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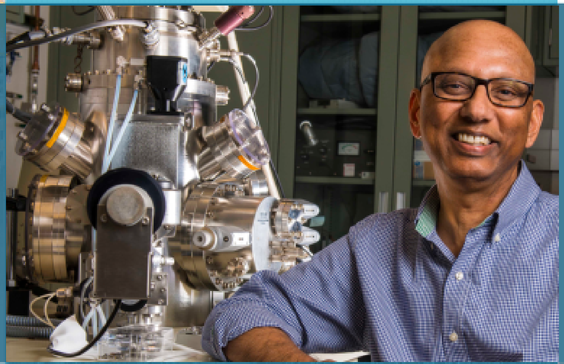
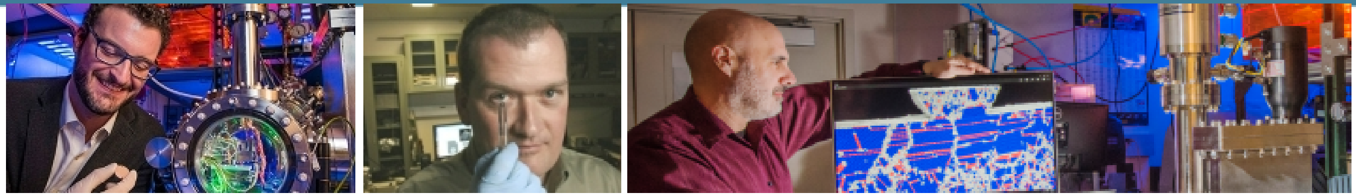
SAND2022-2190C

Sandia National Laboratories

Tribochemical formation of diamond-like carbon films on catalytically-active noble alloys





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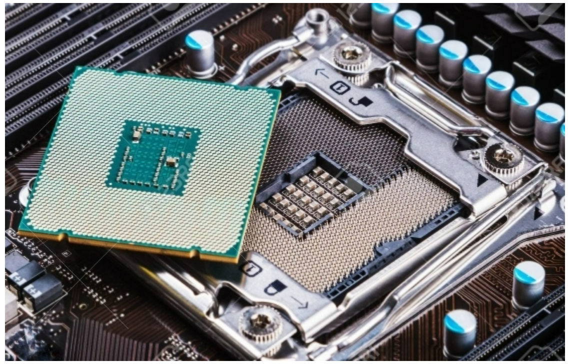
Problem statement: friction and wear in electrical contacts

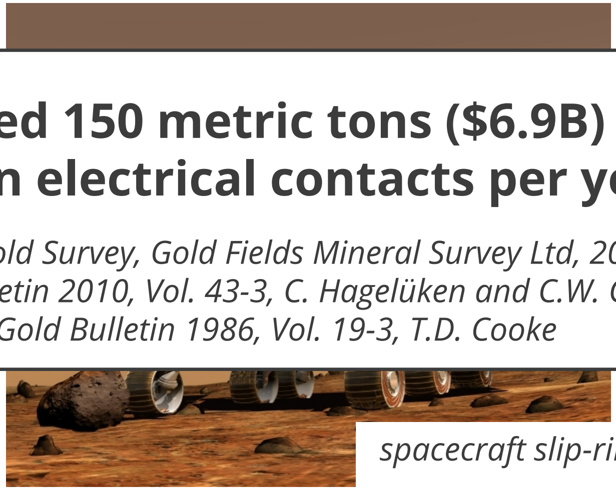
wind turbine slip-rings (sensors and blade pitch motors)

PCB sockets

cell phones

CPU sockets



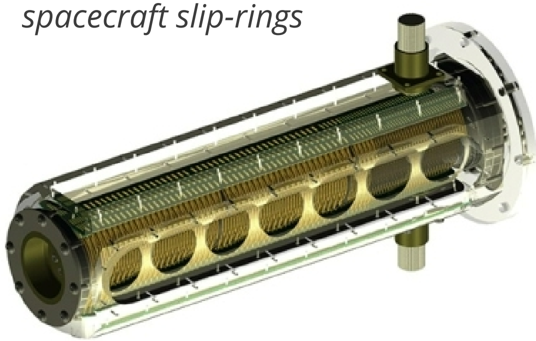


Estimated 150 metric tons ($6.9B) of Au used in electrical contacts per year.

Refs: Gold Survey, Gold Fields Mineral Survey Ltd, 2011
Gold Bulletin 2010, Vol. 43-3, C. Hagelüken and C.W. Corti,
Gold Bulletin 1986, Vol. 19-3, T.D. Cooke

