SAND2018-3004PE

The Promise of Stable Nanocrystalline Metals:

Ultra-low Wear and Diamond-like Carbon from Thin Air

PRESENTED BY

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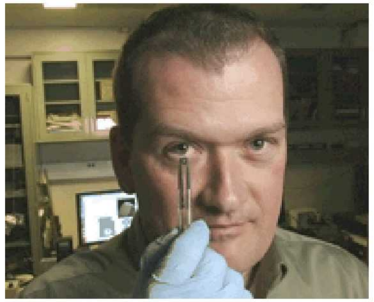
The Team

Experiments


Nic Argibay


Mike Dugger


Andrew Kustas


Tim Furnish


Brad Boyce


Brendan Nation


Minh Pham


Blythe Clark


John Curry


Tomas Babuska

Simulations


Mike Chandross
("Heisenberg")


Adam Hinkle


Chris O'Brien

Synthesis


Dave Adams


Kathy Sobczak

Microscopy

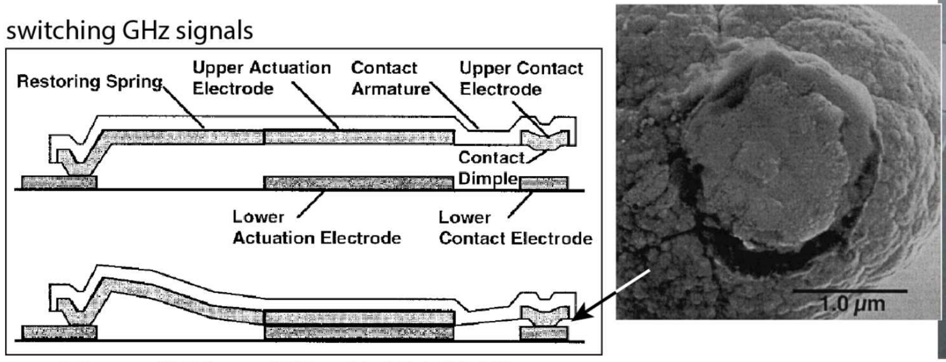

Ping Lu


Mark Rodriguez

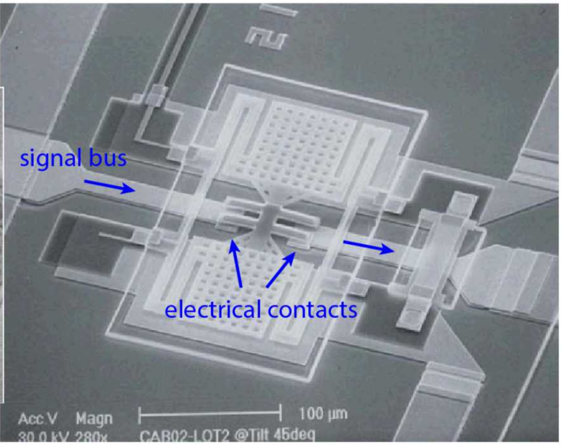
Where Metals Matter in Tribology - Electrical Contacts

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

Phone Interconnects

Electronics (e.g. PCB blade connectors):

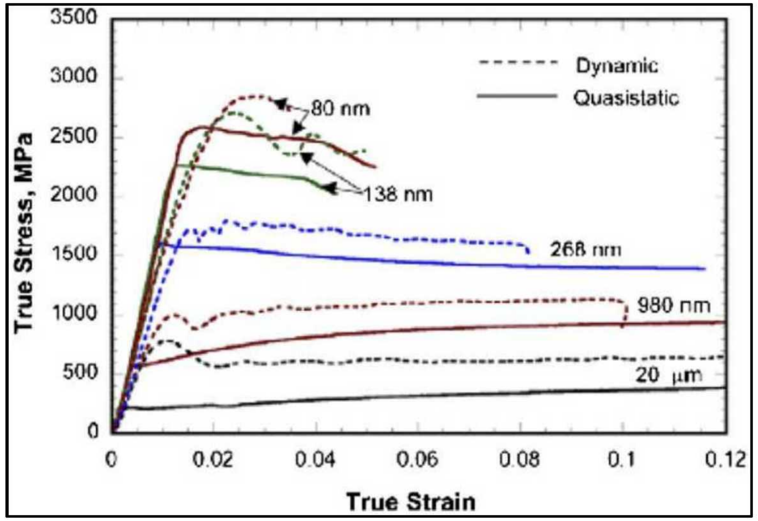
200 - 500 nm thick electroless hard gold

Aerospace and Energy

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

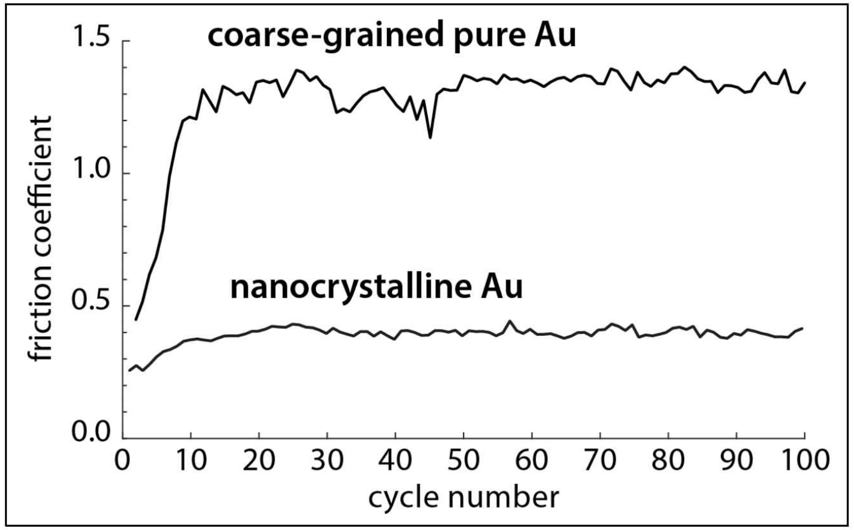
The Nanocrystalline Promise

ref: D. Jia, et al. Acta Mat 2003.



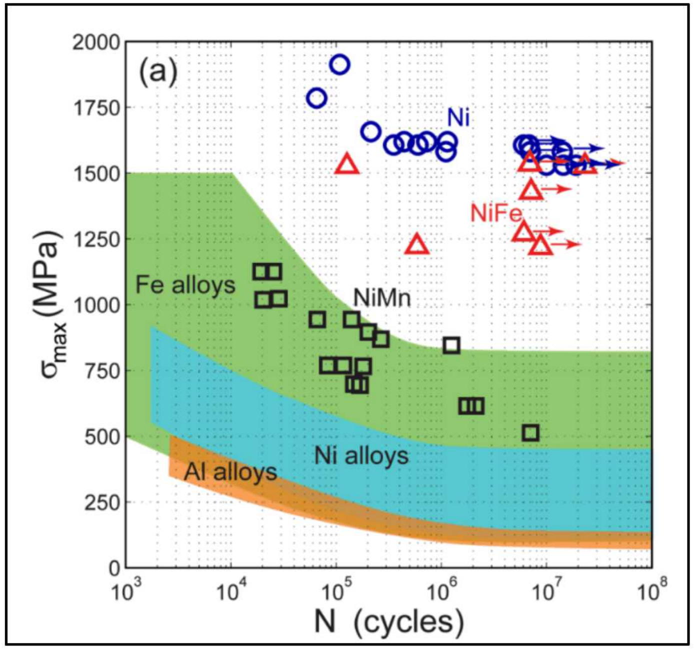
High Tensile Strength

Nanocrystalline metals have many advantages…



Low friction (& wear)

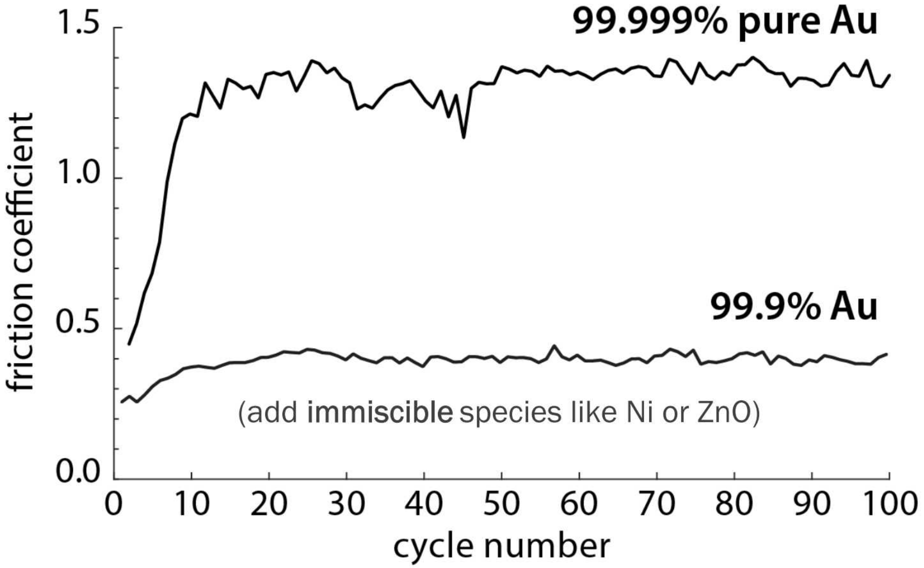
ref: B. L. Boyce et al. Met Trans 2011.



High Fatigue Strength

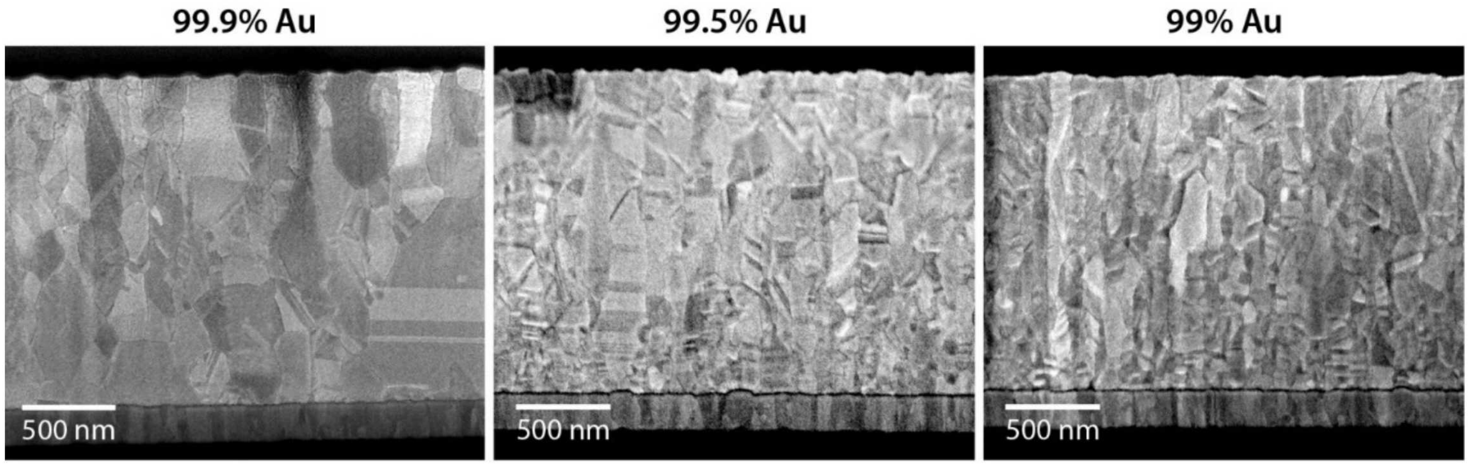
Reduced friction and wear of nanocrystalline metals

Alloying reduces friction coefficient:

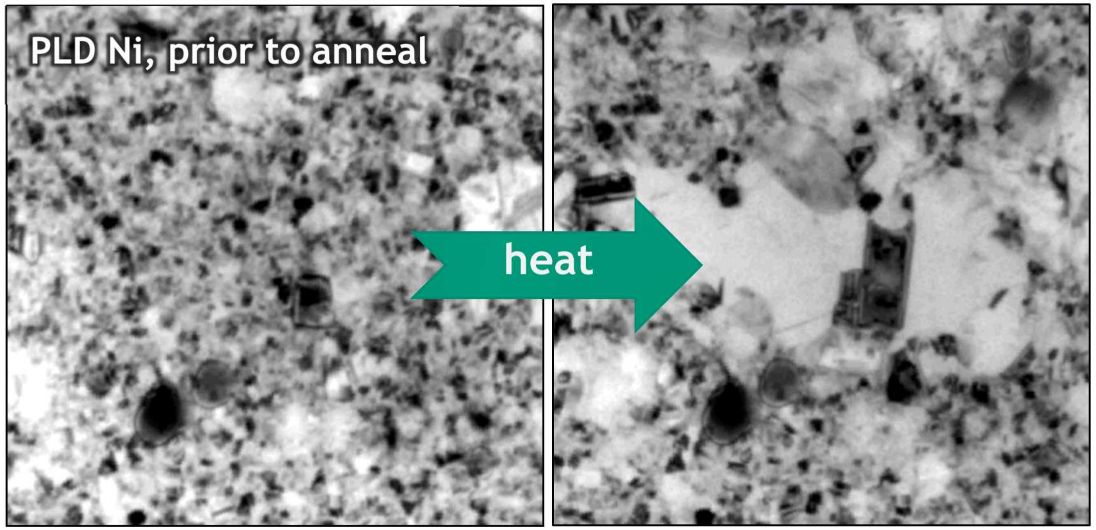


Alloying improves friction & wear performance by reducing **and stabilizing** grain size

…by reducing and stabilizing grain size:



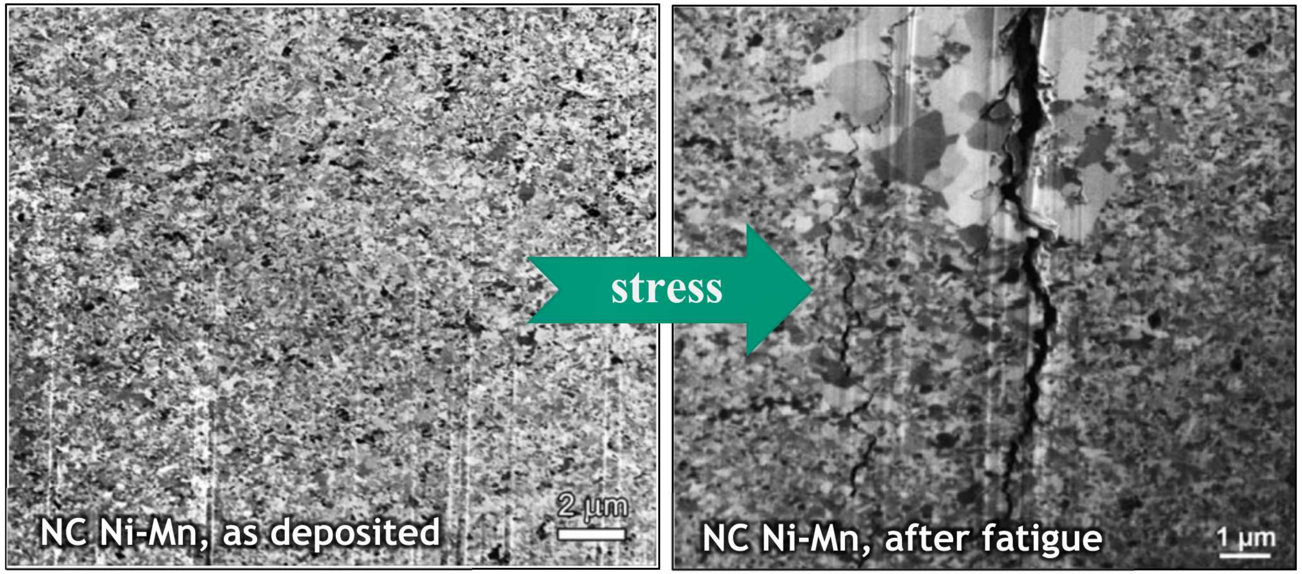
The challenge of grain size instability…



S. Rajasekhara, K. Hattar, P. Ferreira, A. Kinghorn, B. G. Clark, unpublished.

Nanocrystalline metals are driven to grain growth *thermally…*

…and mechanically



H. A. Padilla and B. L. Boyce, Exp. Mech. (2010).

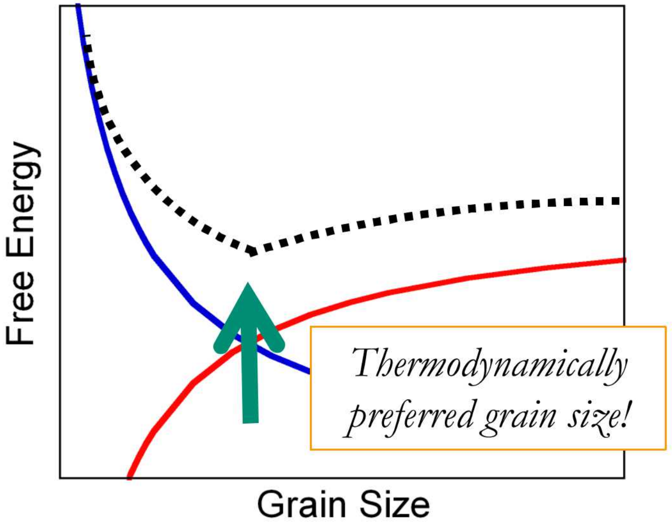
Intrinsically thermodynamically stable nanocrystalline alloys

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

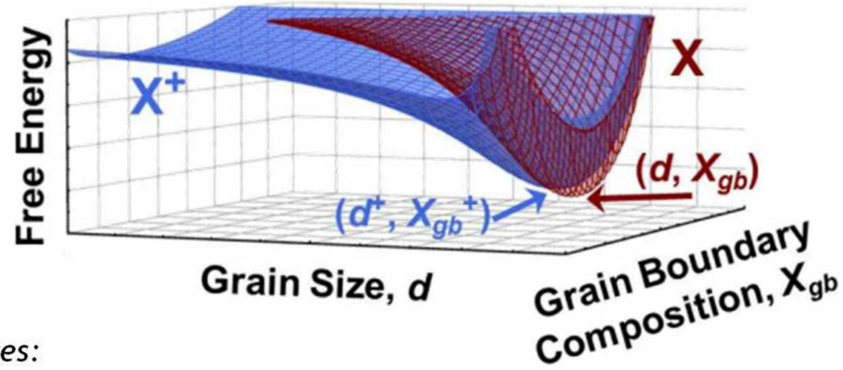
Classic grain growth model (GB speed): $v = \boxed{M} \cdot \boxed{P} = \underbrace{\boxed{M_o \exp\left(-\frac{Q_m}{kT}\right)}}_{\text{kinetics}} \cdot \underbrace{\boxed{\frac{2\gamma_o}{r}}}_{\text{thermodynamics}}$

RNS Model (Chris Schuh Group at MIT)

Slide courtesy of C. Schuh and H. Murdoch (MIT)

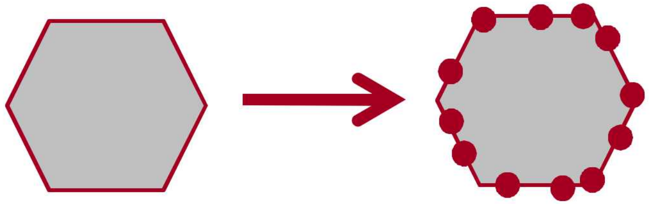


Thermodynamically preferred grain size!



