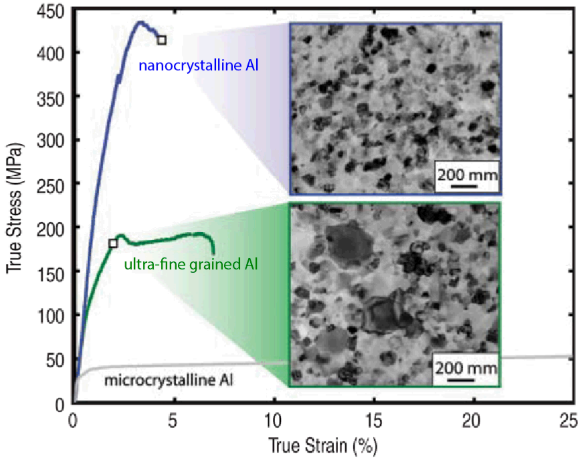
ref: Lo, Augis and Pinnel, JAP (1979)

higher fatigue strength (endurance limit)

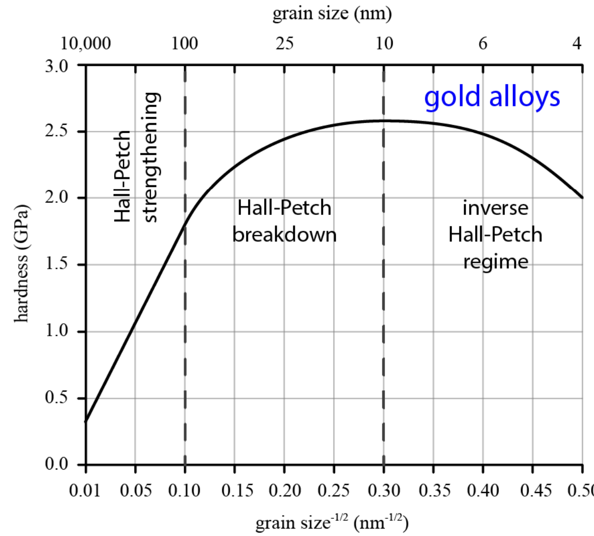


Engineering advantages of NC metals, alloys and metal-matrix composites

higher yield strength

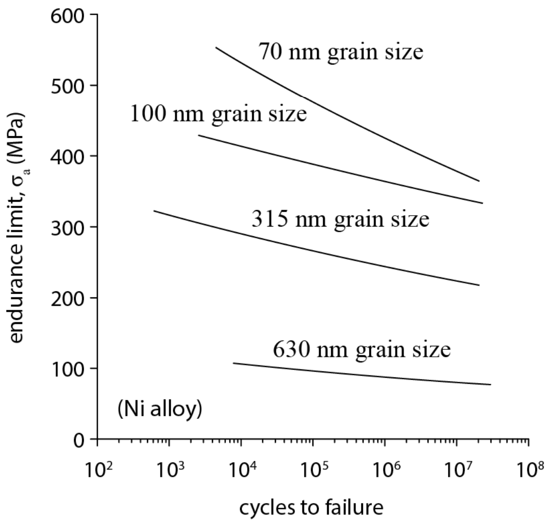


higher hardness

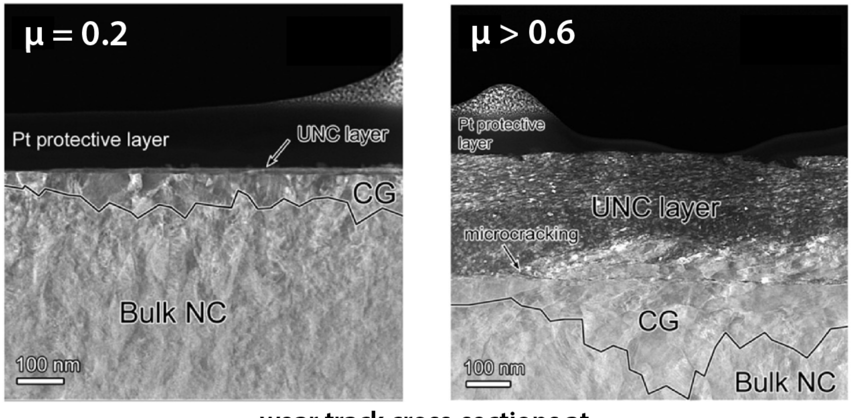


ref: Lo, Augis and Pinnel, JAP (1979)

higher fatigue strength (endurance limit)



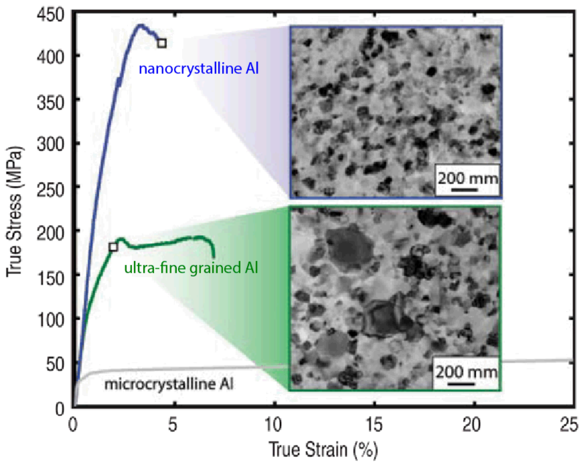
lower friction and wear rates



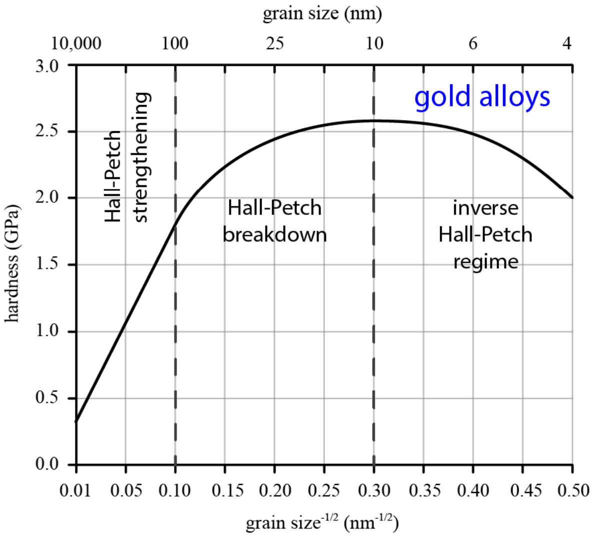
wear track cross-sections at steady-state sliding conditions

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

higher yield strength

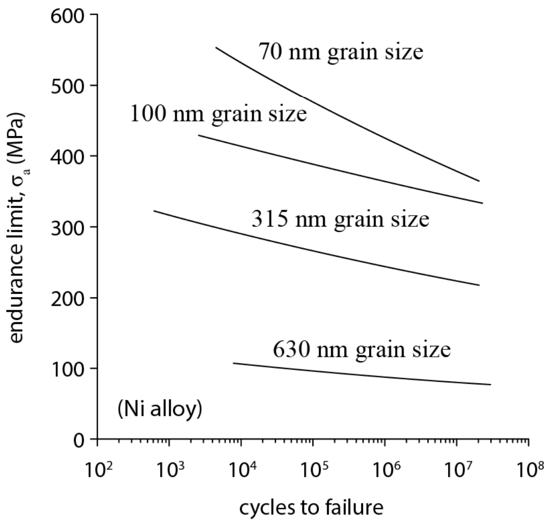


higher hardness

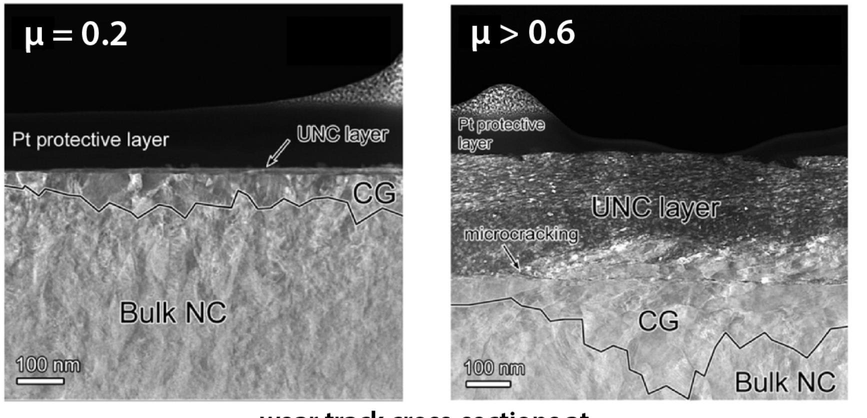


ref: Lo, Augis and Pinnel, JAP (1979)

higher fatigue strength (endurance limit)



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

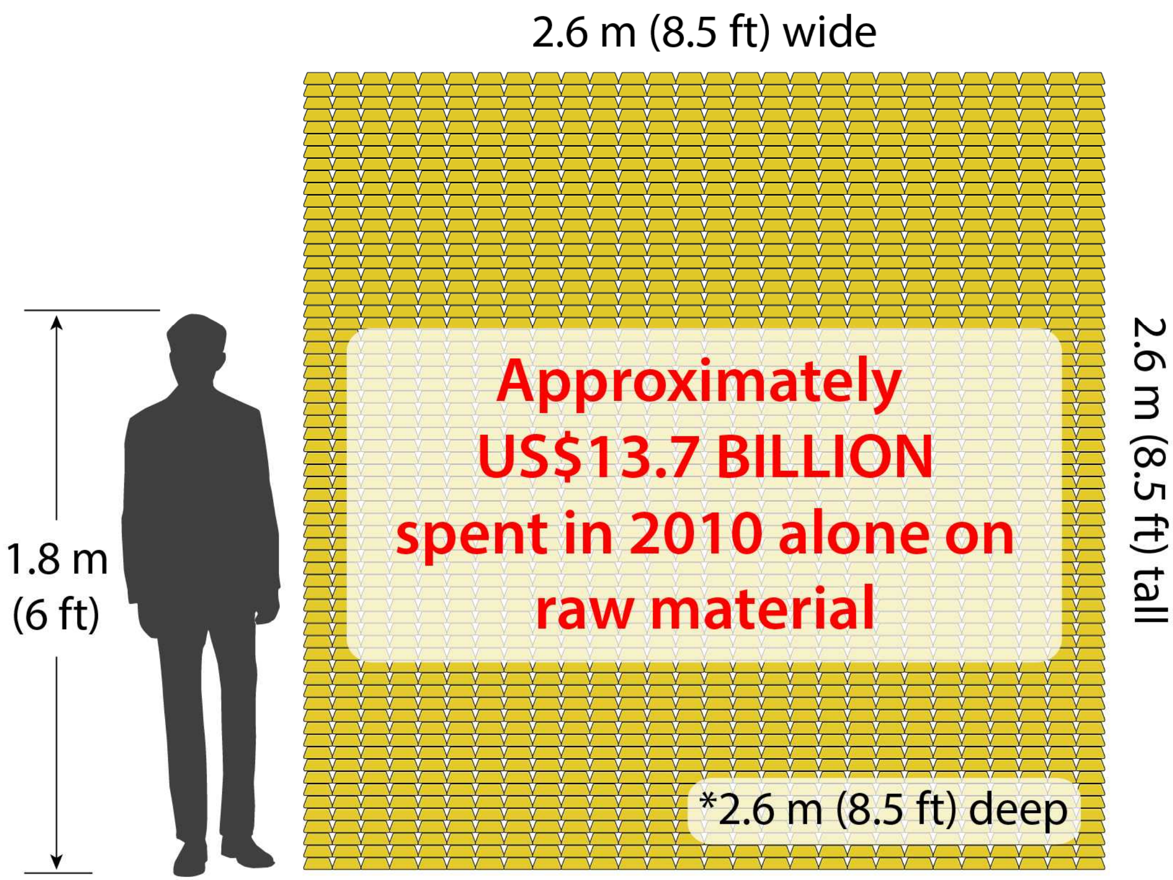


wear track cross-sections at steady-state sliding conditions

Investigations will focus on noble metal films – high impact and simpler (no oxides)

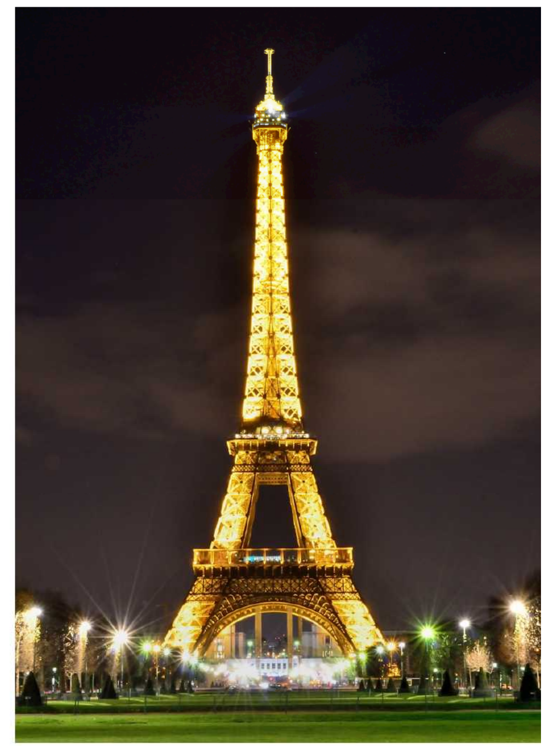
An estimated **300 metric tons/year** of gold used in electronics related applications, most of it in electroplated connectors and contacts (**11% of yearly amount mined**)

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



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***



Investigations will focus on noble metal films – high impact and simpler (no oxides)

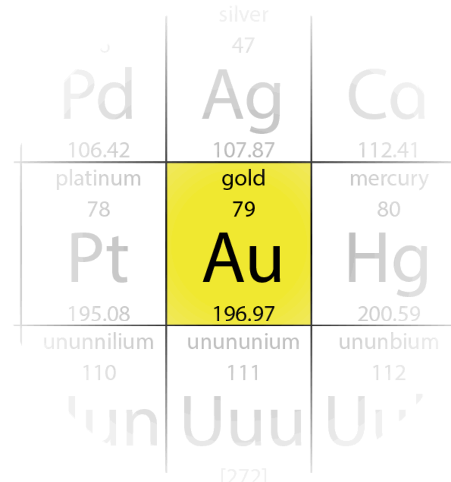
Characteristics of <u>pure</u> gold thin films:

- oxidation resistance

- high ductility

- high electrical conductivity

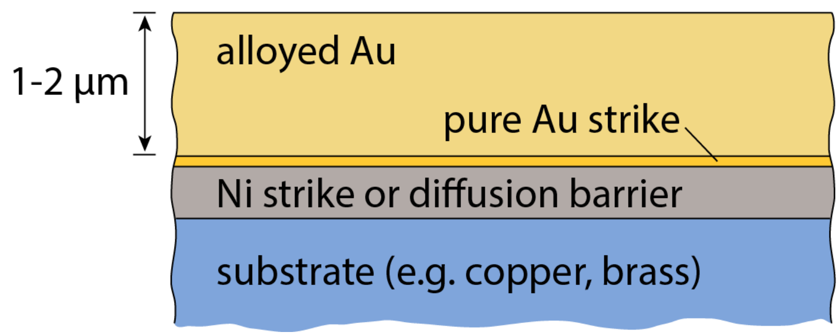
...but low friction/wear? ***no***



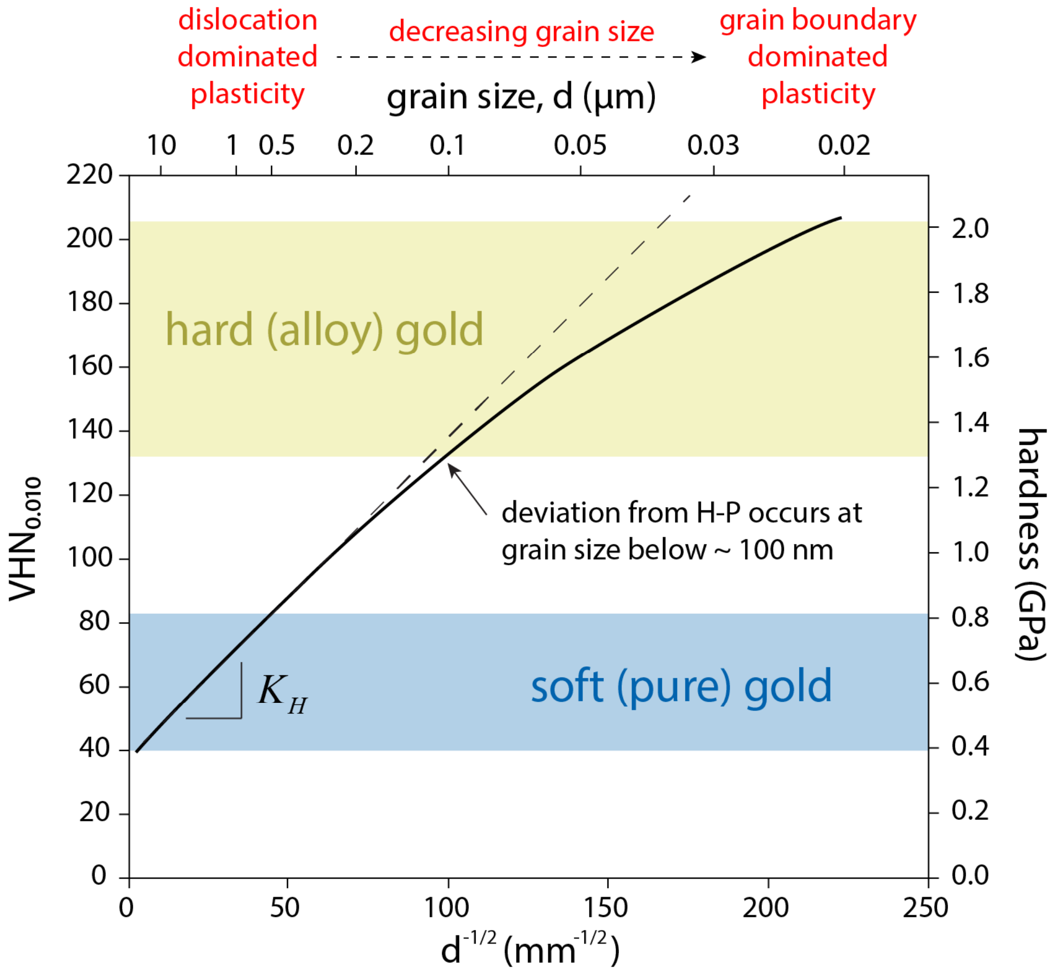
Solution: alloying/metal-matrix composites

alloy or composite ("hard") gold:

Gold that is alloyed with up to 1 wt. % of Ni/Co/Fe, creating a fine-grained, Hall-Petch Strengthened wear-resistant coating.



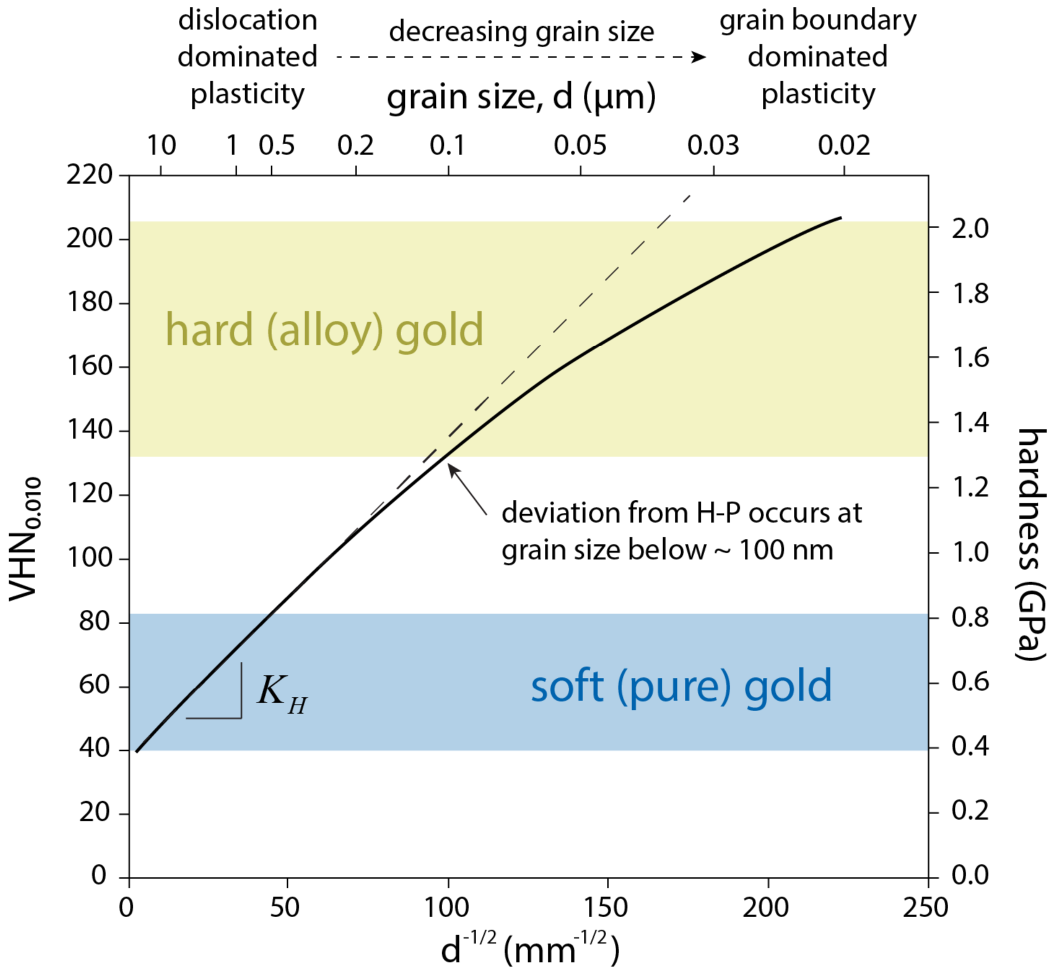
Why “hard” Au? Hardness increase associated primarily with grain size reduction