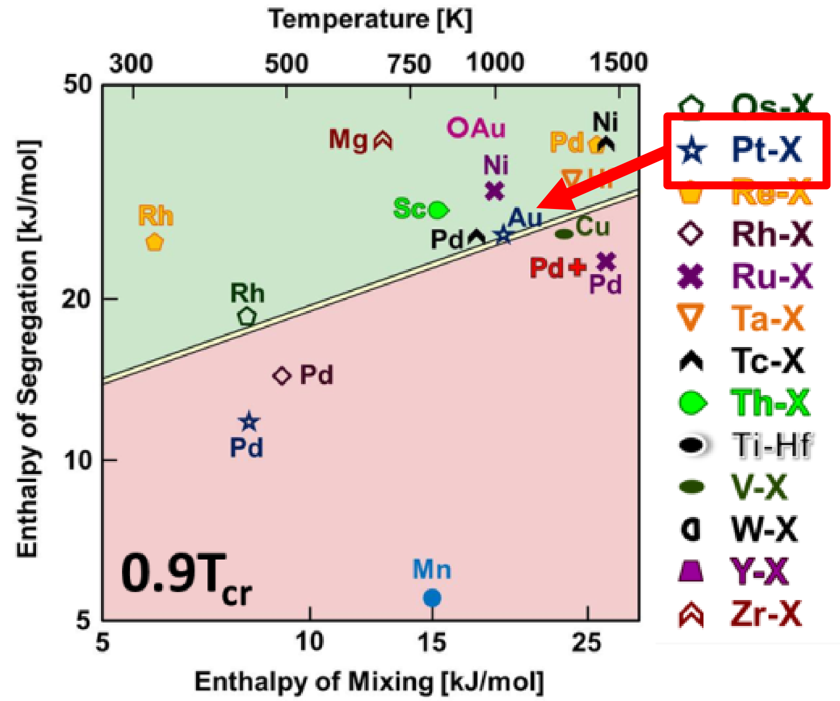
RJ45 connectors

spacecraft slip-rings



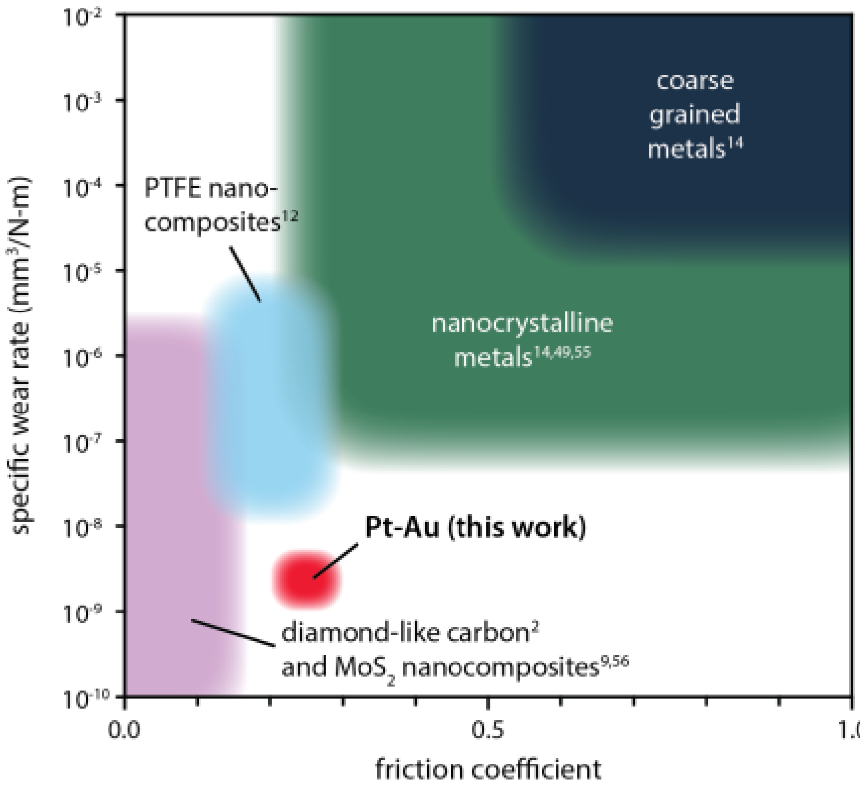
EV charging

Proposed solution: ultra-low wear Pt-Au alloys



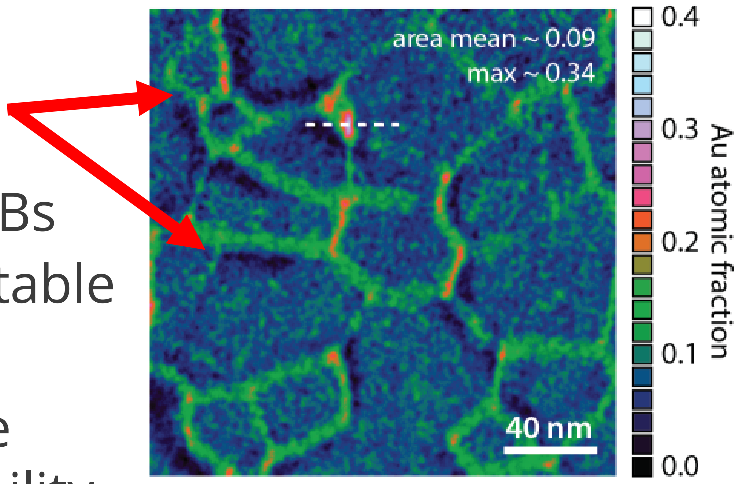
Benefits

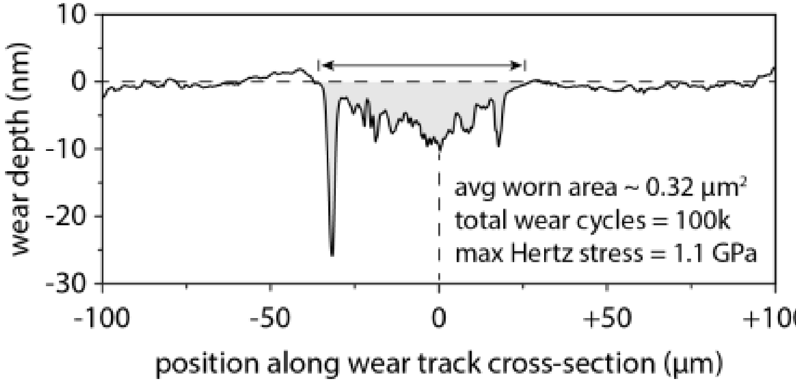
- Mitigate cyclic stress-driven coarsening.
- Increase fatigue resistance.
- Reduce delamination driven wear.



segregation of solute to GBs

- Developed thermodynamically stable binary metal alloy (Pt & Au).
- Bet on thermodynamically stable alloys exhibiting mechanical stability.

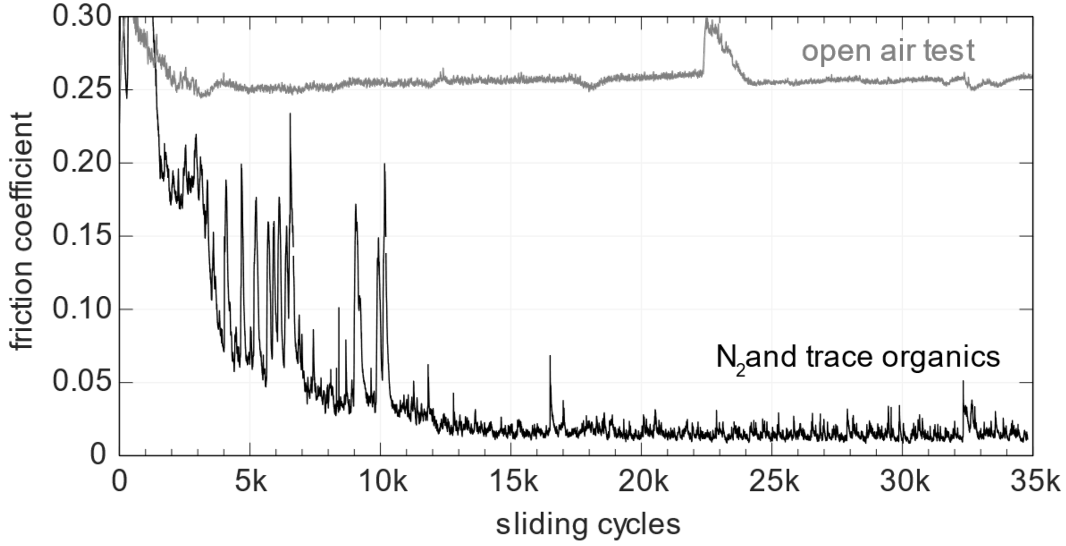




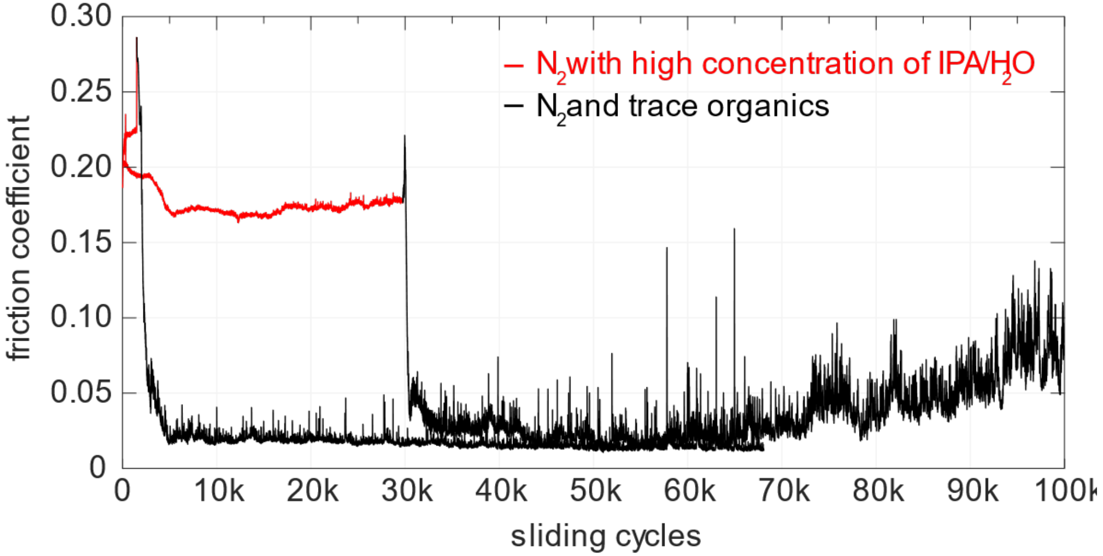
Curry et al., Adv. Mater. 2018
Murdoch and Schuh, J. Mat. Research 2013