References:
Kirchheim, Acta Materialia, 2002
Weissmuller, J. Materials Research, 1994
T. Chookajorn, et al., Science, 2012
D.S. Gianola et al., Acta Materialia, 2006

Solute segregation at grain boundaries:



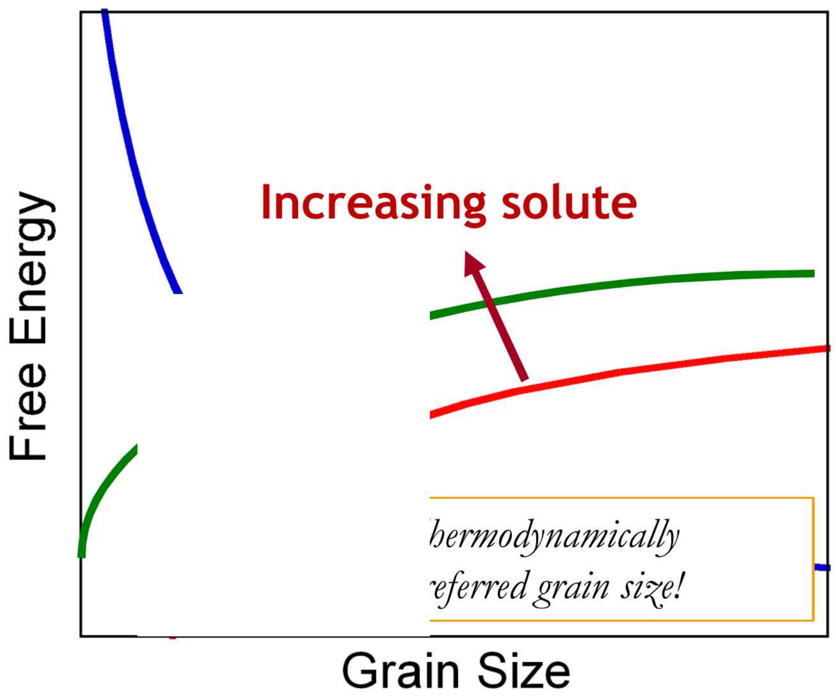
$$dG = \left[\gamma - \frac{N_\beta}{A} \Delta G_{seg} \right] dA$$

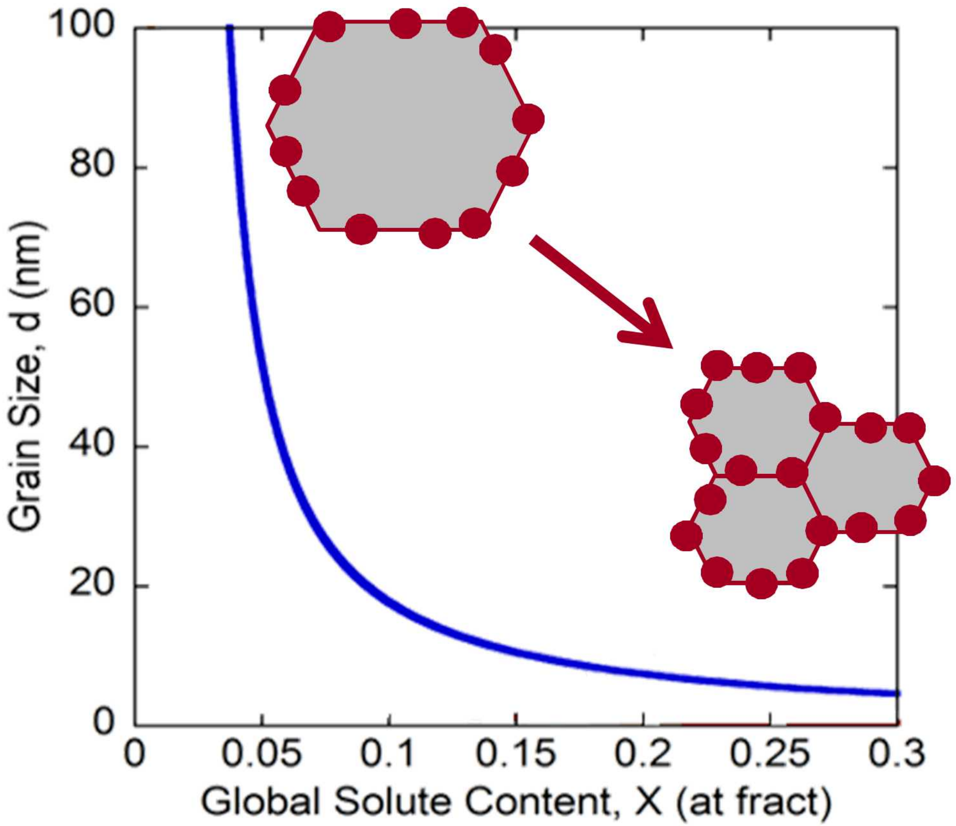
Are thermally stable alloys also mechanically stable?

Is thermo-mechanical stability achievable?

GB solute segregation reduces thermodynamic drive for growth

Reference: Murdoch and Schuh, Science (2012)

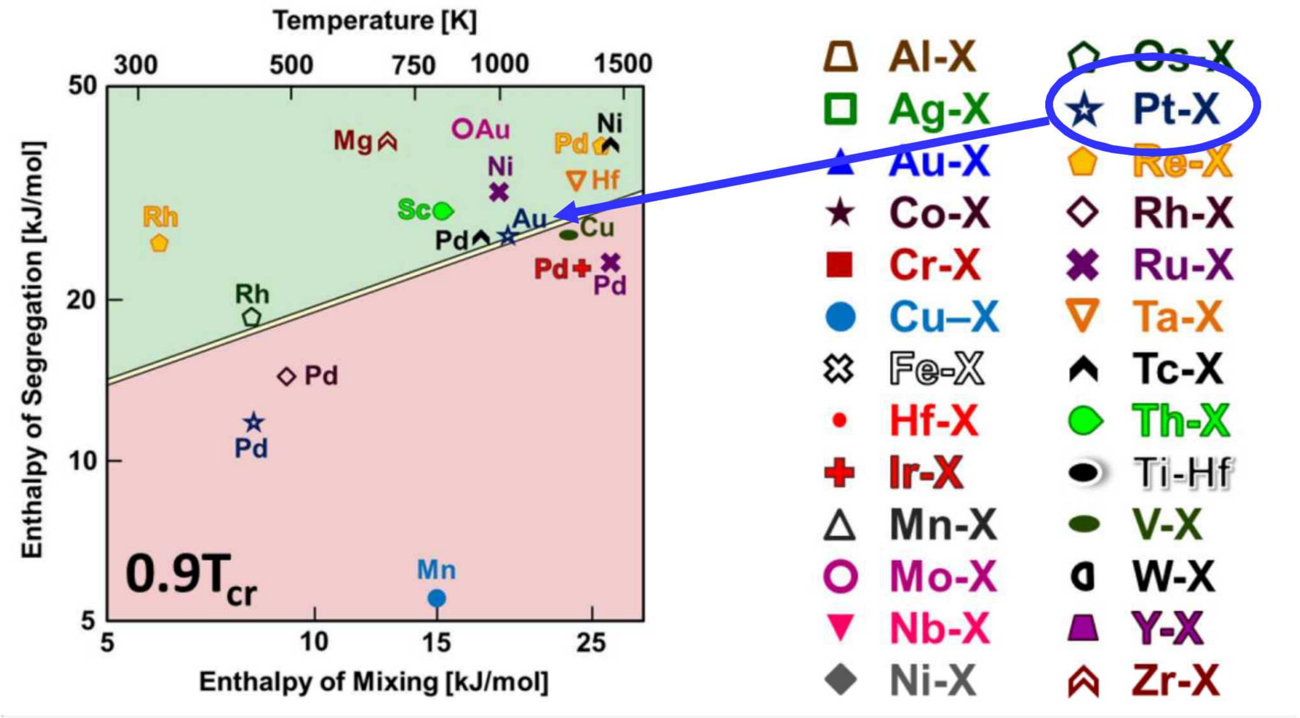




Increasing solute lowers the grain boundary energy and reduces the stable grain size

Binary metal alloys with favorable segregation

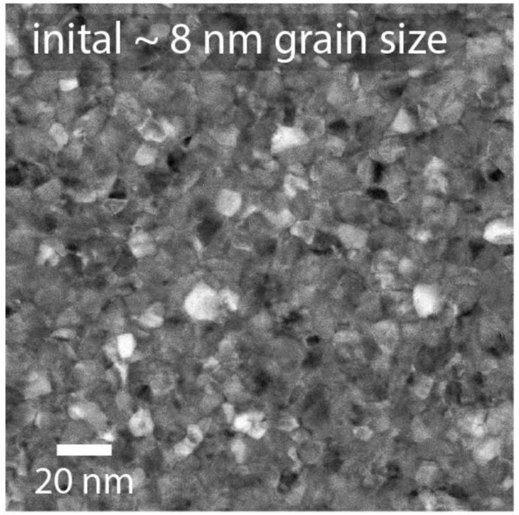
Reference: Murdoch and Schuh, J. Mat. Research (2013)



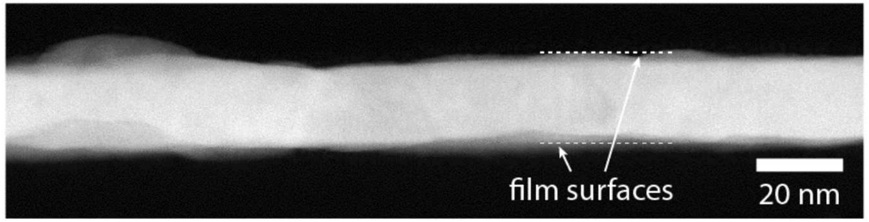
Sputter-deposited two types of **Pt-10 at. % Au** films

Freestanding 18 nm thick films, lifted from rock salt, transferred to TEM grids:

Plan view:

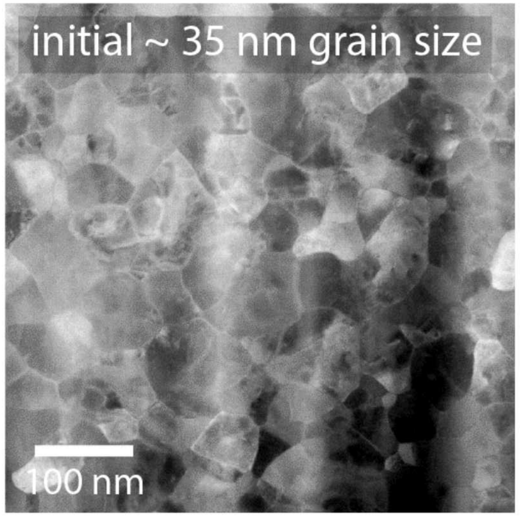


cross-section view:

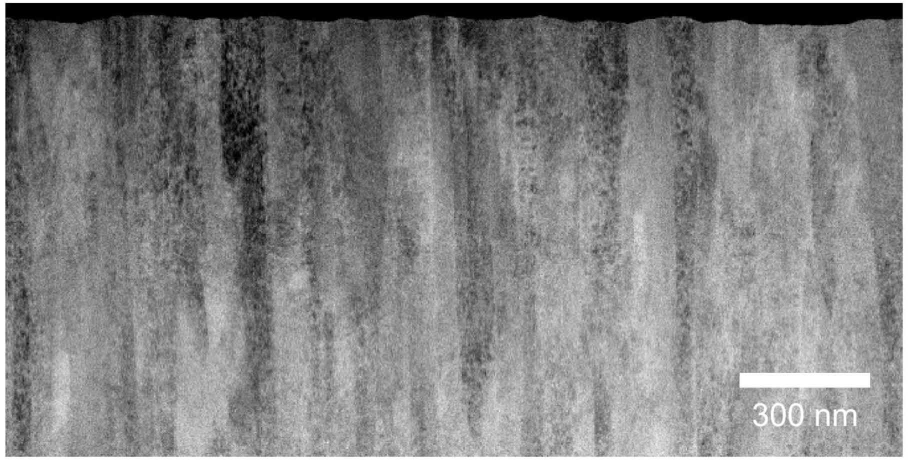


2 µm thick films on silicon wafers:

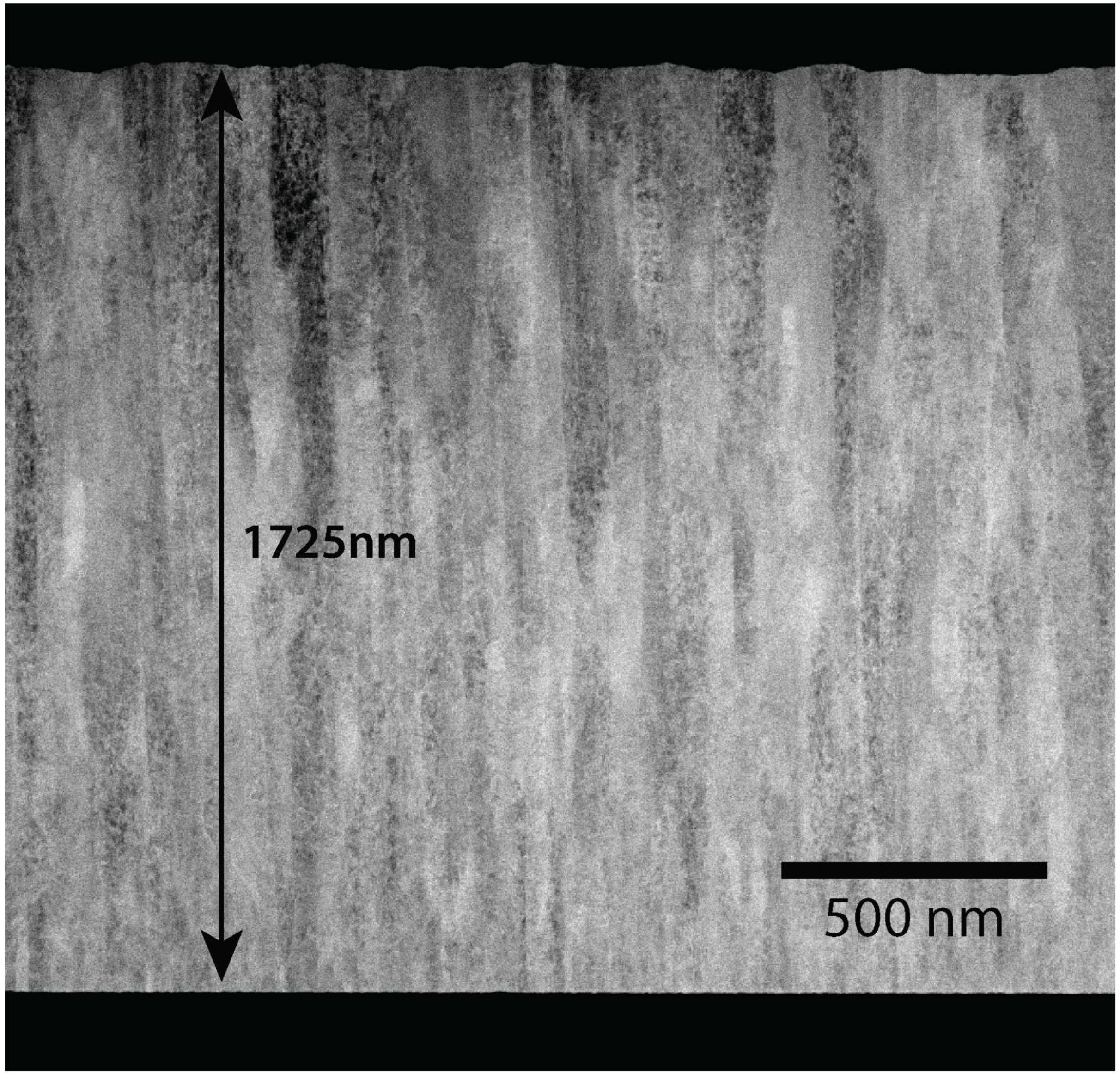
Plan view:

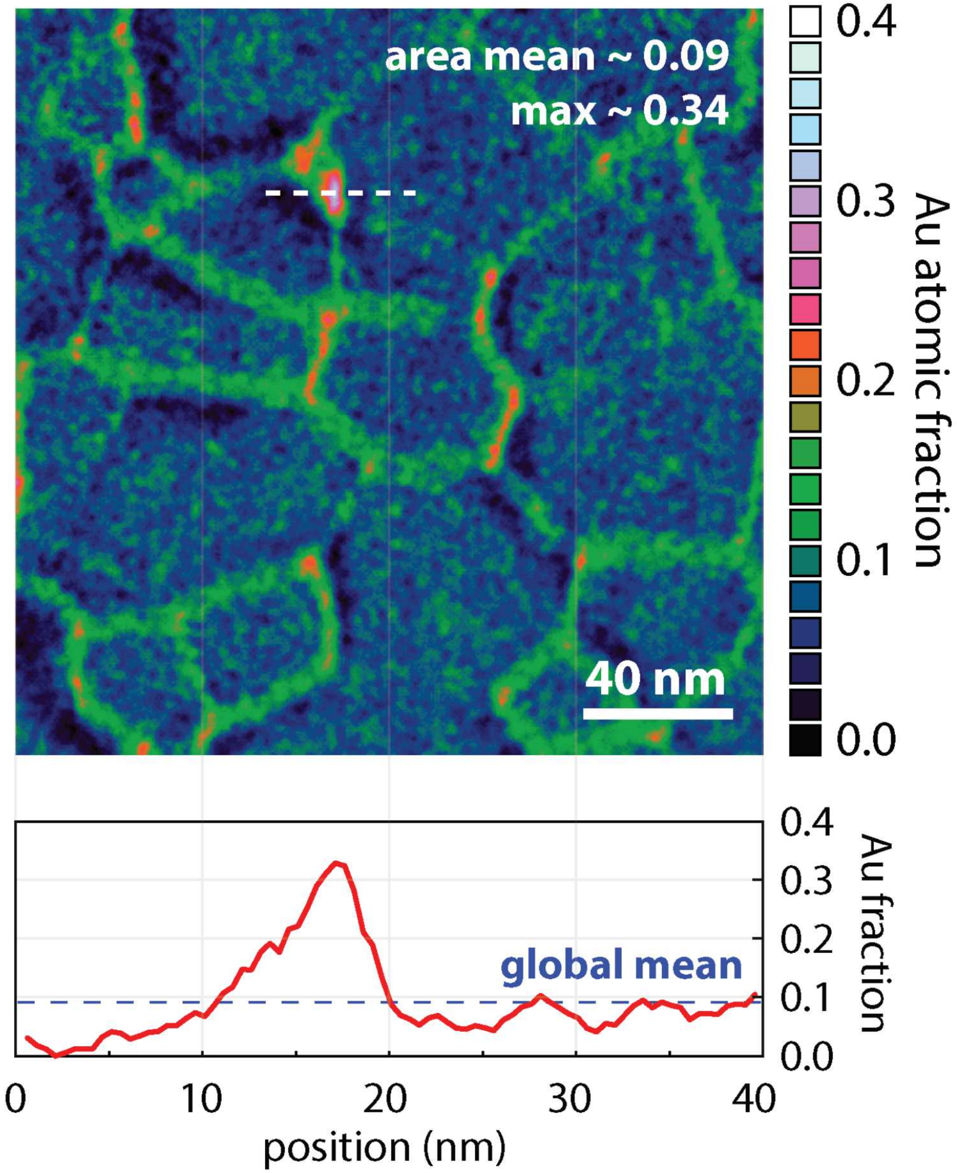


cross-section view:



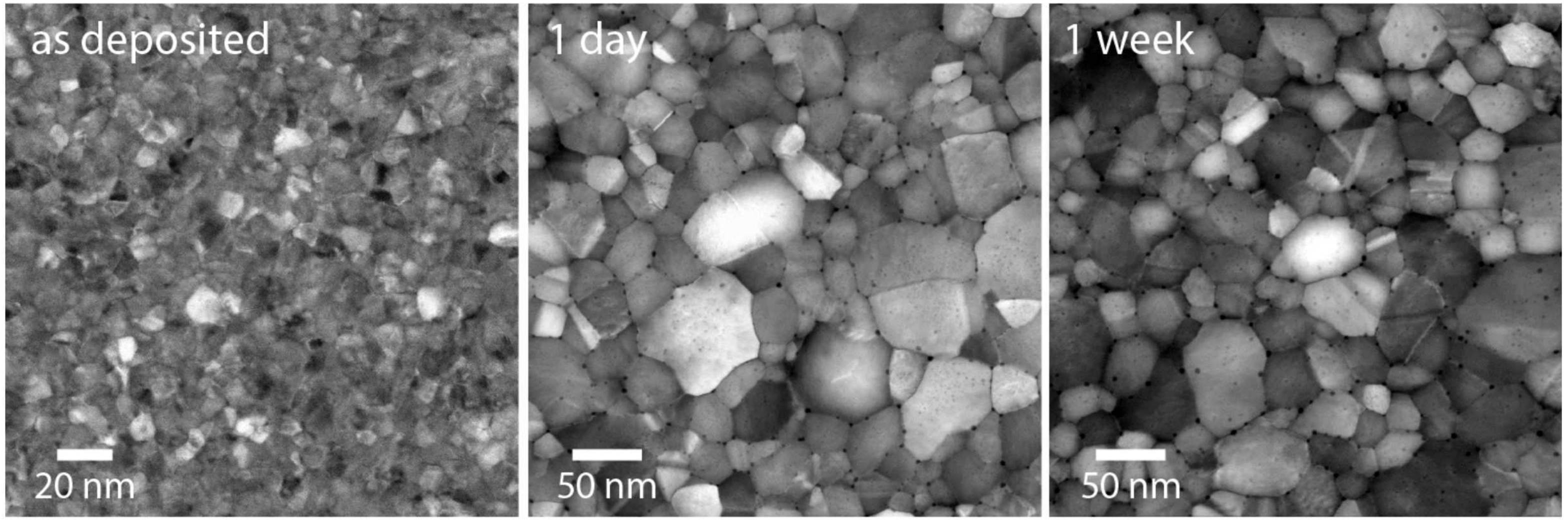
Heterogeneity, denuded zones, preferential segregation to triple junctions



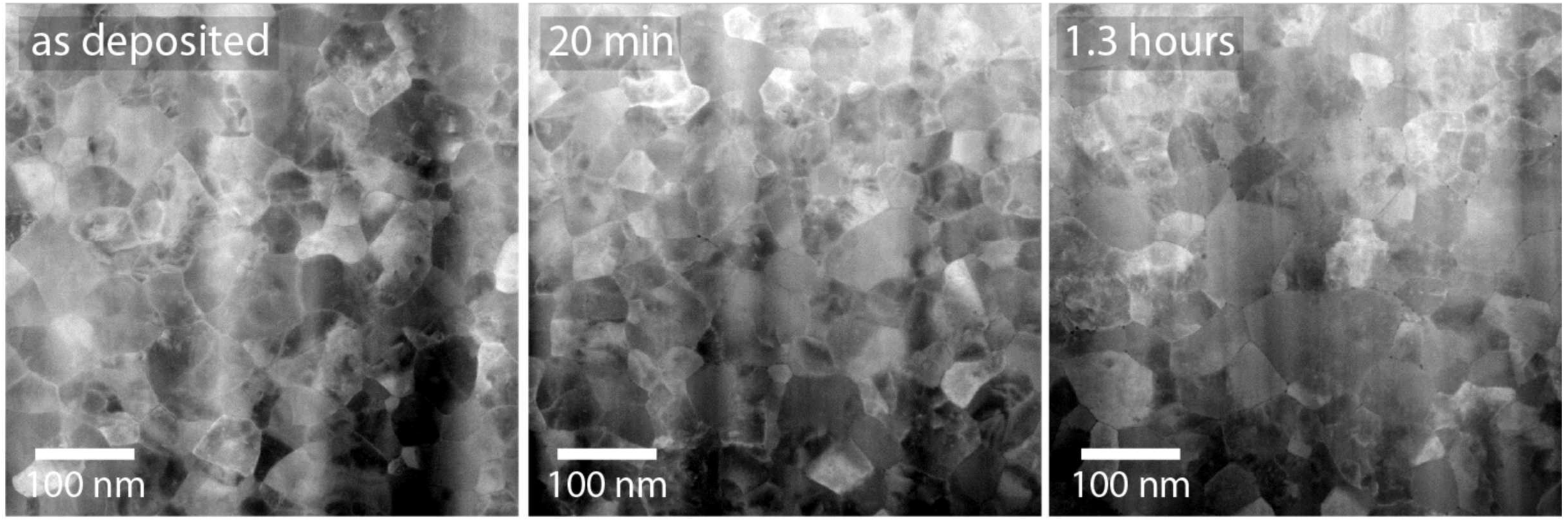


Comparing thin (freestanding) and thick (columnar) film 500°C anneals

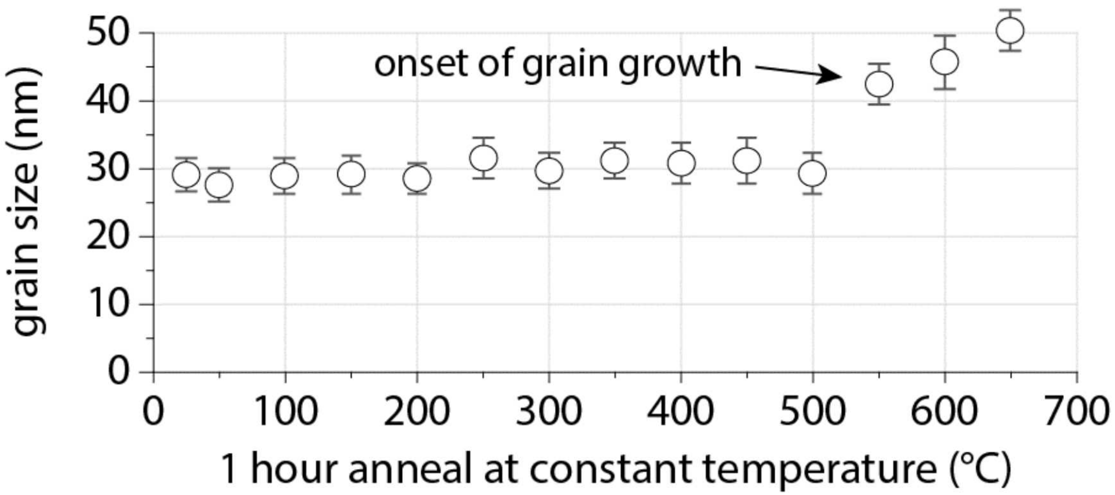
freestanding 18 nm thick films



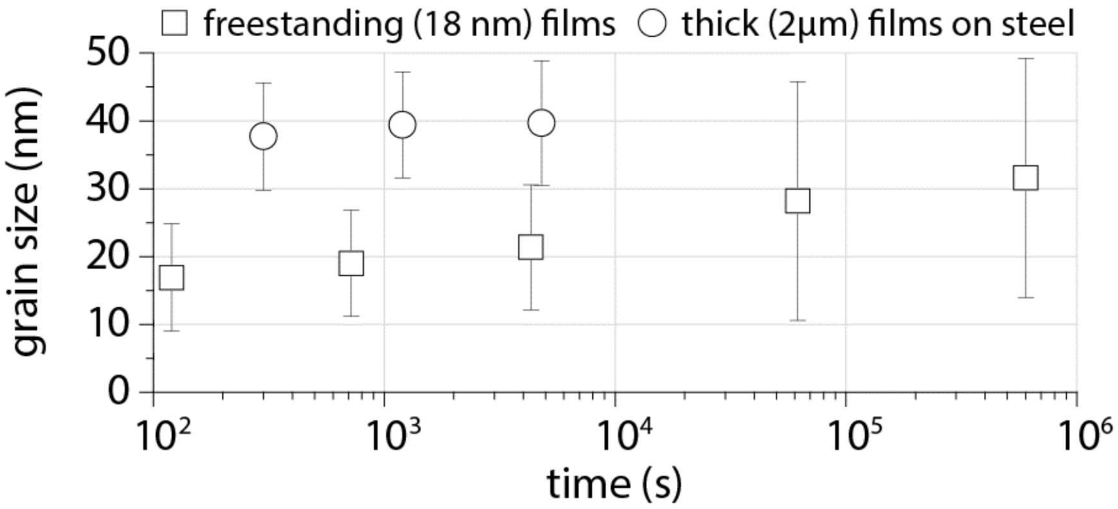
2 µm thick films on Si wafers



PtAu alloy nanocrystalline microstructures are thermally stable



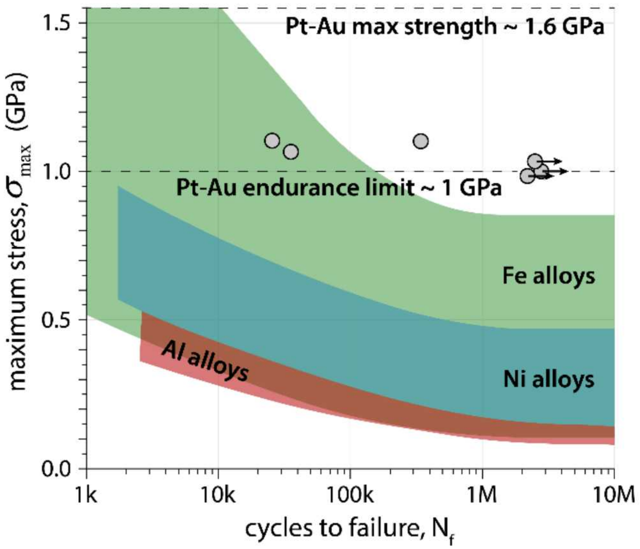
XRD in situ grain growth



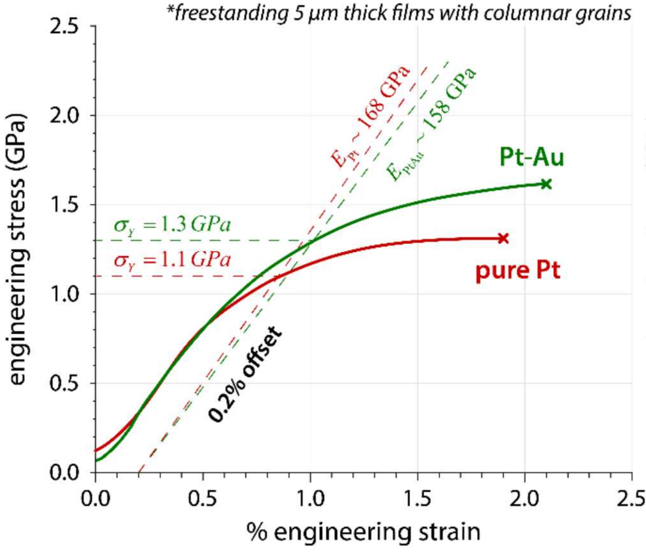
TEM in situ grain growth at 500°C

PtAu alloys have high yield strength and remarkable fatigue resistance

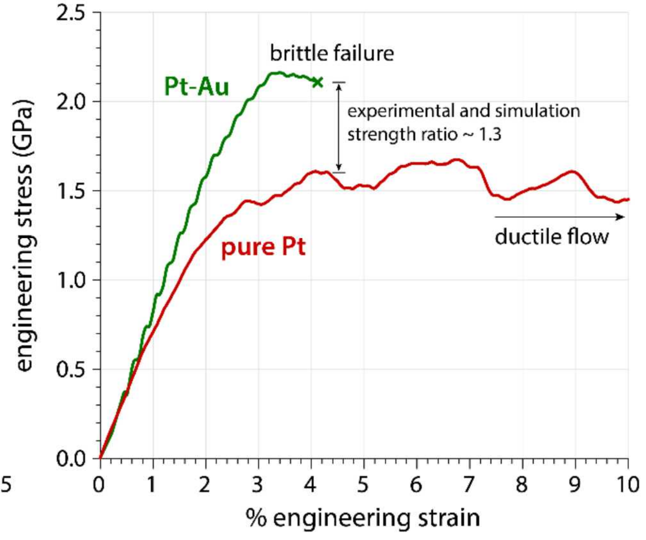
Experimental Tensile Fatigue:



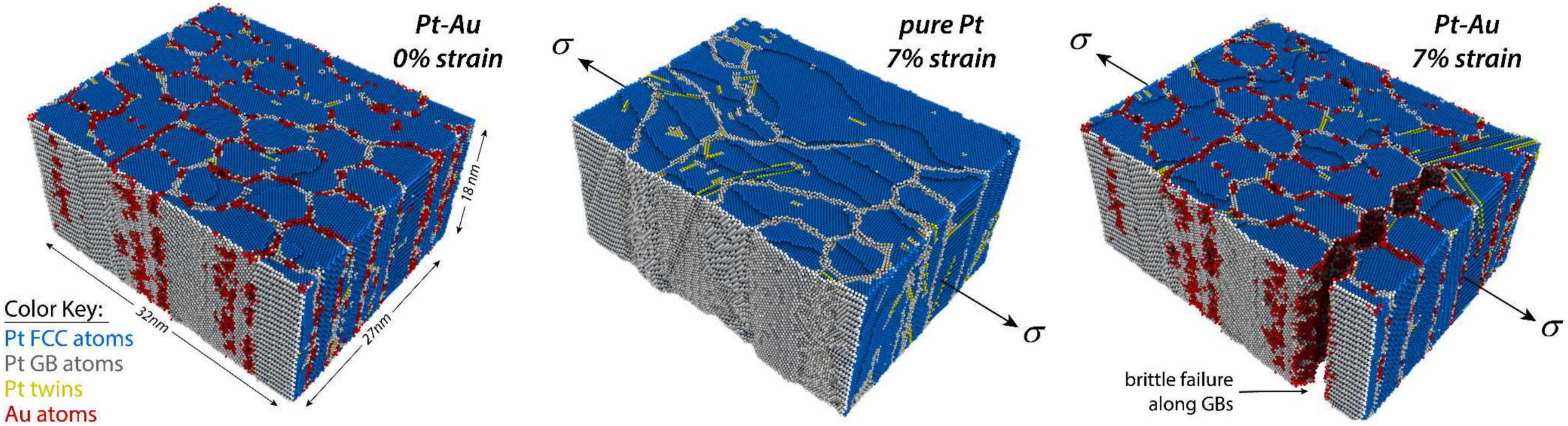
Experimental stress-strain data:



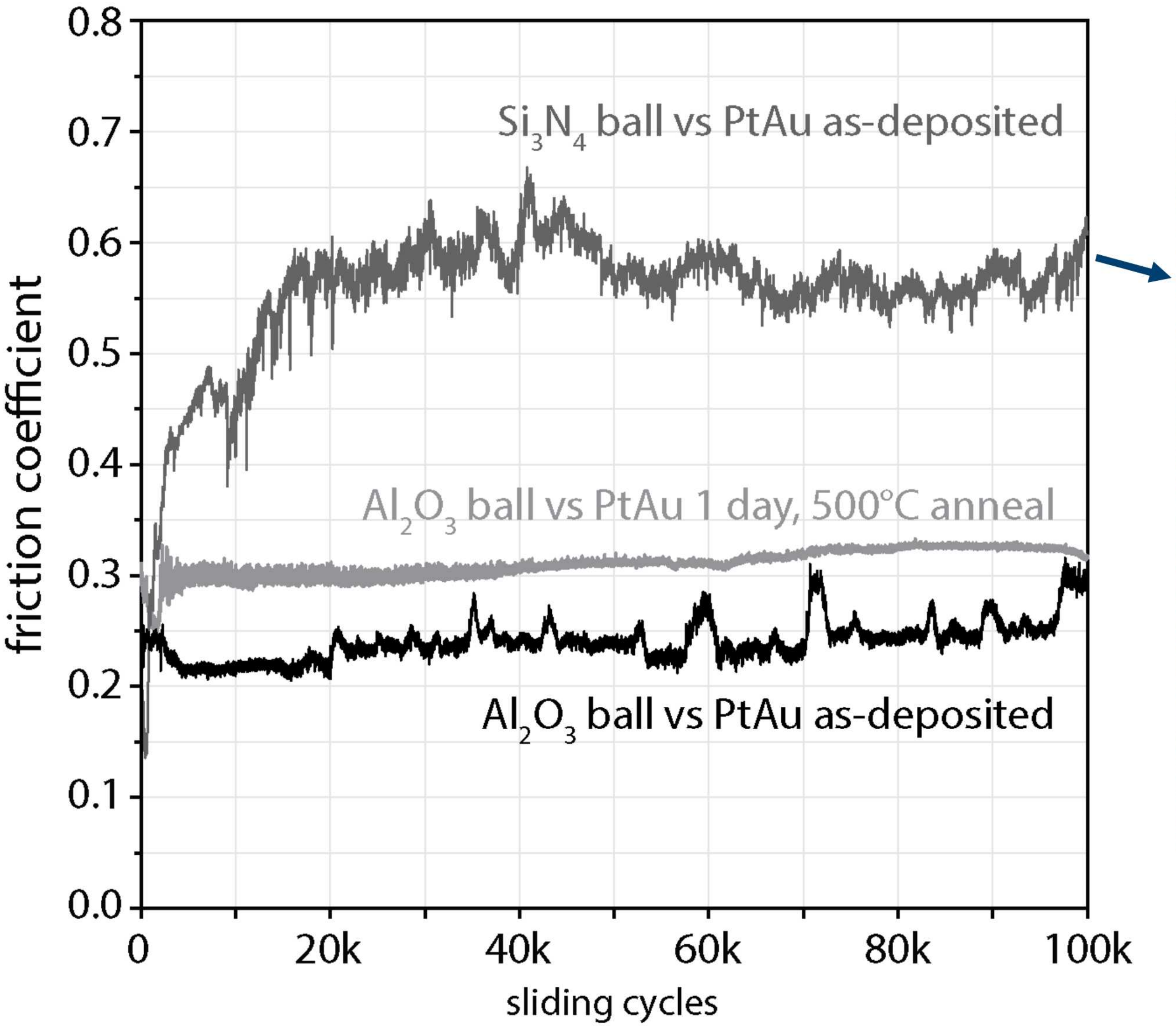
Simulation stress-strain data:



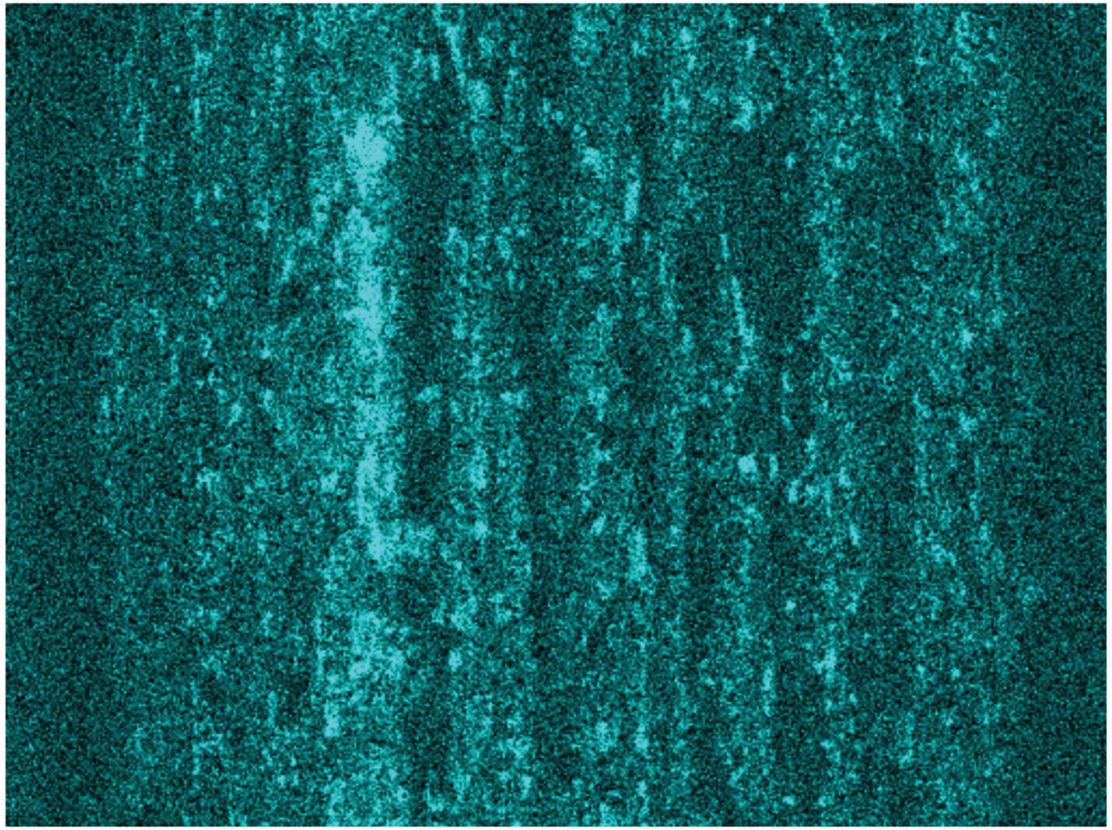
MD Simulation Snapshots (grain growth during uniaxial tensile stress exposure):



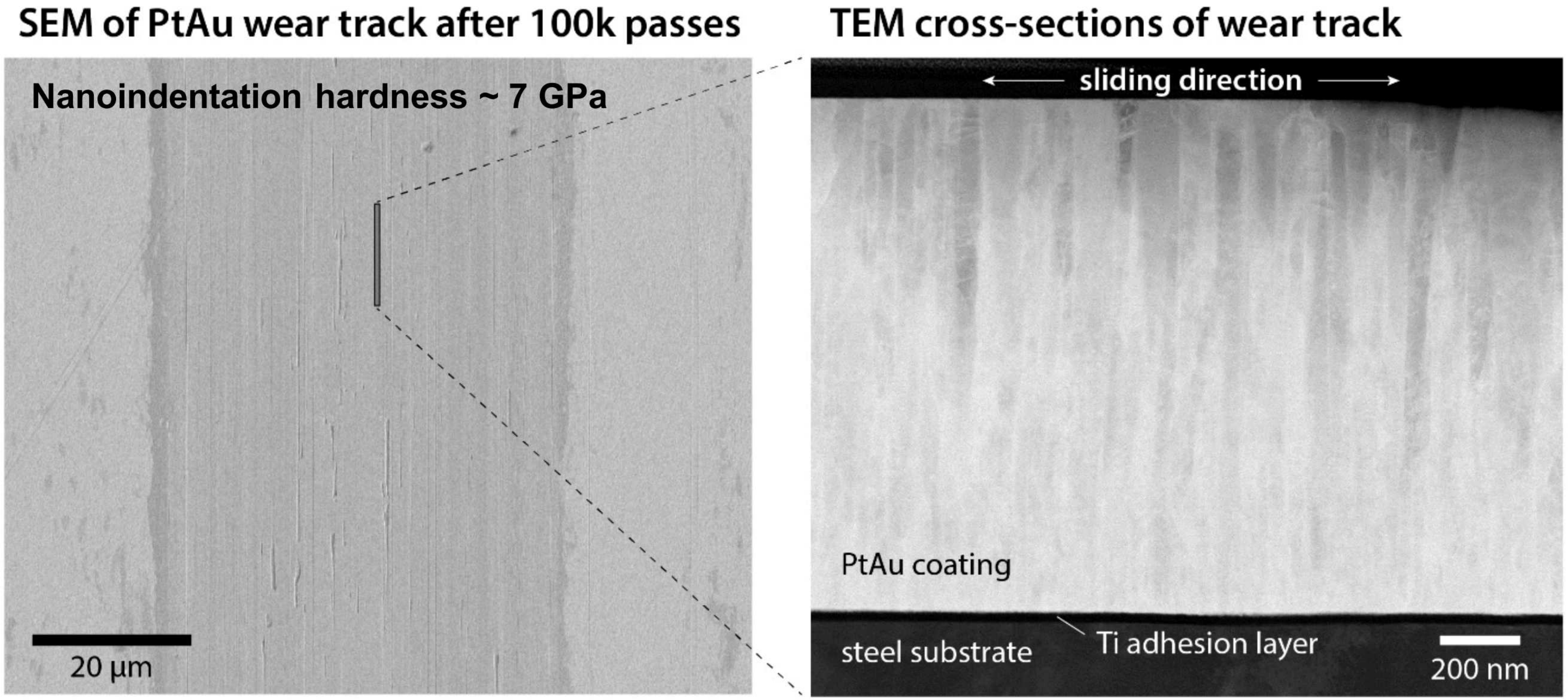
Stable nanocrystalline PtAu exhibited low friction(against sapphire)



Si EDS map

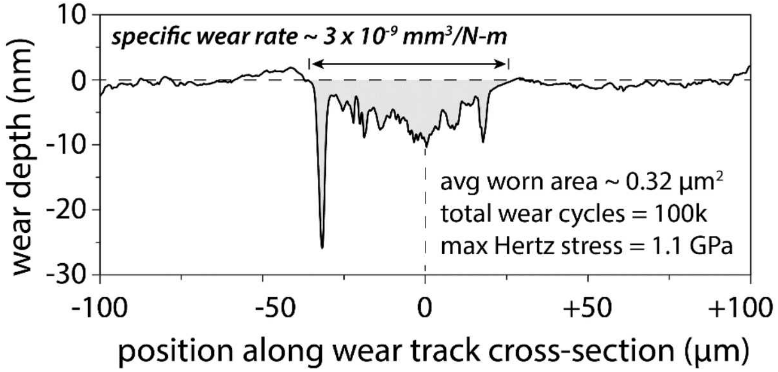


Also, *extremely* low wear rate – 3x10^{-9} mm^3/N-m


SEM of PtAu wear track after 100k passes

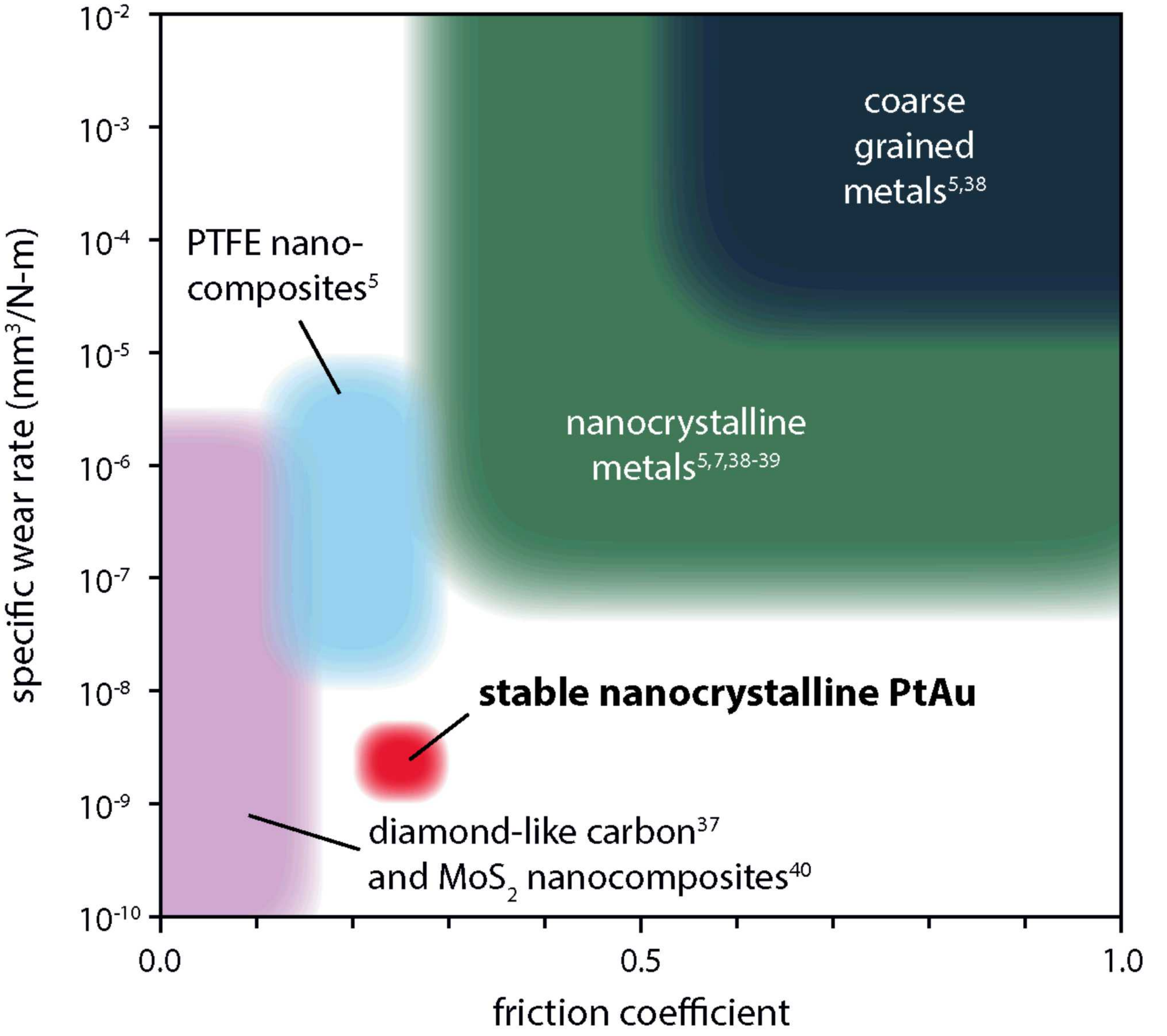
TEM cross-sections of wear track

Average Wear Track Cross-section:

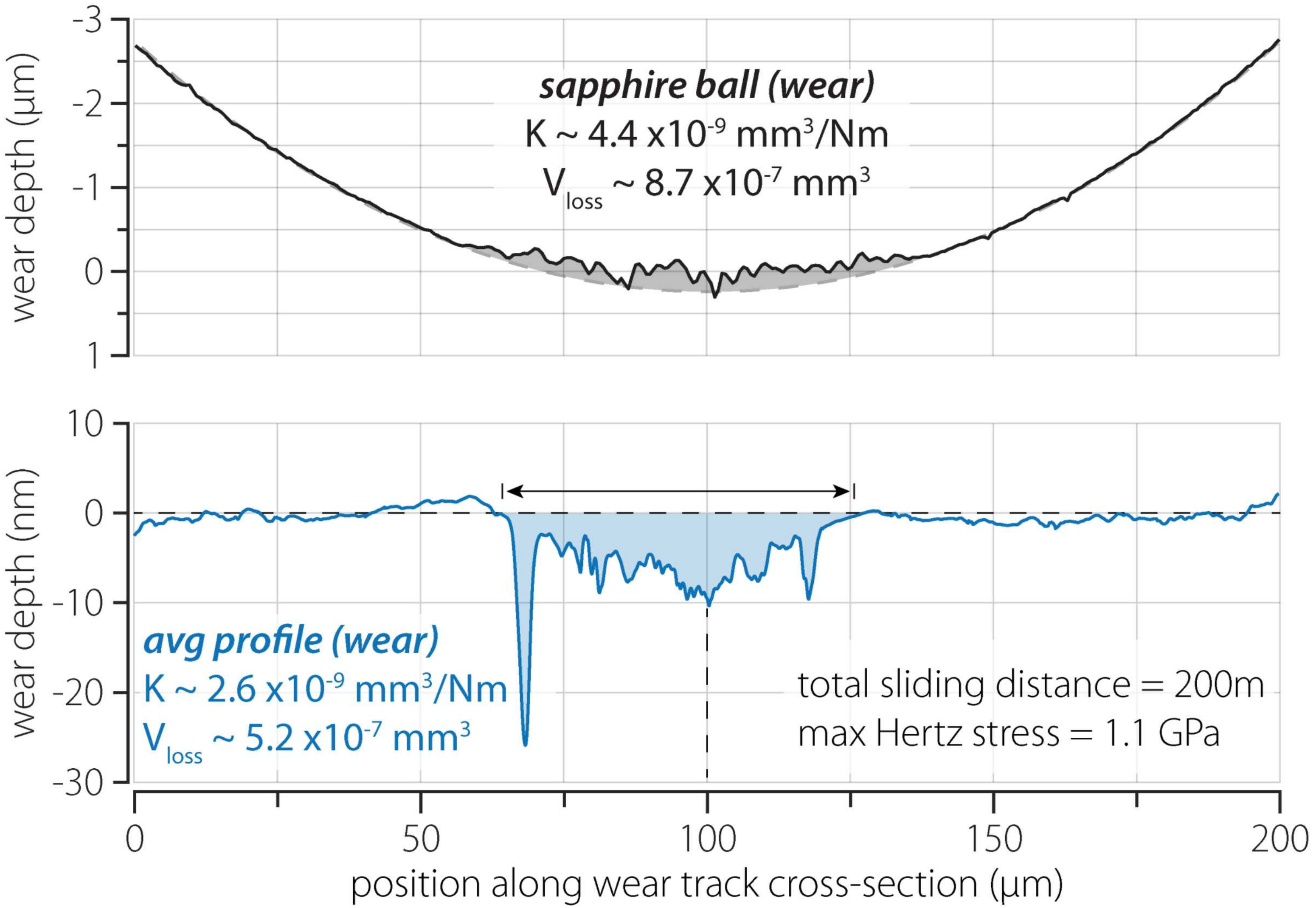


Ultra-low wear and
no evidence of grain size evolution
at peak Hertz stress of 1.1 GPa

Remarkable Improvement in Wear Resistance

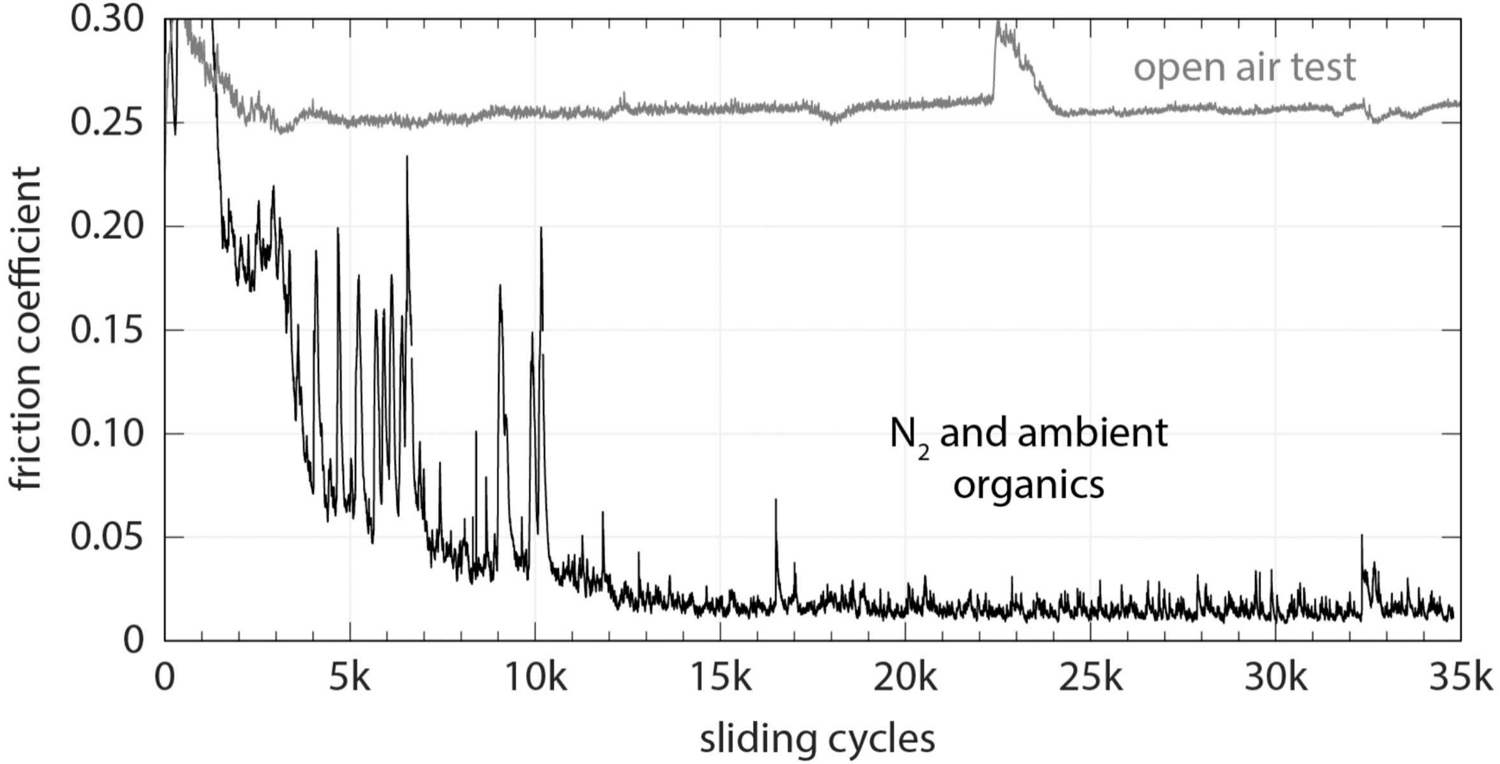


When scissors beat rock!



Friction Behavior in Non-Oxygenated Environment

N_2 w/ trace organics

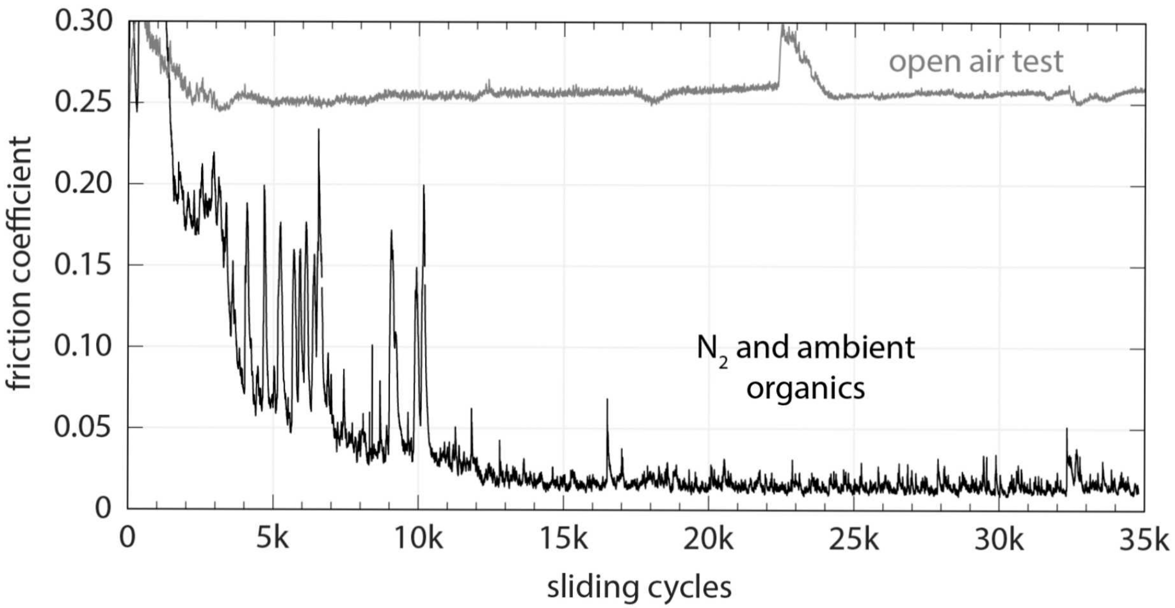


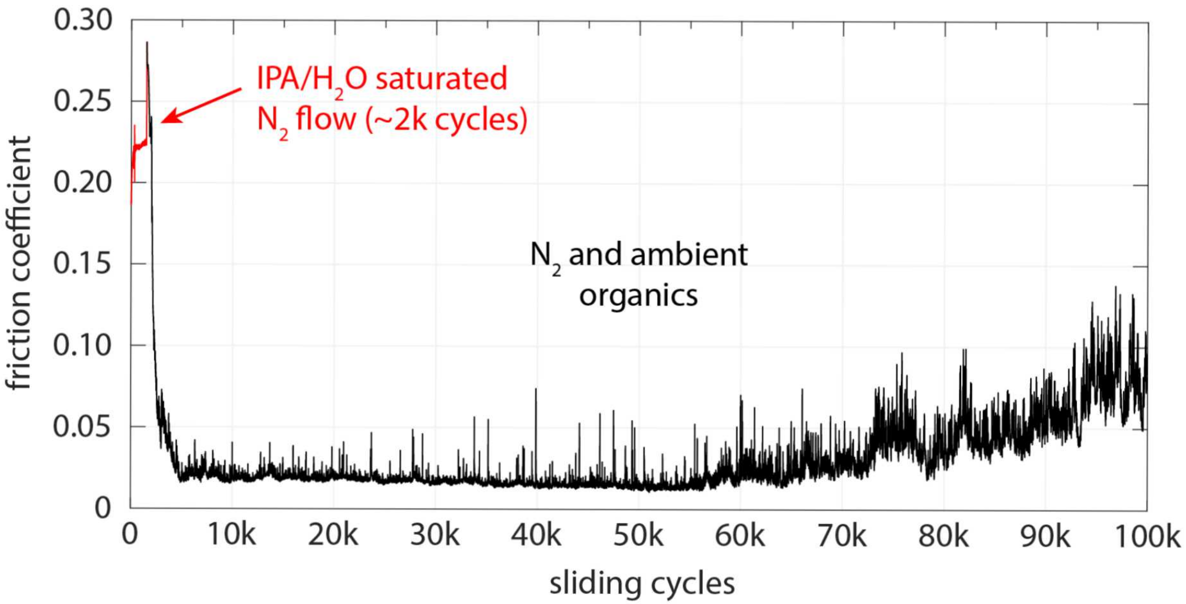
Compounds Identified
trichloroethylene
acetic acid
benzaldehyde
tridecane
phenol
acetophenone
2-heptyl-1,3-dioxolane
butylated hydroxytoluene
benzoylformic acid
phenylmaleic anhydride

(20-100 ng/L)

… in situ tribo-chemical formation of DLC films from "thin air"!
(Albuquerque is at 6,000ft/1,800m of elevation, after all…)

Alcohol Fixes Everything…



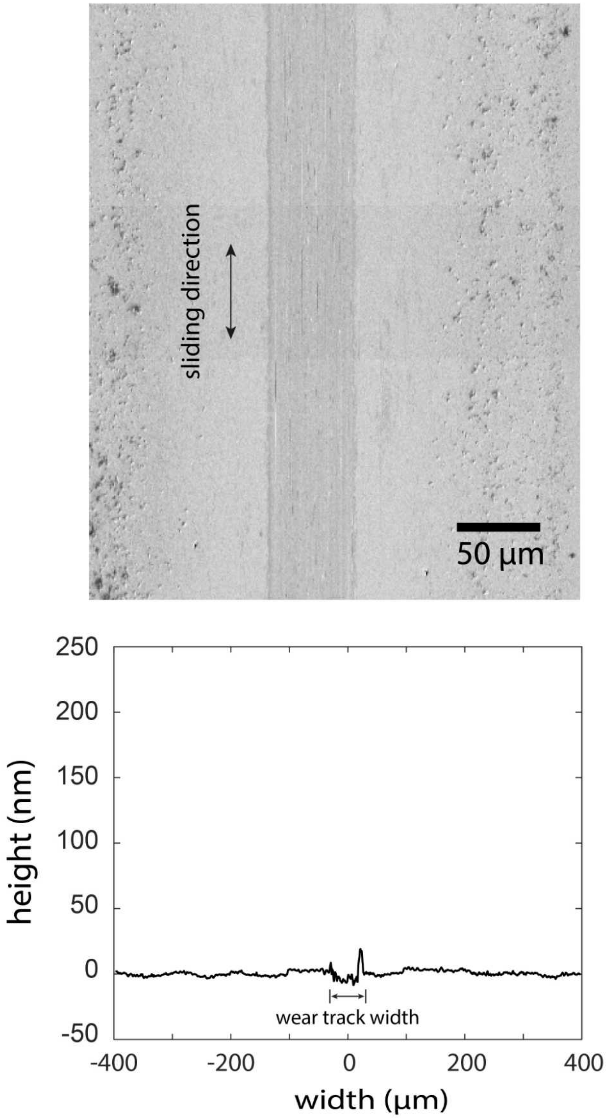


Unfortunately, water complicates interpretation.
Was addition of humid IPA enhancing or inhibiting?

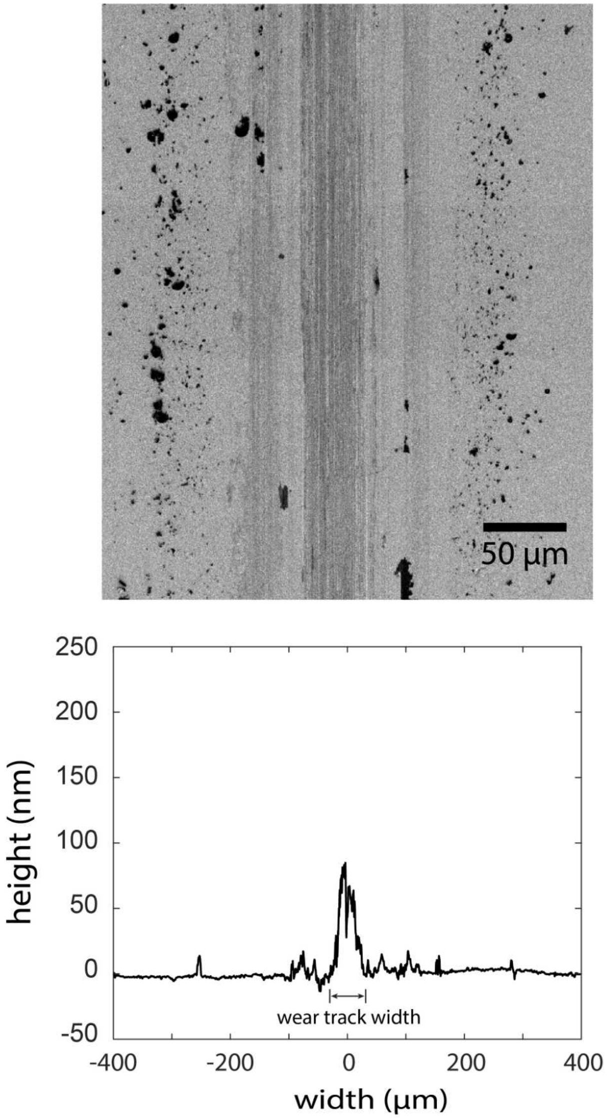
More on this…

SEM and Profilometry Reveal Thick, Well-Adhered, Persistent Films

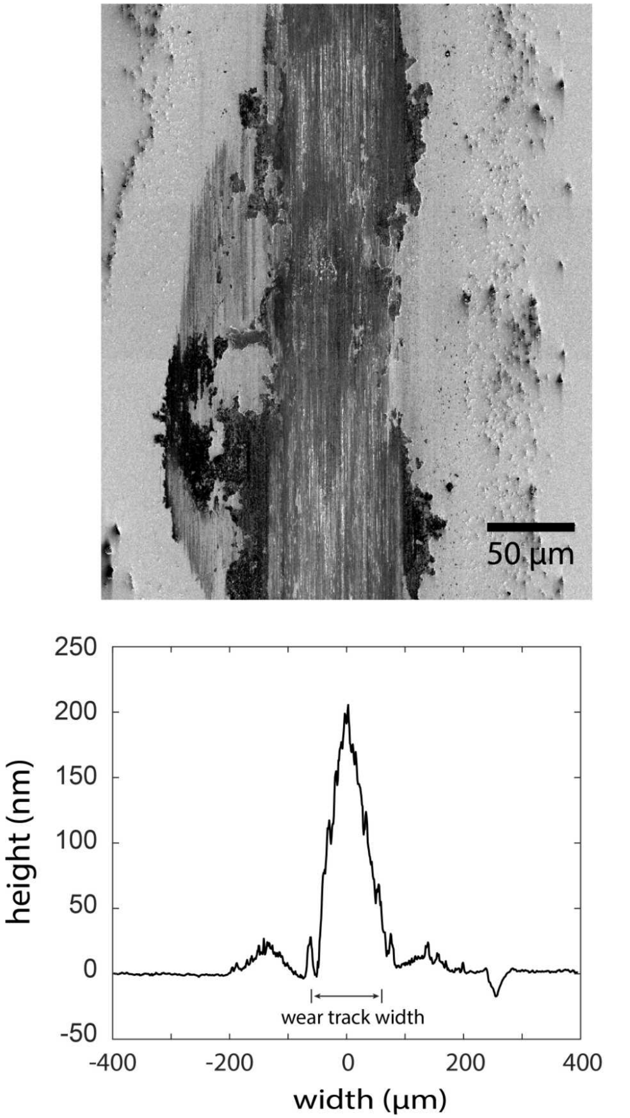
lab air



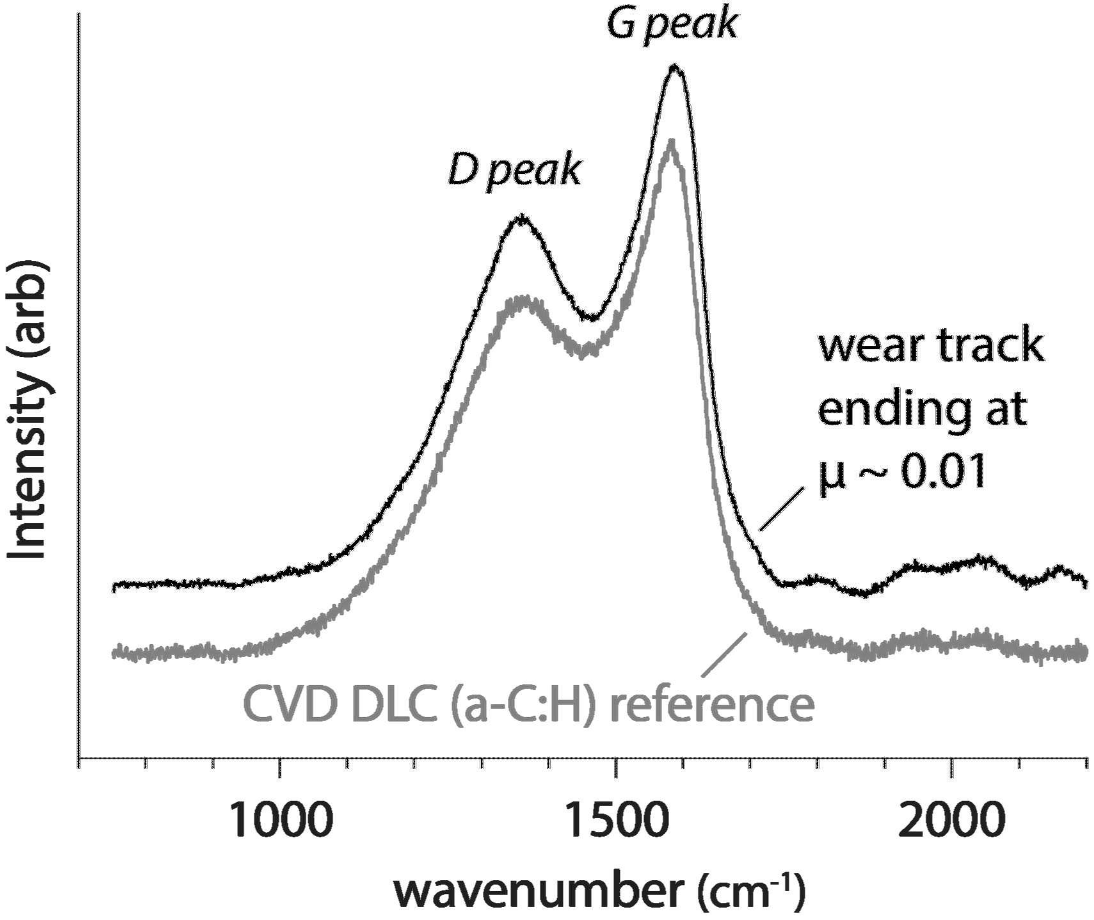
N_2 and ppb trace organics

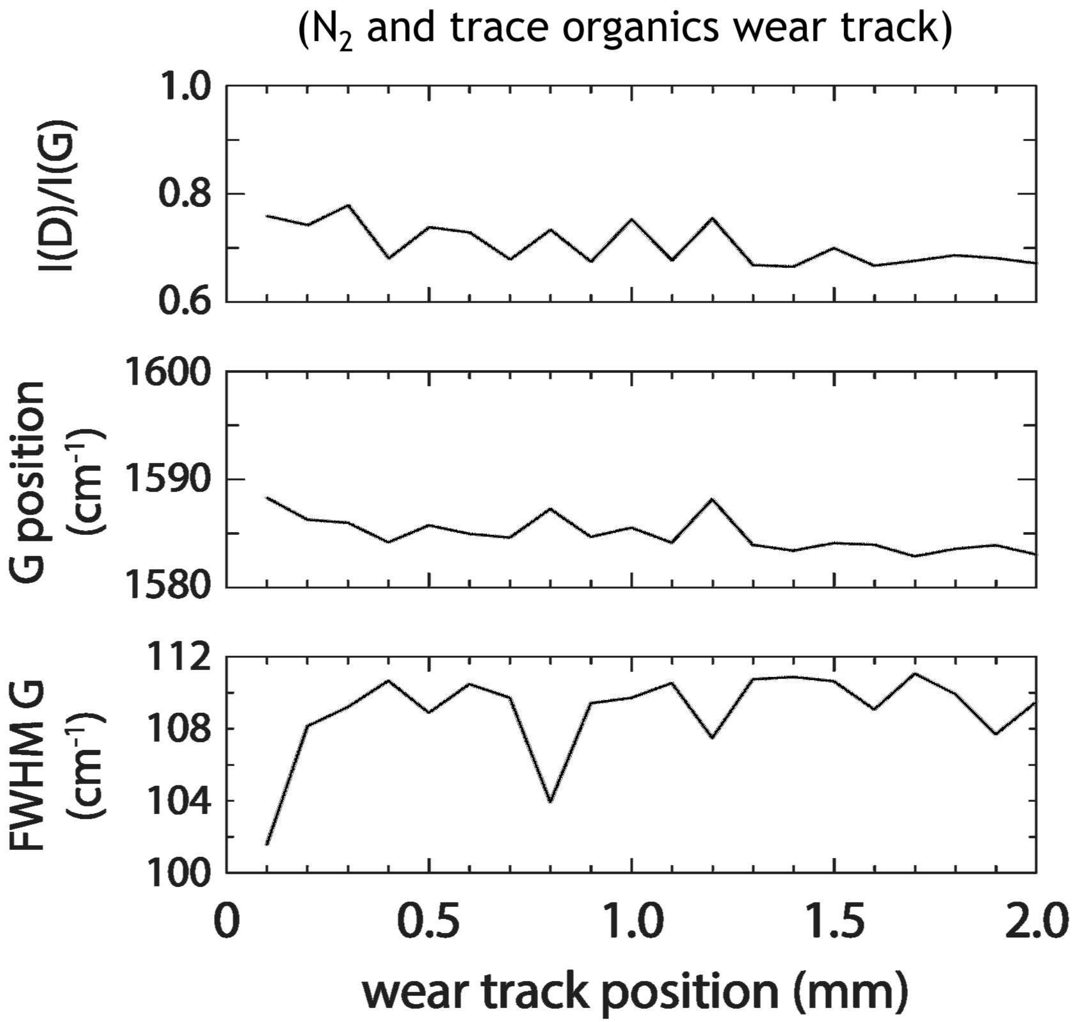


N_2 and concentrated IPA/H_2O vapor



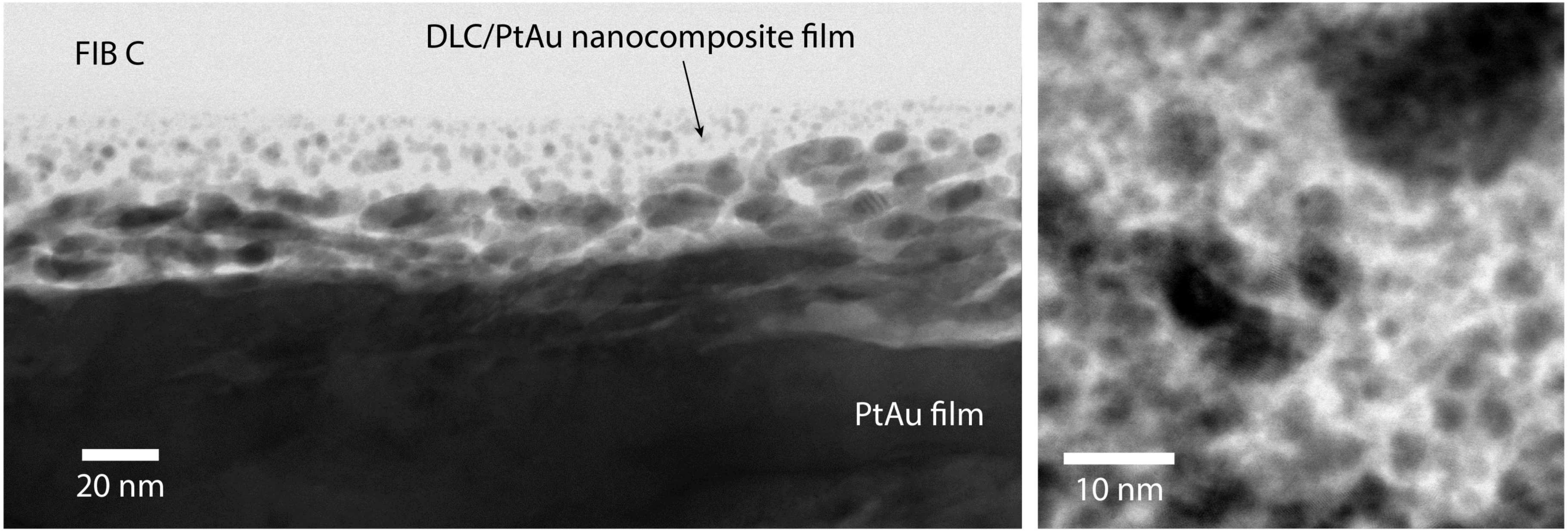
Raman Spectroscopy -- Highly Graphitic Hydrogenated (20%) DLC



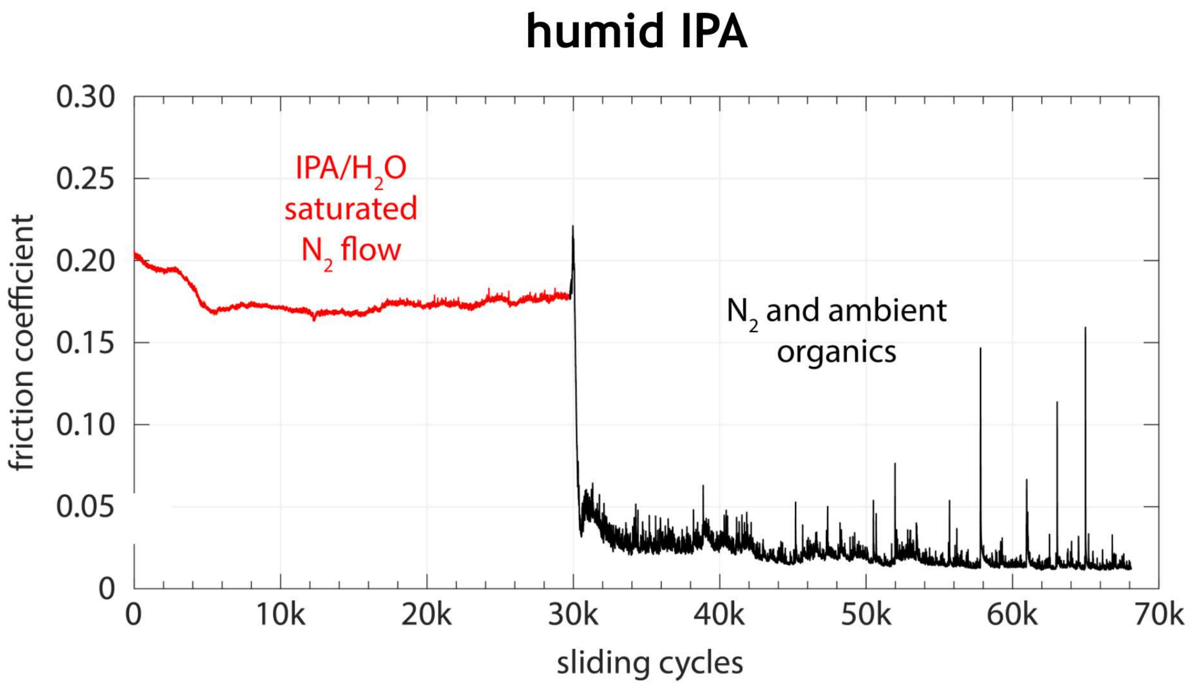

(N_2 and trace organics wear track)

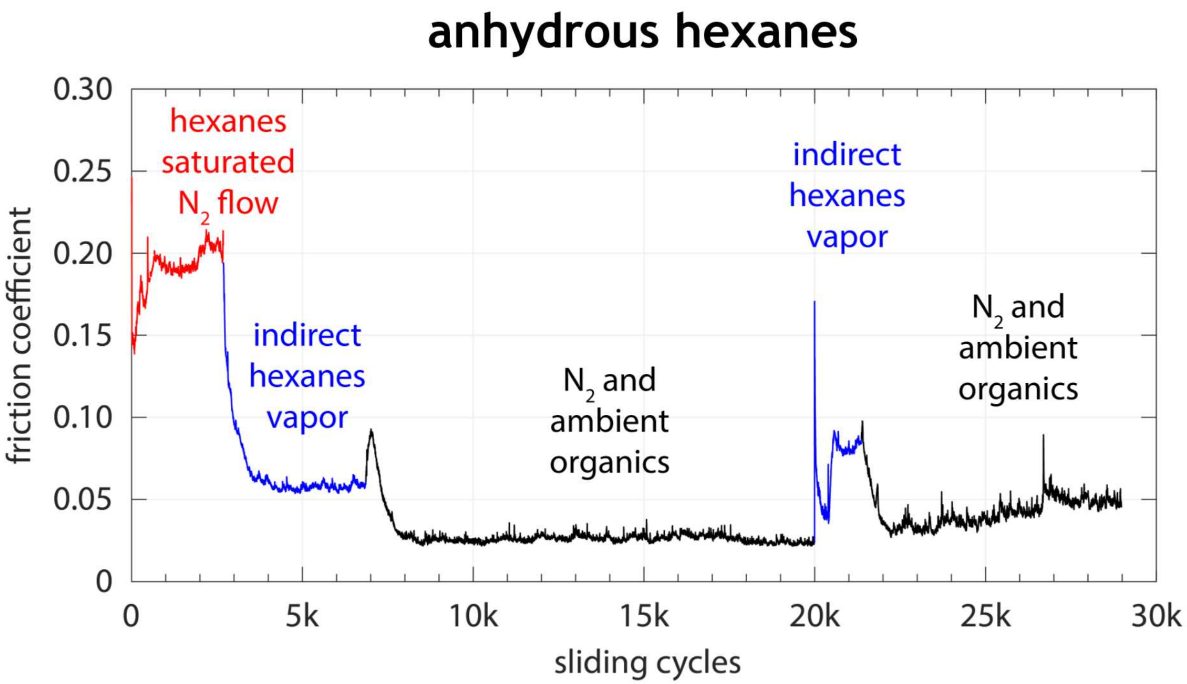
elastic recoil shows ~ 20% H

TEM Reveals a Nanocomposite Structure (DLC/PtAu Nanoparticles)



Anhydrous hexanes





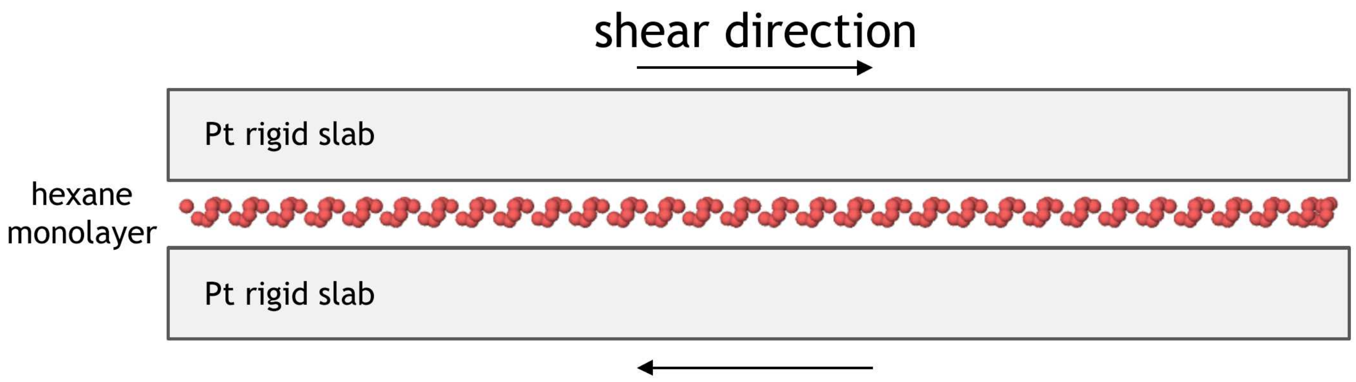
elevated concentration of organics
results in high friction

Alcohol helps, but only in moderation

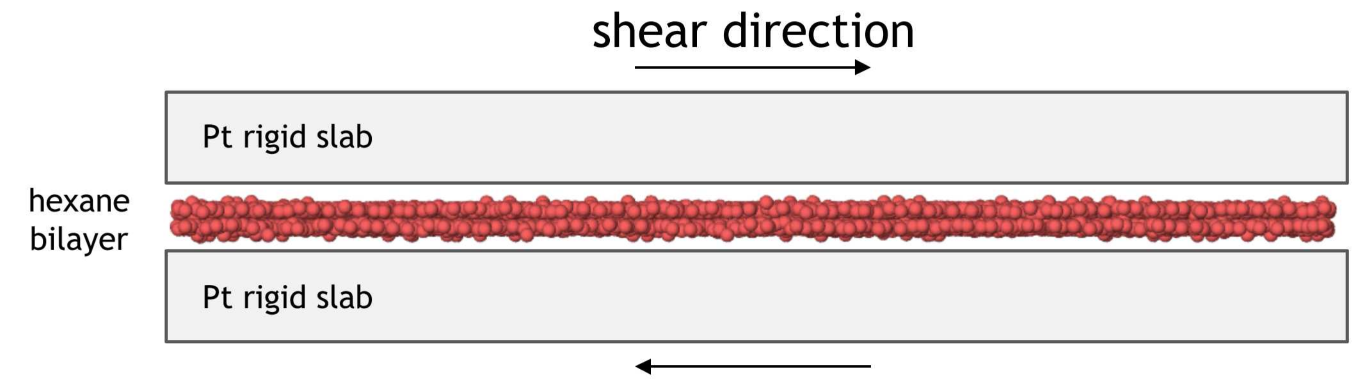
… and don’t water down your alcohol.

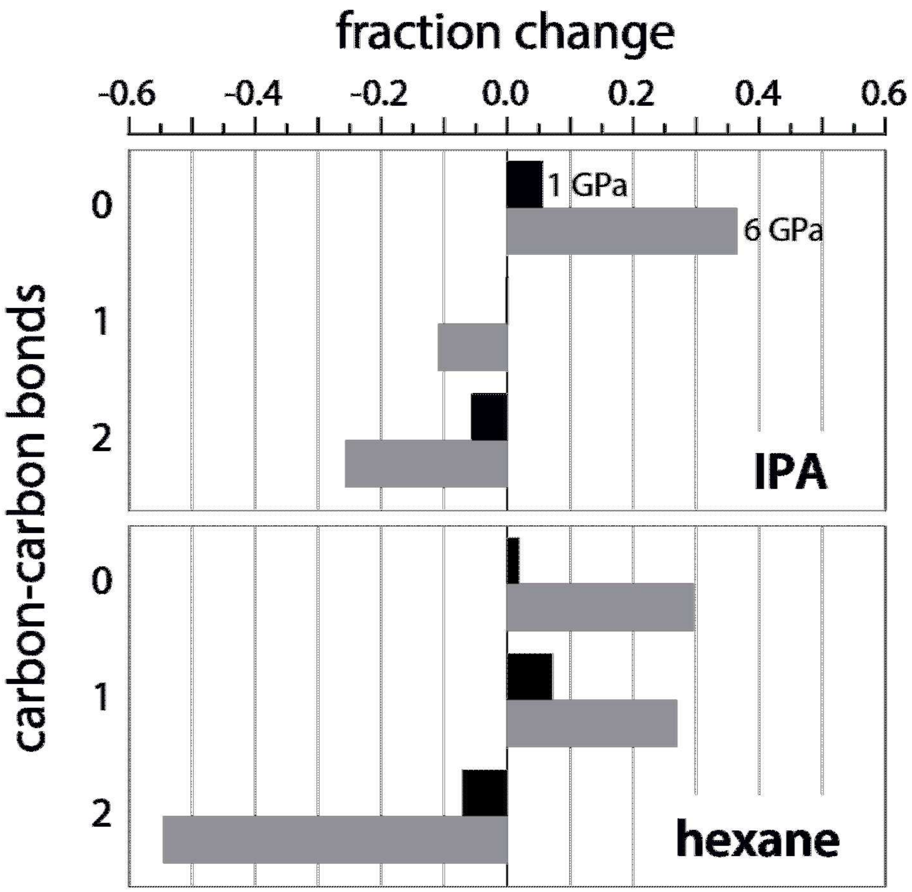
MD Simulations Show Chain Scission and Possibly a Stress Threshold

Initial Configuration (Pre-Sliding):



After Shearing for ~ 8 ns:



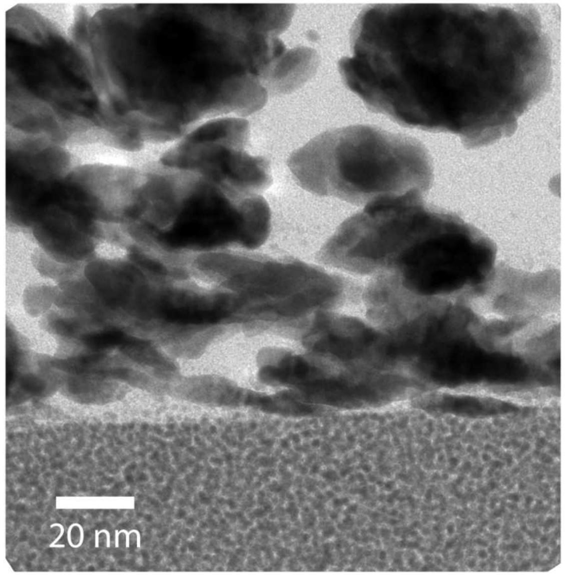


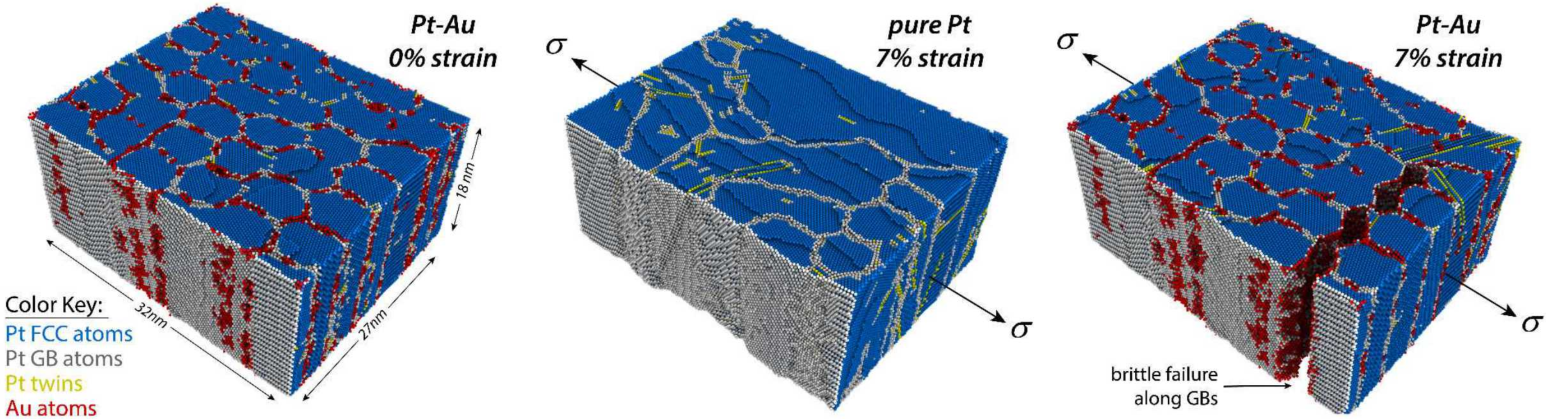
reactive force field – meant for hydrocarbon catalysis on Pt, not tribo-chemistry…

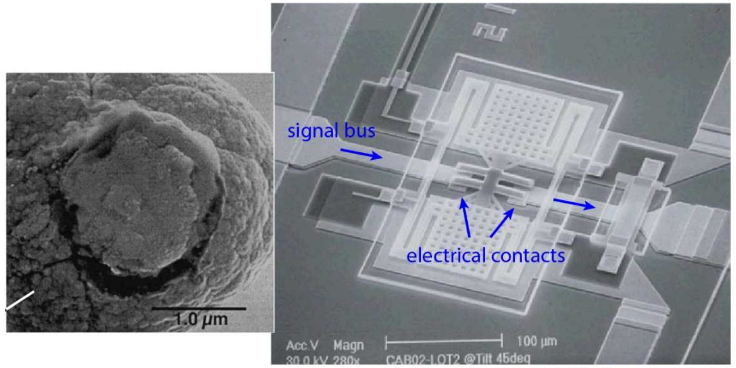
Potential Reference: Y. Shin et al., J. Phys. Chem. A, 2016

Closing Remarks

- Demonstration of highly stable nanocrystalline PtAu alloy
- Stable nanocrystalline alloys show promise for tribological applications in thin film form under cyclic stress and annealing
- Noble metal exemplar addresses confounding arguments like the presence of metal-oxides (i.e. Zener pinning)
- Ultra-low wear with a metal alloy at relatively high stress!
- Tribo-chemical pathway for in situ DLC film formation from ambient hydrocarbons was found with wear resistant PtAu… wide range of possible engineering implications (additives, electrical contacts?)





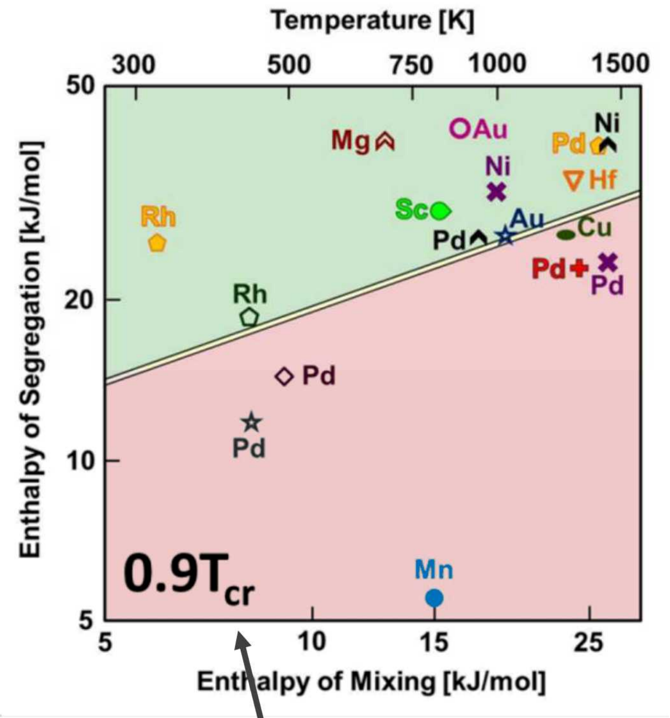


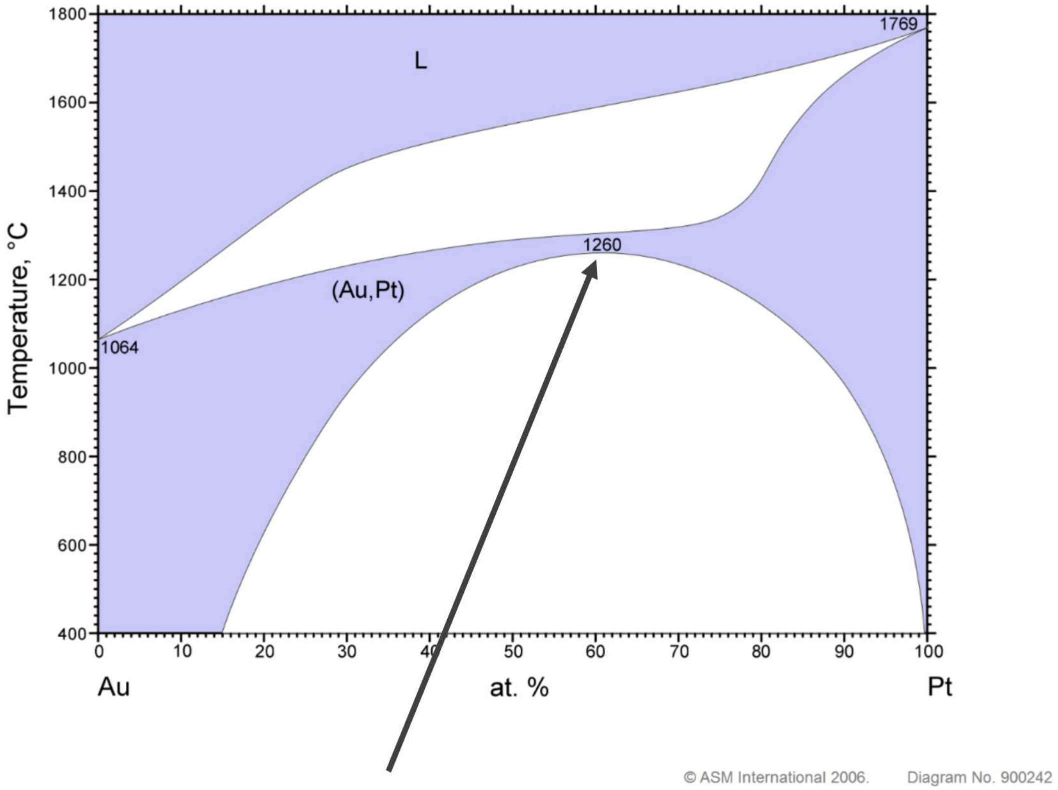
Source: Rockwell Scientific metal-metal switch

Supplementary Slides

Nanocrystalline stability maps: enthalpy of segregation> enthalpy of mixing

Reference: Murdoch and Schuh, J. Mat. Research (2013)





critical temperature = apex of miscibility gap

Two routes to stabilize nanocrystalline metals – kinetics and thermodynamics

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

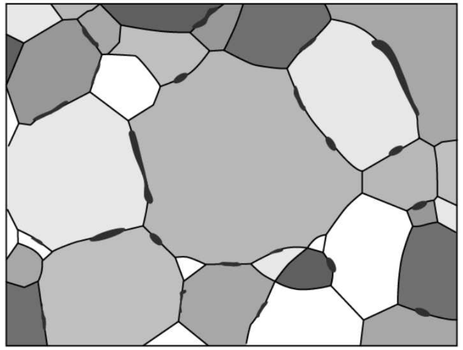
P = pressure on grain boundary

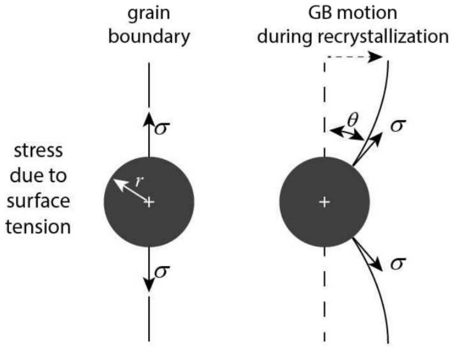
γ_o = interfacial energy per unit area

r = mean grain radius

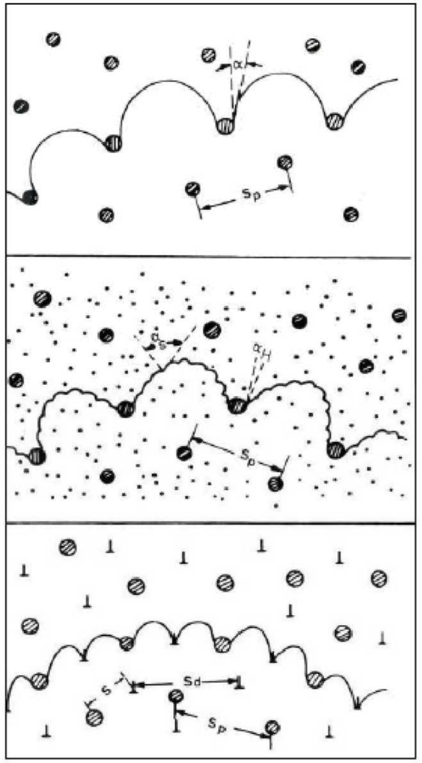
Limit the ***kinetics*** of recrystallization (traditional quasi-stability)

e.g. Zener pinning, solute drag, porosity





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



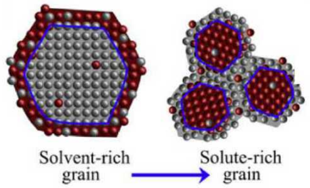
Weissmüller (1993), Kirchheim (2002), and Schuh (2012) have made significant contributions toward understanding and achieving ***thermodynamic*** stability by lowering grain boundary energy through solute segregation

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

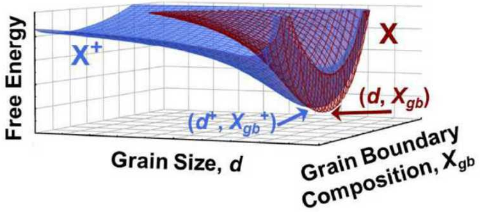
$$\Delta G^{\text{mix}} = (1 - f_{\text{gb}})\Delta G_{\text{c}}^{\text{mix}} + f_{\text{gb}}\Delta G_{\text{gb}}^{\text{mix}} + z\nu f_{\text{gb}}(X_{\text{gb}} - X_{\text{c}})\left[(2X_{\text{gb}} - 1)\omega_{\text{gb}} - \frac{1}{zt}(\Omega^{\text{B}}\gamma^{\text{B}} - \Omega^{\text{A}}\gamma^{\text{A}})\right]$$

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

Grain structure model:
segregated 2-phase metal system



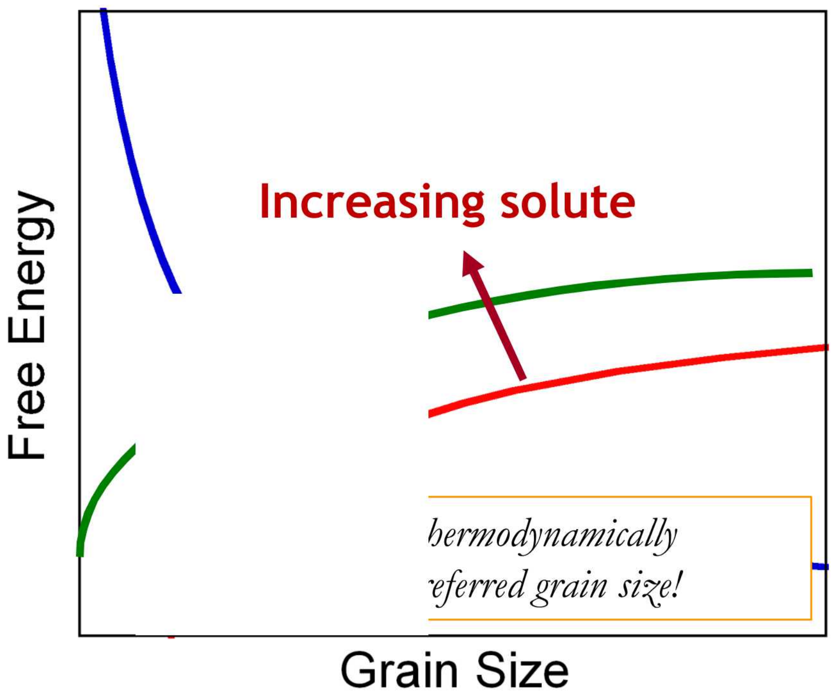
ref: Murdoch et al., Acta Mat. (2013)

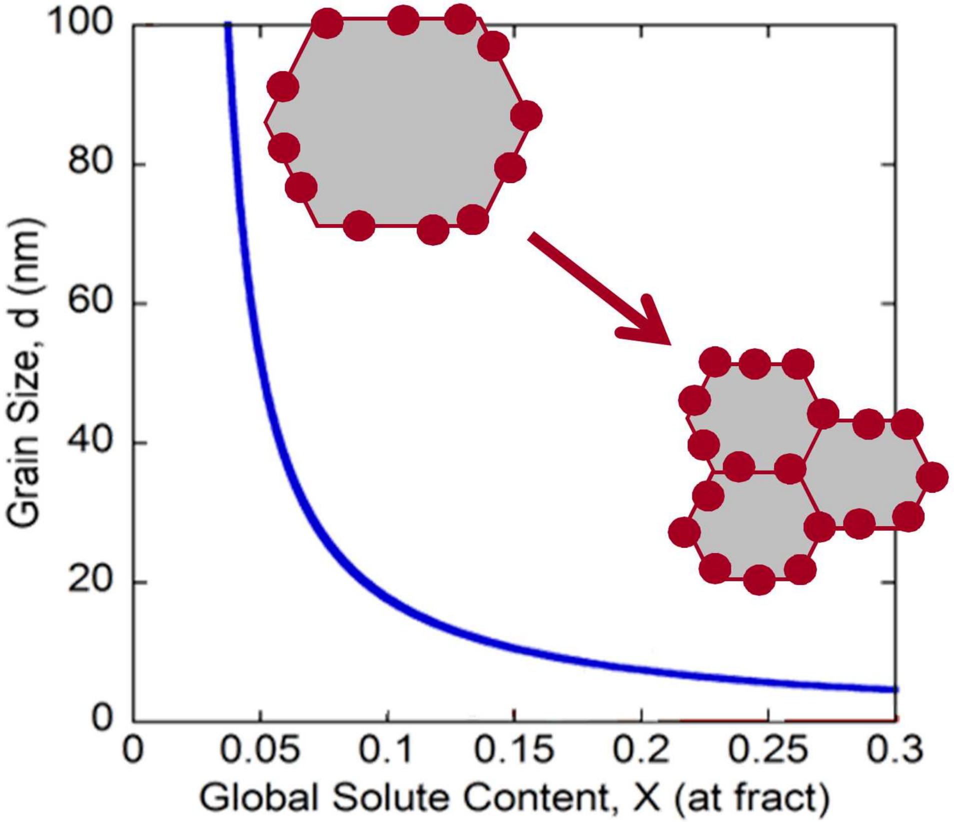


ref: Murdoch et al., Acta Mat. (2013)

GB solute segregation reduces thermodynamic drive for growth

Reference: Murdoch and Schuh, Science (2012)

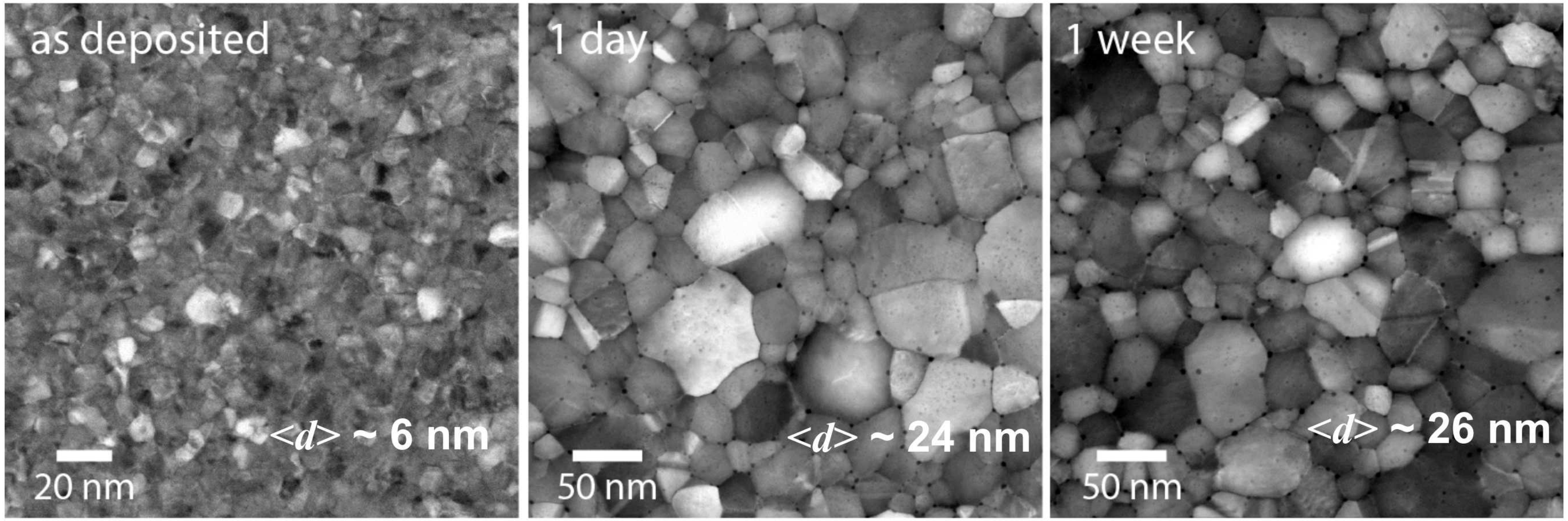


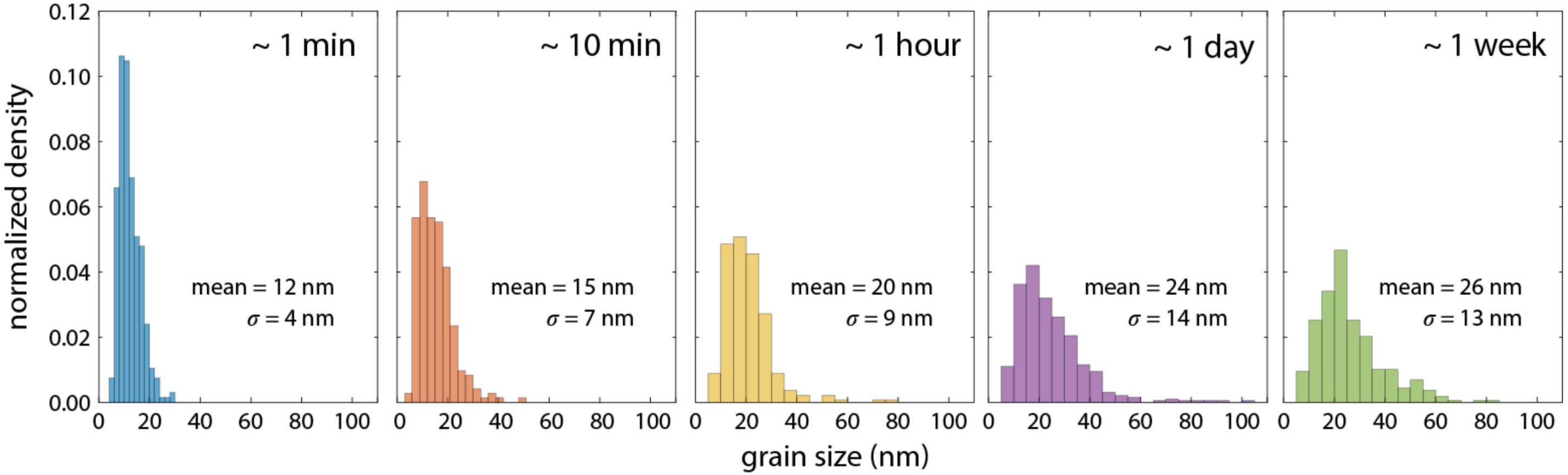


Increasing solute lowers the grain boundary energy and reduces the stable grain size

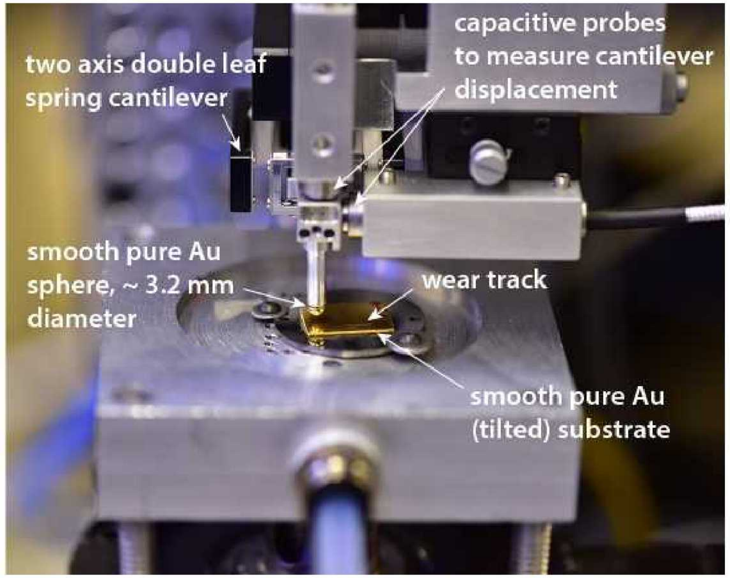
TEM grain growth studies of Pt-Au thin films by annealing at 500°C

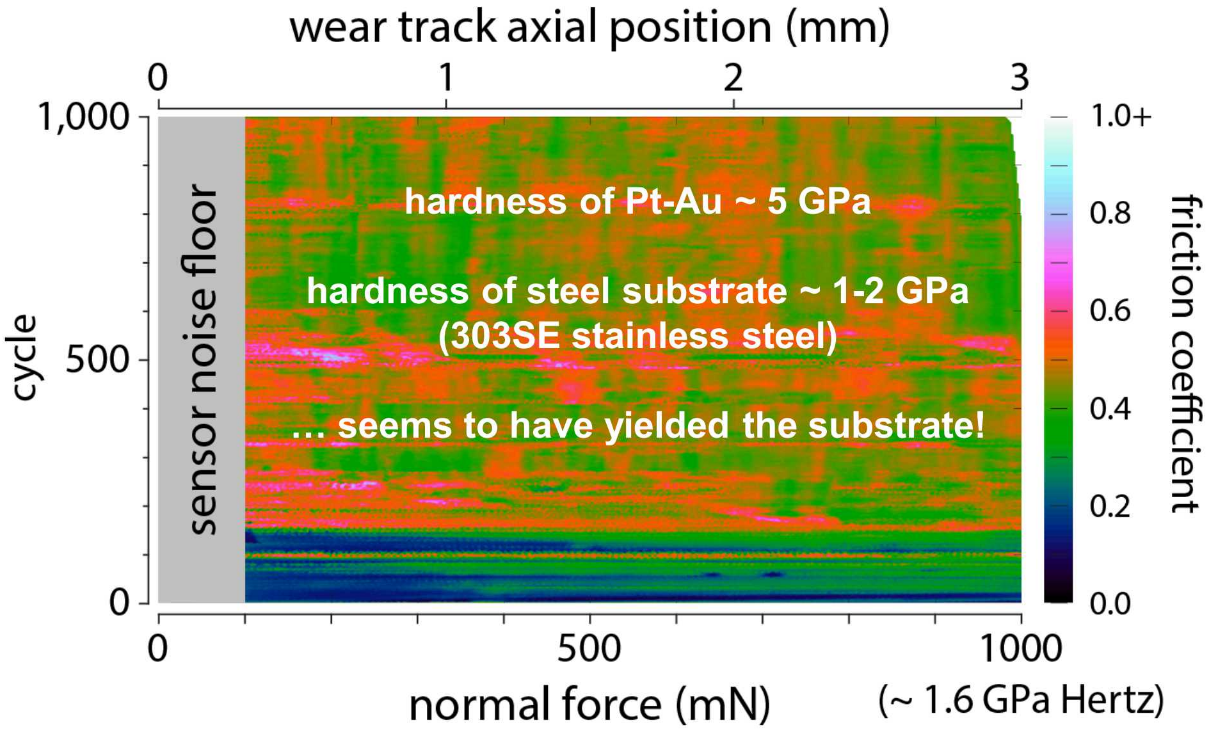
freestanding 18 nm thick films





What about *mechanical* stability? Preliminary tribological testing is promising





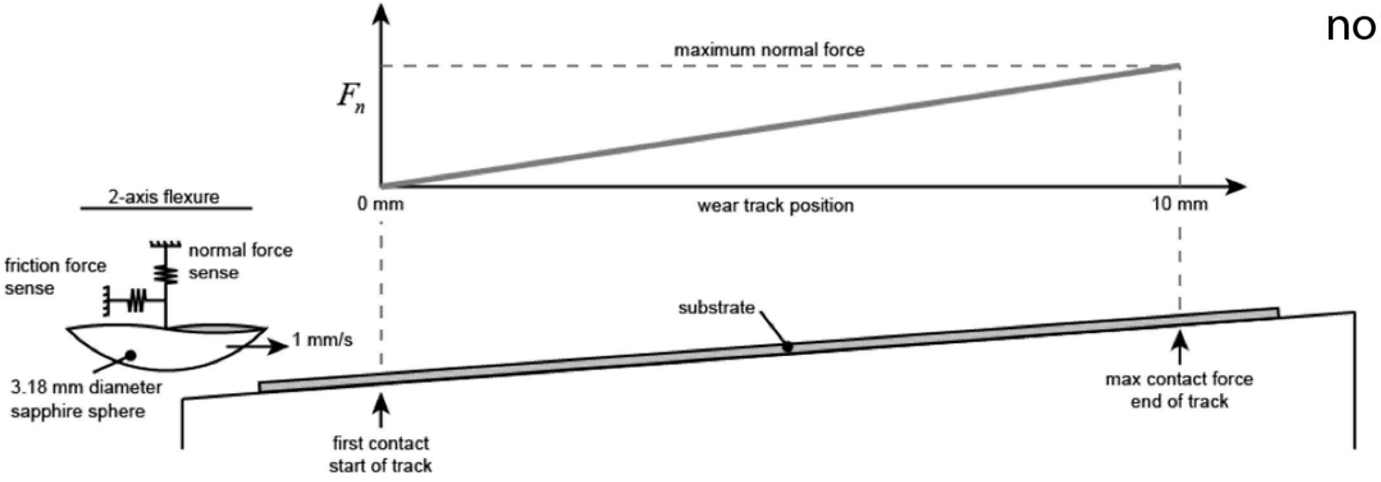
hardness of Pt-Au ~ 5 GPa

hardness of steel substrate ~ 1-2 GPa (303SE stainless steel)

… seems to have yielded the substrate!

(~ 1.6 GPa Hertz)

Diagram of ramped contact force experiment



Friction maps of self-mated PtAu show contact stress dependence

Ramped force experiments on initially nanocrystalline Pt and Pt-Au films (using hard Au-alloy probes):

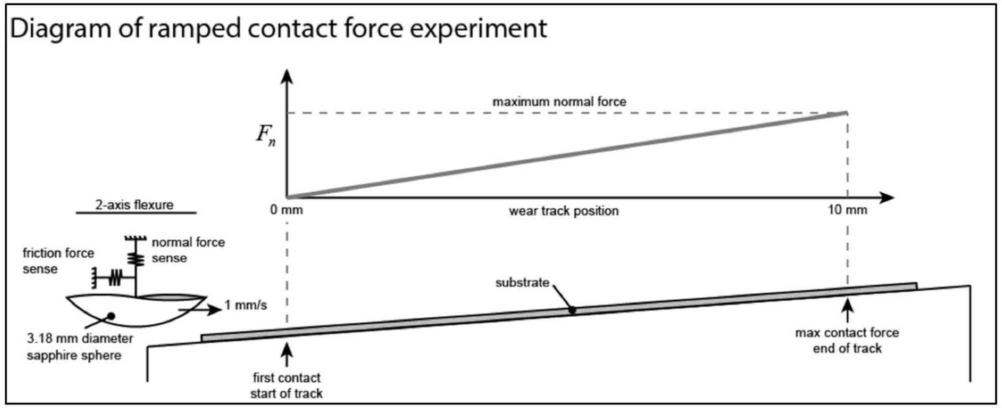
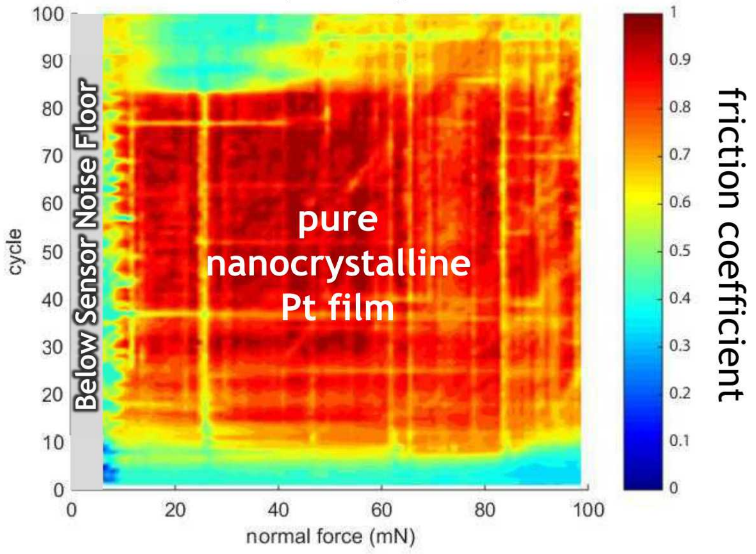
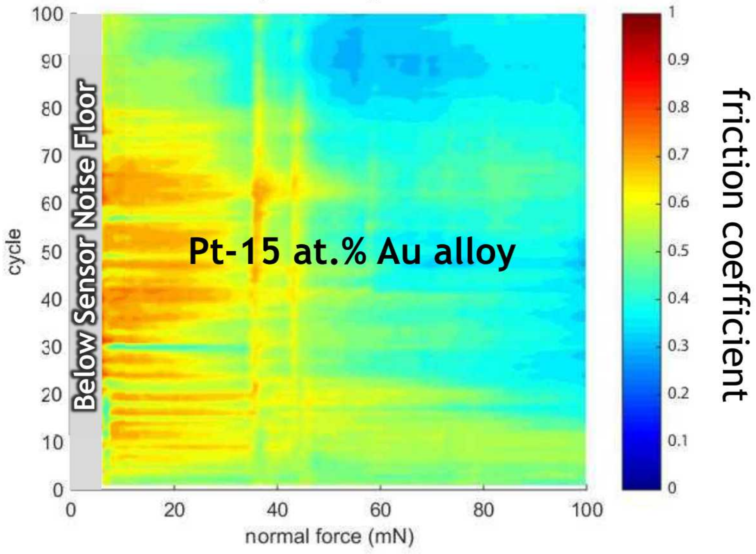


Diagram of ramped contact force experiment

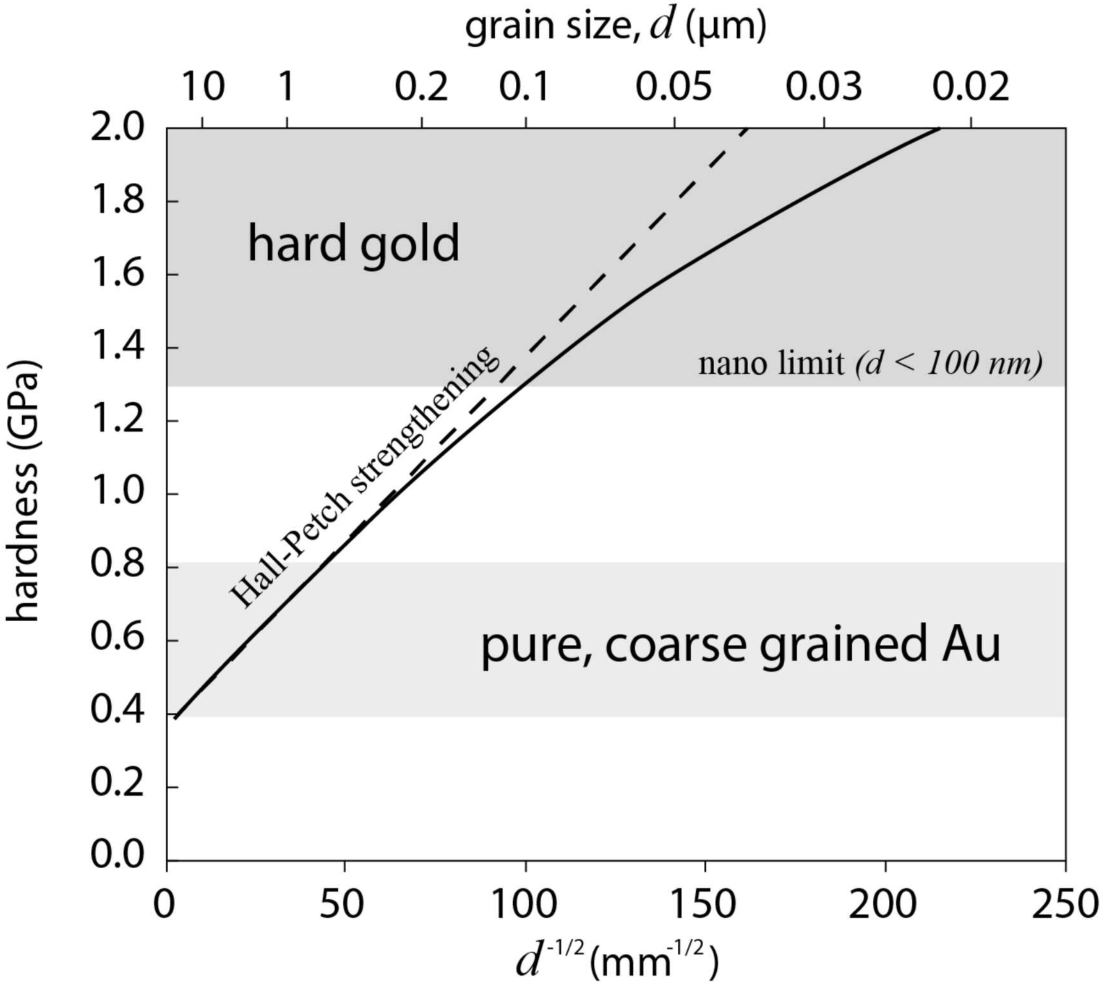
high friction (> 0.8)
after prolonged run-in



low friction (< 0.3)
after prolonged run-in

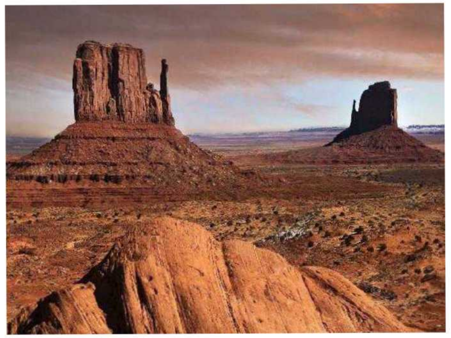


Therefore, reduced friction due to high hardness… right?

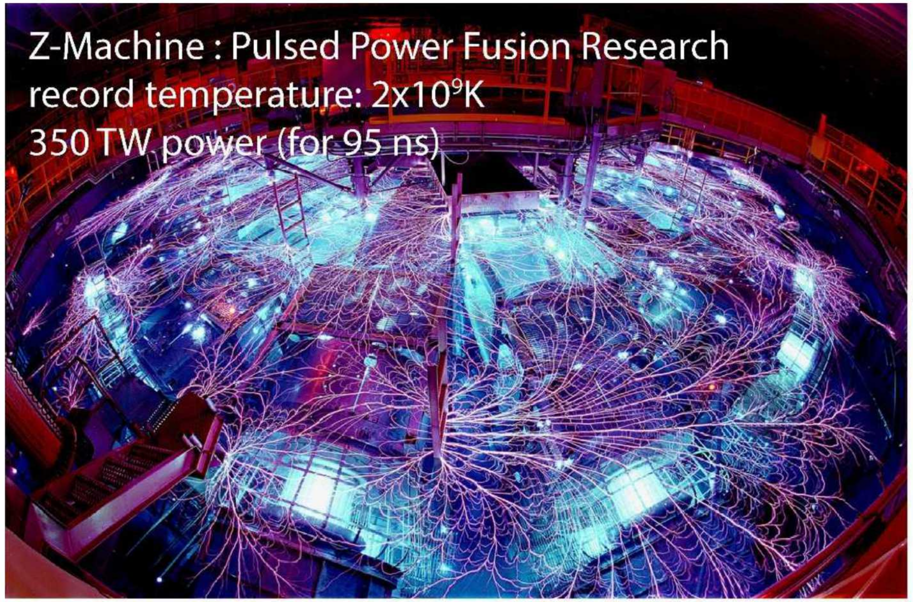


Reference: C. Lo, J. Augis, and M. Pinnel, JAP (1979)

Albuquerque, NM:

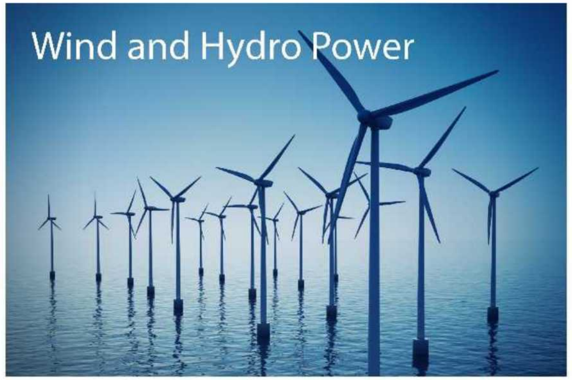


Sandia National Laboratories – Some Highlights



Z-Machine : Pulsed Power Fusion Research
record temperature: 2x10^{9}K
350 TW power (for 95 ns)

Col. John Stapp
46.2G Deceleration



Wind and Hydro Power

Solar Tower - Molten Salt - 6 MW

Annual Budget (2016) : $2.4B
Employees: ~ 10k
HQ: Albuquerque, NM