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

Hall-Petch hardness to grain size relationship: $H = H_0 + K_H d^{-1/2}$

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



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

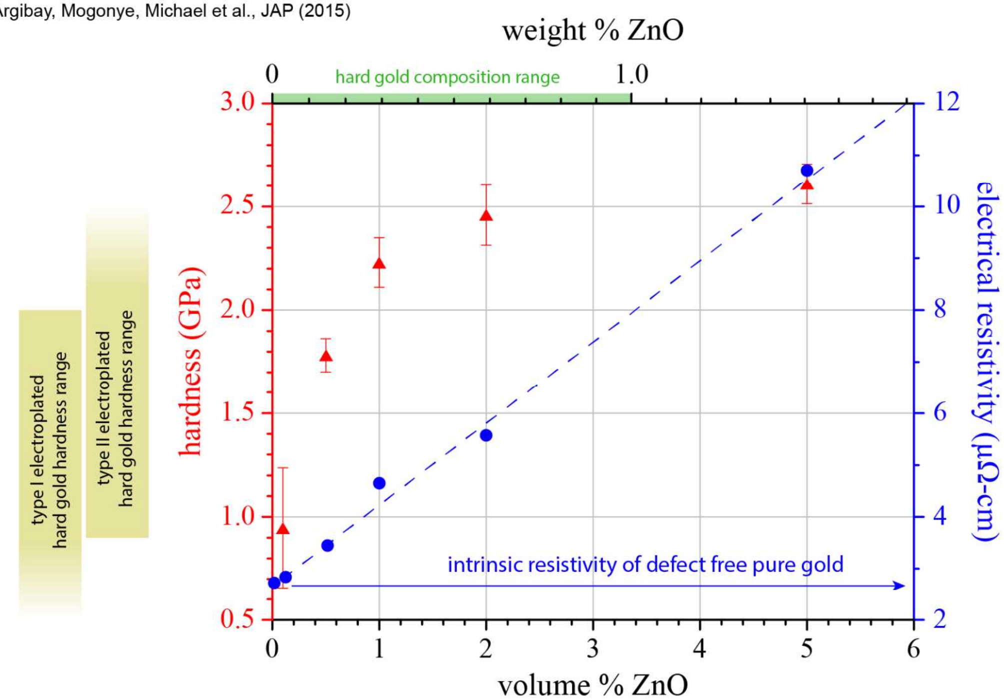
The widely held misconception that <u>hardness increase is the source of low wear and friction</u> is loosely attributed to the notion that real contact area drops with hardness:

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

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

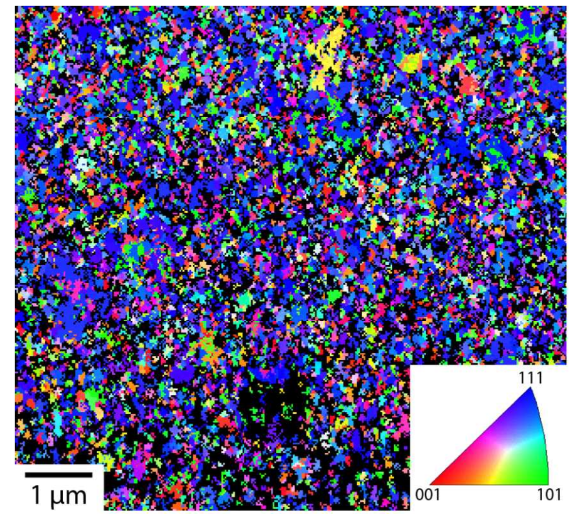
Recently published work showed oxide nanoparticles work just as well as Ni or Co

ref 1: Argibay, Prasad, Dugger, et al., Wear (2013)
ref 2: Argibay, Mogonye, Michael et al., JAP (2015)



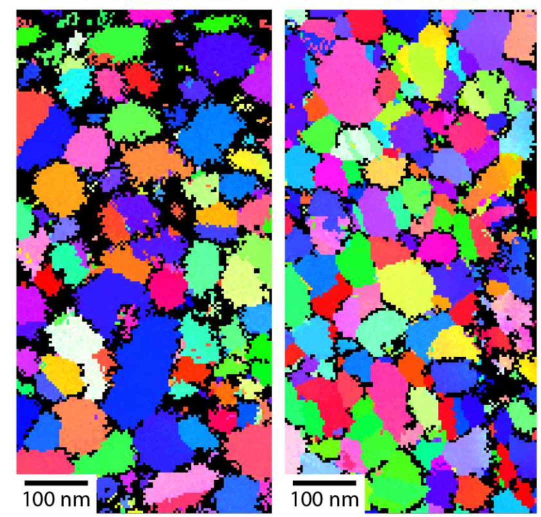
Film surface-normal EBSD mapping:

0.1 vol. % ZnO film



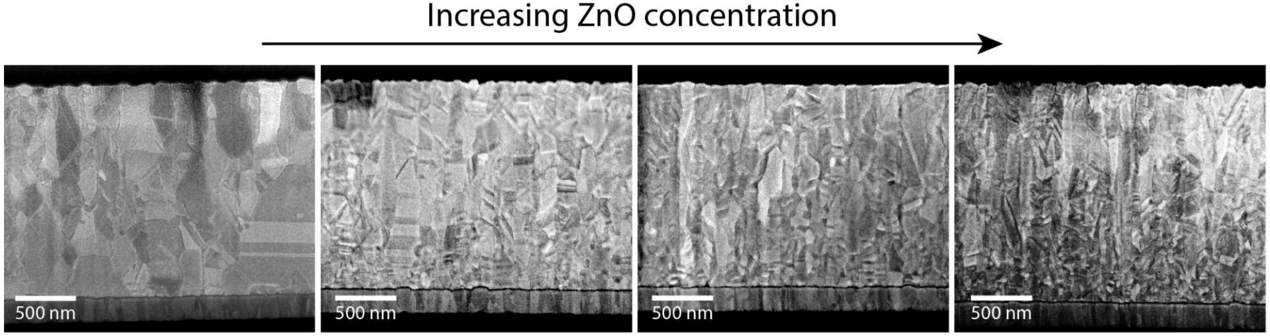
Transmission Kikuchi diffraction:

1.0 vol. % ZnO film | 2.0 vol. % ZnO film



SEM of FIB milled and etched cross-sectional views:

Increasing ZnO concentration



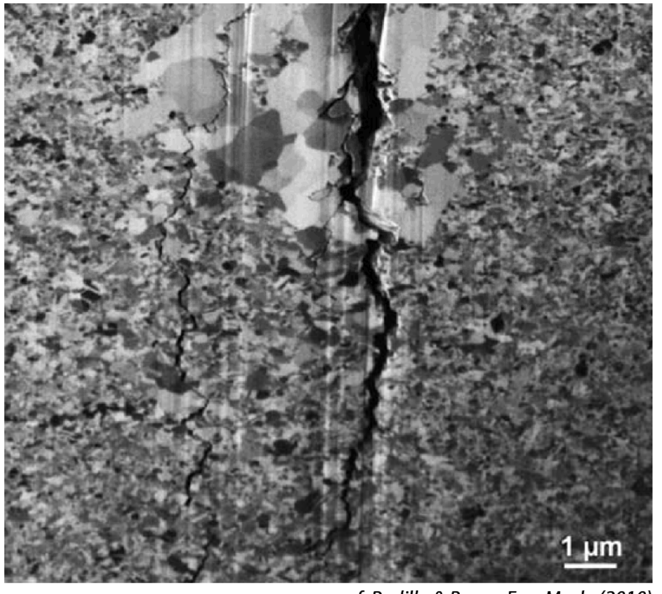
0.1 vol. % ZnO film | 0.5 vol. % ZnO film | 1.0 vol. % ZnO film | 2.0 vol. % ZnO film

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

Mechanical (strain) induced grain growth and recrystallization

Fatigue driven grain growth in NC Ni-Mn; initially NC grain structure

Crack initiated in a region where grain growth occurred



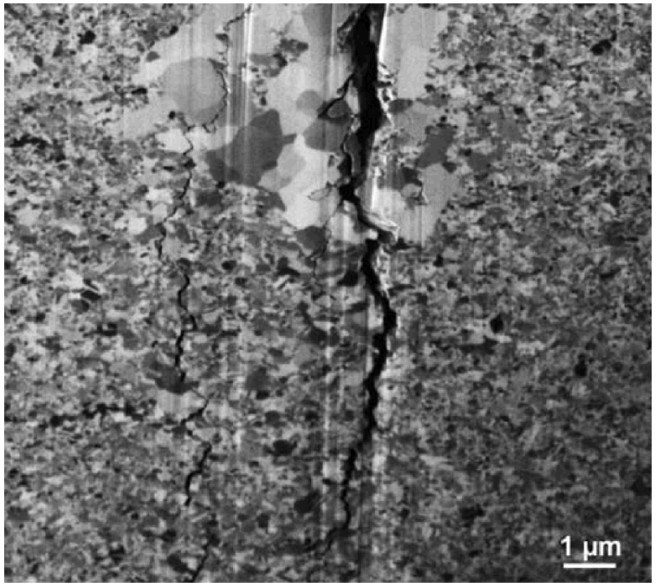
ref: Padilla & Boyce, Exp. Mech. (2010)

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

Mechanical (strain) induced grain growth and recrystallization

Fatigue driven grain growth in NC Ni-Mn; initially NC grain structure

Crack initiated in a region where grain growth occurred

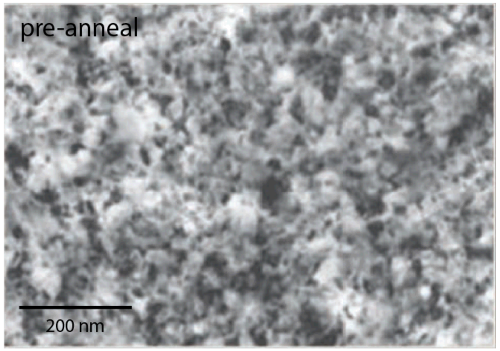


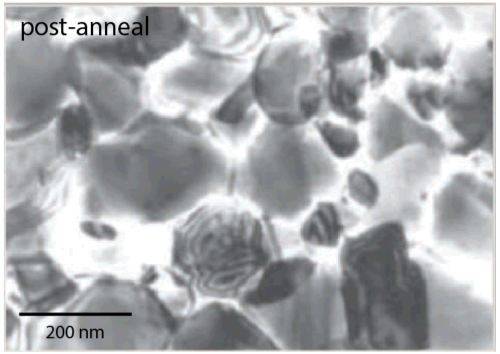
ref: Padilla & Boyce, Exp. Mech. (2010)

Thermally induced grain growth and recrystallization

Ni that was initially nanocrystalline after exposure to 300°C for 30 minutes exhibits typical explosive grain growth

This behavior (Ostwald ripening) is driven by thermally activated solid diffusion



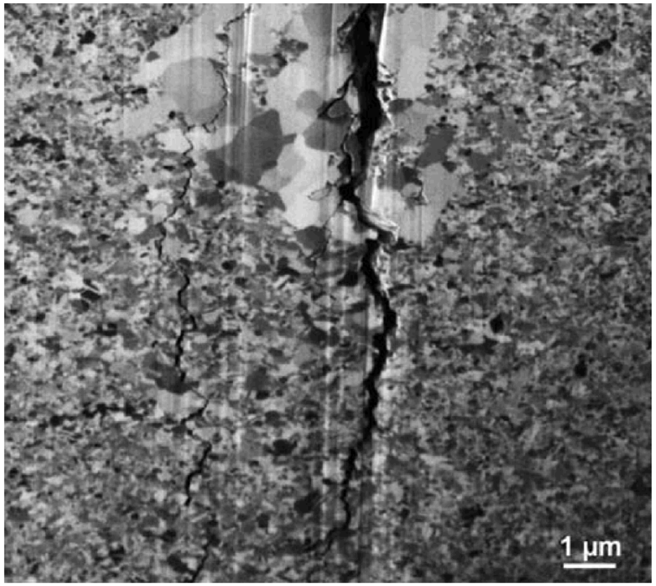


Grain size **stability** remains the key challenge to widespread adoption of NC metals

Mechanical (strain) induced grain growth and recrystallization

Fatigue driven grain growth in NC Ni-Mn; initially NC grain structure

Crack initiated in a region where grain growth occurred



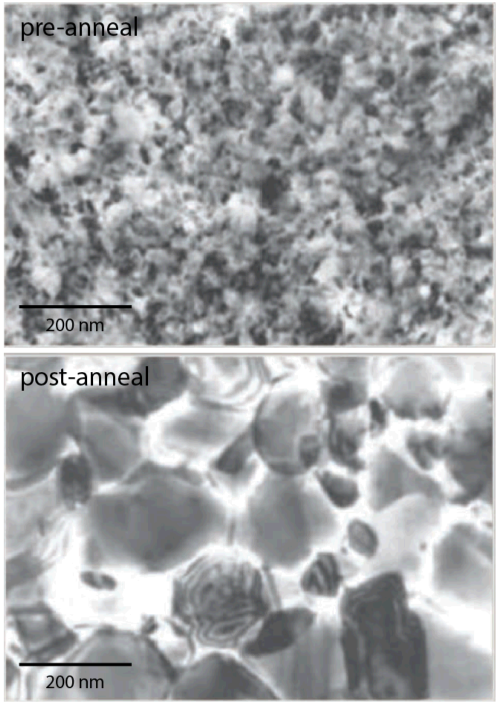
ref: Padilla & Boyce, Exp. Mech. (2010)

This implies contact stress can drive coarsening...

Thermally induced grain growth and recrystallization

Ni that was initially nanocrystalline after exposure to 300°C for 30 minutes exhibits typical explosive grain growth

This behavior (Ostwald ripening) is driven by thermally activated solid diffusion



... and contact heating can drive coarsening (e.g. Lim and Ashby)

Two routes to stabilize nanocrystalline metals – kinetic and thermodynamic

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

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

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

M = grain boundary mobility

P = pressure on grain boundary

γ_o = interfacial energy per unit area

r = mean grain radius

Two routes to stabilize nanocrystalline metals – kinetic and thermodynamic

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

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

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

M = grain boundary mobility

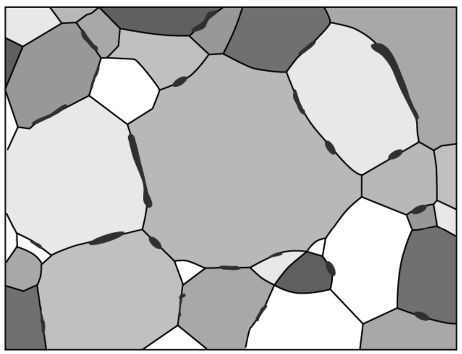
P = pressure on grain boundary

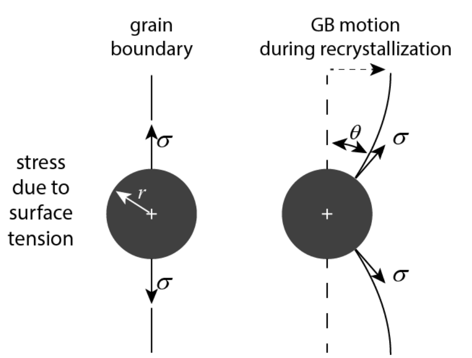
γ_o = interfacial energy per unit area

r = mean grain radius

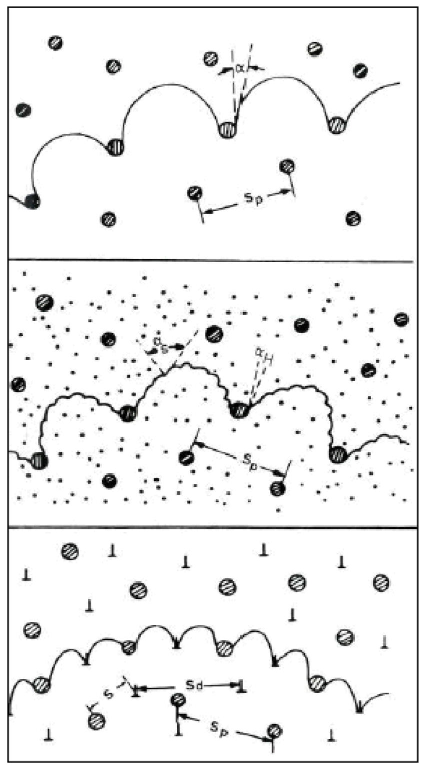
Limit the ***kinetics*** of recrystallization (traditional quasi-stability)

e.g. Zener pinning, solute drag, porosity





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



Two routes to stabilize nanocrystalline metals – kinetic and thermodynamic

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

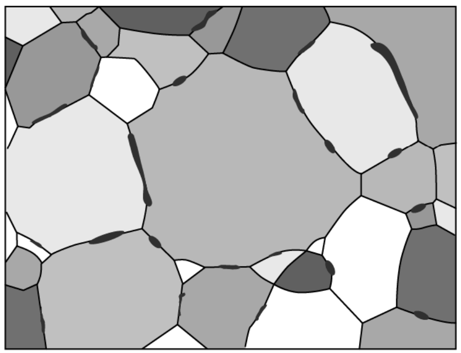
Grain growth is essentialy driven by grain boundary described by speed of grain boundary motion (speed), v

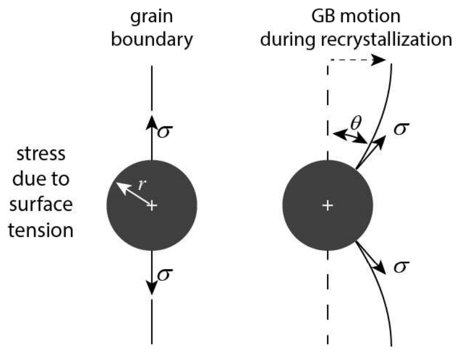
$$v = M \cdot P = M_o \exp\left(-\frac{Q_m}{kT}\right) \cdot \frac{2\gamma_o}{r}$$

M = grain boundary mobility
P = pressure on grain boundary
γ_o = interfacial energy per unit area
r = mean grain radius

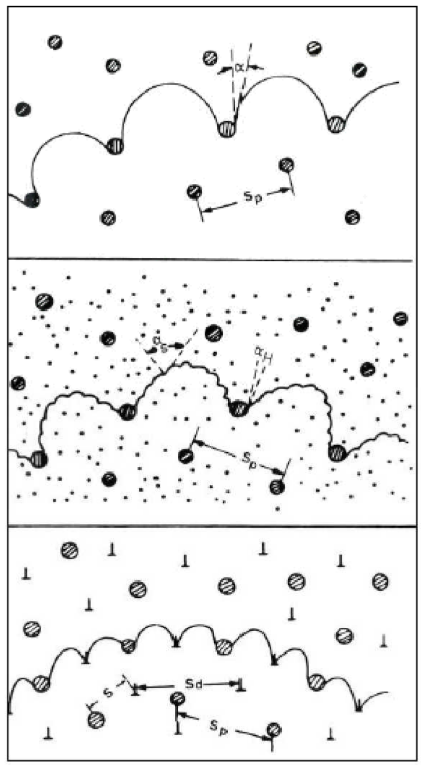
Limit the *kinetics* of recrystallization (traditional quasi-stability)

e.g. Zener pinning, solute drag, porosity





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



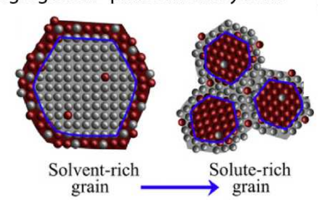
Weissmüller (1993), Kirchheim (2002), and Schuh (2012) have made significant contributions toward understanding and achieving *thermodynamic* stability by lowering grain boundary energy through solute segregation

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

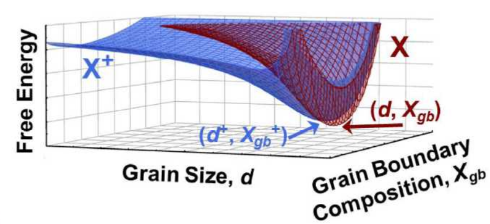
$$\Delta G^{mix} = (1 - f_{gb})\Delta G_c^{mix} + f_{gb}\Delta G_{gb}^{mix} + z\nu f_{gb}(X_{gb} - X_c)\left[(2X_{gb} - 1)\omega_{gb} - \frac{1}{zt}(\Omega^B\gamma^B - \Omega^A\gamma^A)\right]$$

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

Grain structure model:
segregated 2-phase metal system

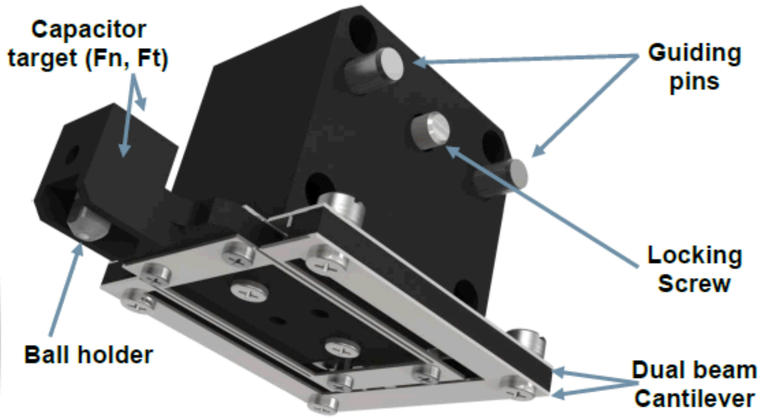


ref: Murdoch et al., Acta Mat. (2013)



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

Modified CSM Nanotribometer – friction and wear testing platform

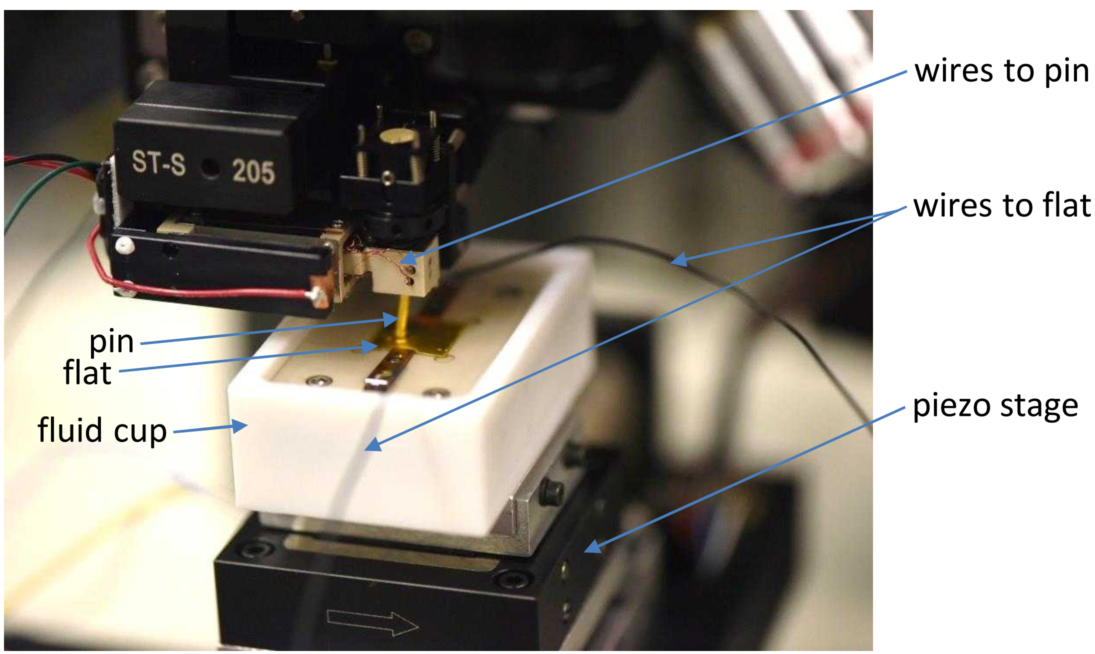


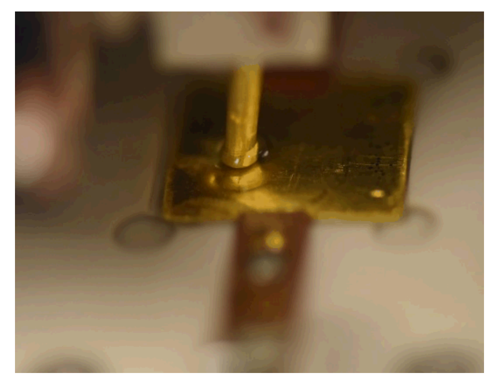
CSM nanotribometer modified for 4-wire ECR measurement