Low friction and wear linked to trace organics

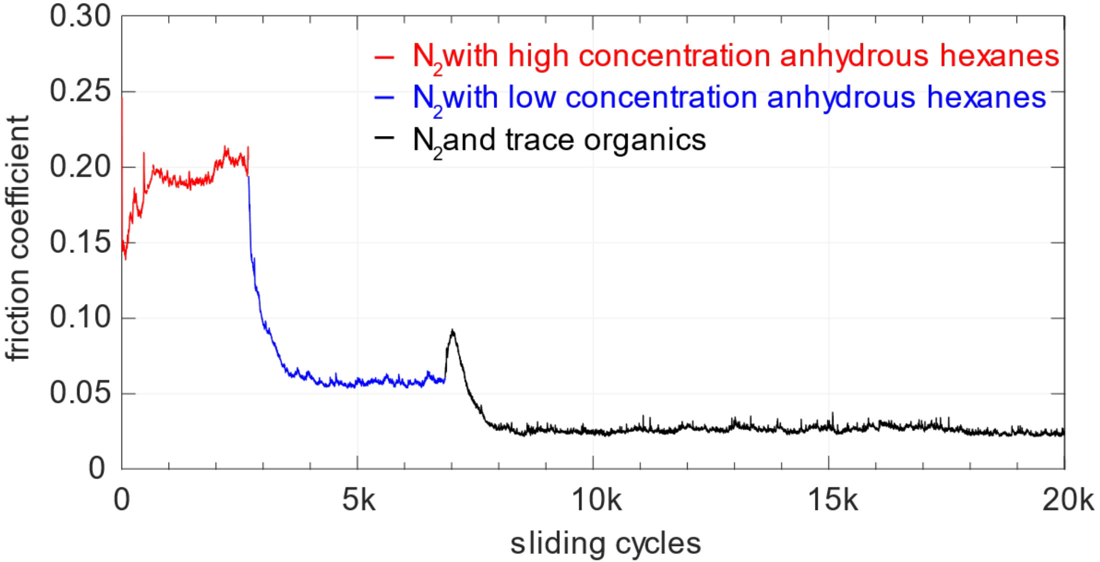
inert gas and lab air comparison



inert gas with water and alcohol vapor



inert gas with anhydrous hexanes

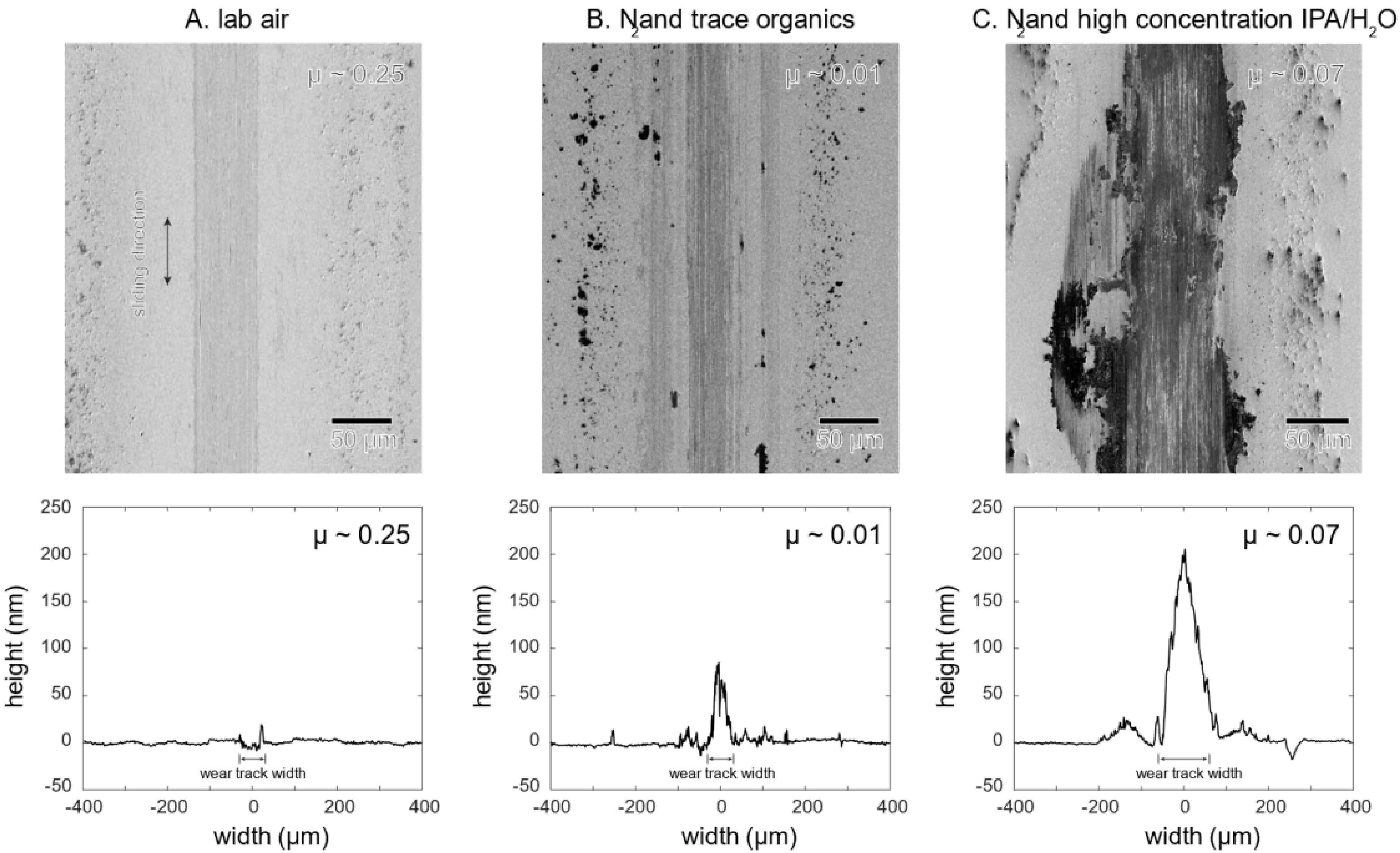


- Testing in inert environments lowers friction?
- Priming the enclosure with hydrated IPA accelerates drop… and prolongs it.
- Any amount of anhydrous hexanes increased friction, with higher/lower friction at higher/lower concentrations.
- Unclear what role water/oxygen play.

Argibay et al., Carbon 2018

Tribofilm accumulation is key to the behavior

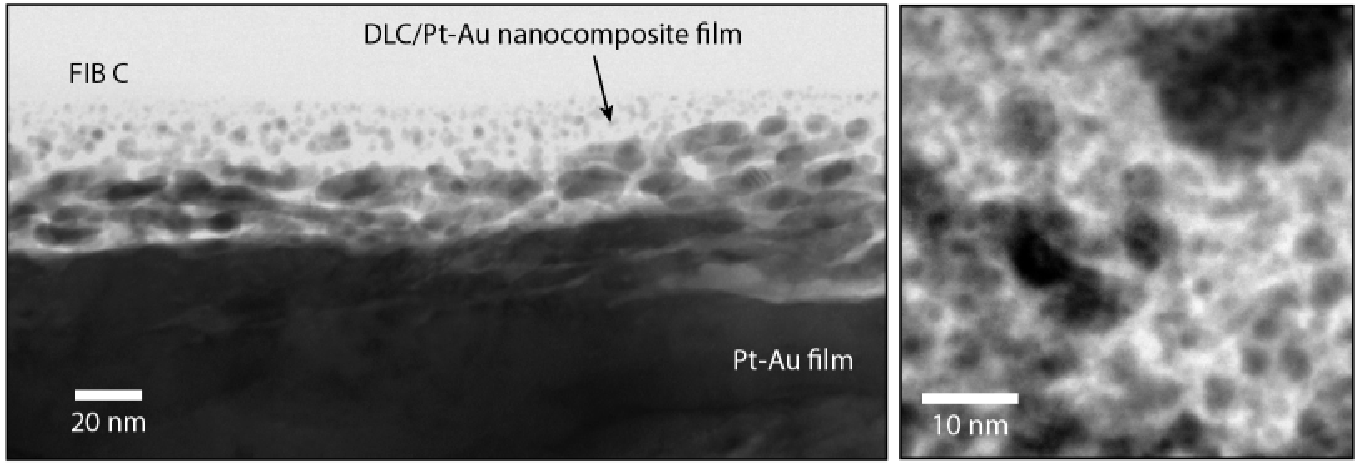
- Film thickness not sustained in air; likely influence of oxygen or water.
- Ultra-high purity N_2: films grow to about 50 nm; low friction achieved.
- Hydrated IPA: film thickness increased to 200 nm; friction increased.