- DC power supply
- nano-ohm meter

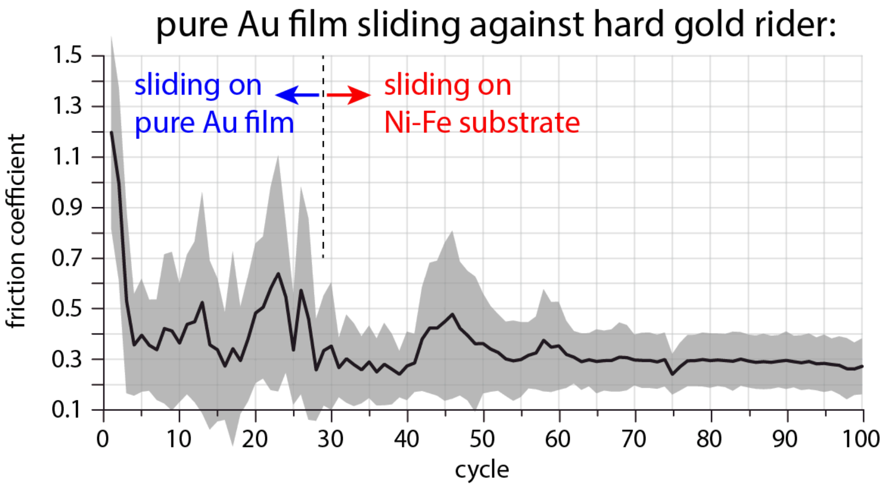
Test parameters:

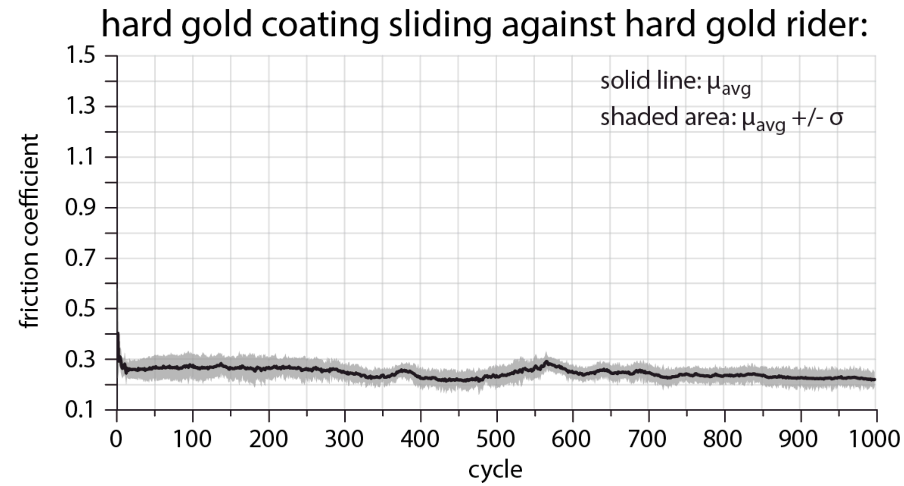
- Fn = 100 µN to 1000 mN
- pin radius = 1.6 mm
- track length = 0.1 to 10 mm
- v = 0.01 to 10 mm/s



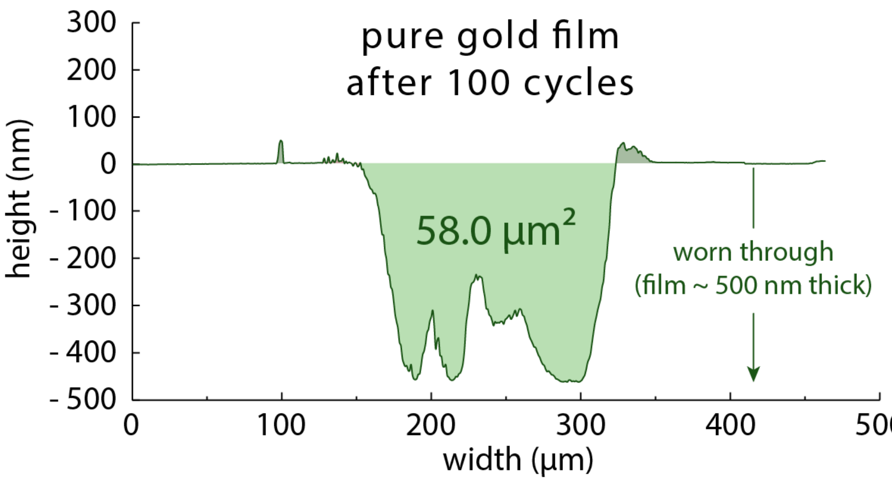


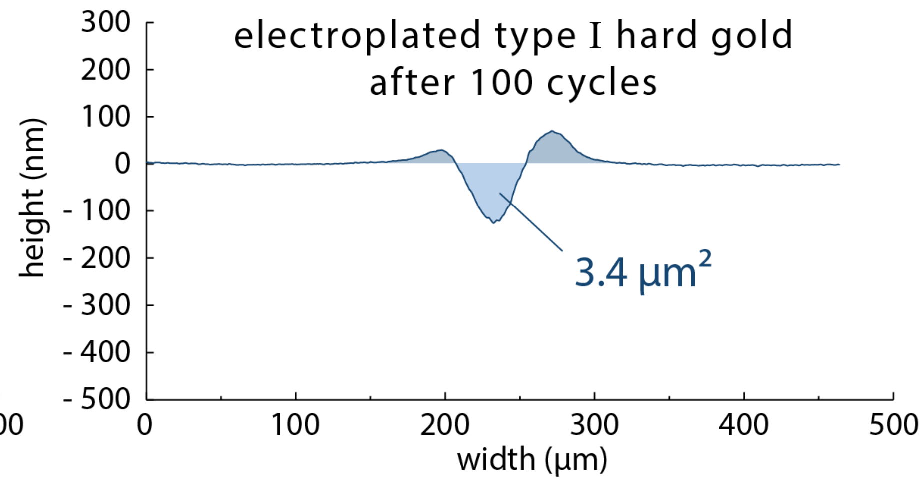
Macro-scale experiments on pure and alloy gold (electroplated Ni-hardened Au)





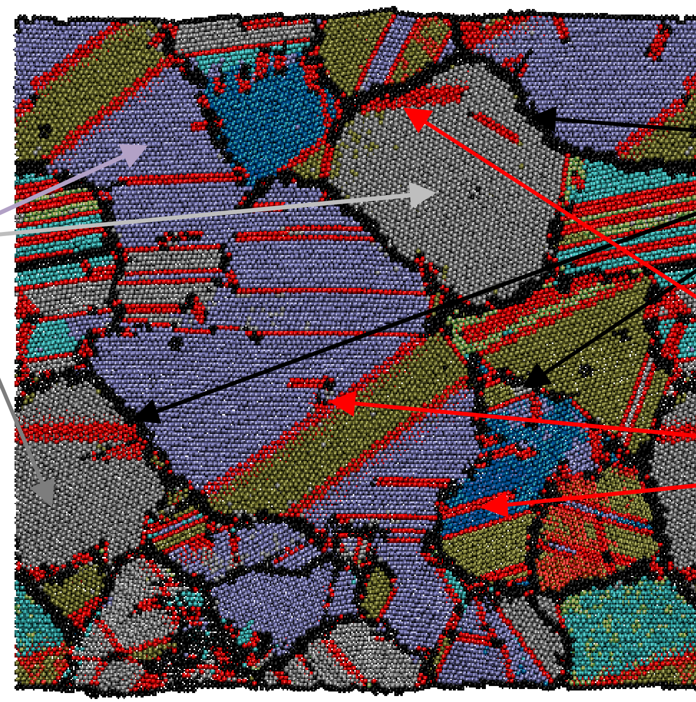
Average wear track cross-section in same sliding conditions against bulk hard gold alloy rider:





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

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

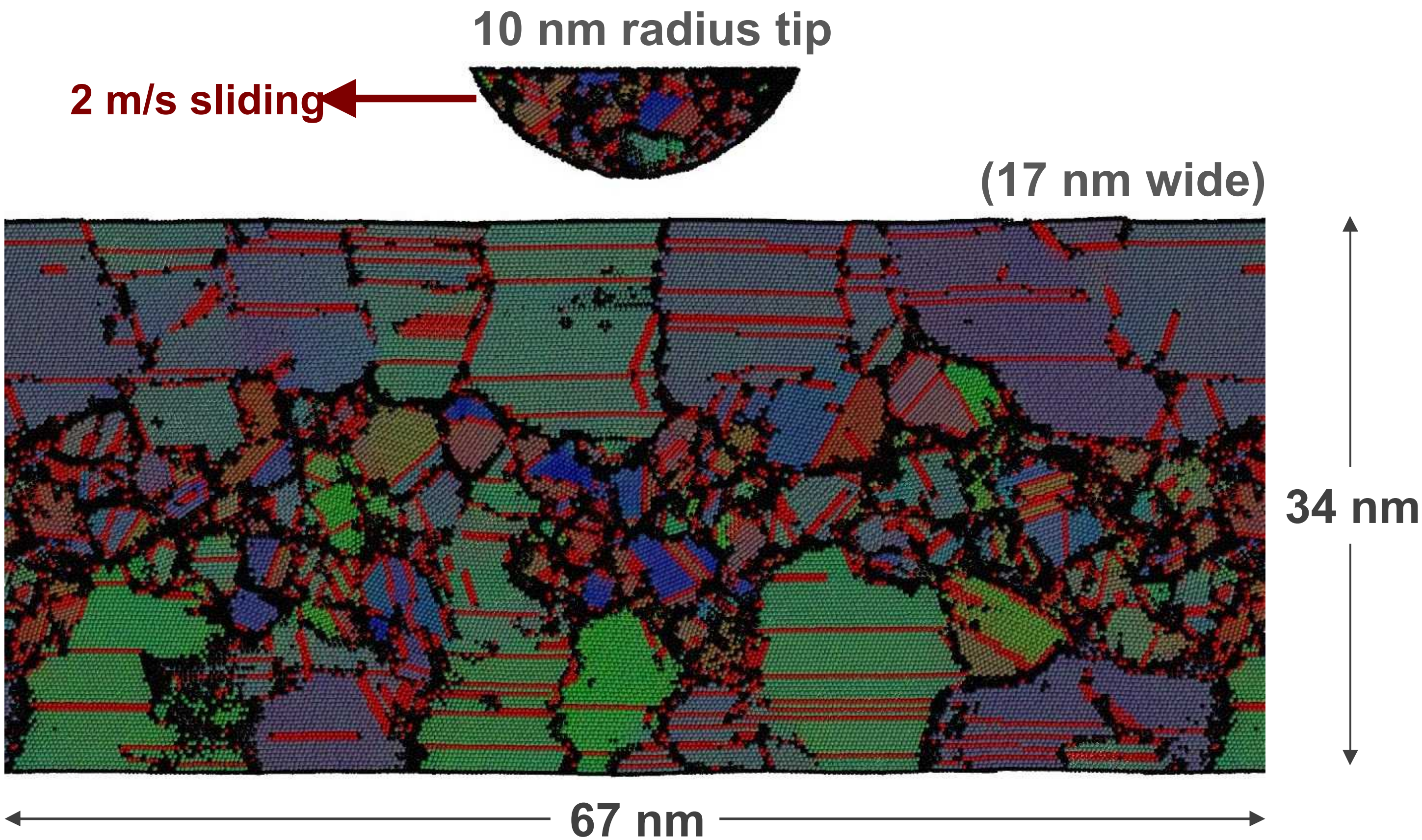


grain boundaries (black)

stacking faults & twins (red)

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

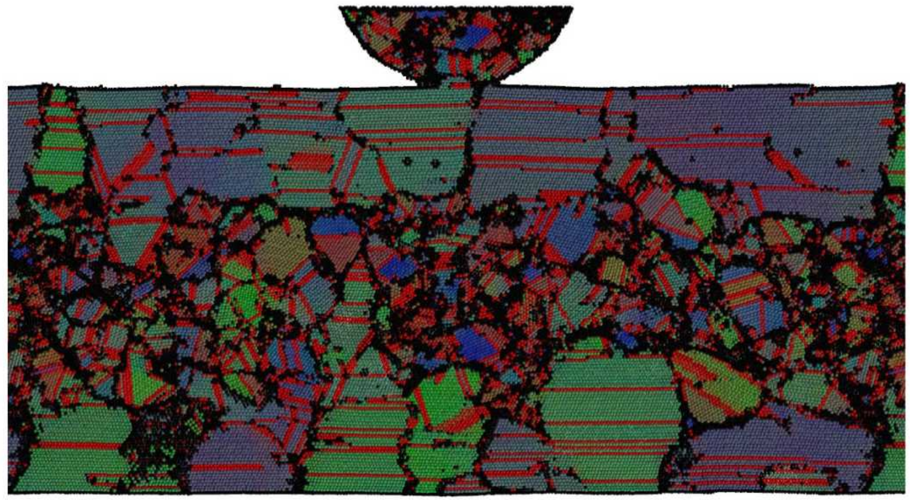
Tip based friction simulations : this is what the initial condition looks like



Substrate: nanocrystalline Ag
Constraint 1: constant velocity
Constraint 2: constant separation ***or*** normal force

Comparison between pure and alloyed Ag grain evolution

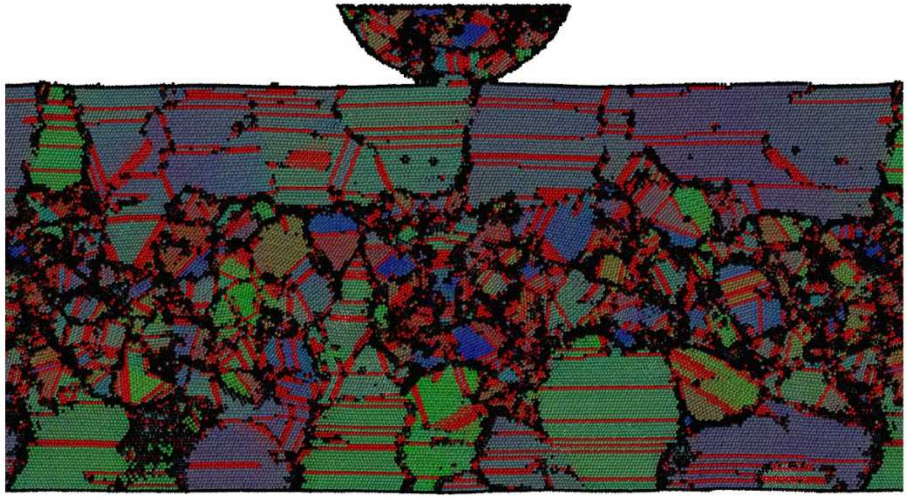
initial microstructure
of Ag and Ag-Cu alloy
(no sliding yet)



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

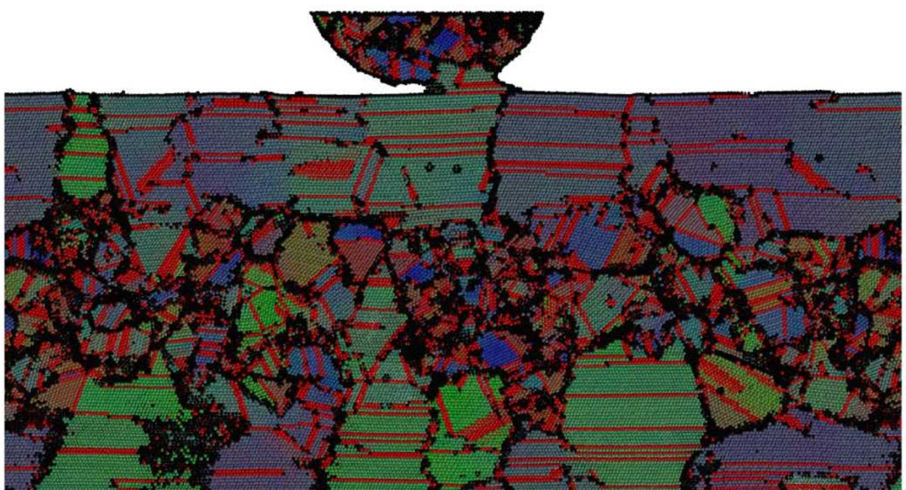
Comparison between pure and alloyed Ag grain evolution

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

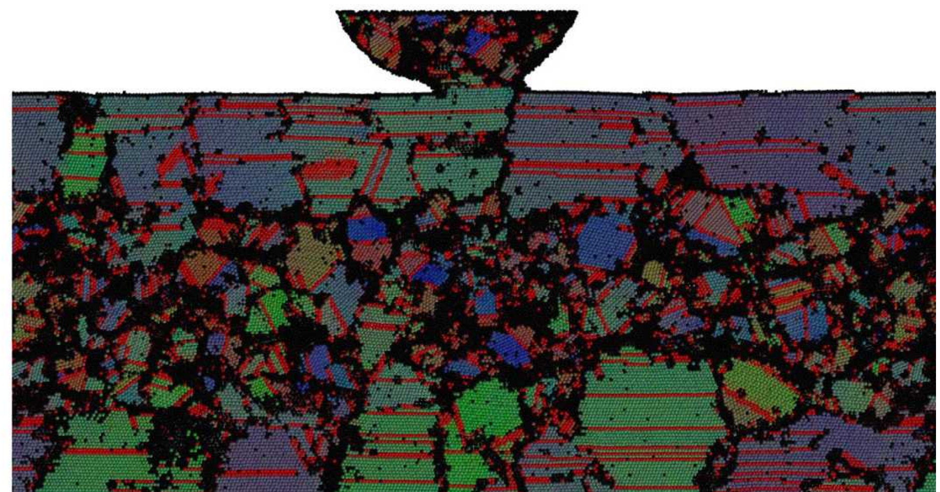


300 MPa contact stress
300 K temperature
2 m/s sliding speed

pure Ag after 4 nm of sliding

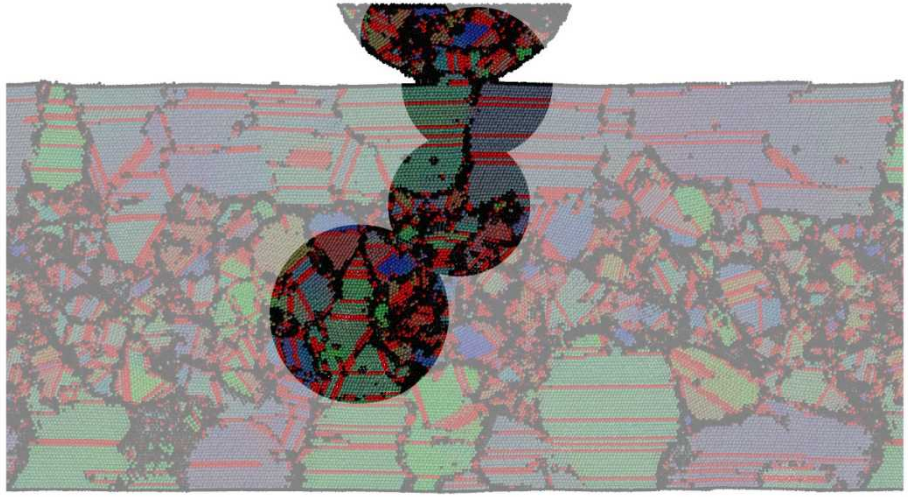


Ag-10% Cu alloy after 4 nm of sliding



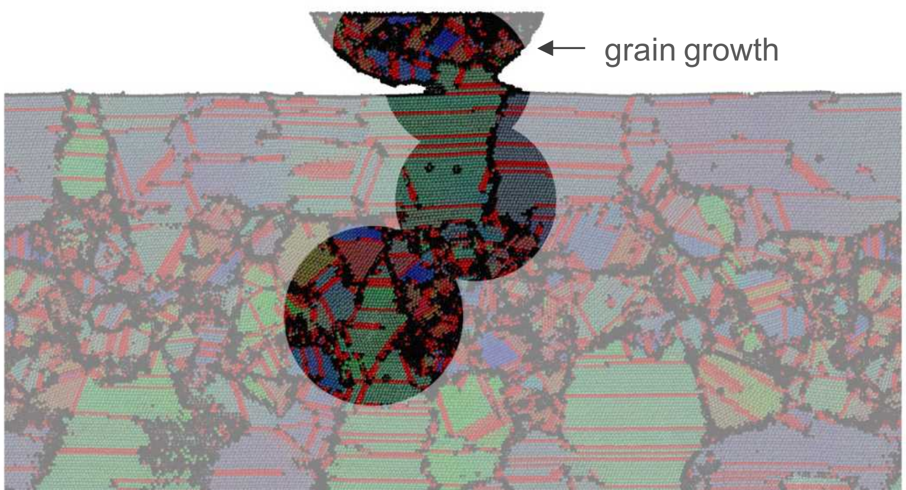
Comparison between pure and alloyed Ag grain evolution: stabilization thru alloying!

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



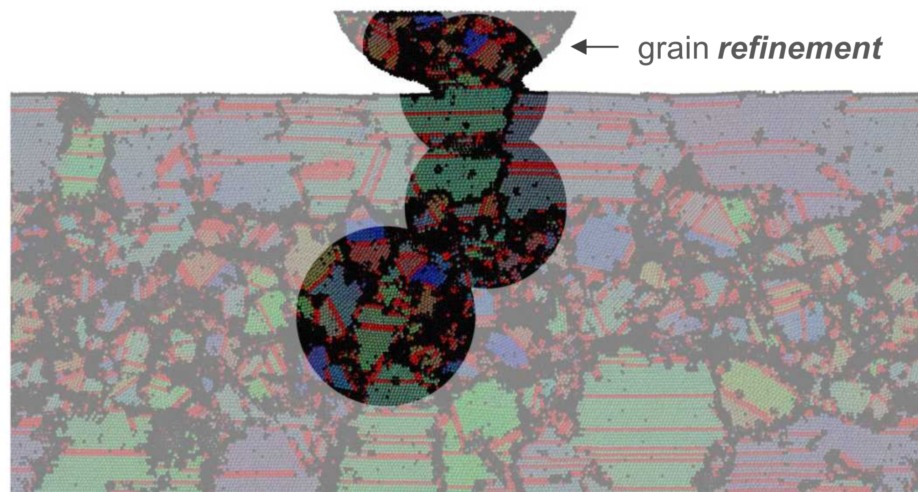
300 MPa contact stress
300 K temperature
2 m/s sliding speed

pure Ag after 4 nm of sliding



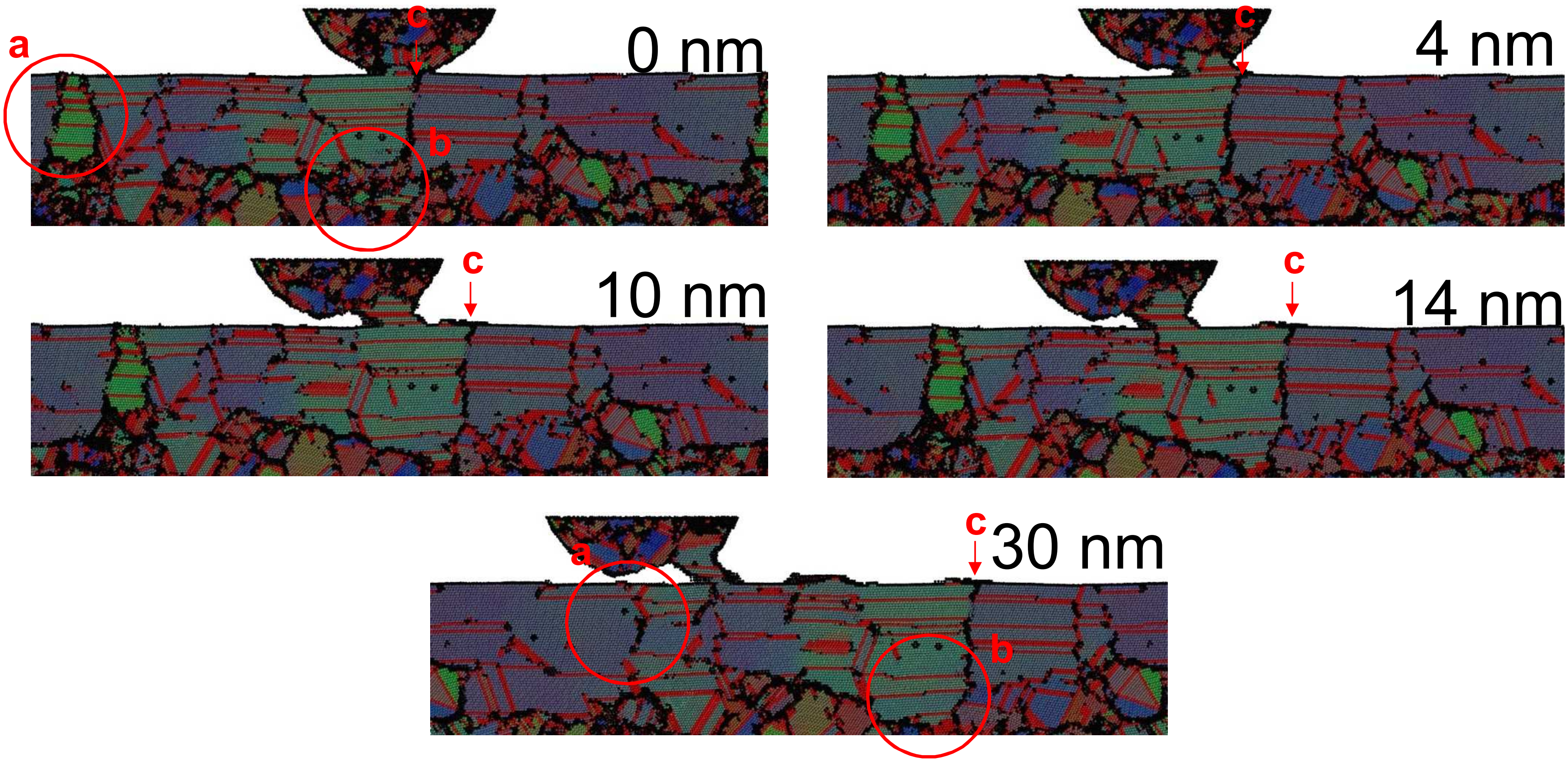
← grain growth

Ag-10% Cu alloy after 4 nm of sliding



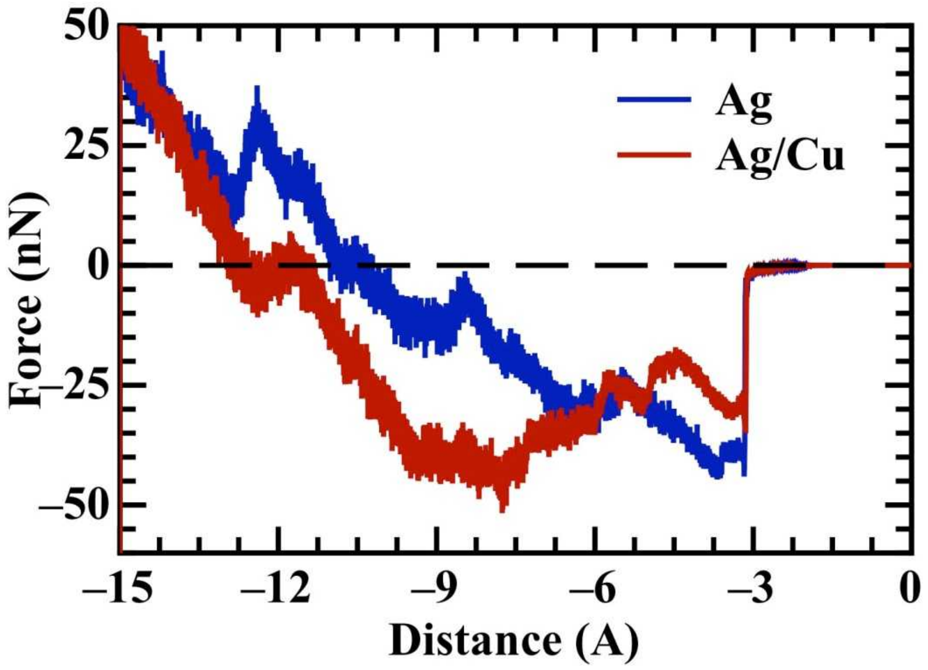
← grain ***refinement***

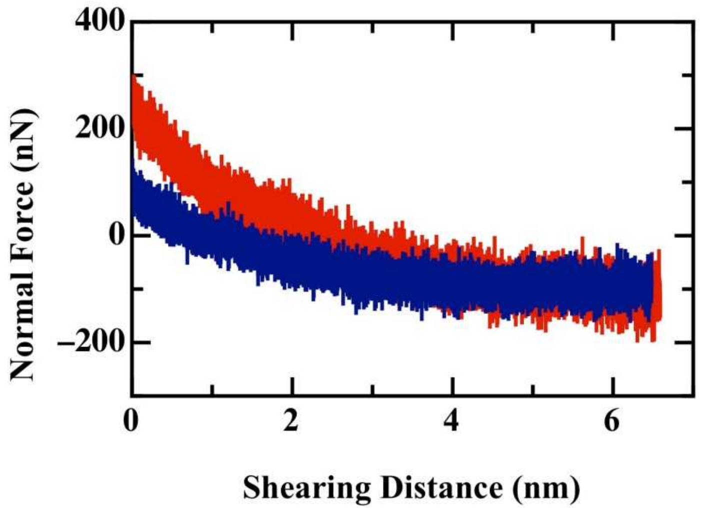
Looking at pure Au tip/slab contact evolution over a longer sliding time

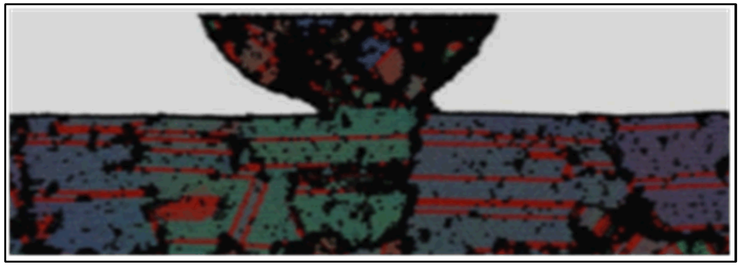


- Initially distinct grains
- After shear (adhesive load), coalescence – now a mode II crack
- Single grain forms across interface – stress induced grain growth

Summary of “tip/slab” contact with pure and alloyed Ag

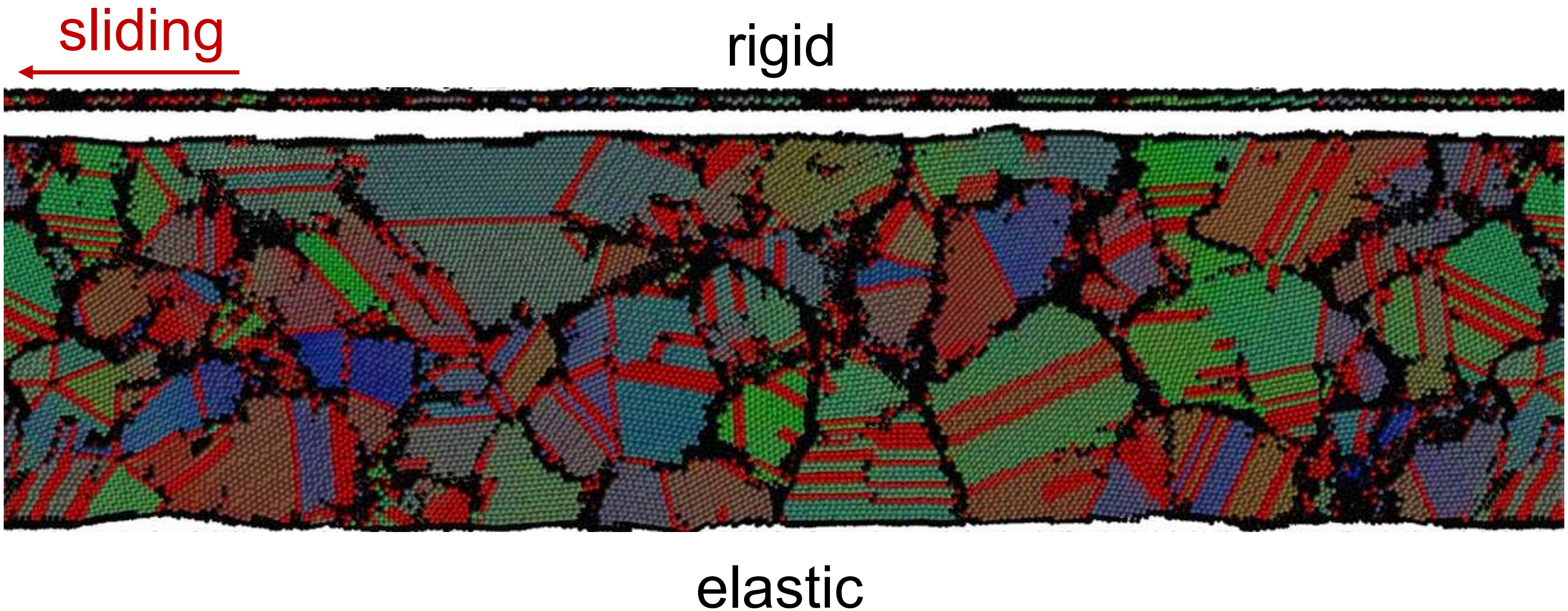






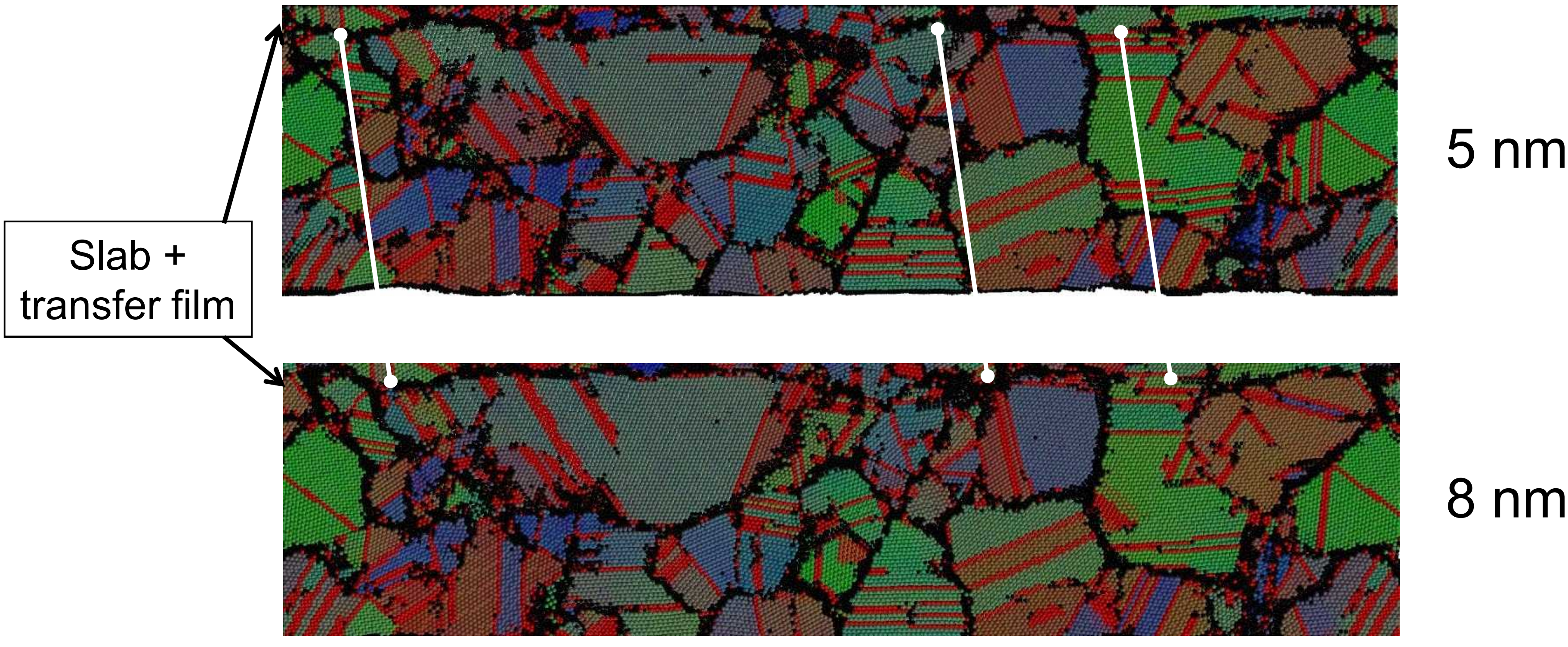
- Alloy is more adhesive (work of adhesion twice that of Ag)
- Can’t measure friction with tip/slab geometry
  - load decays to equivalent adhesive value… tip wear
- Alloys suppress commensurate contacts

Slab-on-slab sliding contact simulations



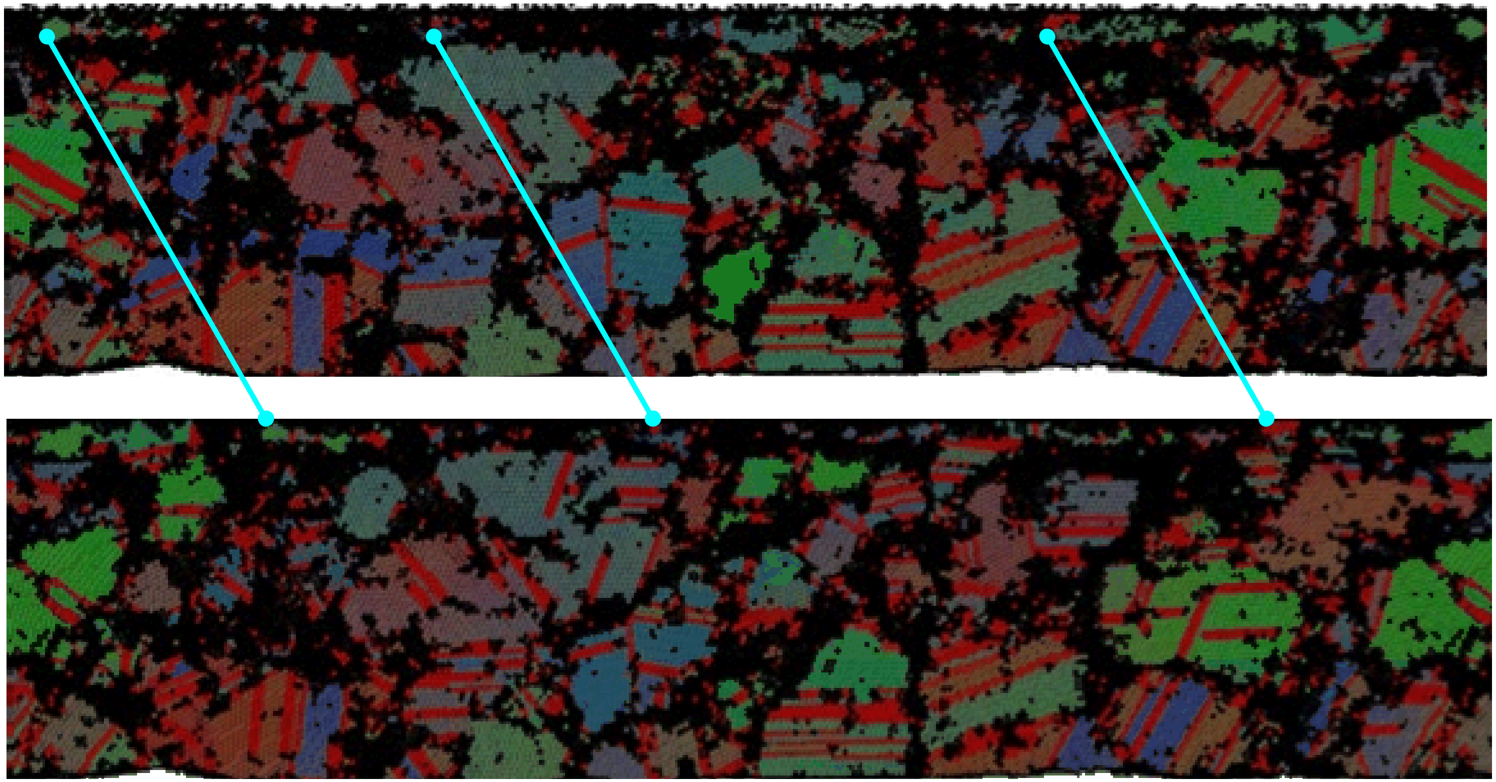
- Rigid slabs suppress grain growth
- No plowing is possible/reduced contact stress

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



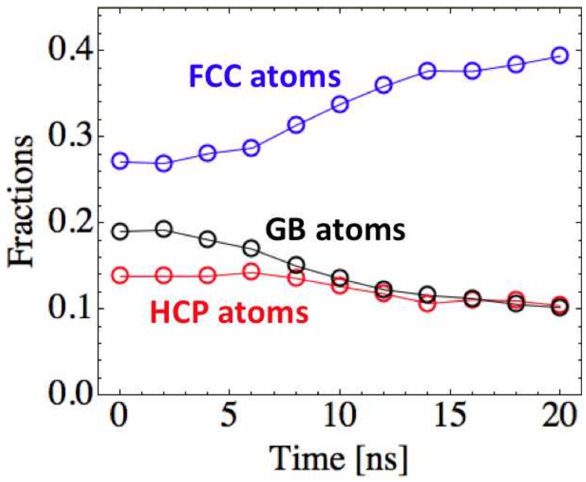
6 nm

16 nm

- 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!)

Grain size stabilization (refinement!) observed for alloys with *miscibility gap* only

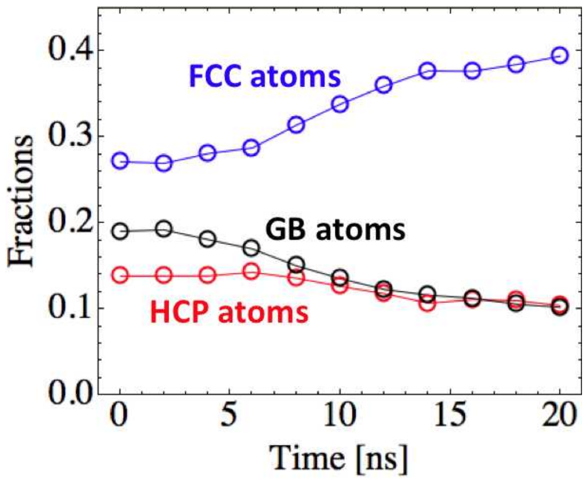
pure Ag slabs



grain coarsening

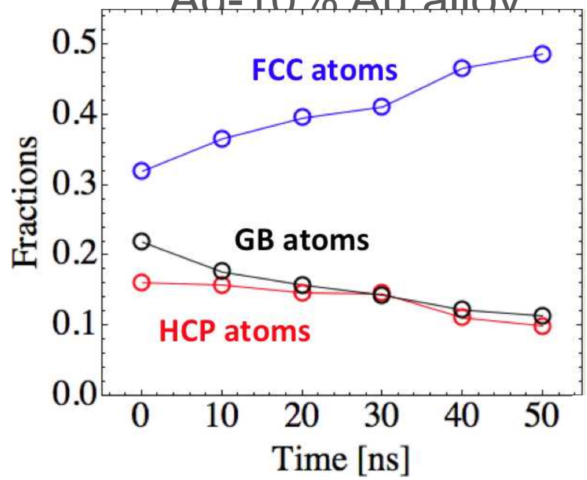
Grain size stabilization (refinement!) observed for alloys with ***miscibility gap*** only

pure Ag slabs



grain coarsening

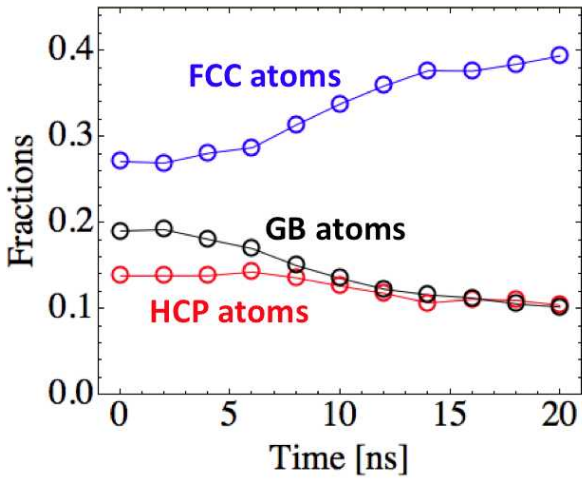
high solubility
system
Ag-10% Au alloy



grain coarsening

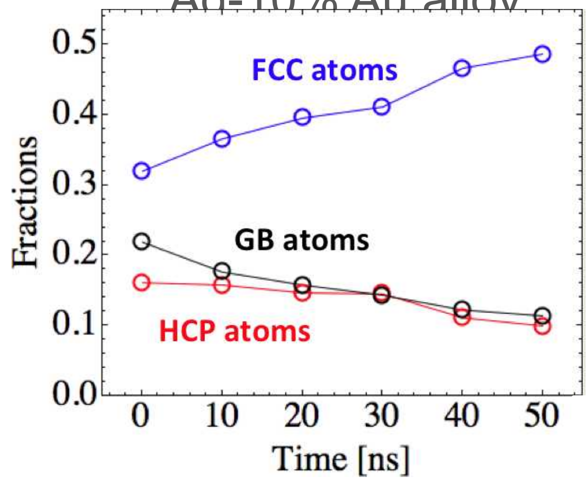
Grain size stabilization (refinement!) observed for alloys with ***miscibility gap*** only

pure Ag slabs



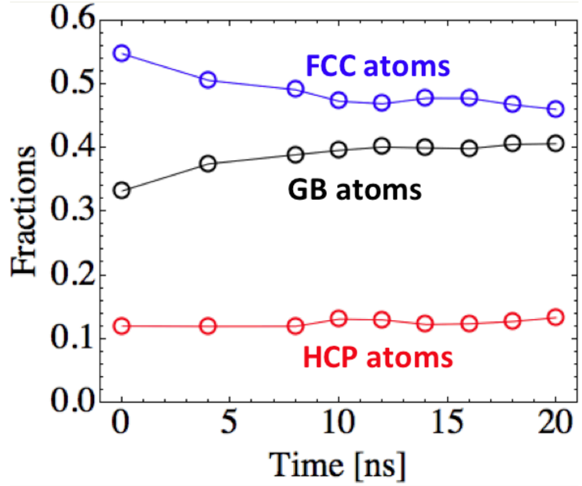
grain coarsening

high solubility system
Ag-10% Au alloy



grain coarsening

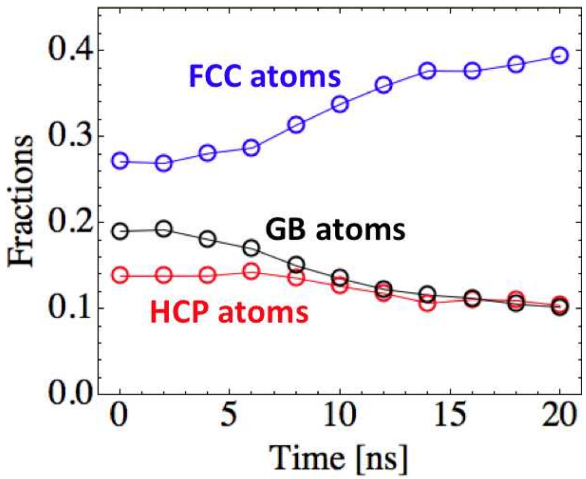
negligible solubility system
Ag-10% Cu alloy



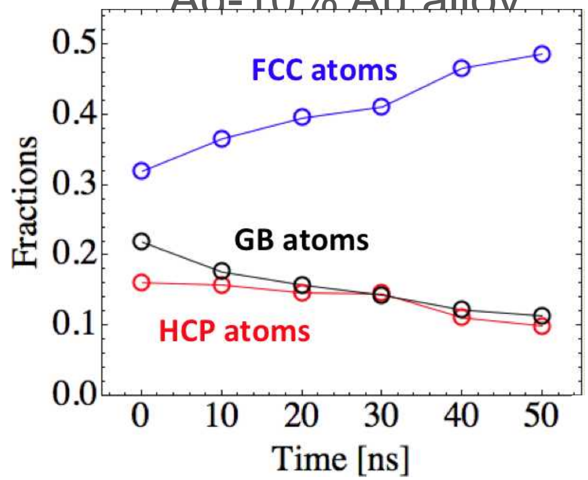
grain refinement!