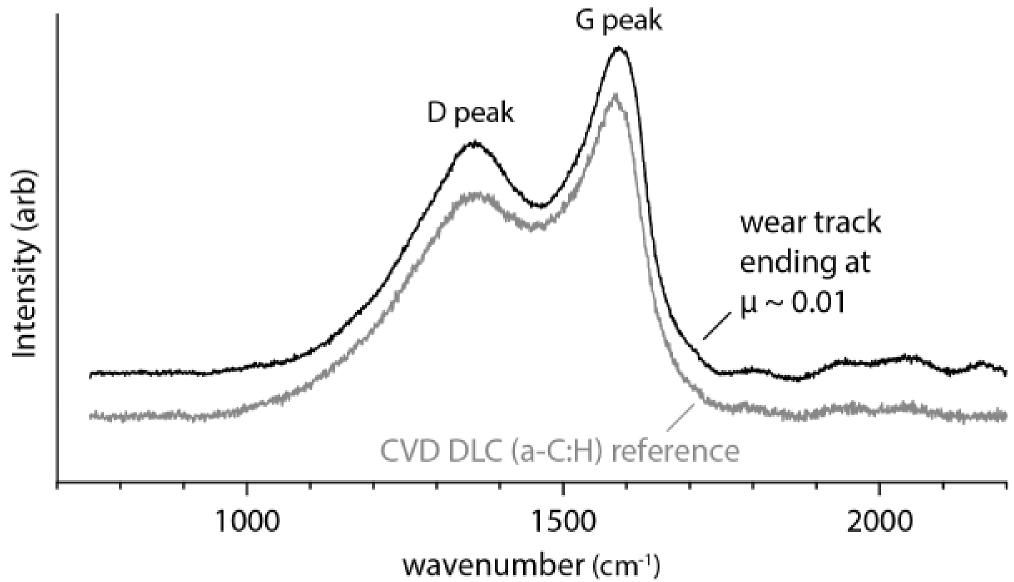


Argibay et al., Carbon 2018

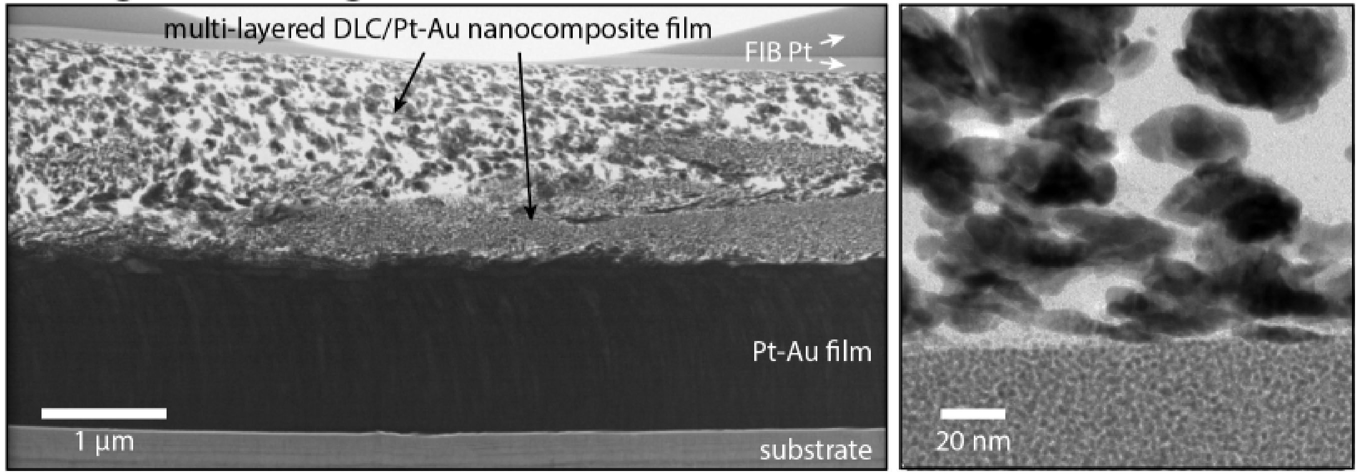
Tribofilms are diamond-like carbon nanocomposites

nitrogen and trace organics





nitrogen and high concentration of IPA/H_2O



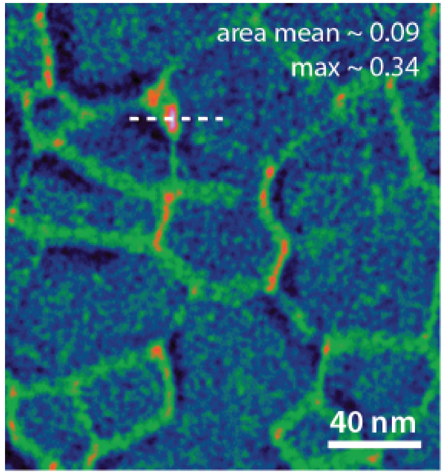
- Tribofilms are DLC and Pt-Au particles, confirmed by TEM and Raman.
- High concentrations exhibit larger, less mixed/layered particles, possibly limiting mixing and Pt interaction.
- Need to characterize stress- and time-dependent formation!

Argibay et al., Carbon 2018

How do we study the tribofilm structure and properties?

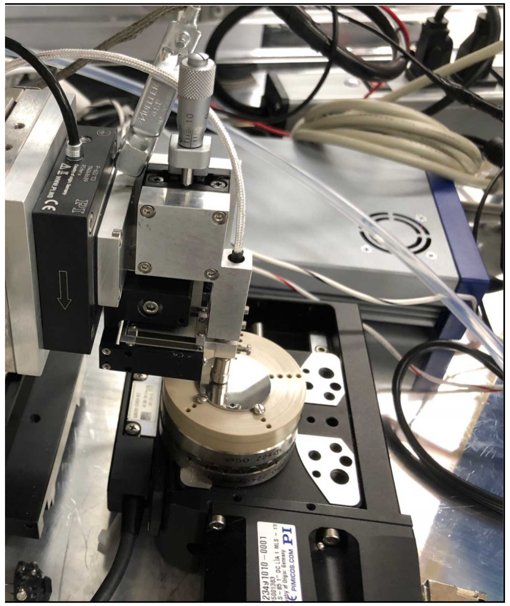
Pt-Au Deposition

- DC magnetron sputtering
- Thickness: 1 μm to 2 μm
- Film composition verified via electron microprobe: 90 at.% Pt and 10 at.% Au.



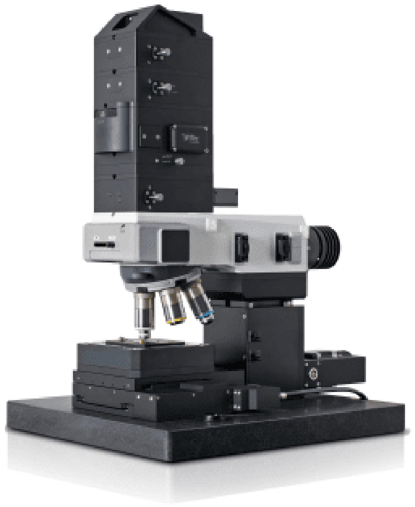
Macroscale Tribology

- Anton Paar Tribometer
- 3.2 mm sapphire spheres
- 0.55 to 1.2 GPa pressure
- N_2 environment at 25 °C



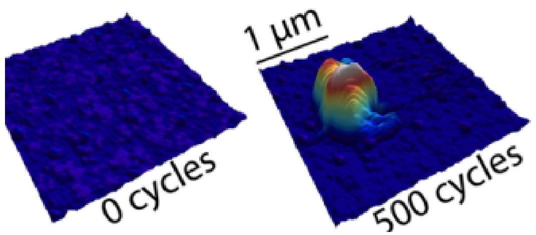
Raman Spectroscopy

- WiTec alpha 300R Raman
- 532-nm incident laser
- Spectral accuracy of 1 cm^{-1}
- Spatial resolution of 2 μm
- Carbon concentration was estimated by quantifying the strength of the G-mode peak near 1580 cm^{-1}.