Grain size stabilization (refinement!) observed for alloys with *miscibility gap* only

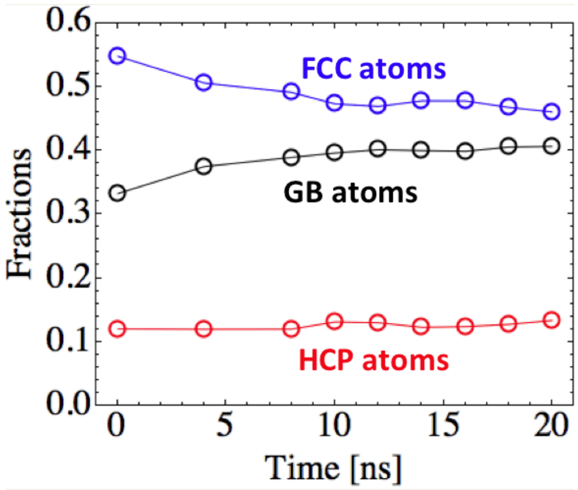
pure Ag slabs



high solubility system
Ag-10% Au alloy



negligible solubility system
Ag-10% Cu alloy



- Experiments: alloys stabilize grain boundaries, prevent grain growth
- Simulations: alloys prevent grain growth through lattice mismatch
- Both: Lack of grain growth avoids formation of commensurate interface, lowering friction

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

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):

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

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; INDENTION CRACKING
ULTRA MILD WEAR	

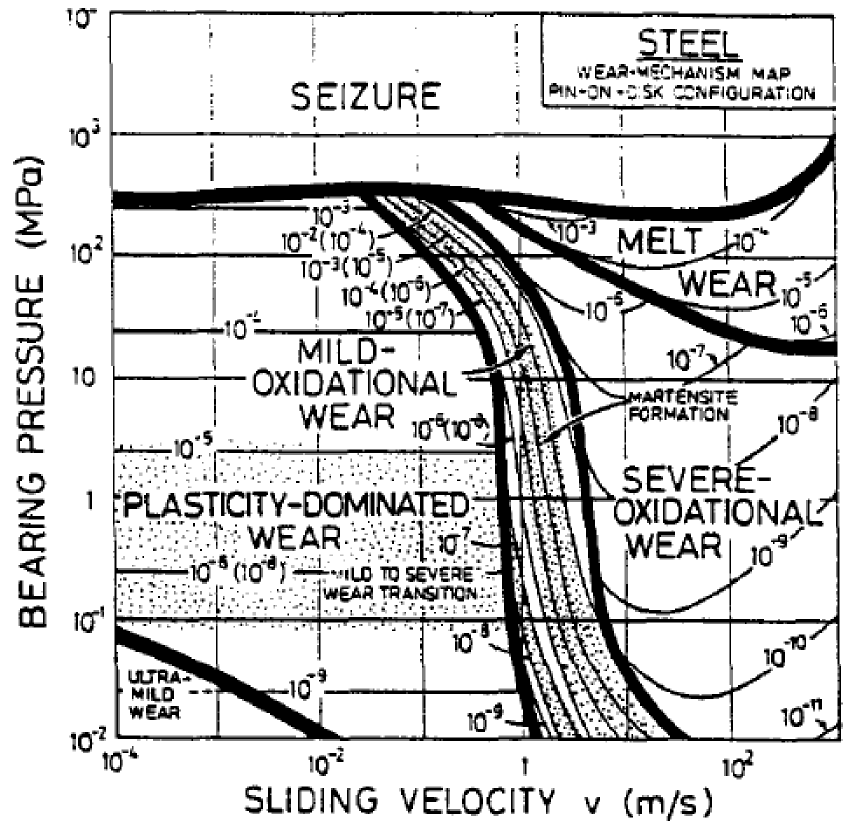
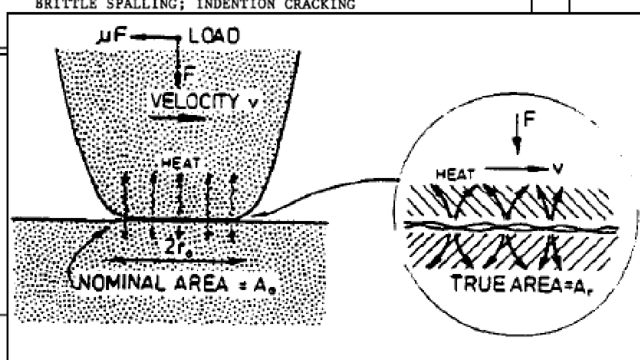
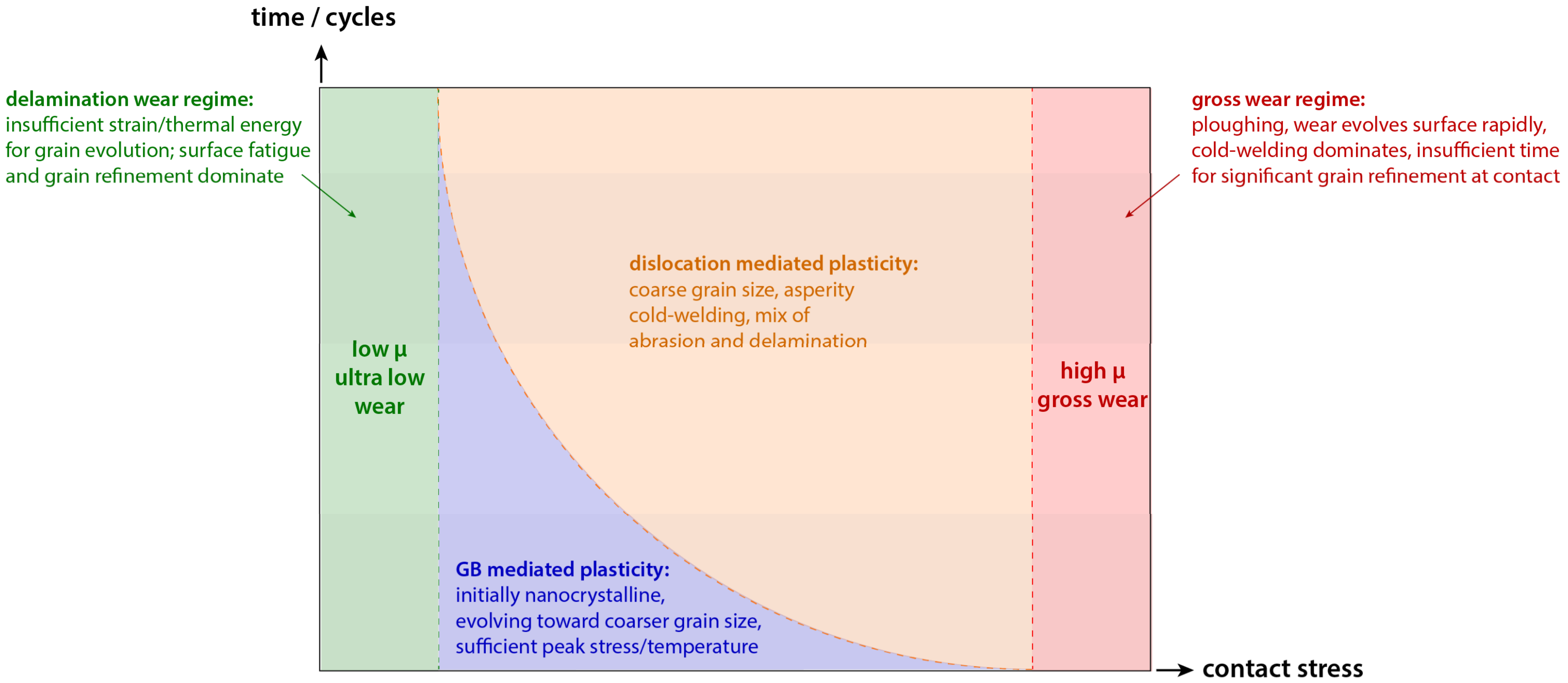


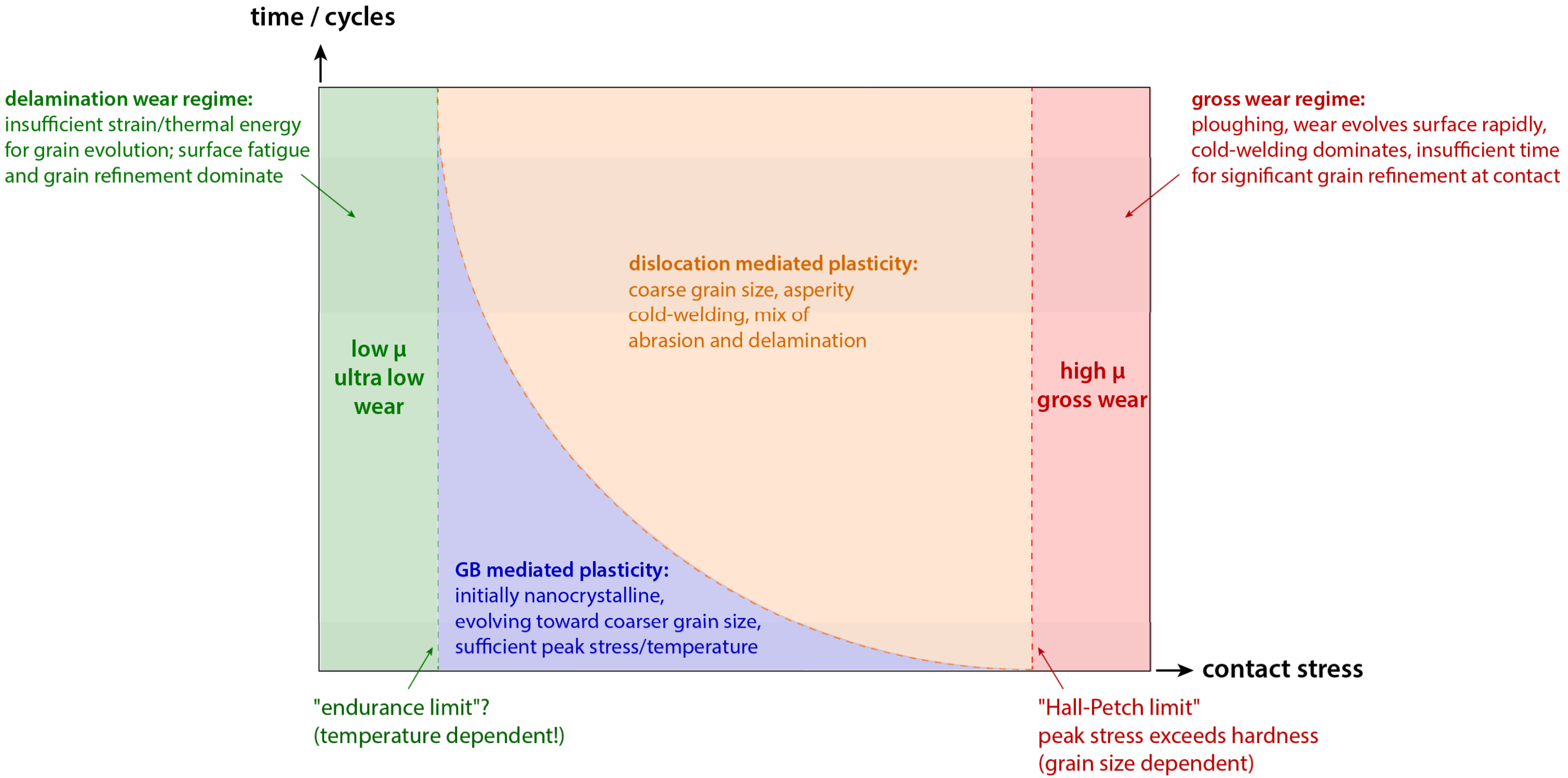
Figure 3. A wear-mechanism map for low-carbon steel based on physical modelling calibrated to experiments. The shaded regions show transitions.



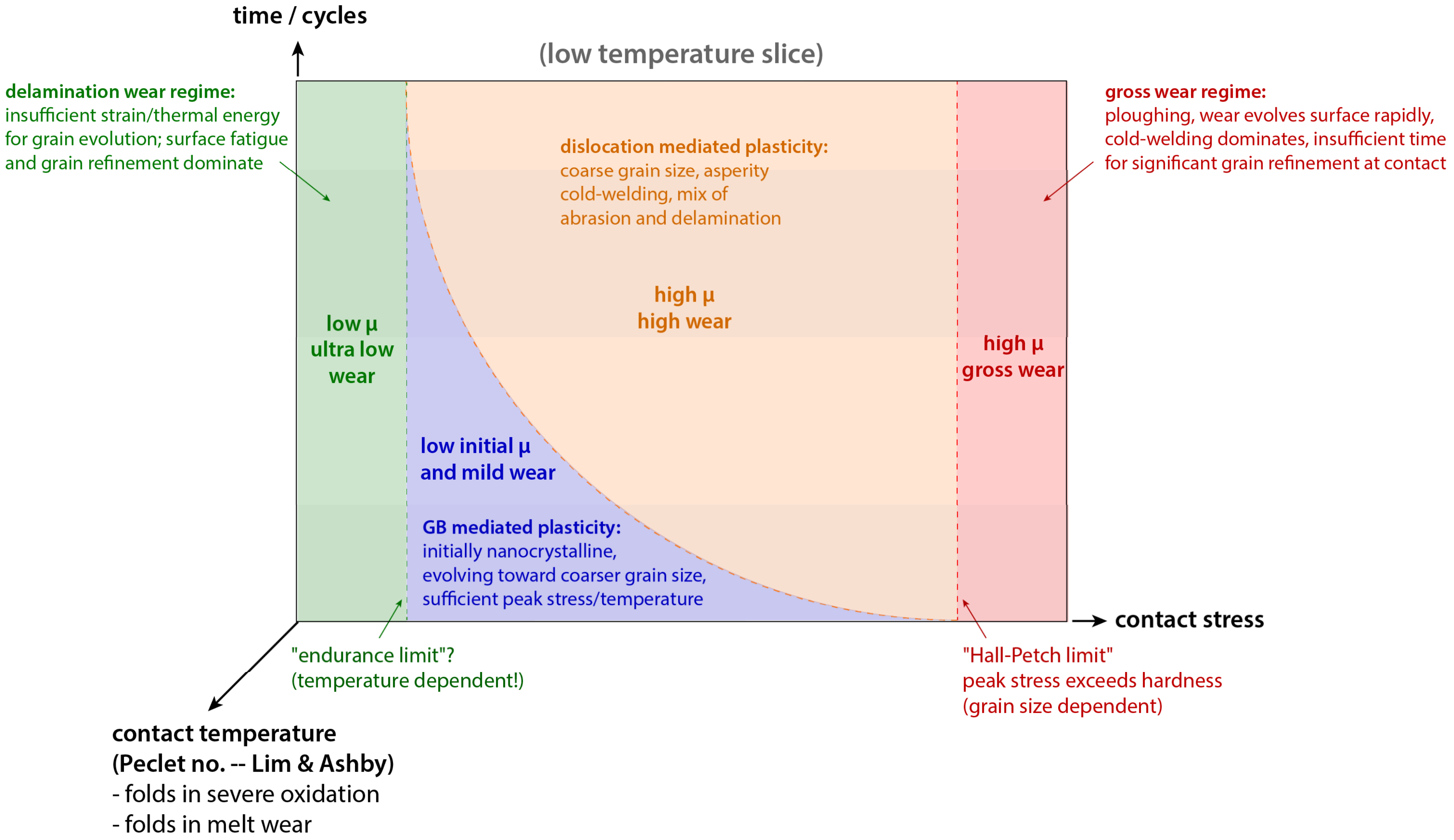
What would a metals tribological behavior map look like founded on GB stability?



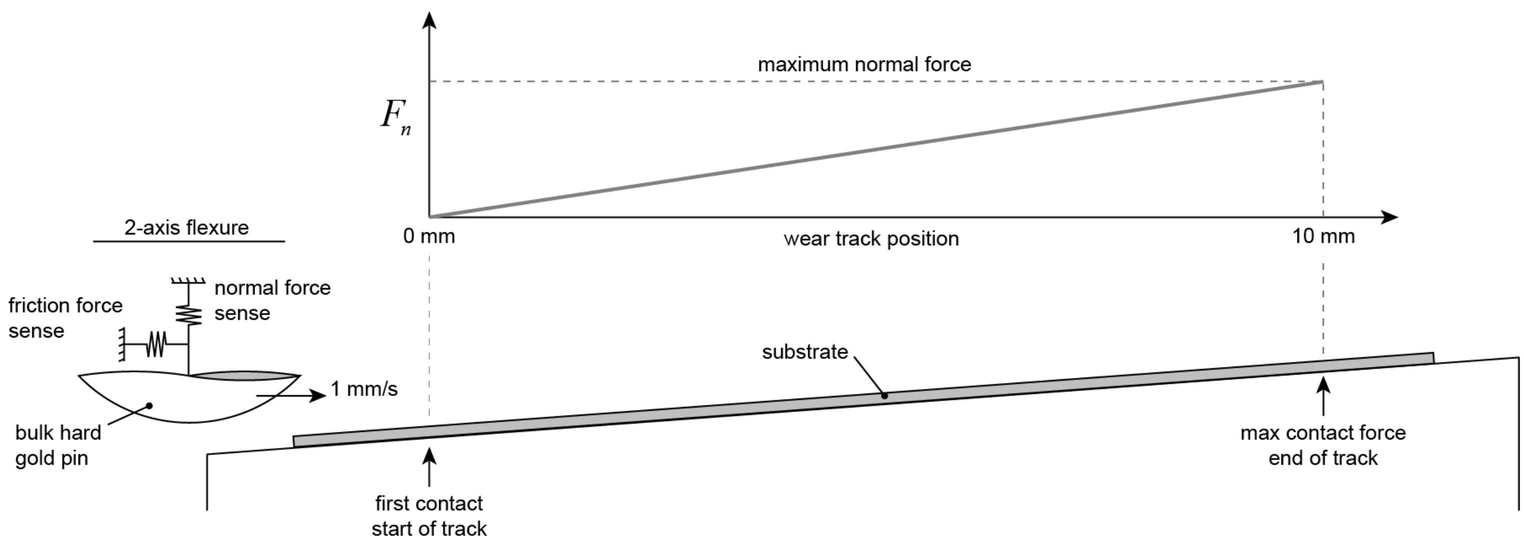
What would a metals tribological behavior map look like founded on GB stability?



What would a metals tribological behavior map look like founded on GB stability?

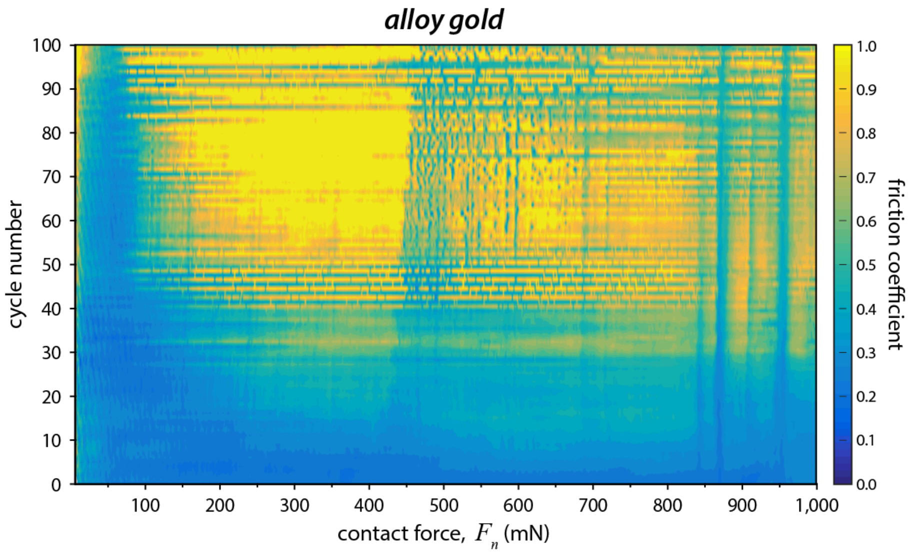


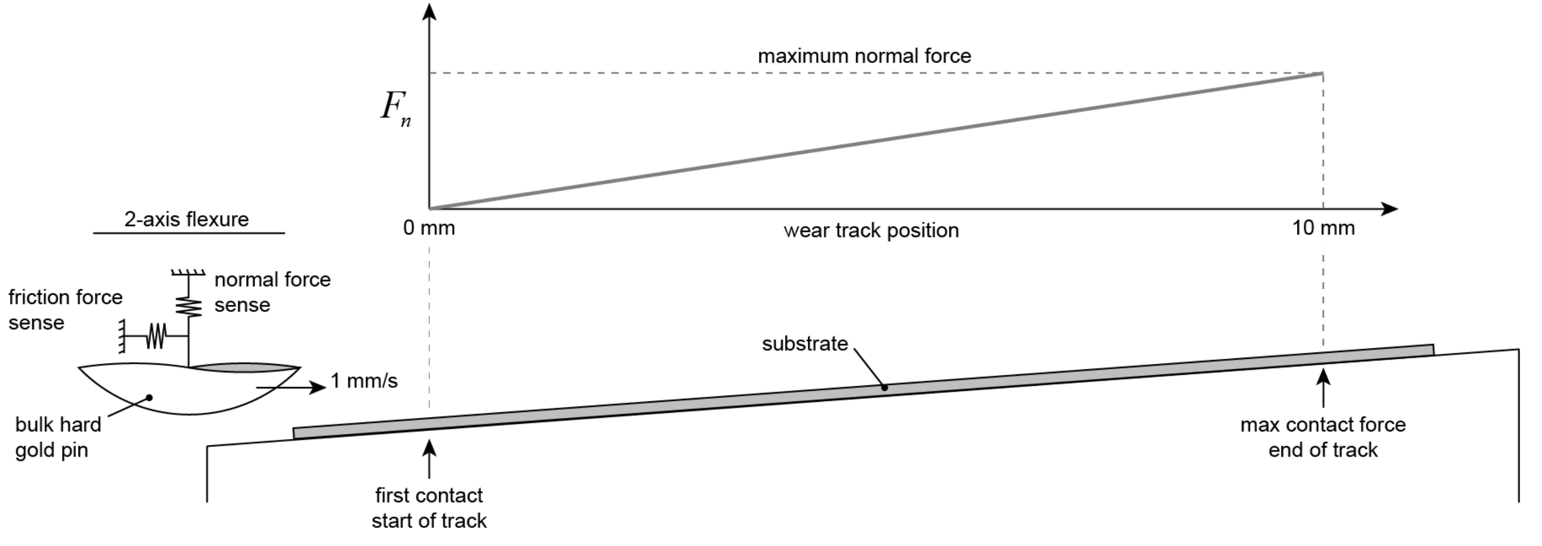
Ramped contact force experiments with self-mated pure and alloyed gold



Friction maps for bulk alloy gold vs electroplated hard gold supports the model!

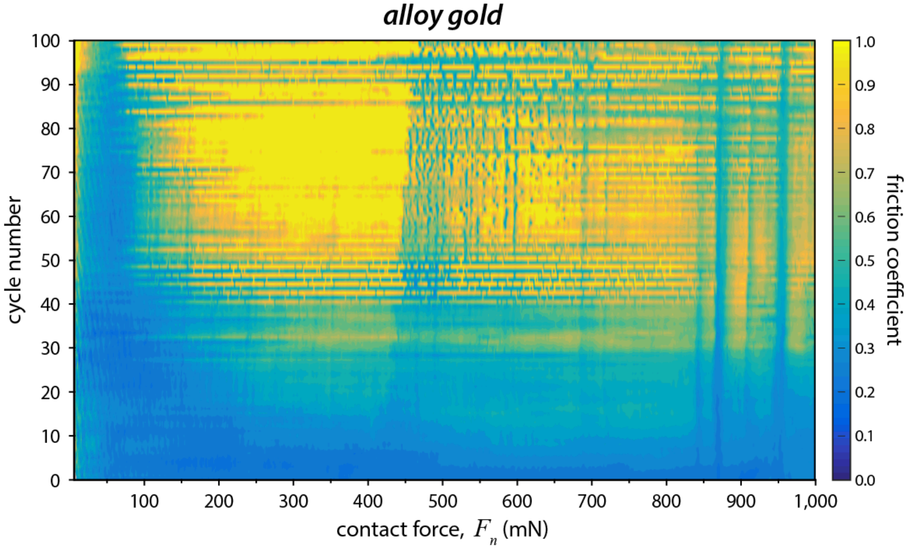
Contact force ramped from 0 to 1N along 10 mm long wear track
1 mm/s sliding speed

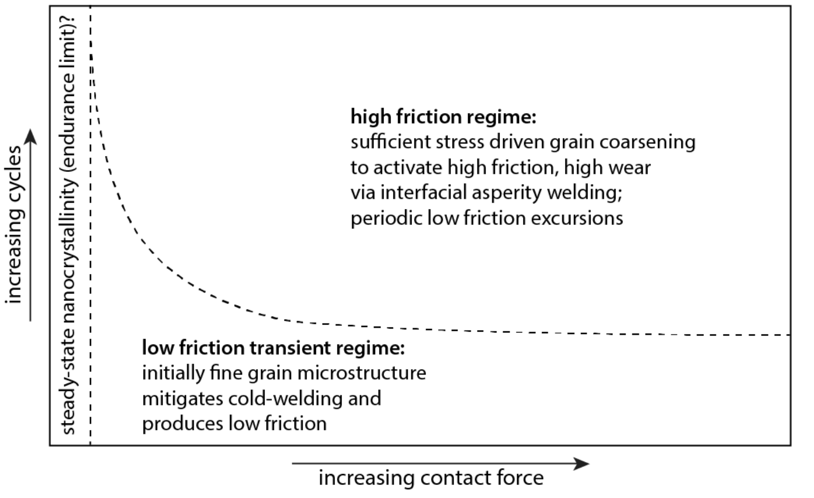




Friction maps for bulk alloy gold vs electroplated hard gold supports the model!

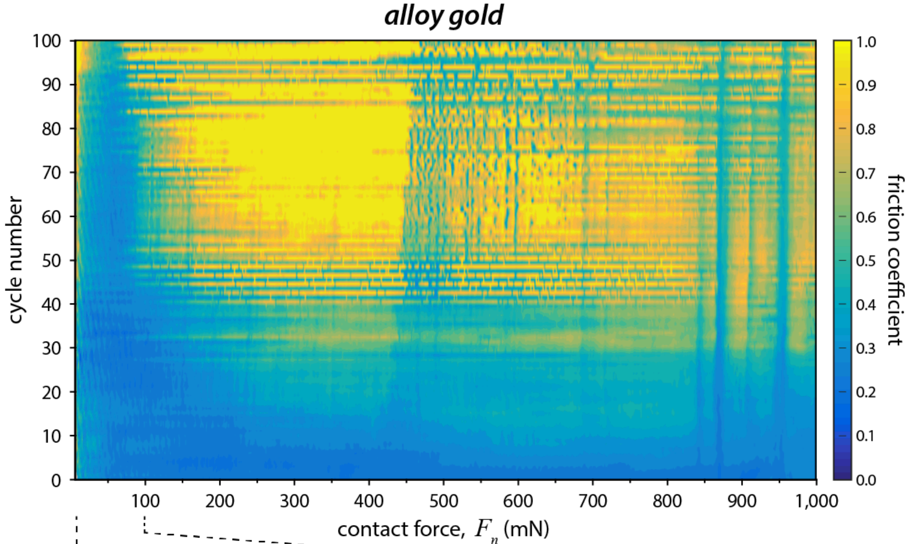
Contact force ramped from 0 to 1N along 10 mm long wear track
1 mm/s sliding speed

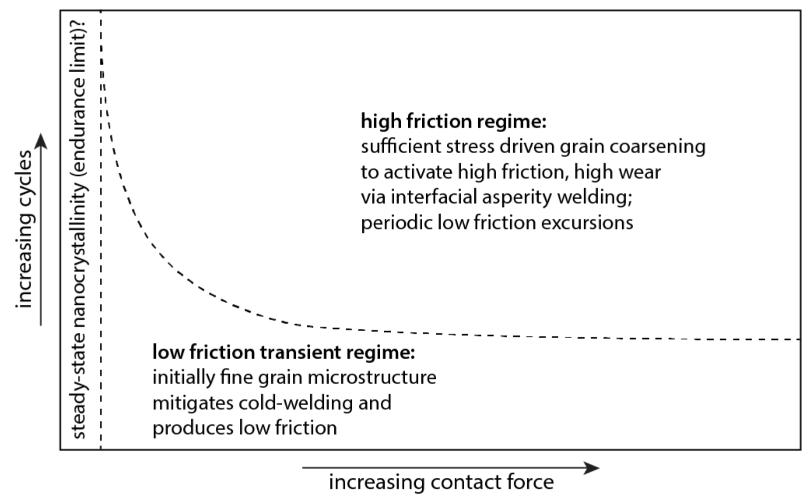


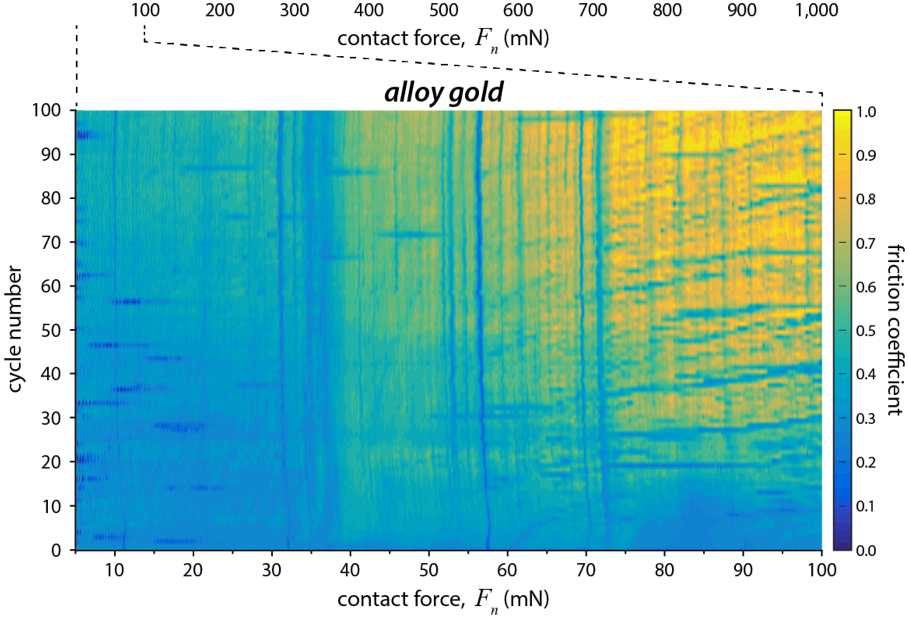


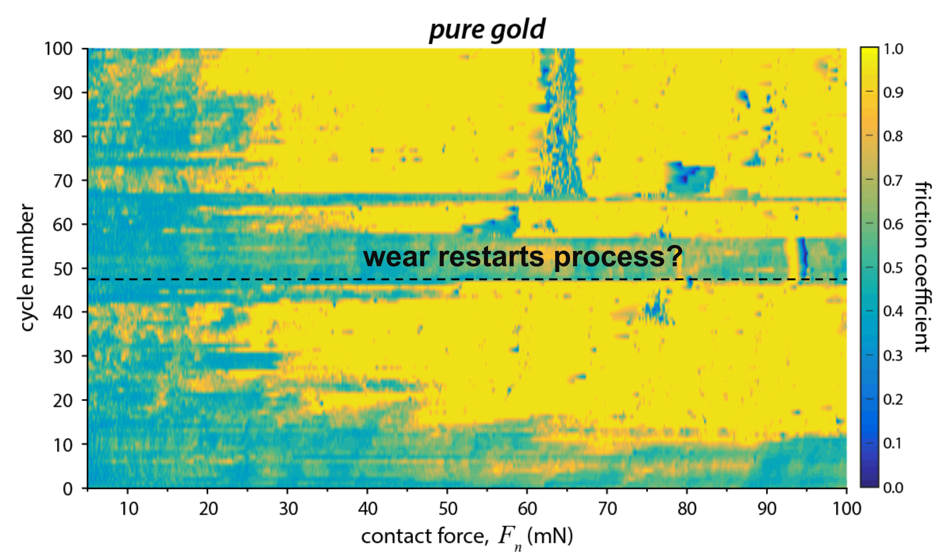
Now comparing hard gold to pure gold… again, envelope is observed

Contact force ramped from 0 to 1N along 10 mm long wear track
1 mm/s sliding speed



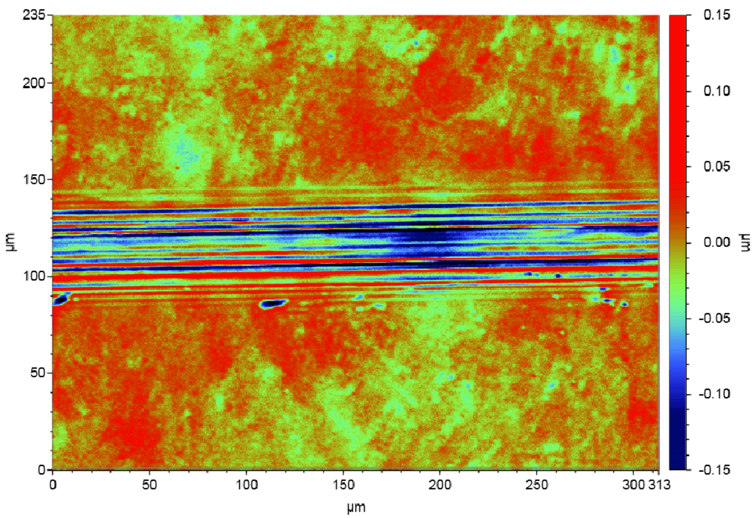






Wear analysis of pure and alloy gold surfaces along wear track for ramped force test

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



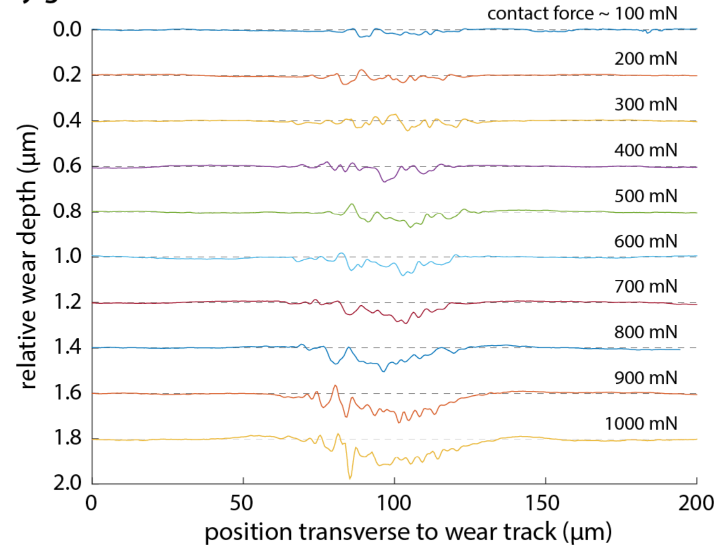
Images taken at 1 mm intervals along 10 mm long wear tracks

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

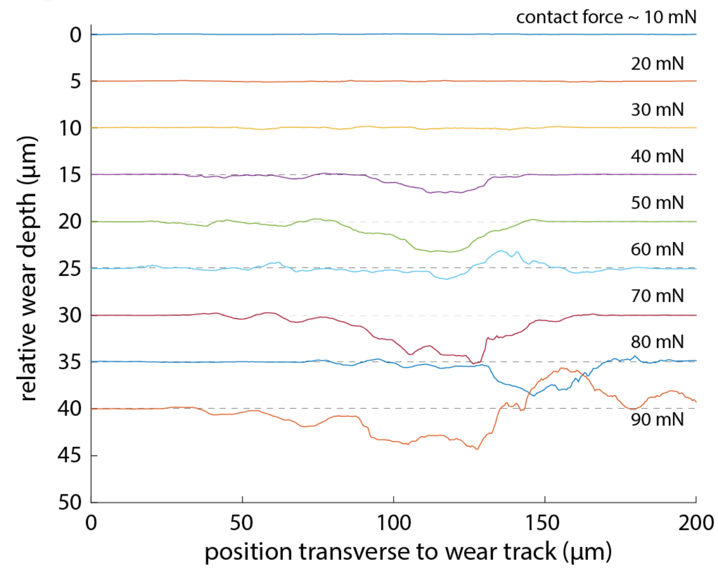
Wear at each interval calculated based on contact force average in this part of the track, number of cycles, and volume loss

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

alloy gold film surface evolution

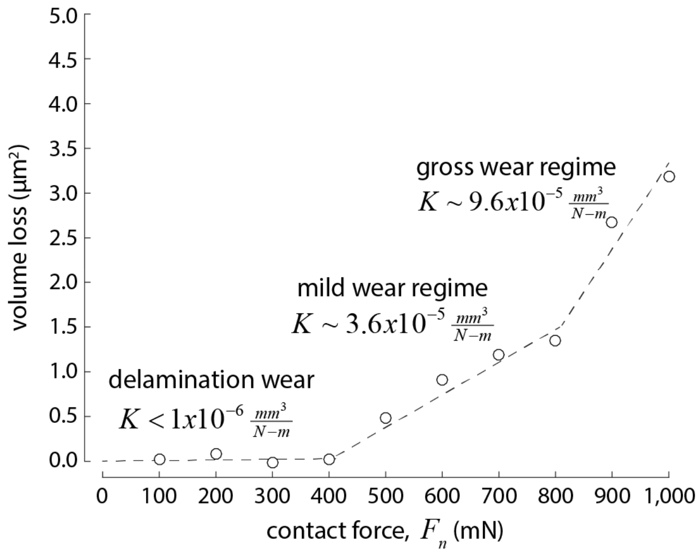


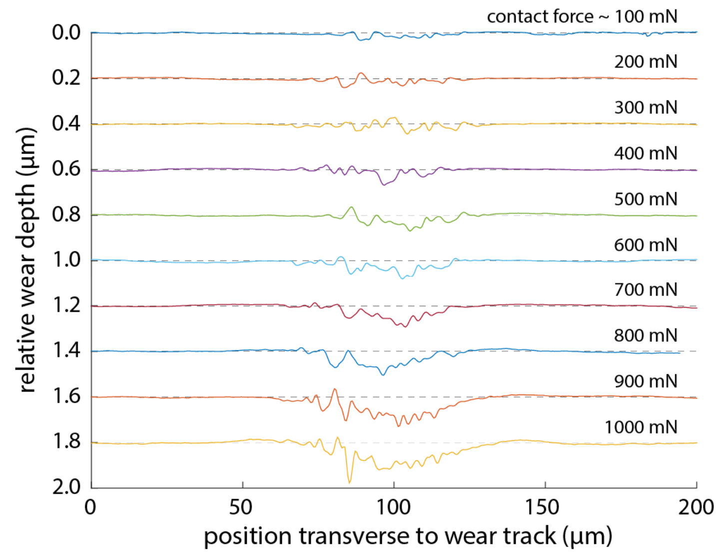
pure gold substrate surface evolution



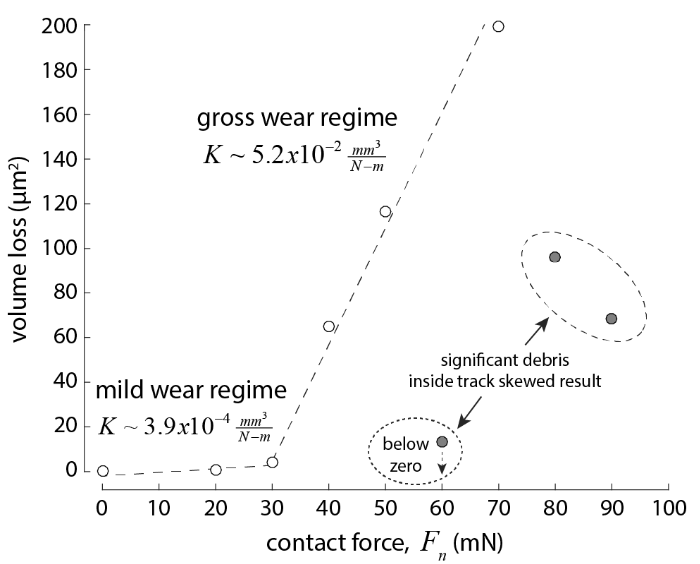
Observed three wear regimes

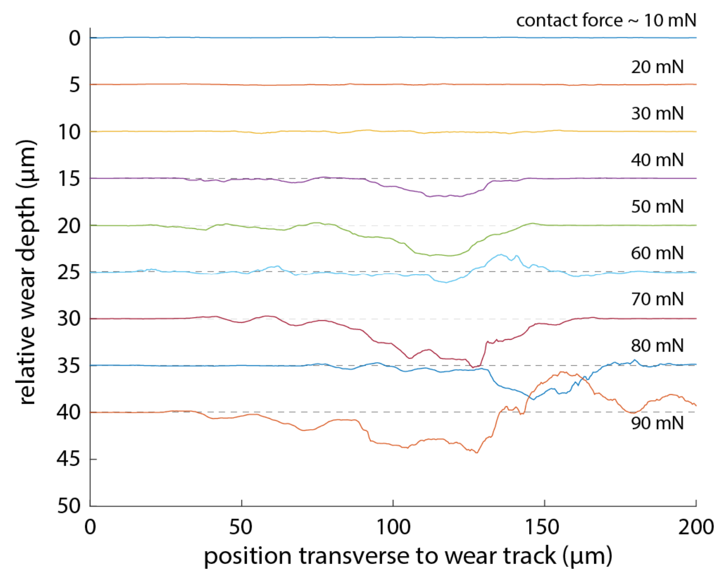
alloy gold film surface evolution





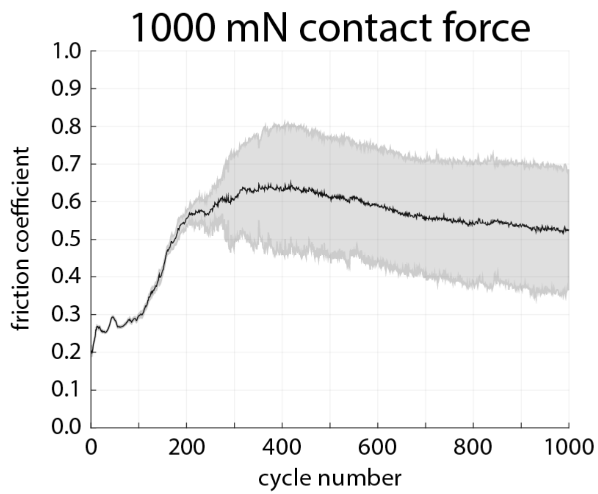
pure gold substrate surface evolution





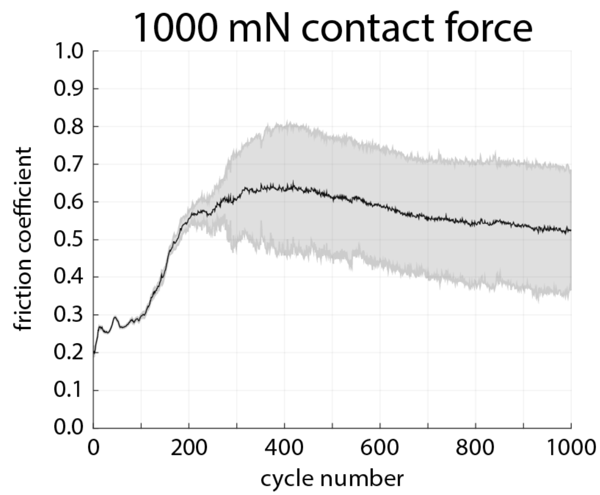
Three regimes observed for 60Ni-40W at.% vs sapphire in oxidizing environment