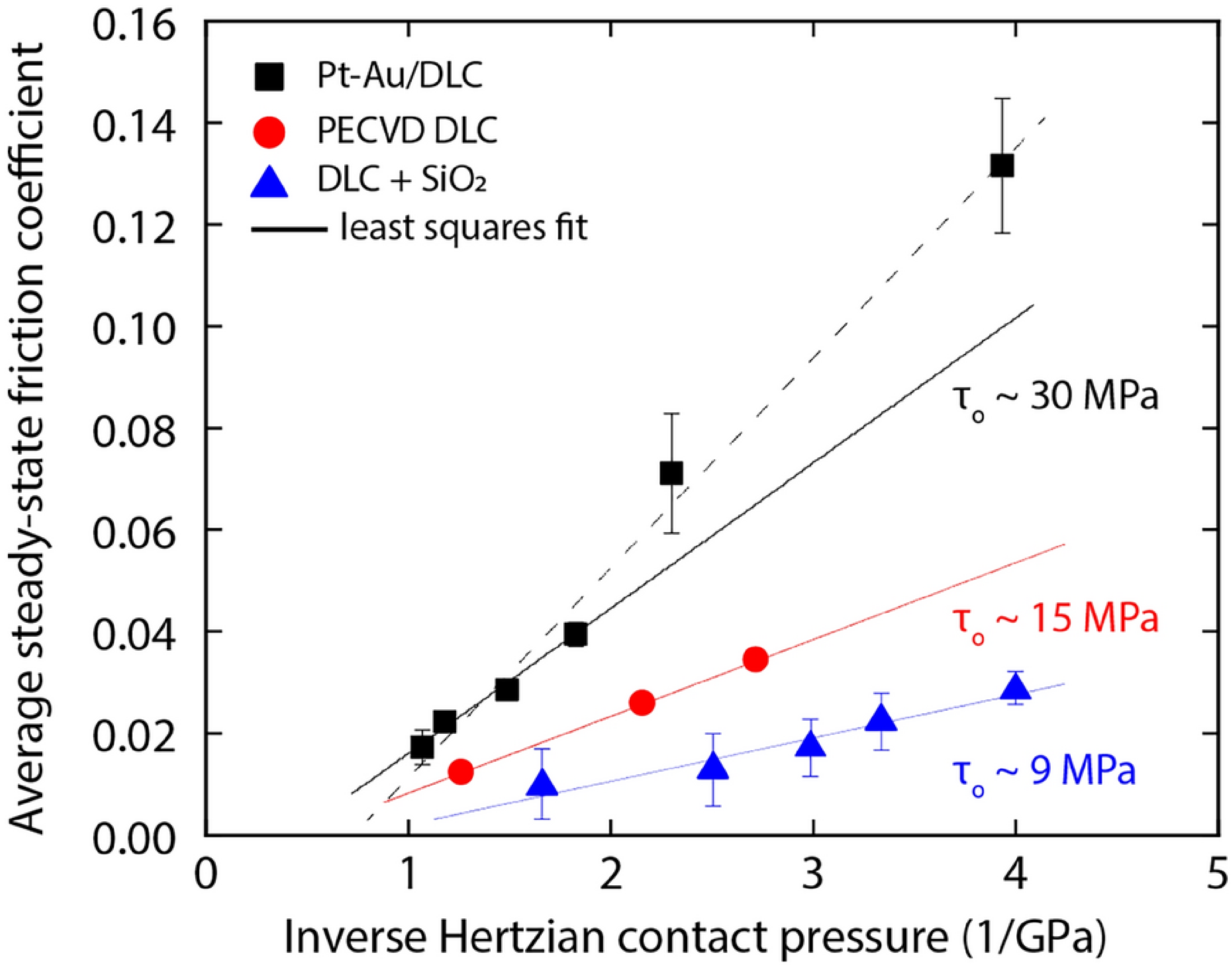
Nanoscale Tribology

- Asylum MFP-3D AFM
- N_2 environment at 25 °C
- Diamond-coated Si tips
- Two-step process: contact mode over 1 μm × 1 μm area and intermittent-contact mode image over 3 μm × 3 μm area.



Tribofilm shear strength comparable to other DLC films

- The slope of the coefficient of friction μ and inverse contact pressure $1/P$ data used to determine shear strength τ.
- τ decreased as P increased due to changes in the structure and properties of the tribofilm.
- τ is comparable to traditional DLC and composite films (10-50 MPa).
- Differences due to varying film thickness, sp2/sp3 carbon content, and the degree of hydrogenation.



Jones et al., JOM 2021

Higher contact pressures result in more disordered films

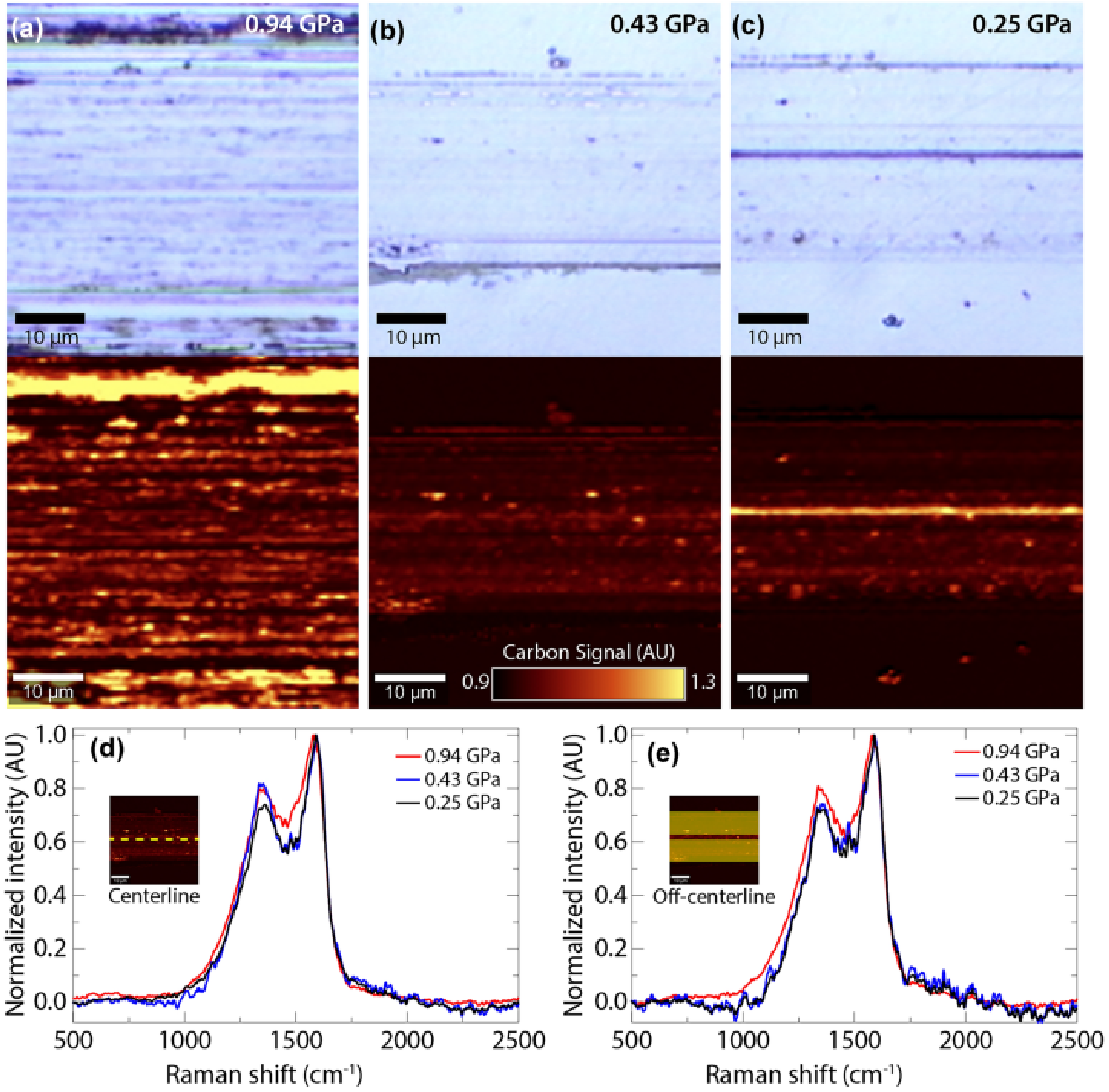
- Optical images and Raman maps of the G-mode (1580 cm^{-1}) intensity were taken as a function of contact pressure.

Coverage and Thickness

- The coverage and thickness increased as the contact pressure increased.

Structure

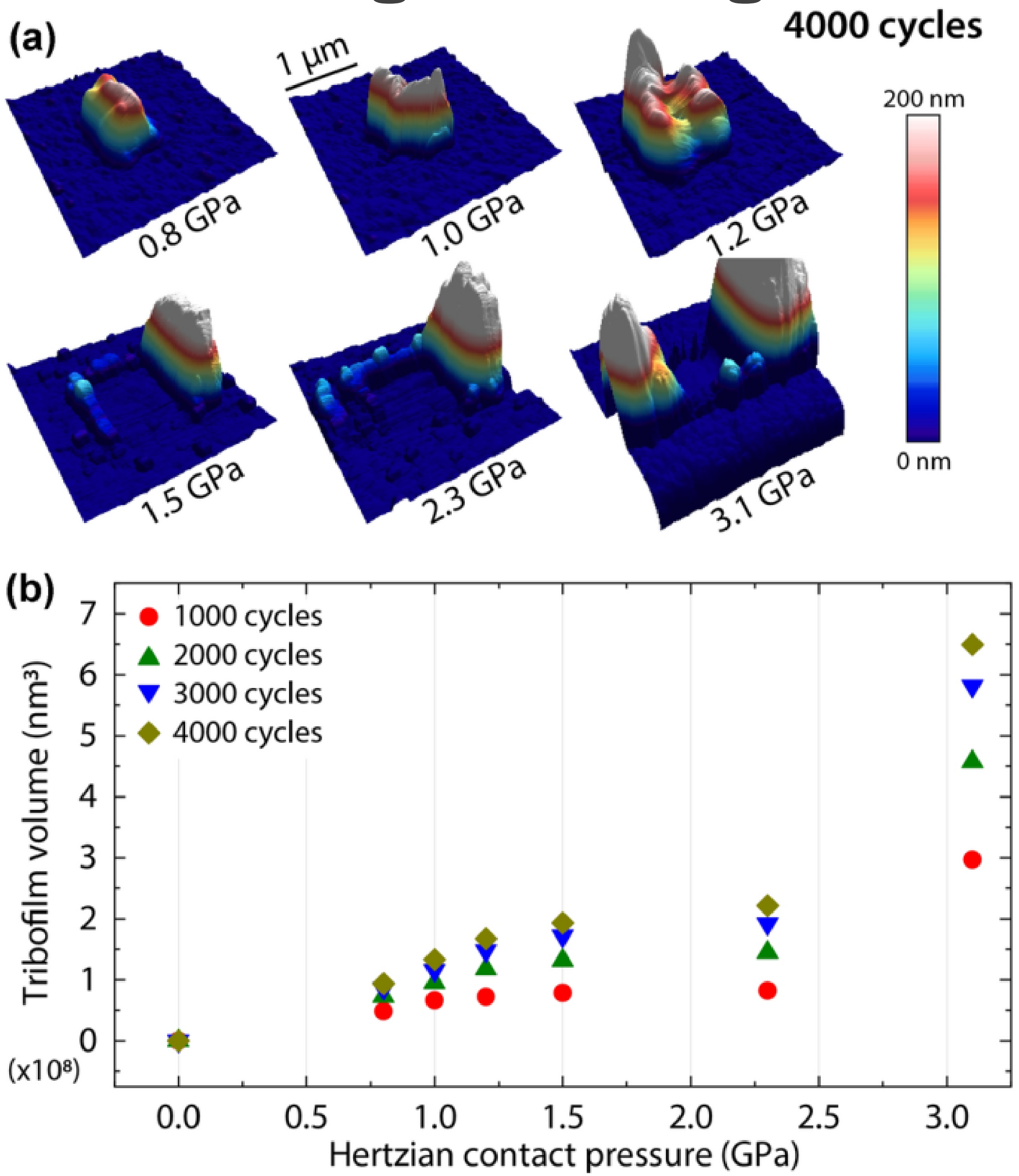
- On the centerline, higher pressures resulted in more disordered sp2 carbon (downshift and broadening of peak).
- Off the centerline, smaller but similar qualitative characteristics (more disorder at higher contact pressures).



Jones et al., JOM 2021

AFM demonstrates two separate tribofilm growth regimes

- Contact-mode scans were generated at pressures from 0.8 GPa to 3.1 GPa and intermittent-contact mode images were taken at 500-cycle increments.



Jones et al., JOM 2021

Two Separate Regimes in Growth

- At small pressures (≤1.2 GPa), tribofilm volume increased linearly, with growth vertically and laterally in the contact region.
- At larger pressures (>1.2 GPa), tribofilm volume increased exponentially due to wear and increased exposure to Pt-Au surface.

Higher cycle counts result in more ordered films

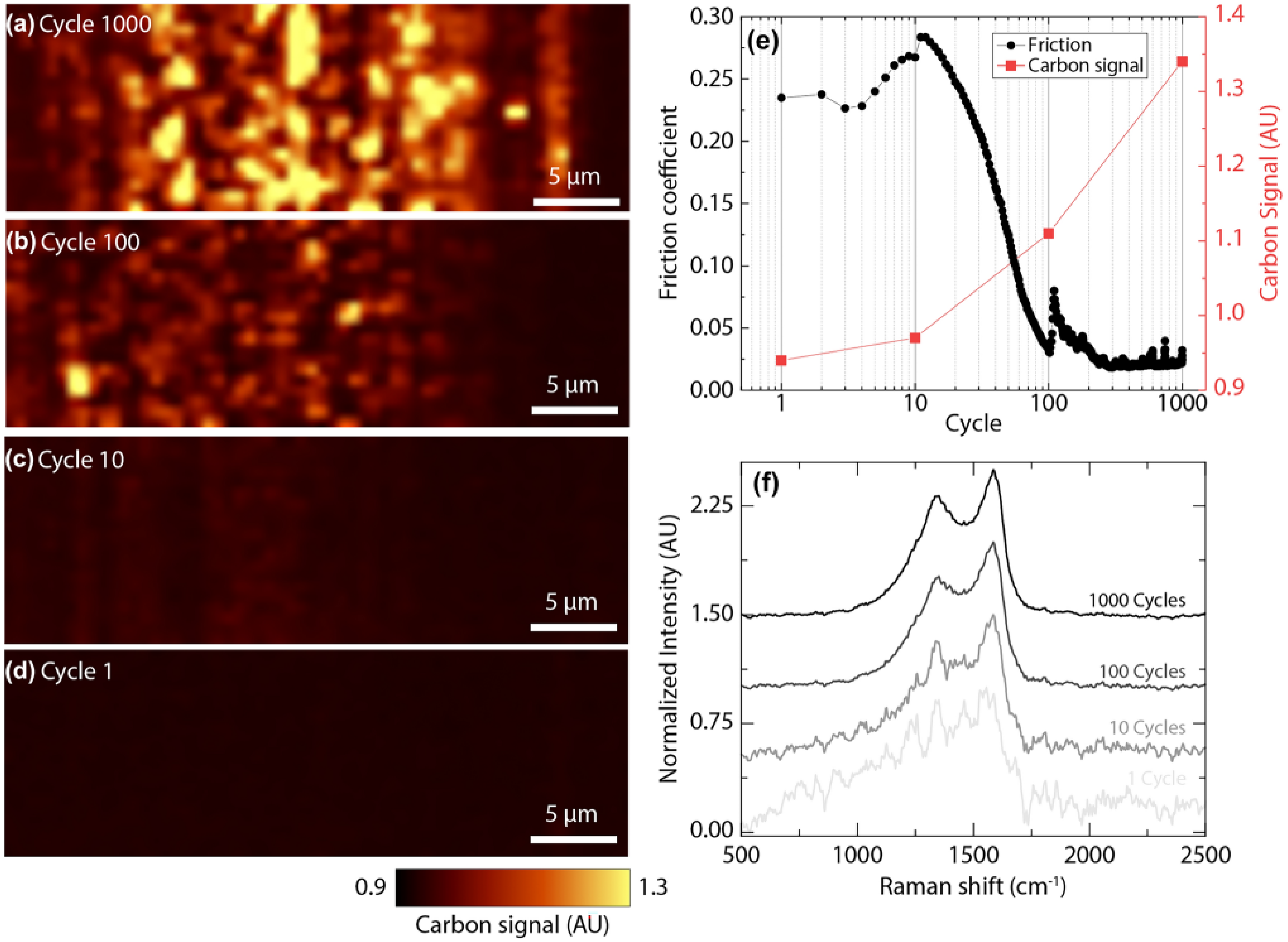
- "Stripe" test was run at 0.55 GPa: 1 cycle over 4 mm, 10 cycles over 3 mm, 100 cycles over 2 mm, and 1000 cycles over 1 mm.

Coverage and Thickness

- The coverage and thickness increased as the cycles increased.

Properties and Structure

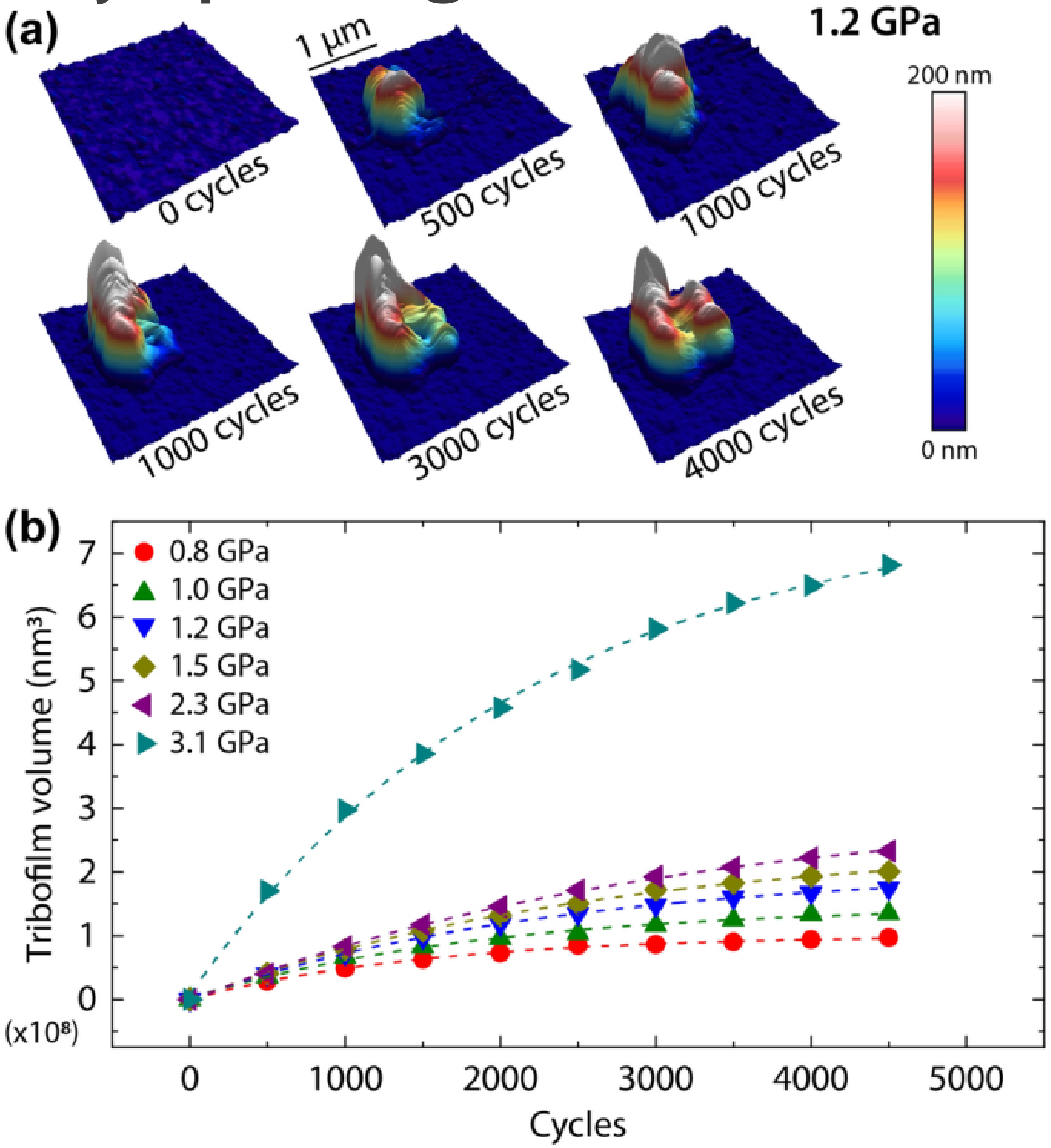
- The lowest friction and highest carbon were at 1000 cycles.
- Spectra show an increase in order with the number of cycles (separation of D and G peaks).



Jones et al., JOM 2021

AFM demonstrates patchy and asymptotic growth

- Contact-mode scans were generated at pressures from 0.8 GPa to 3.1 GPa and intermittent-contact mode images were taken at 500-cycle increments.

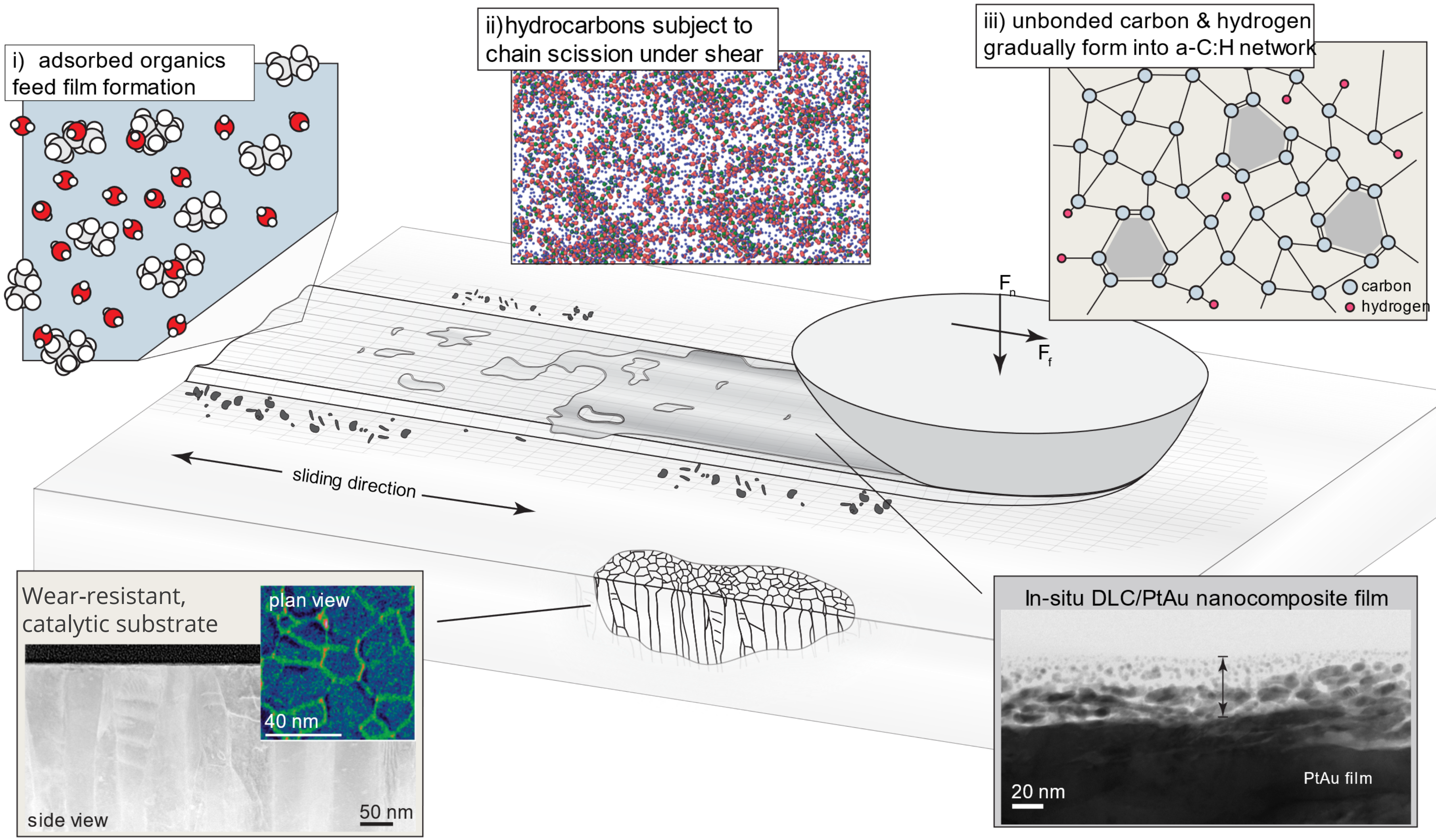


Jones et al., JOM 2021

Growth Morphology and Kinetics

- Patchy growth in the contact region: film nucleation and growth may be dependent on surface roughness and defects.
- Asymptotic growth kinetics: efficacy of the catalytic process for film growth decreased as the number of cycles increased.

Mechanisms of formation



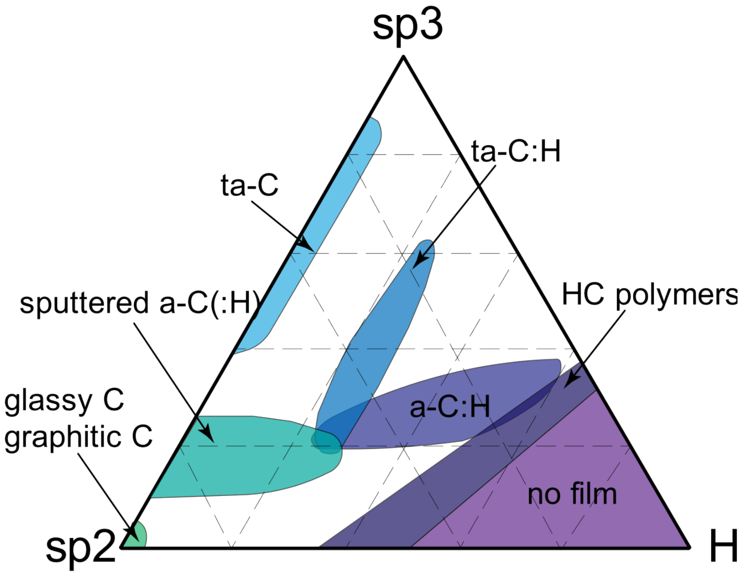
Argibay et al., Carbon 2018

Comparisons to other solid lubricants

solid lubricant	deposition methods	μ_{ss}	F_n	environment
graphite (sp2 bonding)	evaporation, pyrolysis	0.2 - 0.5	0.5 - 1 N	dry N2/UHV
	of HC polymers	0.1 - 0.2	0.5 - 1 N	humid air
DLC (mixed sp2/sp3 bonding)	rf and dc sputtering, ion beam,	0.6 - 0.7 a-C	10 N	dry N2/UHV
	CVD	**0.001 - 0.05 a-C:H**	10 N	dry N2/UHV
		0.1 - 0.2 a-C	10 N	humid air
		0.2 - 0.3 a-C:H	10 N	humid air

* hydrogen content in a-C:H DLC typically between 20-60 at %

- Wide range of definitions for a-C:H/DLC; our tribofilms follow similar friction behaviors in literature (μ=0.01 to 0.05 in dry N_2; μ=0.2 to 0.3 in air/water).
- Elastic recoil detection analysis (ERDA) shows ≈20% hydrogenation (typically 20% to 60%).
- Raman spectra and D/G ratios similar to observed in literature.
- Need better understanding of local structure/ordering (NEXAFS).



Scharf and Prasad, J Mater Sci 2013
Casiraghi et al., Phys Rev B 2005

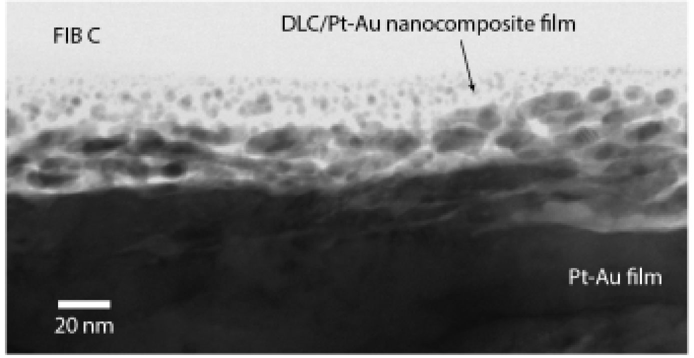
Conclusions and future work

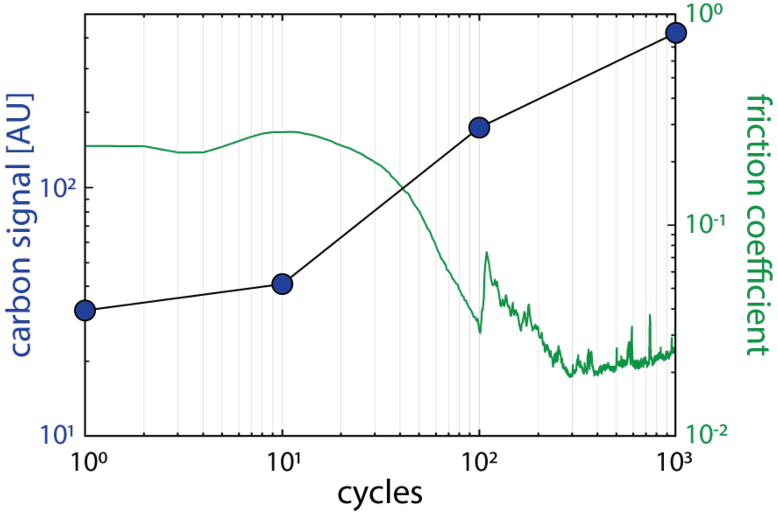
Conclusions

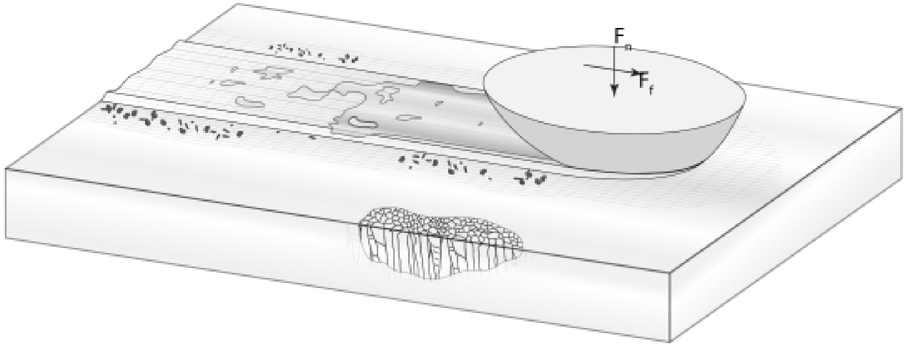
- Carbonaceous tribofilms were formed on Pt-Au surfaces, with μ as low as 0.016 and τ of 30 MPa (similar to other DLC films).
- Raman spectroscopy suggested coverage, concentration, and disorder increased as contact pressure increased.
- AFM highlighted a transition from growth to wear at a pressure of 1.2 GPa and showed the catalytic process decreased with cycles.

Future Work

- Assess relationship between growth rate and temperature for activation energies and reaction rates.
- Need better understanding of local structure and ordering via NEXAFS (better comparisons to DLC films).







Curry et al., Adv. Mater. 2018
Argibay et al., Carbon 2018
Jones et al., JOM 2021