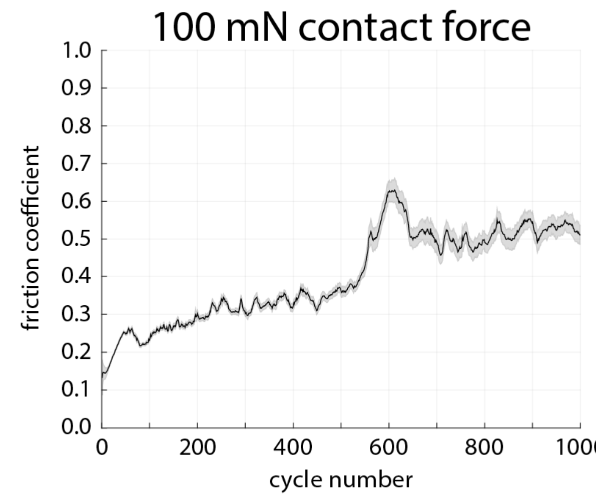
1 mm/s sliding speed
three contact forces used
bidirectional sliding
2mm long track
sapphire ball 1.6 mm diameter
sliding in ***lab air***



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

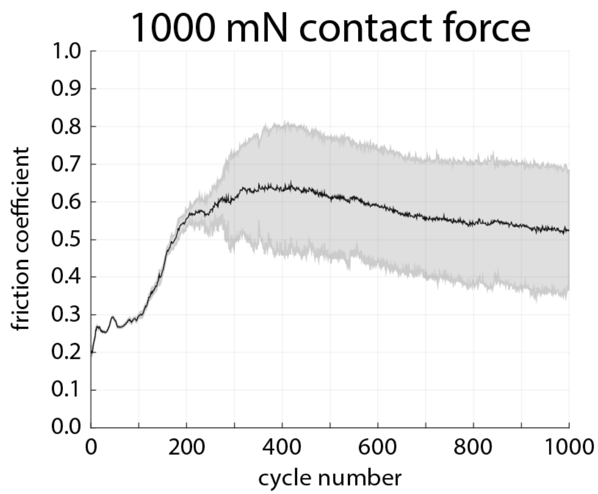
1 mm/s sliding speed
three contact forces used
bidirectional sliding
2mm long track
sapphire ball 1.6 mm diameter
sliding in ***lab air***

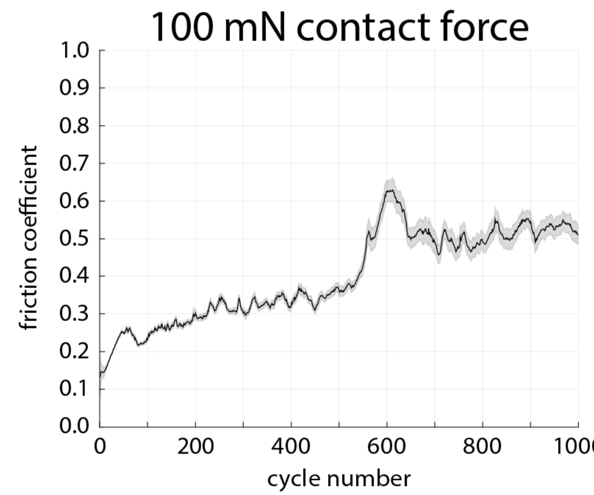


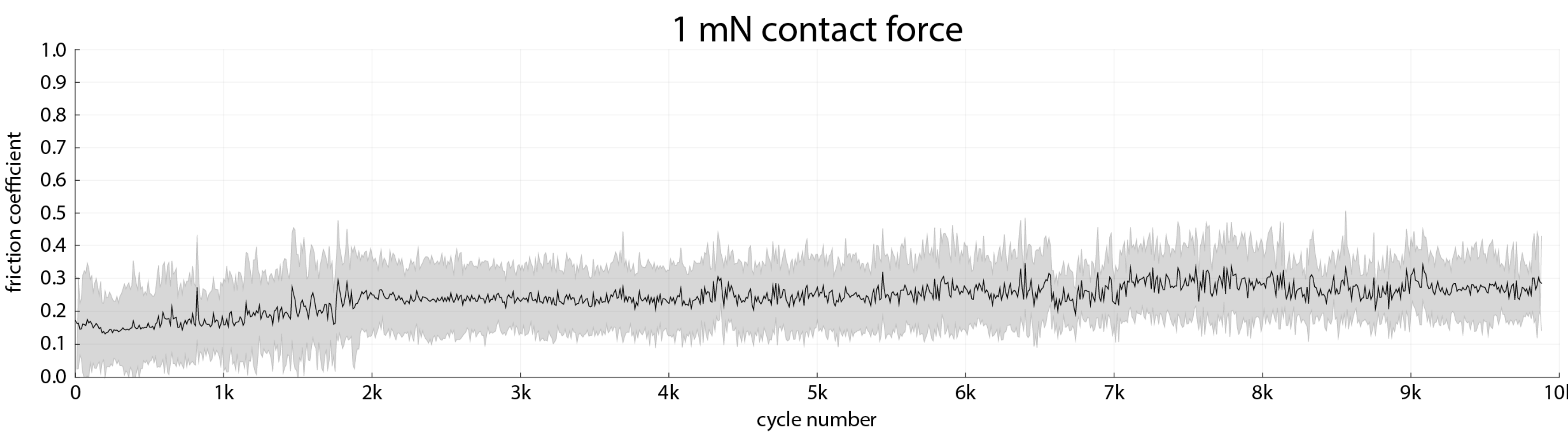


Three regimes observed for 60Ni-40W at.% vs sapphire in oxidizing environment

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

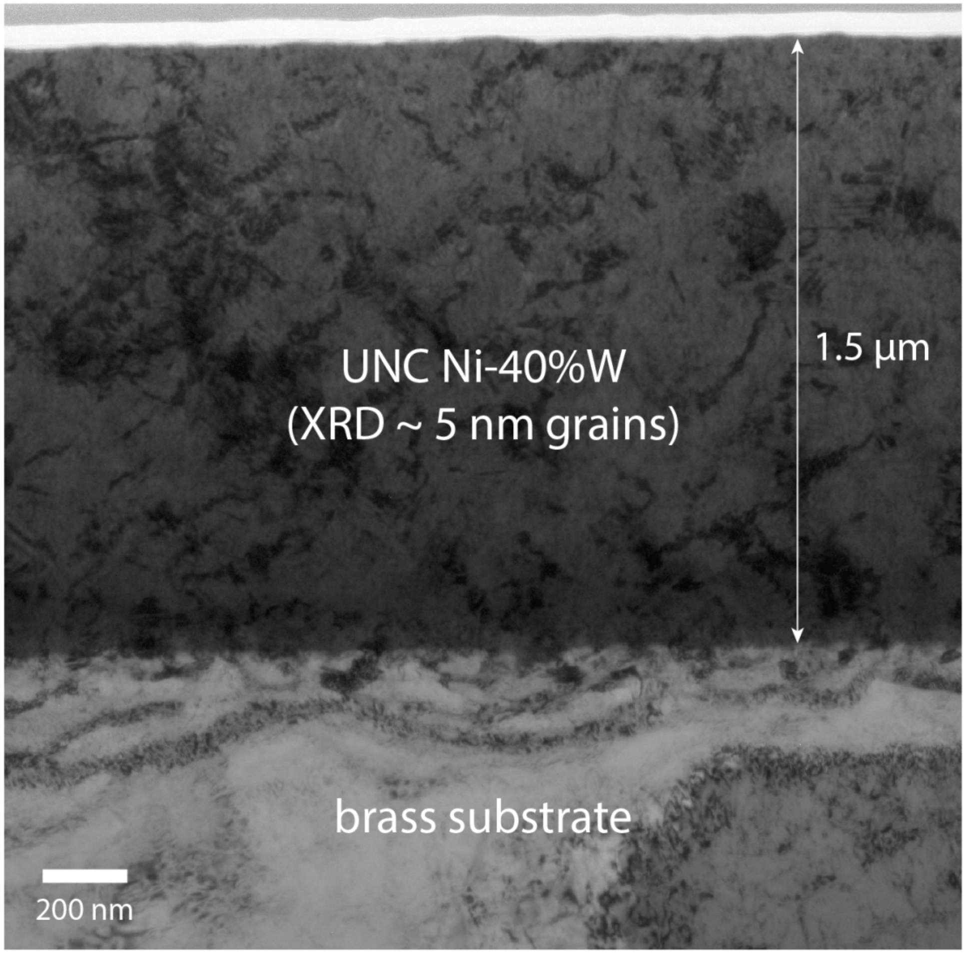






FIB-TEM wear track cross-section of 1 mN normal force / 10k cycle test

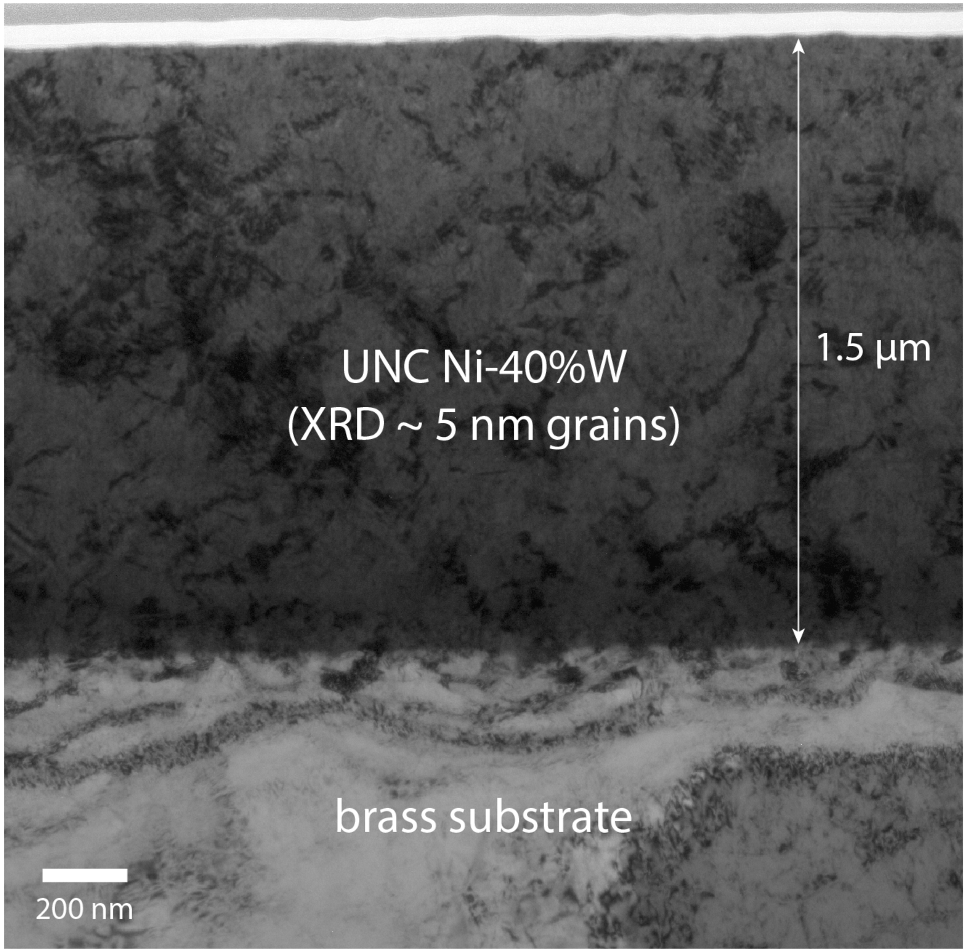
off-track reference



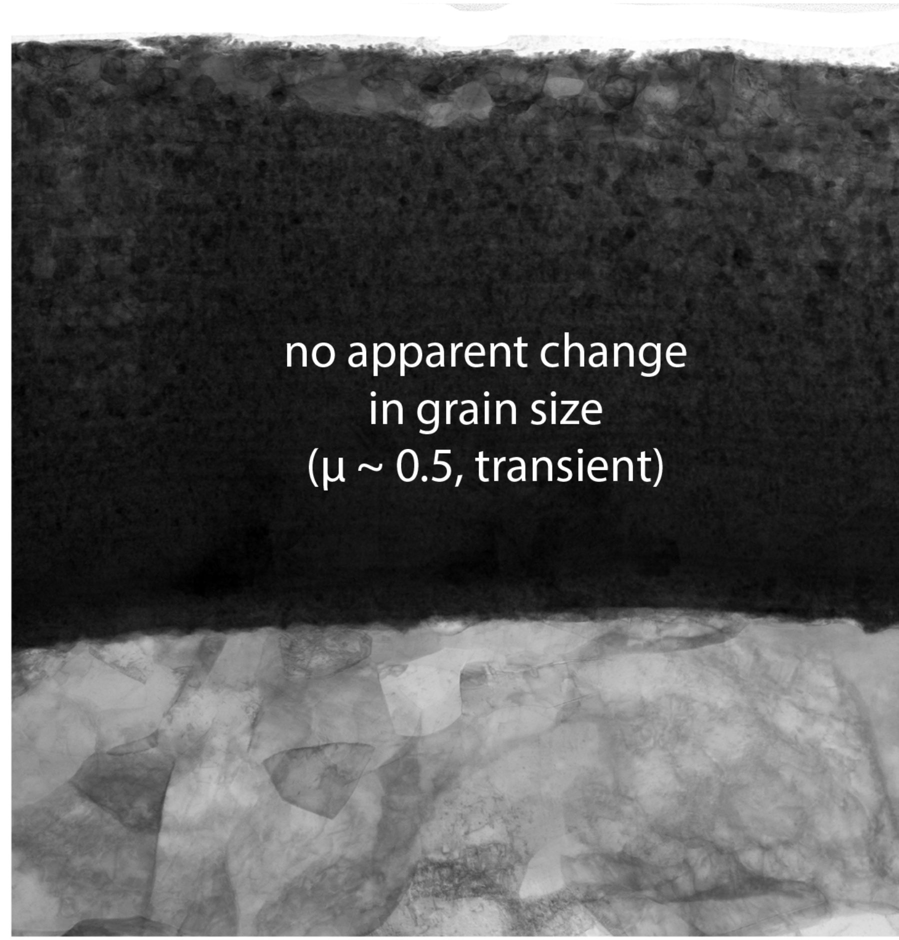
1 mN, 10k cycles track

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

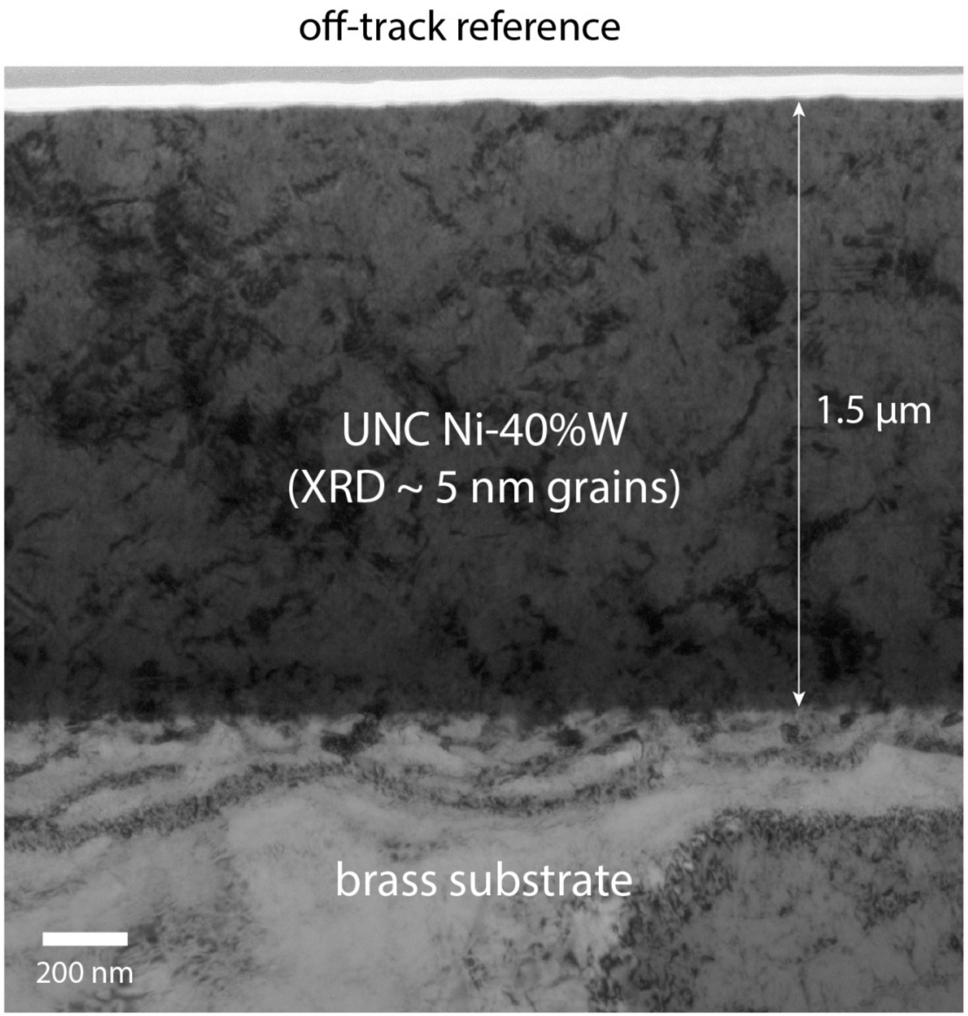
off-track reference

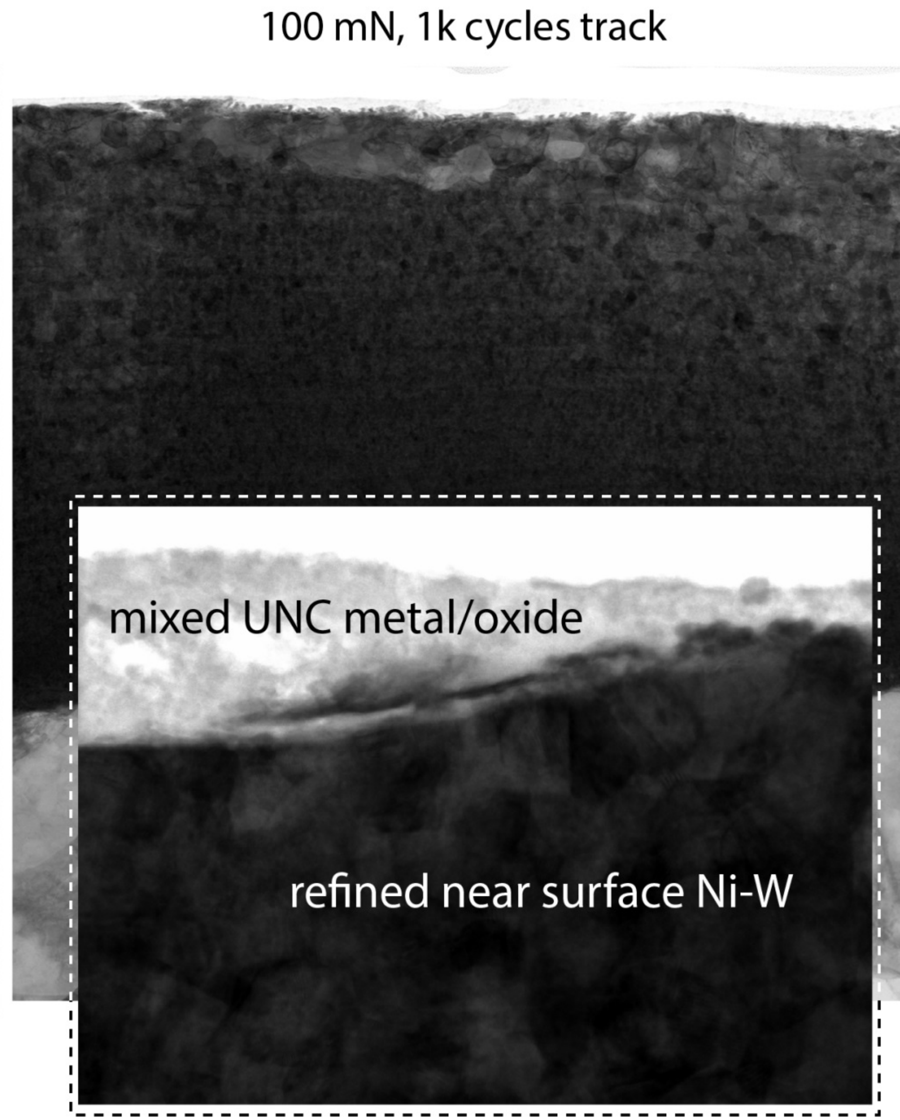


100 mN, 1k cycles track



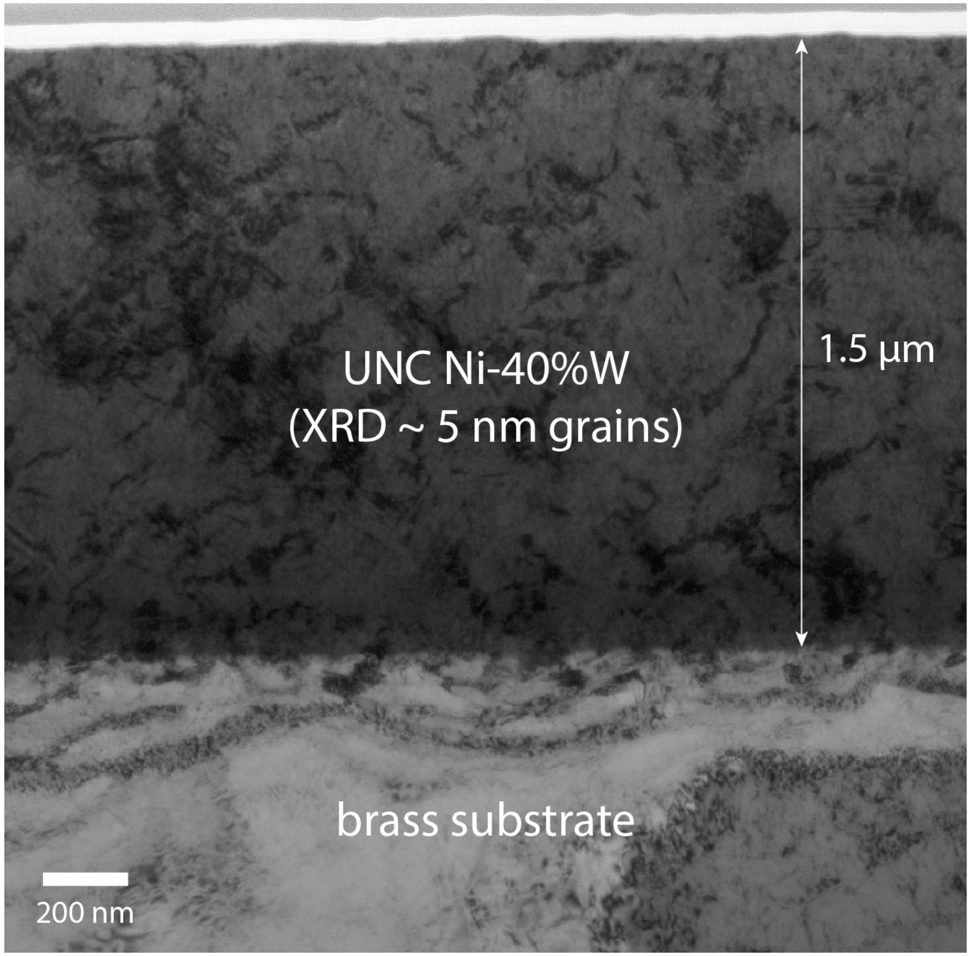
FIB-TEM wear track cross-section of 100 mN normal force / 1k cycle test



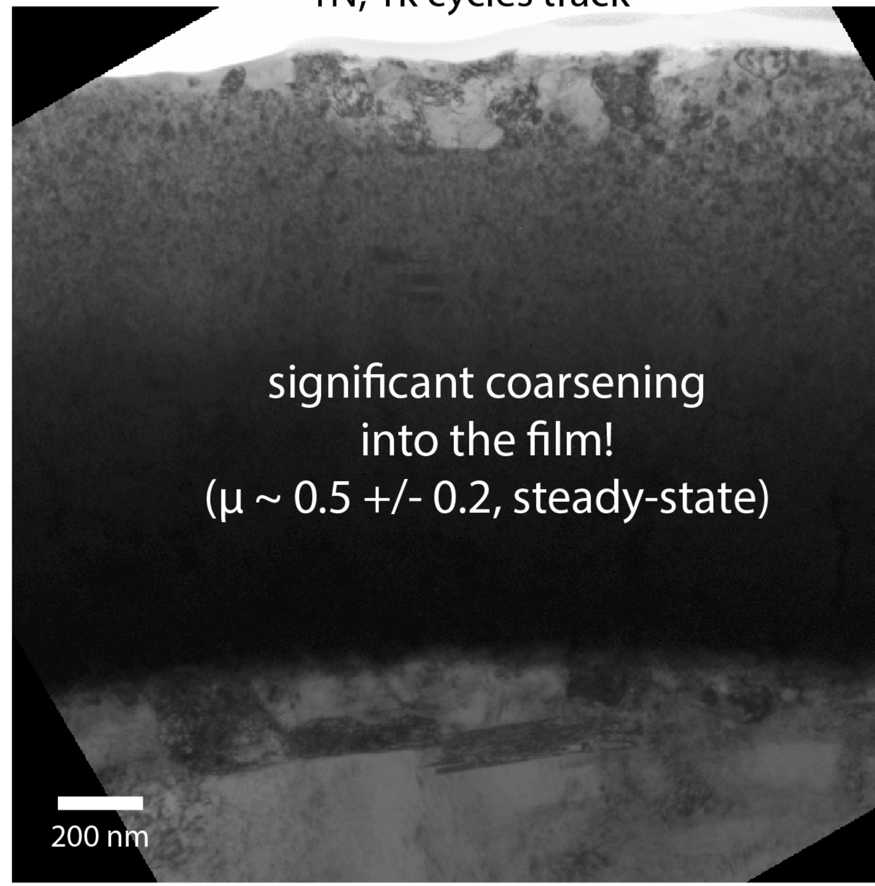


FIB-TEM wear track cross-section of 1000 mN normal force / 1k cycle test

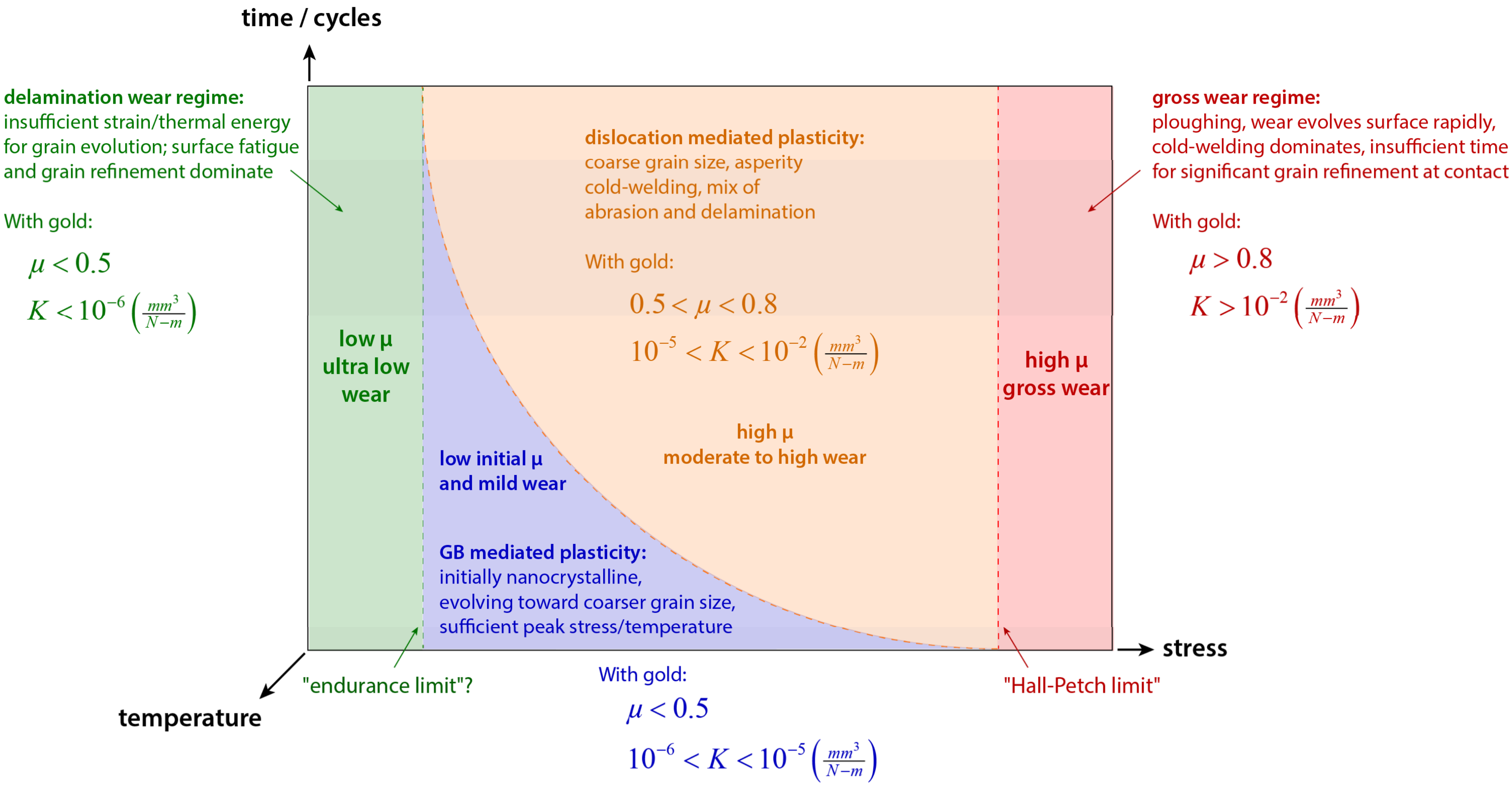
off-track reference



1N, 1k cycles track



General Tribological Behavior Map for Metals, Alloys and Metal-Matrix Composites



General Model: Proposed Dimensionless Parameters… Valid? Others?

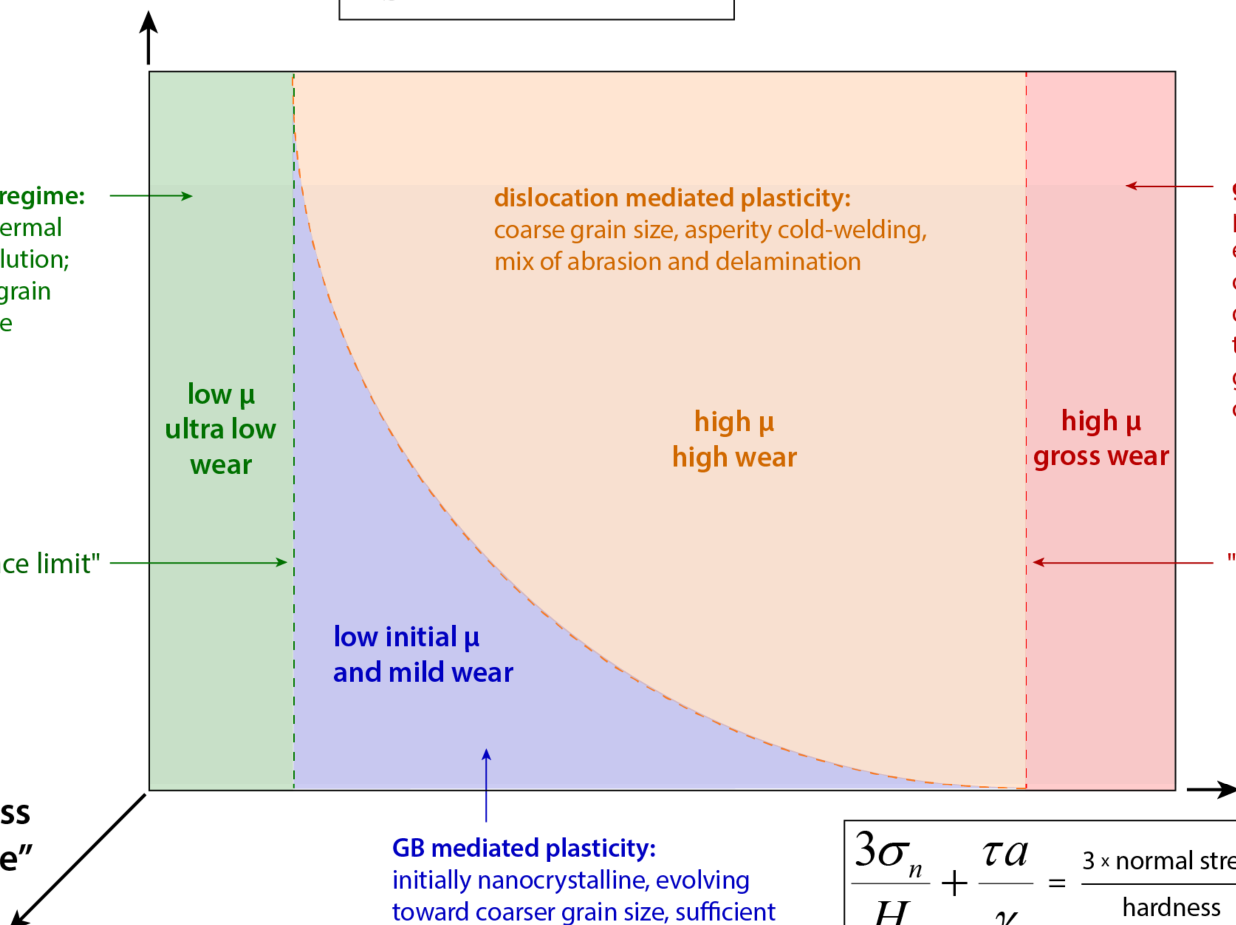
dimensionless "time" parameter,

$$\frac{Mt}{s} = \frac{\text{GB mobility} \times \text{time}}{\text{sliding distance}}$$

delamination wear regime: insufficient strain/thermal energy for grain evolution; surface fatigue and grain refinement dominate

dislocation mediated plasticity: coarse grain size, asperity cold-welding, mix of abrasion and delamination

gross wear regime: ploughing, wear evolves surface rapidly, cold-welding dominates, insufficient time for significant grain refinement at contact



"endurance limit"

"Hall-Petch limit"

dimensionless "stress" parameter,

$$\frac{3\sigma_n}{H} + \frac{\tau a}{\gamma} = \frac{3 \times \text{normal stress}}{\text{hardness}} + \frac{\text{shear stress} \times \text{contact radius}}{\text{GB energy}}$$

GB mediated plasticity: initially nanocrystalline, evolving toward coarser grain size, sufficient peak stress/temperature

dimensionless "temperature" parameter,

$$\frac{kT}{d^2\gamma_o} = \frac{\text{thermal energy}}{\text{grain size}^2 \times \text{GB energy}}$$

Appendix Slides

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

Regular Nanocrystalline Solution (RNS) model

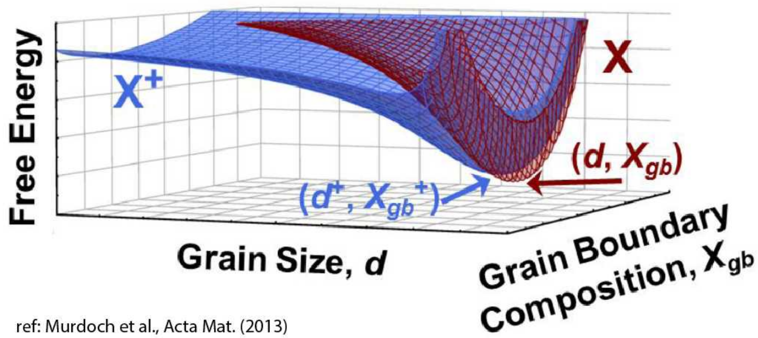
ref: Chookajorn et al., Science, 2012

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

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

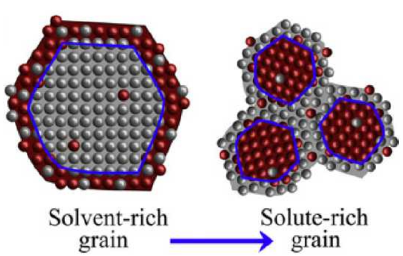
Implications:
Will not drive toward fine grain size, but will remain there

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



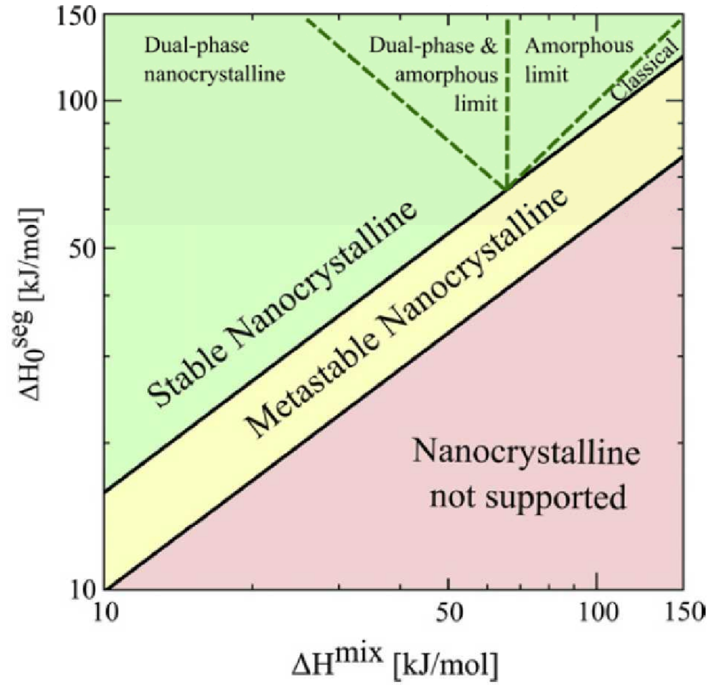
ref: Murdoch et al., Acta Mat. (2013)

Grain structure model: segregated 2-phase metal system:



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

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



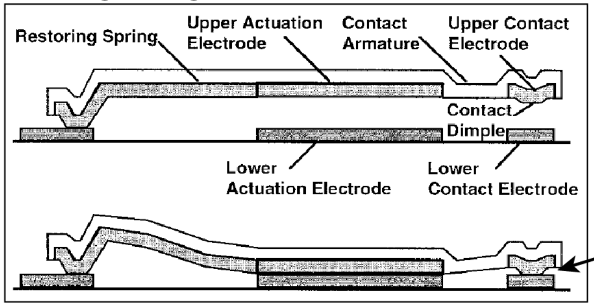
$$\Delta H_o^{seg} = z\left(\omega_c - \frac{\omega_{gb}}{2}\right) \qquad \Delta H^{mix} = z\omega_c X(1 - X)$$

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

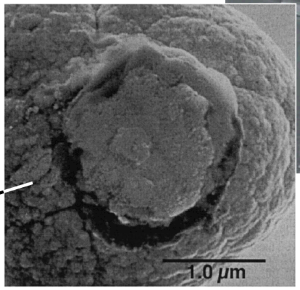
Investigations will focus on noble metal films – high impact and simpler (no oxides)

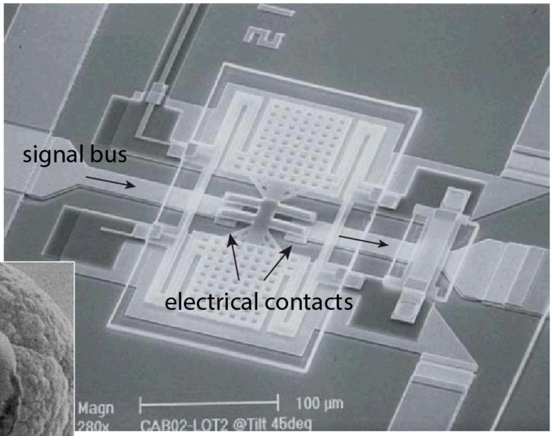
MEMS: 1-2 µm thick <u>pure and alloyed gold</u> films are found in billion cycle life devices

switching GHz signals



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

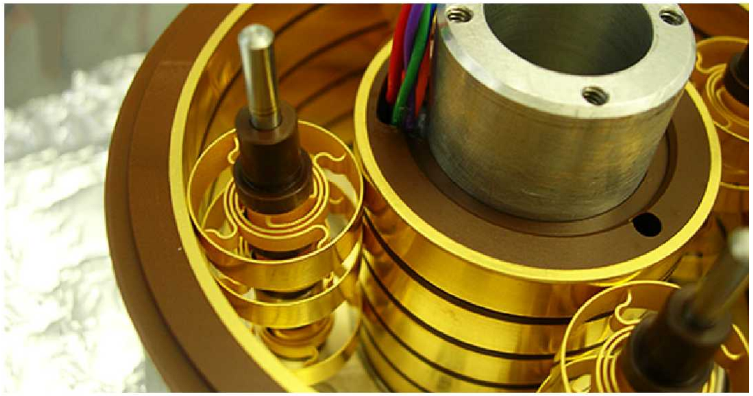




Source: Rockwell Scientific metal-metal switch

Electronics (printed circuit boards, PCBs): 200 - 500 nm thick <u>electroless hard gold</u> films on soldered connections to prevent oxidation on PCBs

Aerospace: 1 - 3 µm thick <u>hard gold</u> (ASTM/MilSpec) used to achieve predictable friction AND contact resistance over years or decades for actuators and signal/power slip rings



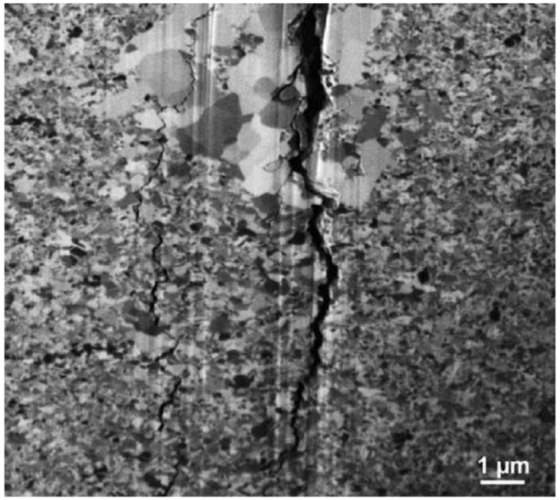
Source: Honeybee Robotics (http://www.honeybeerobotics.com/portfolio/rolling-contact-connector/)

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

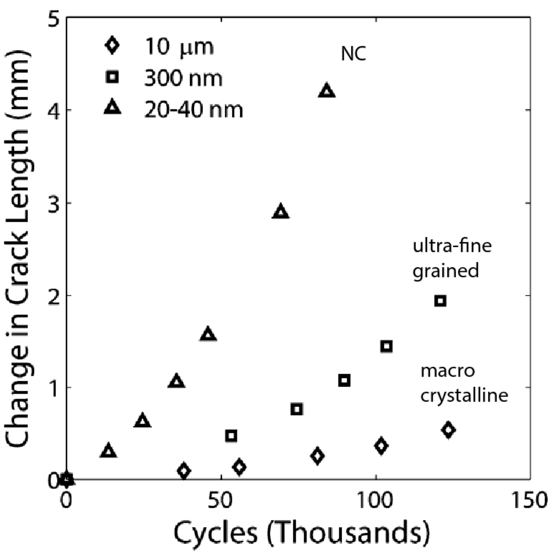
Mechanical (strain) induced grain growth and recrystallization

Fatigue driven grain growth in NC Ni-Mn; initially NC grain structure

Crack initiated in a region where grain growth occurred



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



ref: Hanlon et al., Scripta Mat. (2003)

Crack propagation rates increase with grain refinement

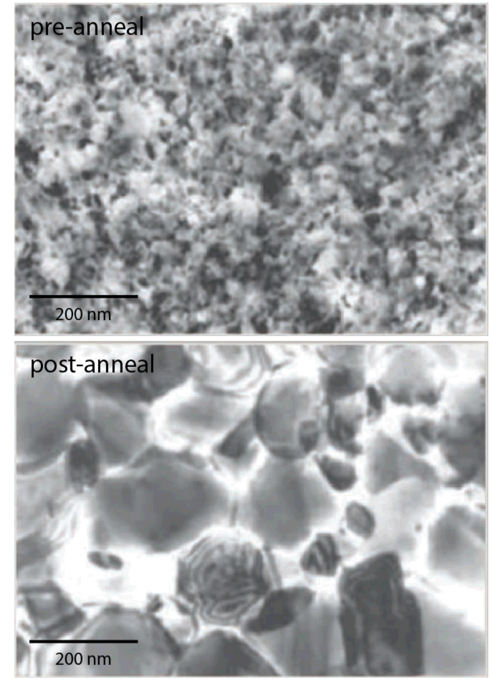
Data collected at stress intensity factor of 11.5 MPa-m$^{1/2}$

Ni system

Thermally induced grain growth and recrystallization

Ni that was initially nanocrystalline after exposure to 300°C for 30 minutes exhibits typical explosive grain growth

This behavior (Ostwald ripening) is driven by thermally activated solid diffusion



Changes in solubility are problematic for stability as well: