Understanding Friction in MoS2, Part 2: Water, Oxidation and Run-in

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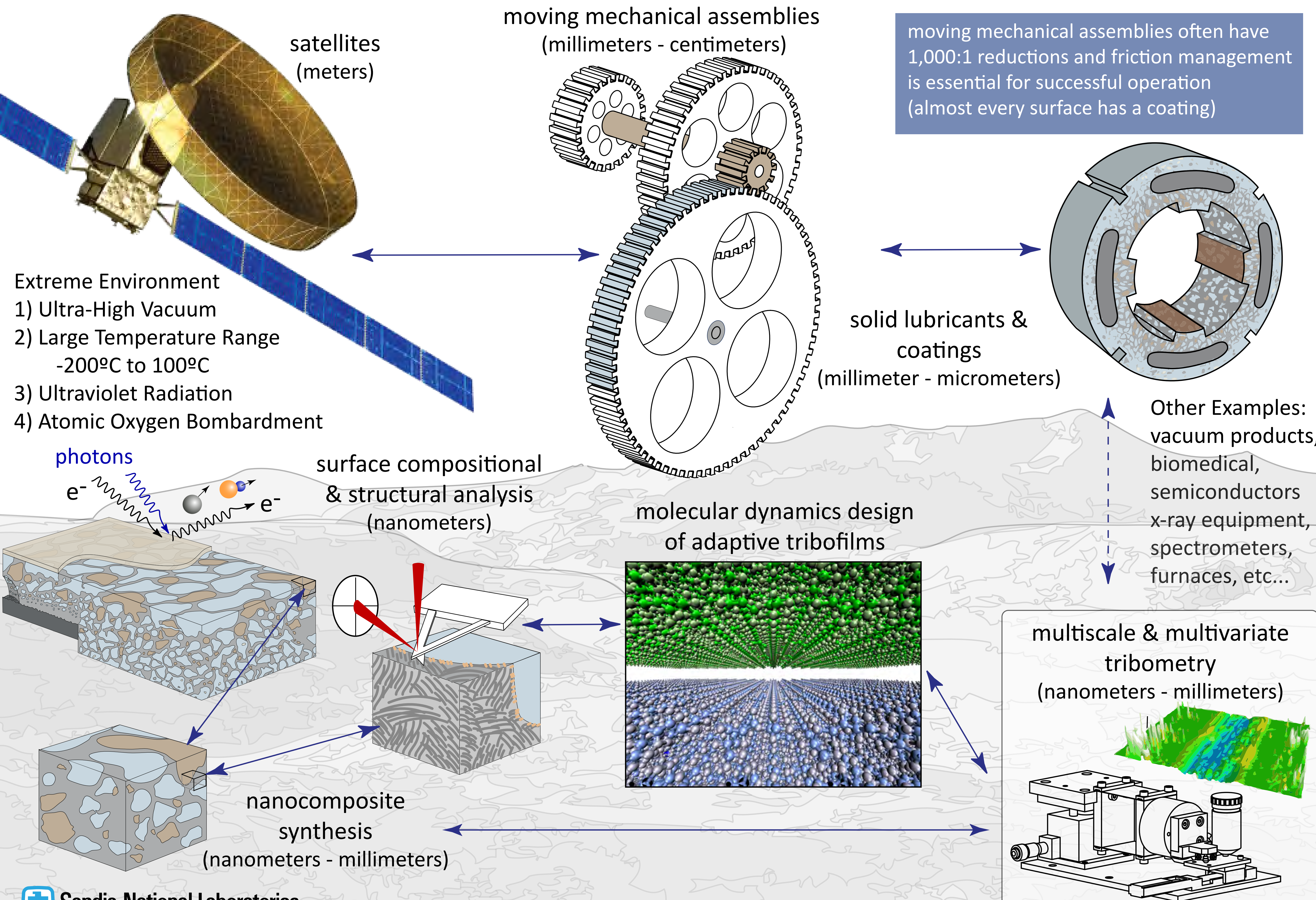
Fundamental Studies and Applied Challenges



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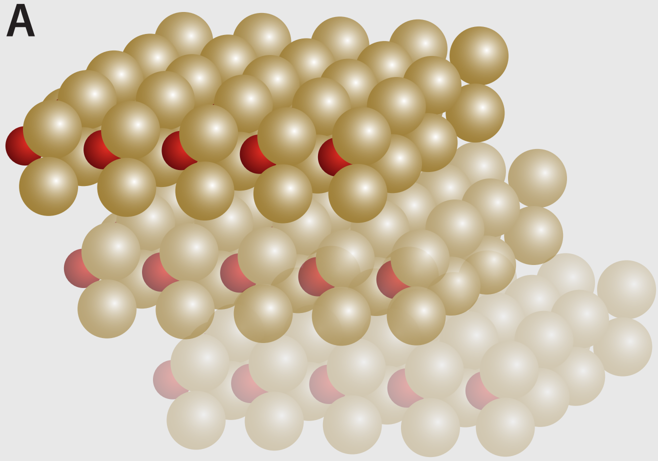
MoS_2 Coatings

molybdenum disulphide

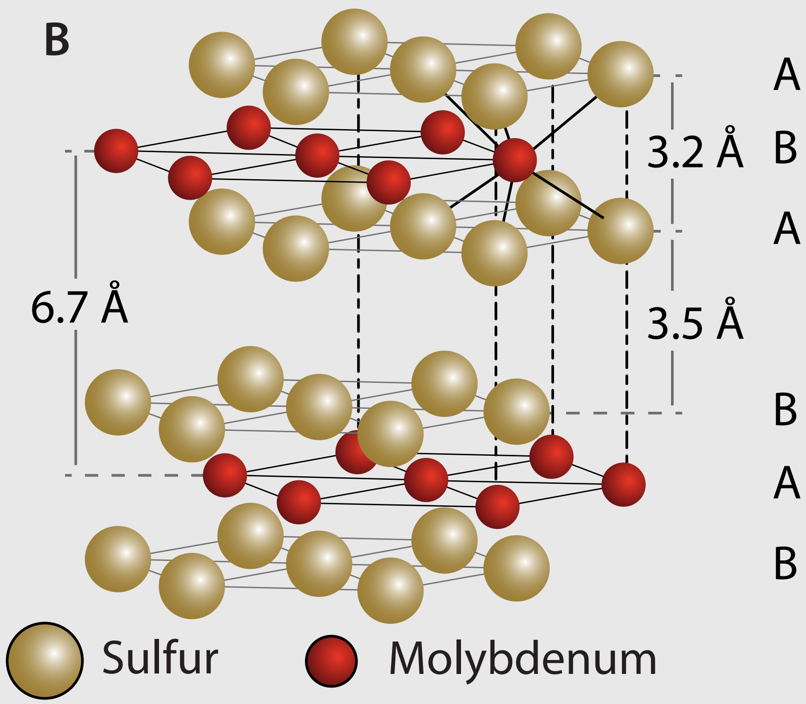
μ = 0.02 - 0.06 (inert @ 1N)

μ = 0.15 - 0.25 (humid air @ 1N)

A

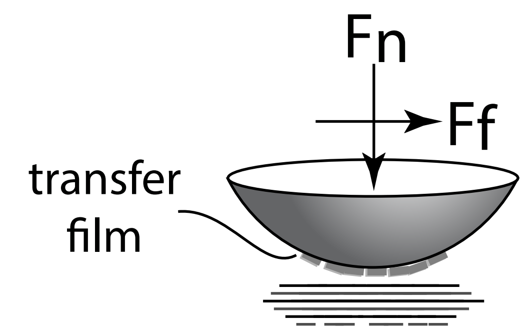


B



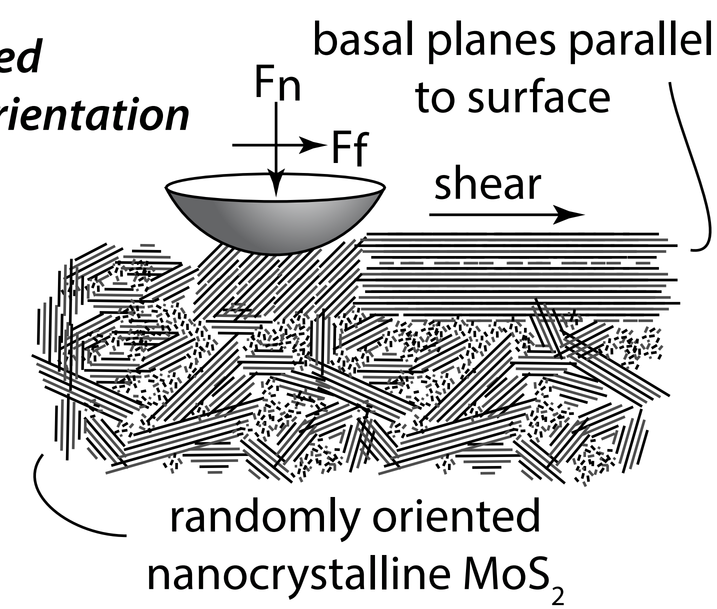
(A) Depiction of the layered structure of MoS_2 lamellae stacked upon one another. (B) Hexagonal stack lattice structure of MoS_2 with atomic spacing and sequencing.

Run-In Processes



1) Transfer Film Formation

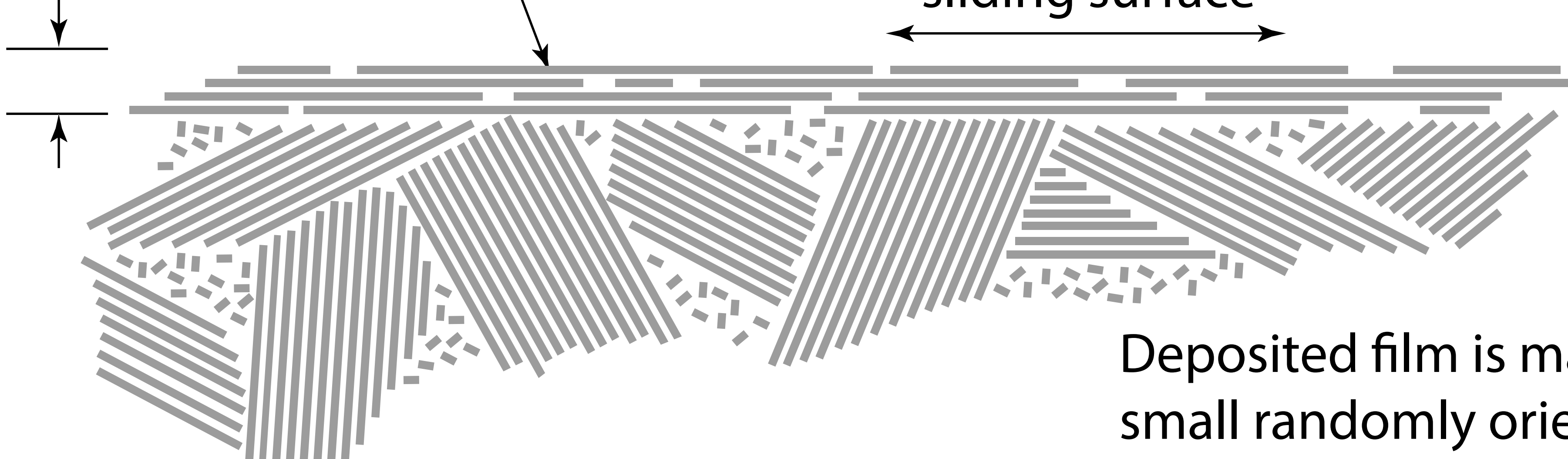
2) Shear-induced crystallite re-orientation



oriented surface layer of 002 basal planes of MoS_2

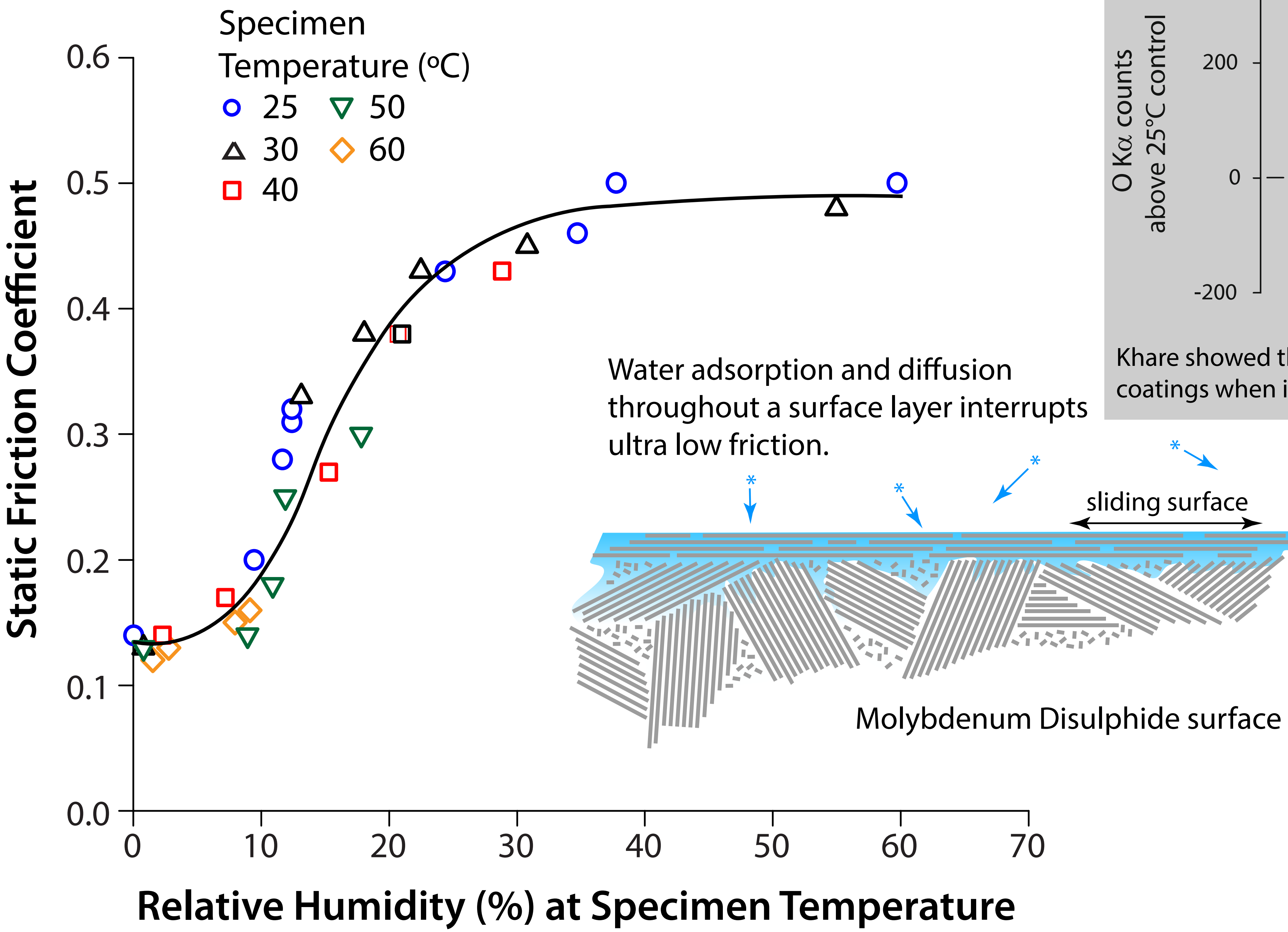
3-10 nm

sliding surface

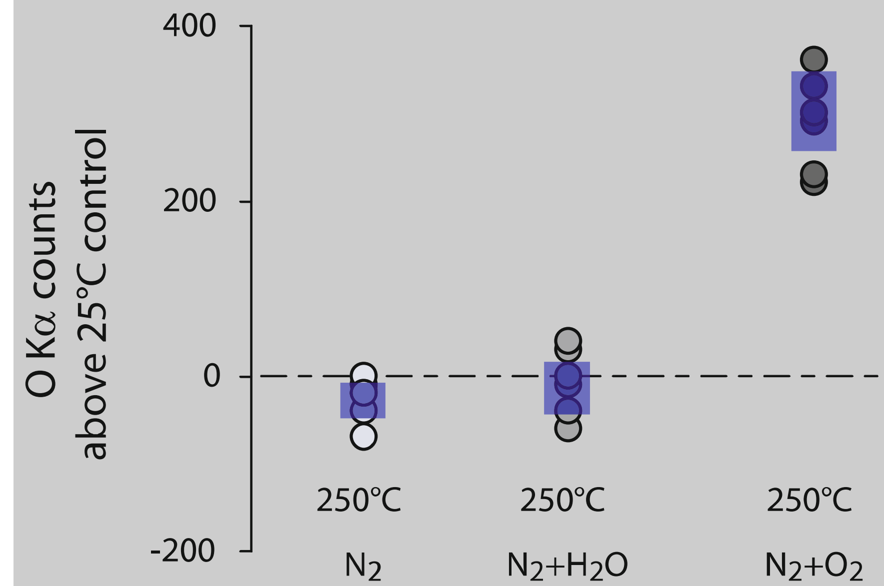


Deposited film is made of many small randomly oriented crystallites of molybdenum disulphide.

Water Vapor Increases Friction in MoS2 Coatings



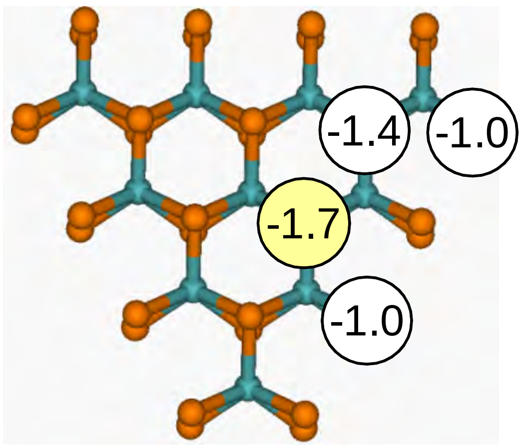
Water adsorption and diffusion throughout a surface layer interrupts ultra low friction.



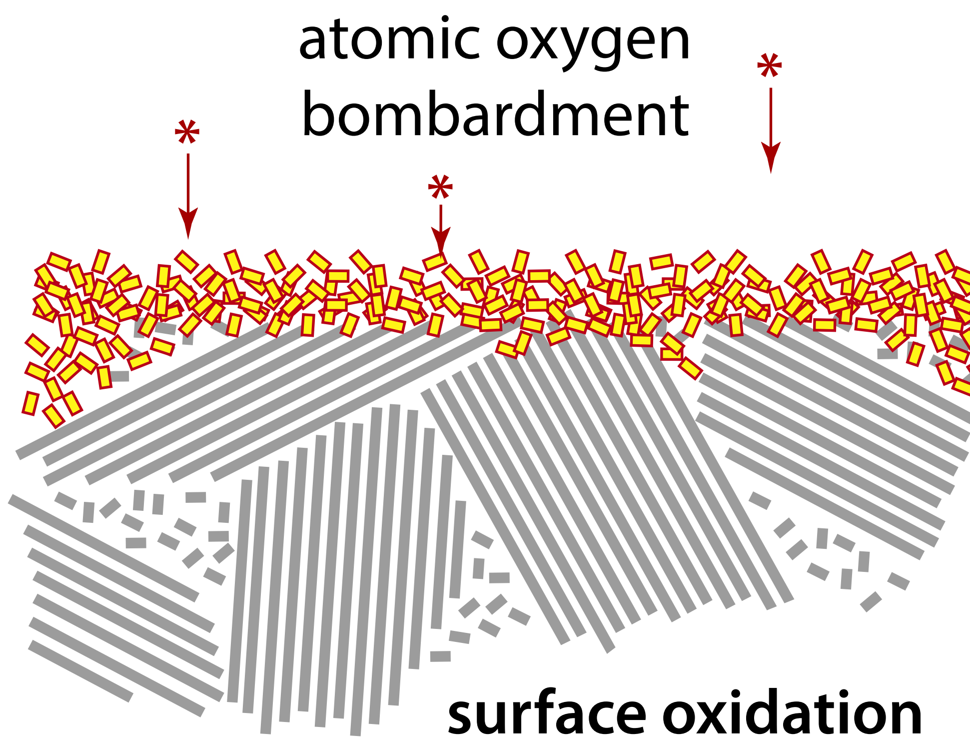
Khare showed that water does not appreciable oxidize coatings when in humid nitrogen environments [2]

[1] Pritchard, C. and J.W. Midgley, The effect of humidity on the friction and life of unbonded molybdenum disulphide films. Wear, 1969. 13(1): p. 39-50.
[2] Khare, H.S., Burris, D.L.: The effects of environmental water and oxygen on the temperature-dependent friction of sputtered molybdenum disulfide. Tribol. Lett. 52, 485–493 (2013).

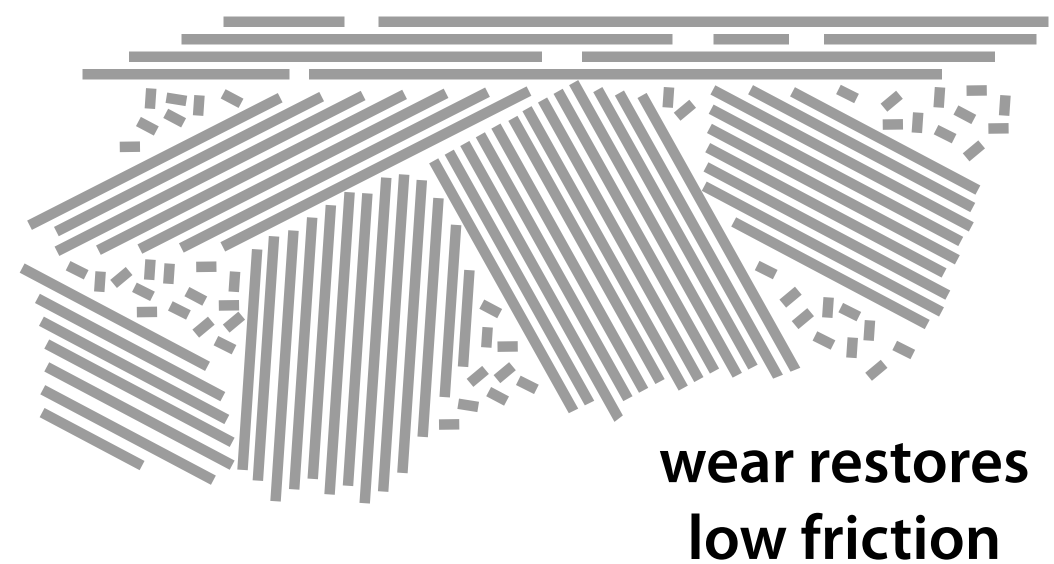
MoS_2 - Oxidation Effects

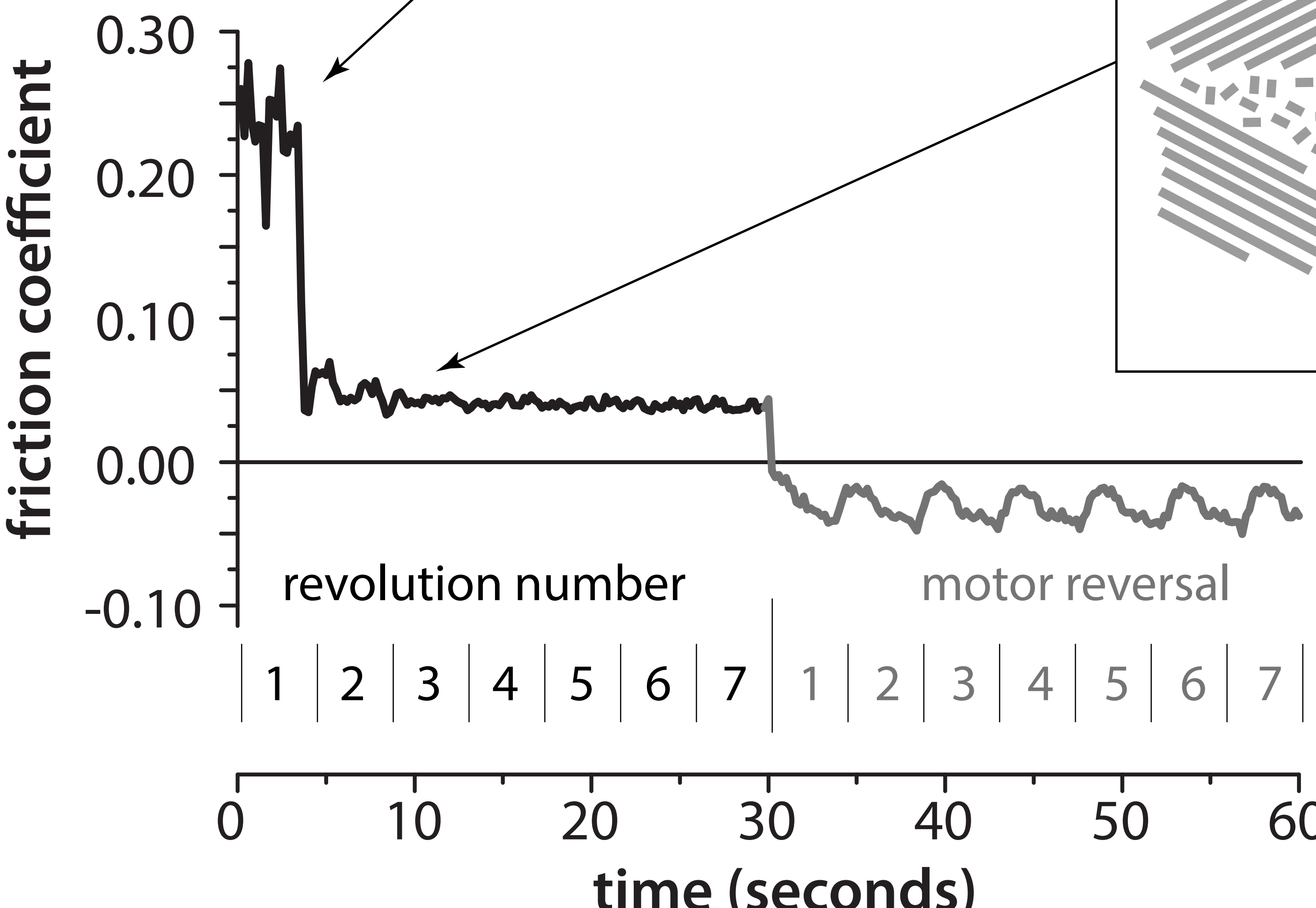


oxidation energies
DFT calculations



Low friction is restored after wear removes the oxidized surface film and restores the lubricous MoS2 surface layer.





data from cycle 140

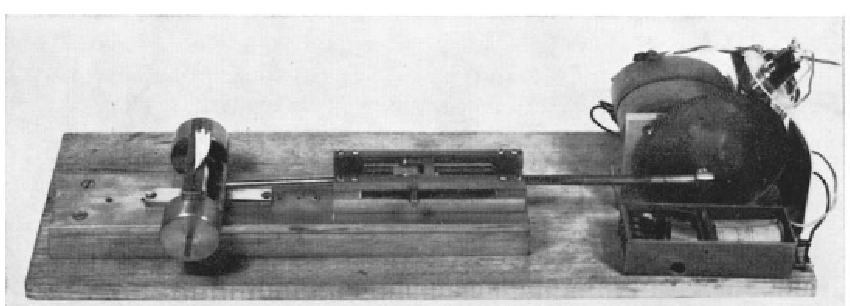
Deposition Techniques - Pros and Cons

Burnishing (1920's - 1960's)

MoS2 powder rubbed onto surface.

Pro
- Inexpensive & simple
- Coating surface is run-in

Con
- Aligns surface of coating, but not bulk
- Poor adhesion
- Difficult to control thickness
- Binding agents outgas in vacuum



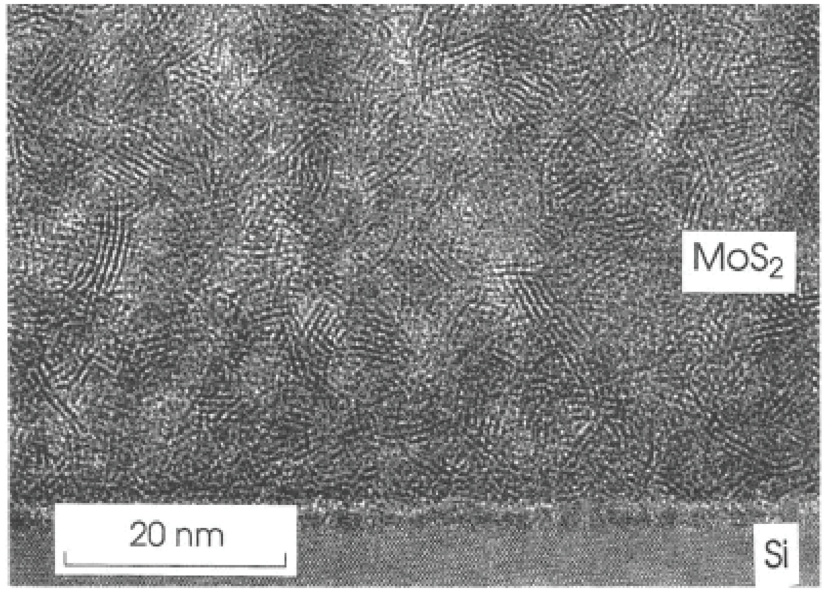
Burnishing machine [4]

Sputtering (1960's - Present)

PVD method where ions ejected from source material impact and coat substrate.

Pro
- Great adhesion
- Fine thickness control

Con
- Nanocrystalline, difficult to control and predict structure
- Expensive & complicated



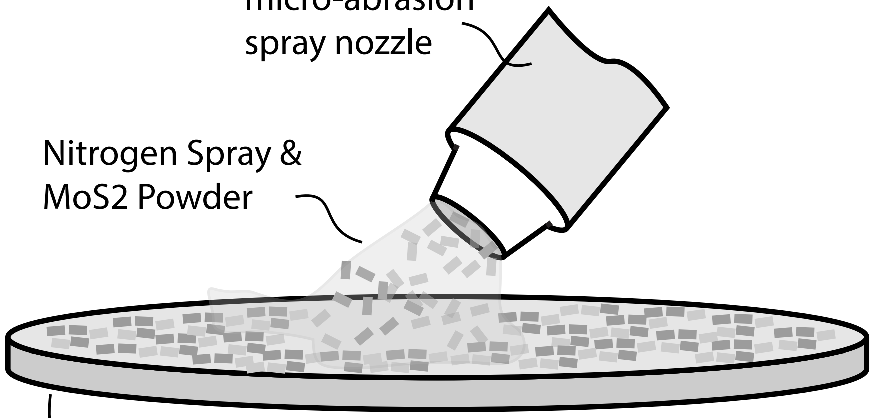
nanocrystalline sputtered MoS2 TEM cross section [5]

Sprayed (Unexplored)

MoS2 powder sprayed onto surface.

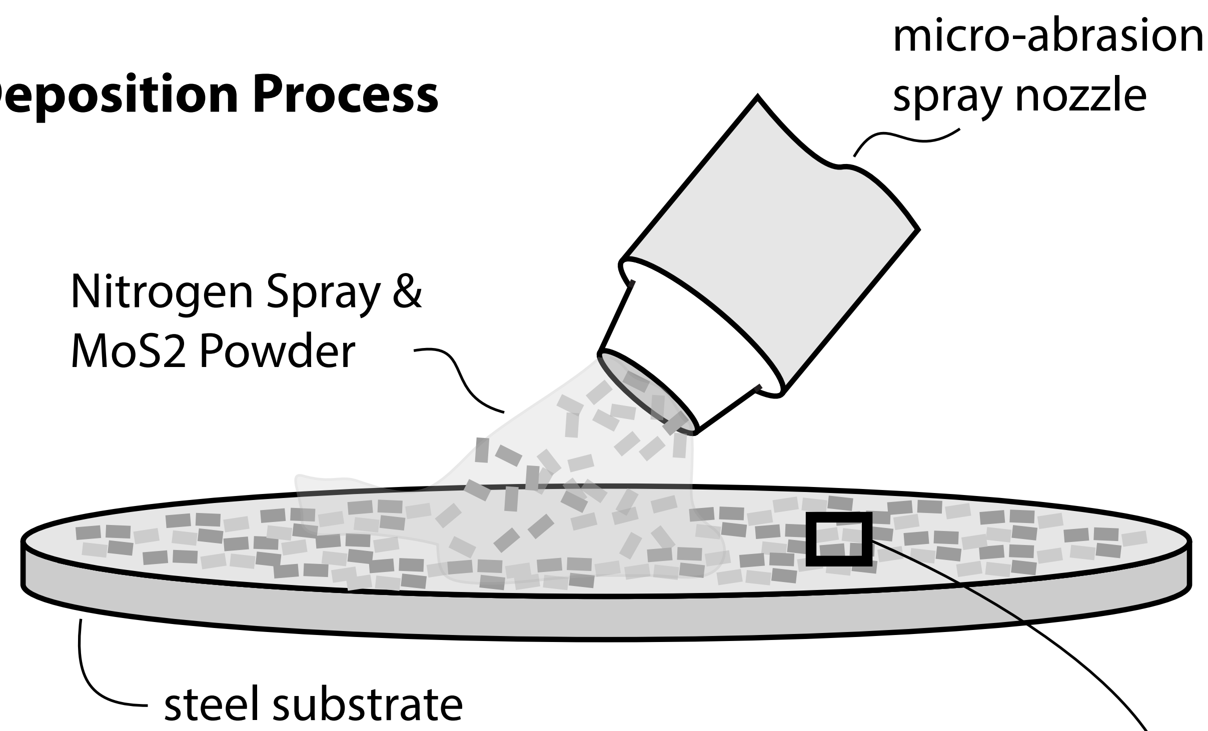
- Should be similar to burnishing
- Typically uses resins to keep adherent

Not much known about structure or performance

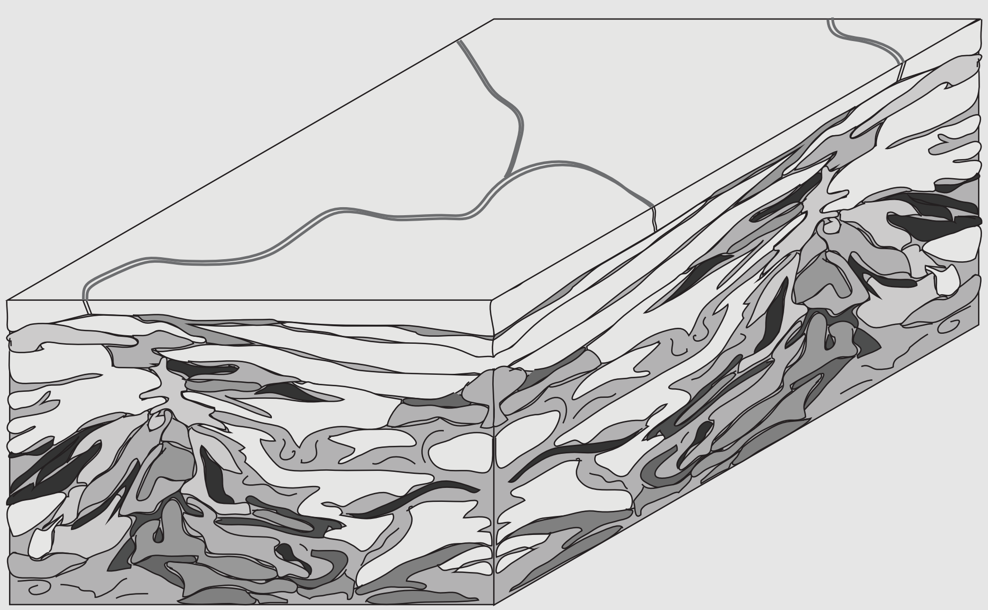


Nitrogen Spray Deposited Coatings

Deposition Process

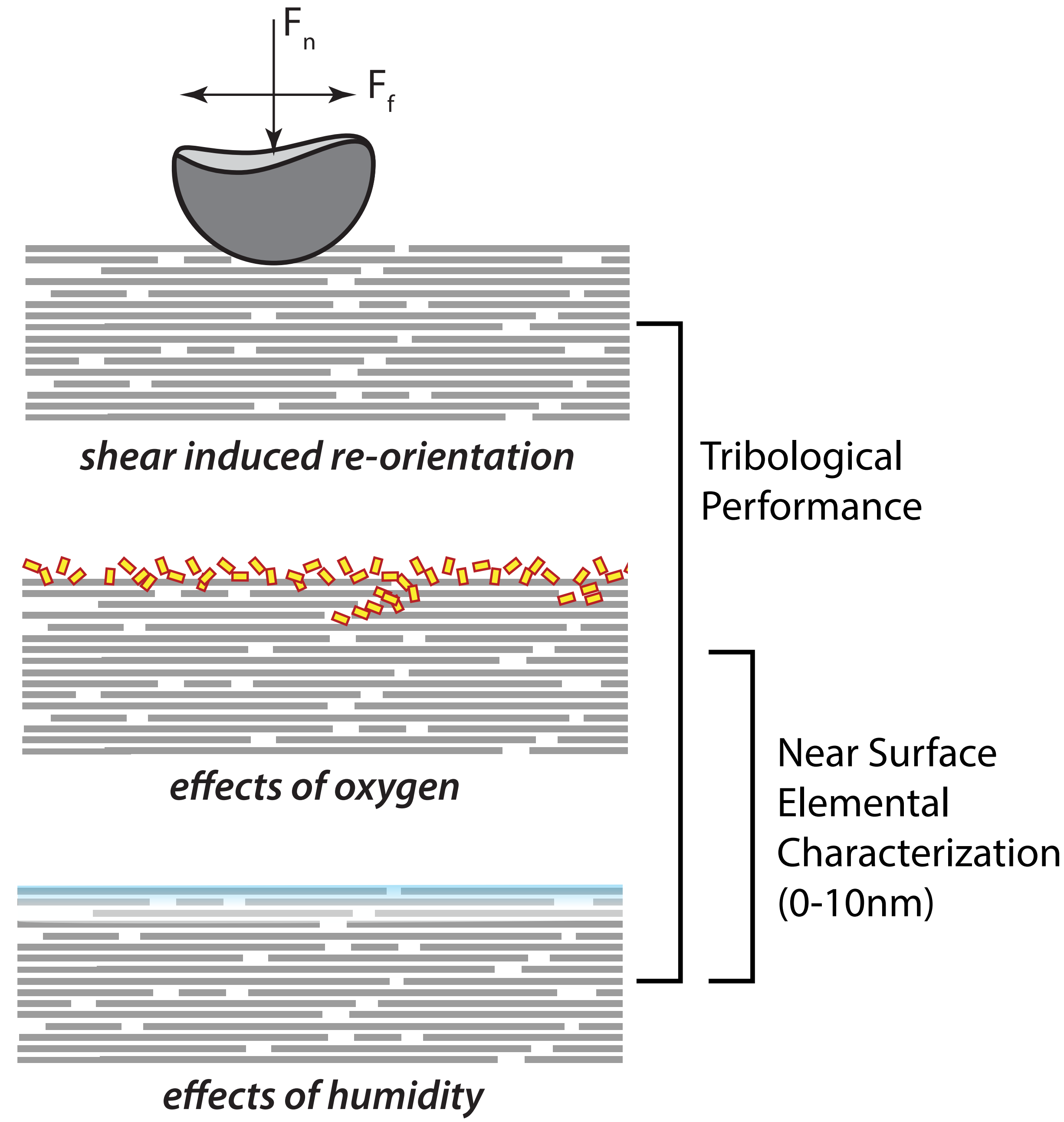


Nitrogen spray deposition process utilizing low pressures allows MoS2 to adhere and build up on the steel surface



Cross section view of MoS2 coating deposited by spray deposition,yielding a preferential crystallographic tetxture (basally oriented). Some in and out of plane twists and kinks most likely exist due to spraying

Synthesis-Structure Relationship

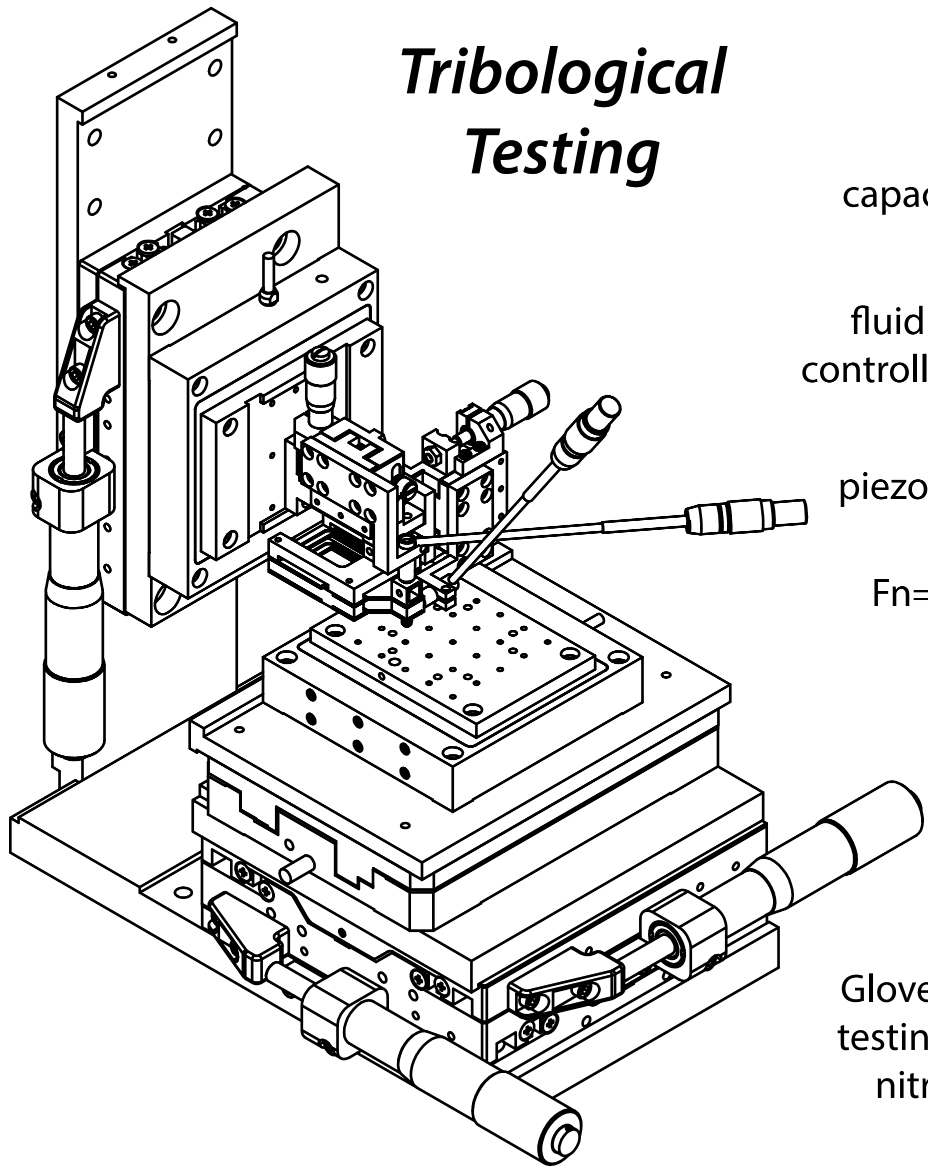


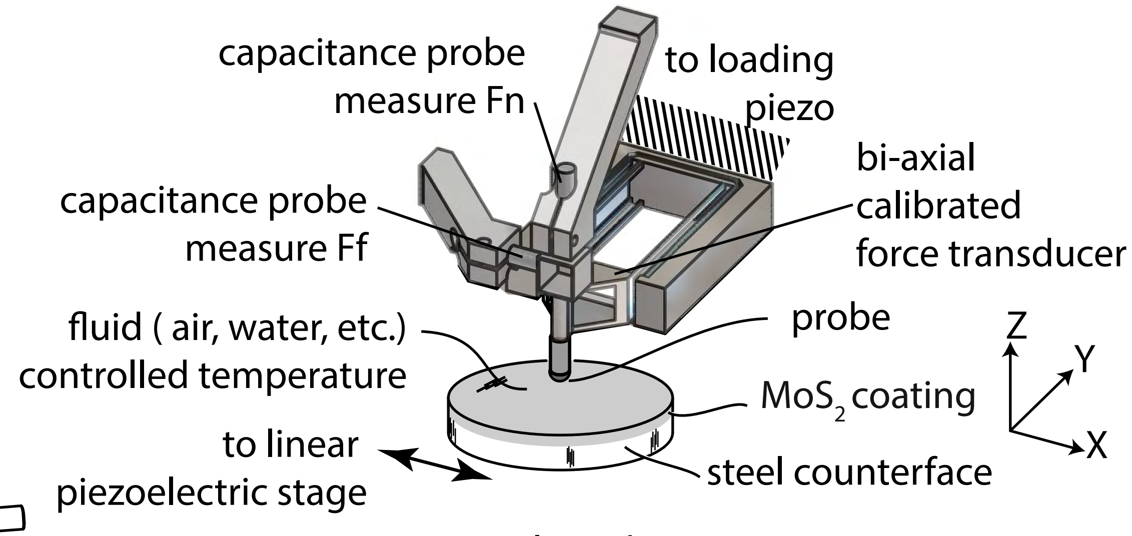
High kinetic energy imparted shears MoS2 onto surface to produce a higher orientation of basal planes.

Hypothesized that large crystallites act as diffusion barriers and diminish aging effects in poor environments

Experimental & Characterization Techniques

Tribological Testing

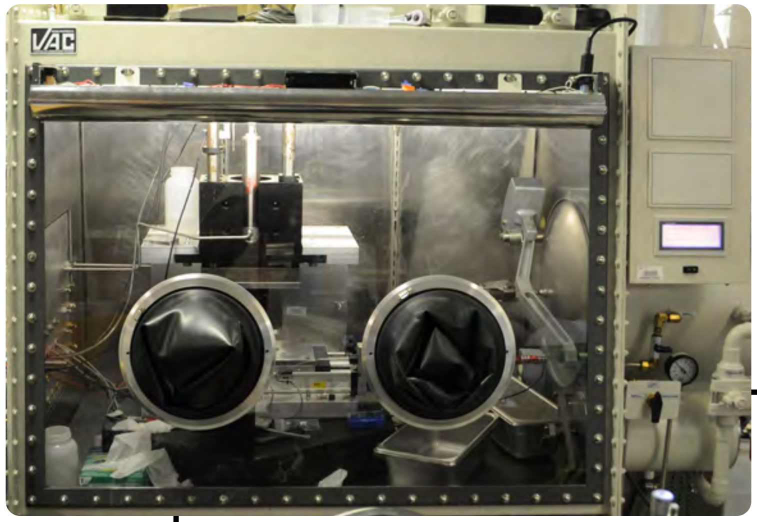




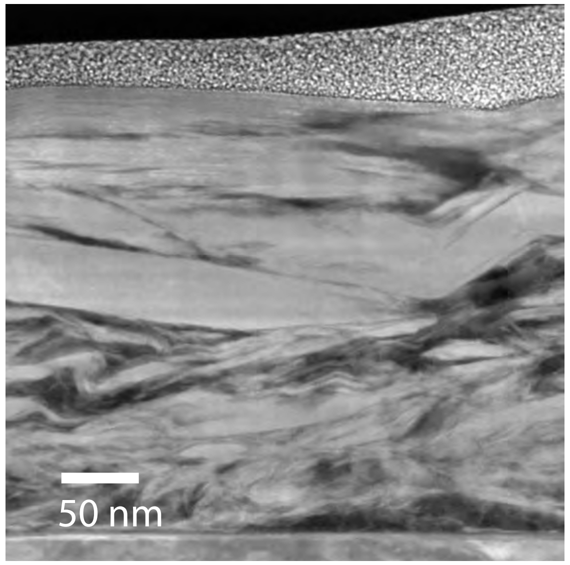
typical conditions:

Fn=0.050-500 mN; stroke=100-800 µm; v=0.1-1000 µm/s

Glovebox for testing in dry nitrogen

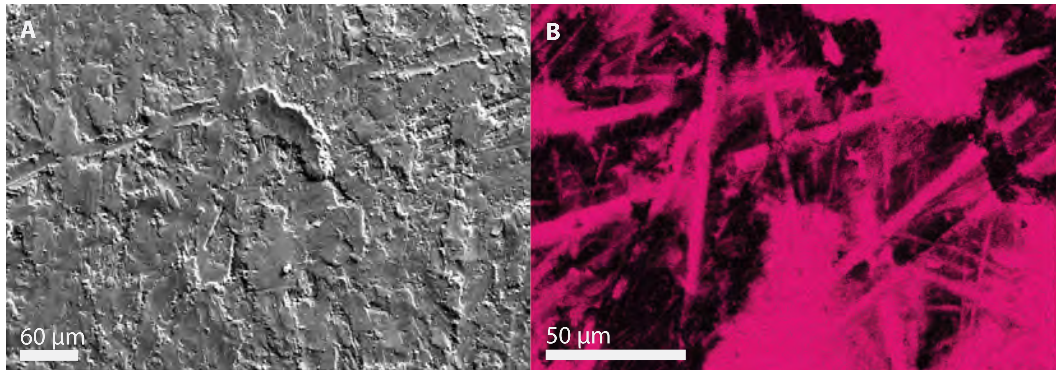


Transmission Electron Microscopy (TEM)



Annular dark-field TEM cross-sections to reveal morphology and thickness

SEM & EDS



(A) Secondary electron (SE) detector images highlighting topography and (B) energy dispersive spectroscopy (EDS) colormaps of the of MoS_2 coverage

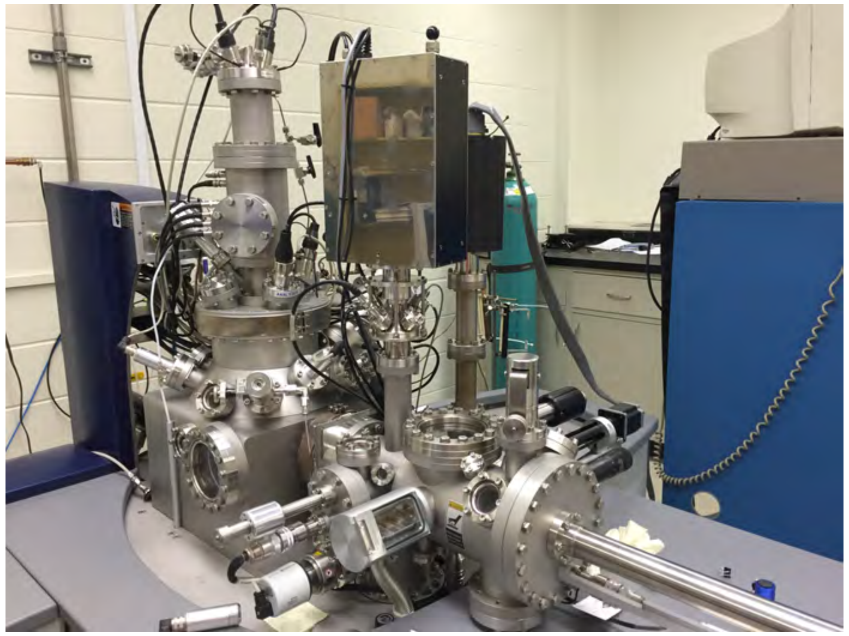
High Sensitivity Low Energy Ion Scattering

aka HS-LEIS

Surface sensitive & near surface elemental depth profiling

Able to quantify the very first atomic layer of a substrate

Only 8 in the world and one in the US (at Lehigh!)



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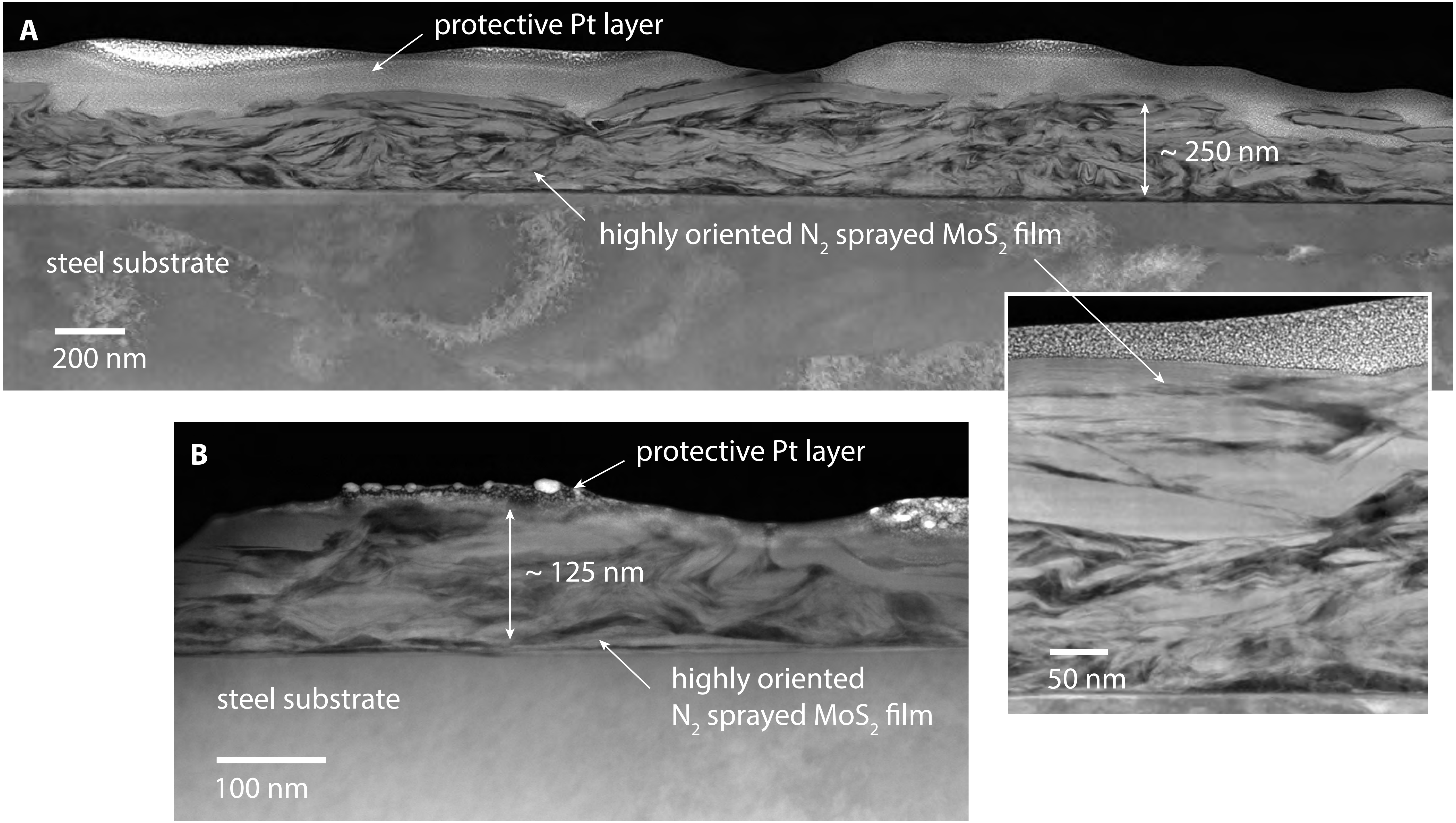
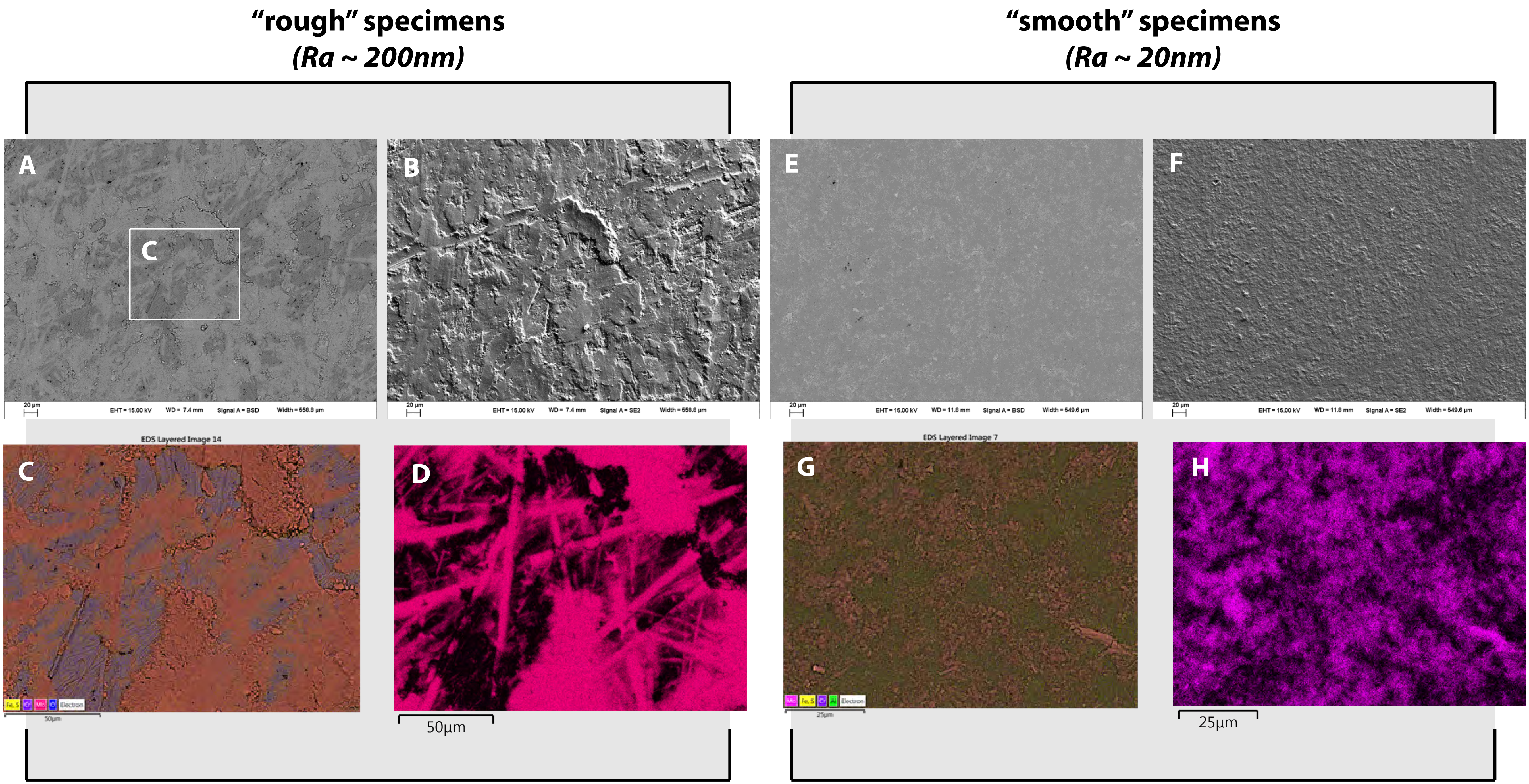


Annular dark-field TEM images of N_2 sprayed MoS_2 cross-sectional views from coated (A) smooth and (B) rough steel coupons; inset is a higher magnification view of a smooth coupon cross-section.

Scanning Electron Microscopy



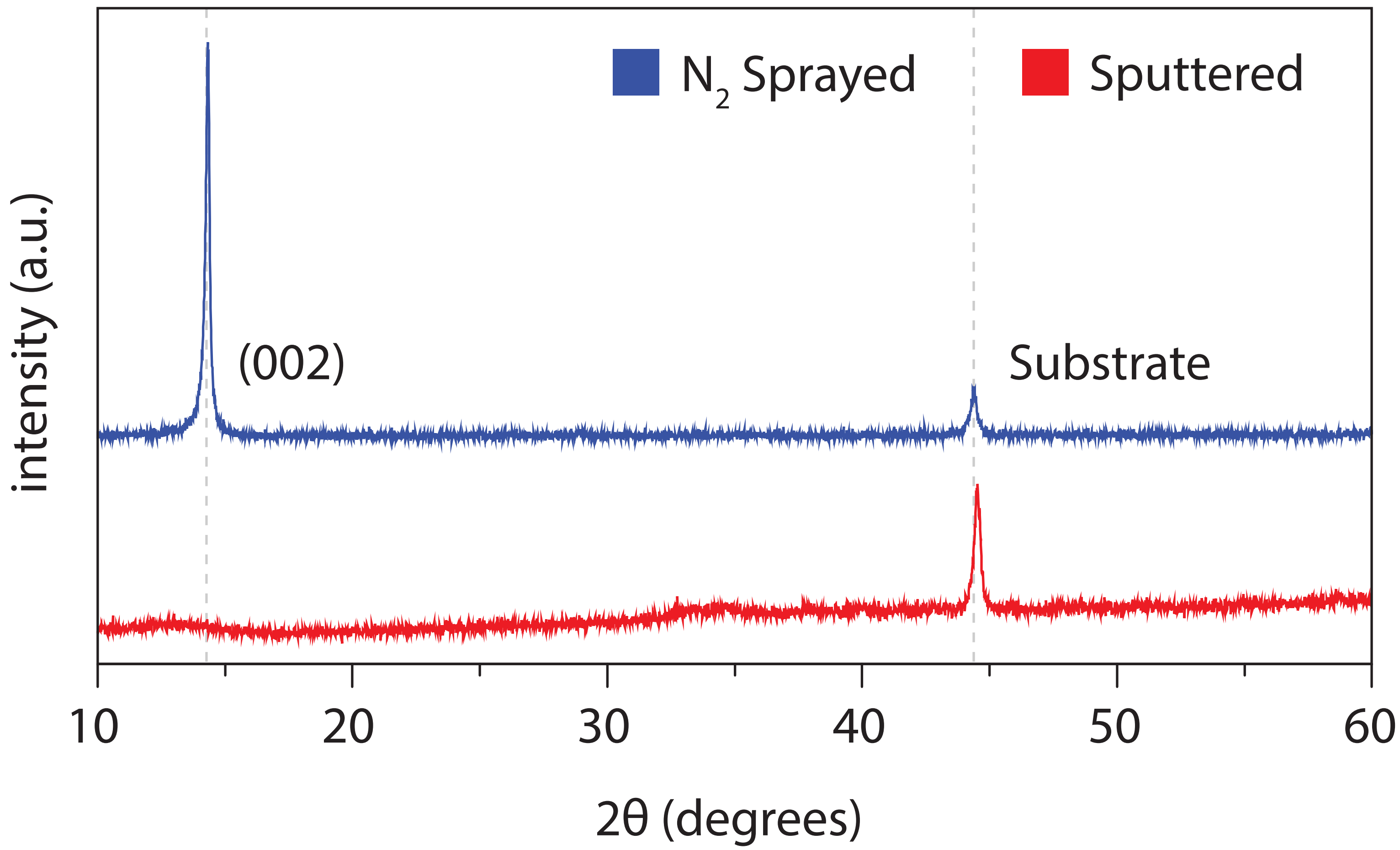
(A,E) : Backscatter Detector (BSD) showing elemental (Z) contrast

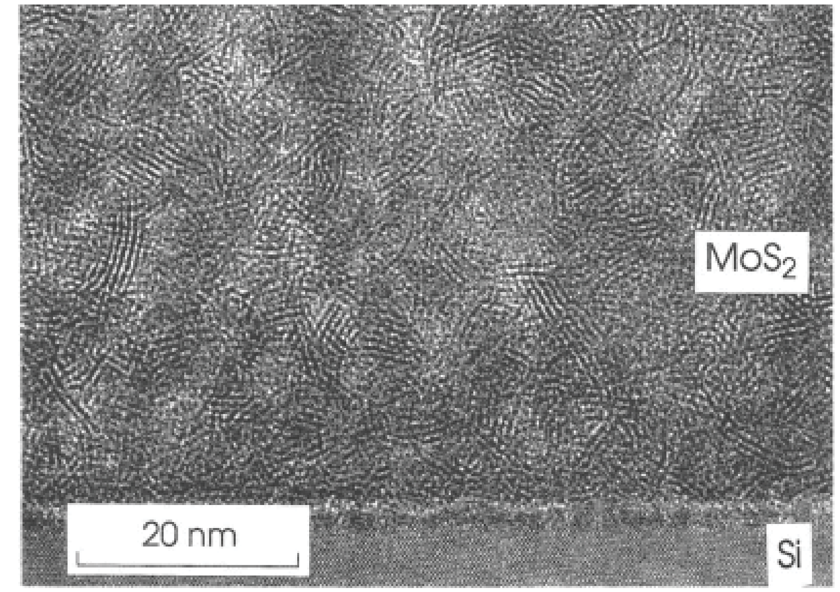
(B,F) : Secondary Electron Detector (SE) showing topographical contrast

(C,G) : Energy Dispersive Spectroscopy (EDS) highlights primary species (Fe, S, Cr, O) and MoS2

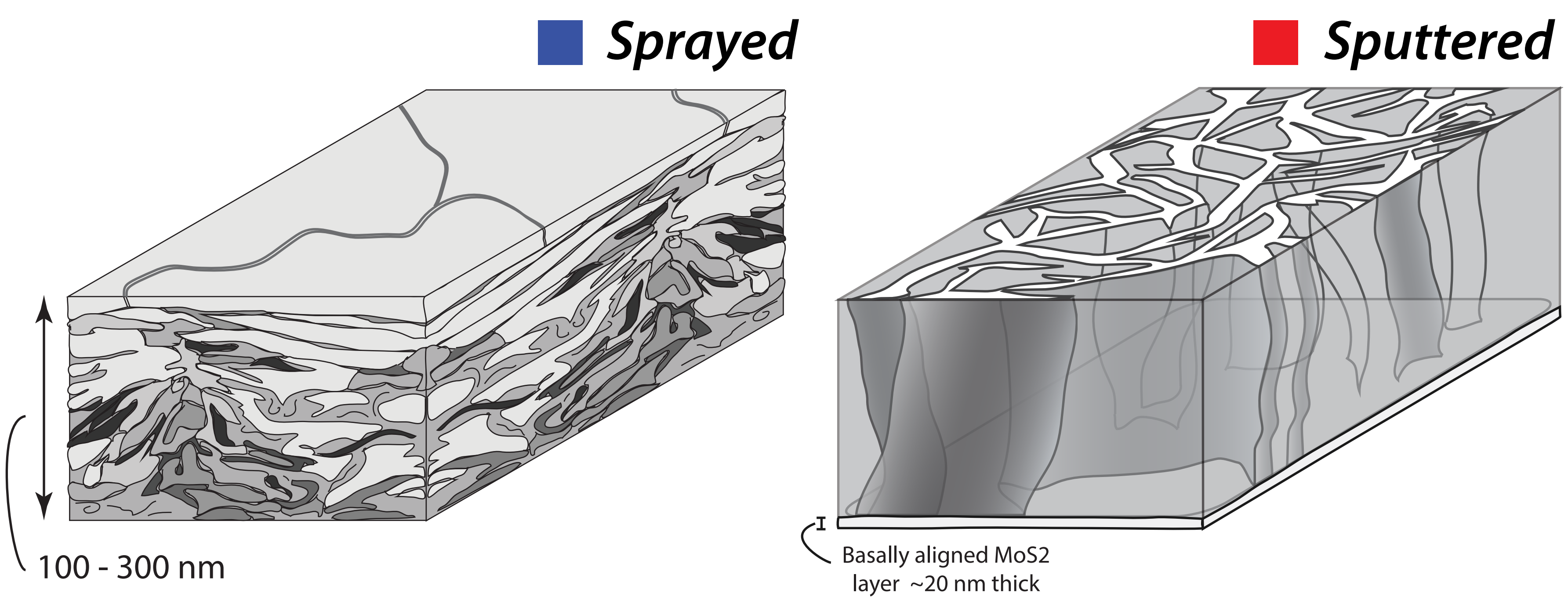
(D,H) : Intensity map of EDS signal showing where Mo (pink/purple) was present

Investigating Structure via XRD

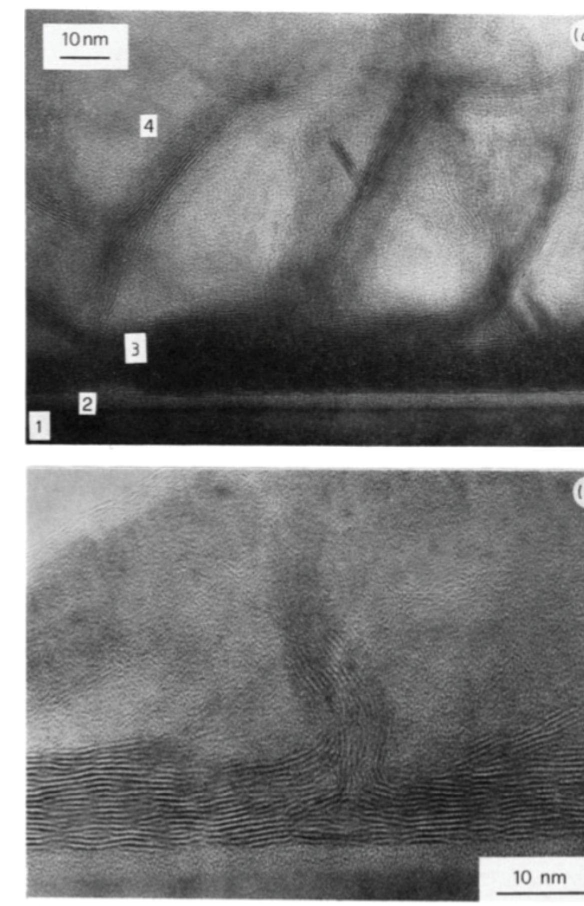




nanocrystalline sputtered MoS2 TEM cross section [5]

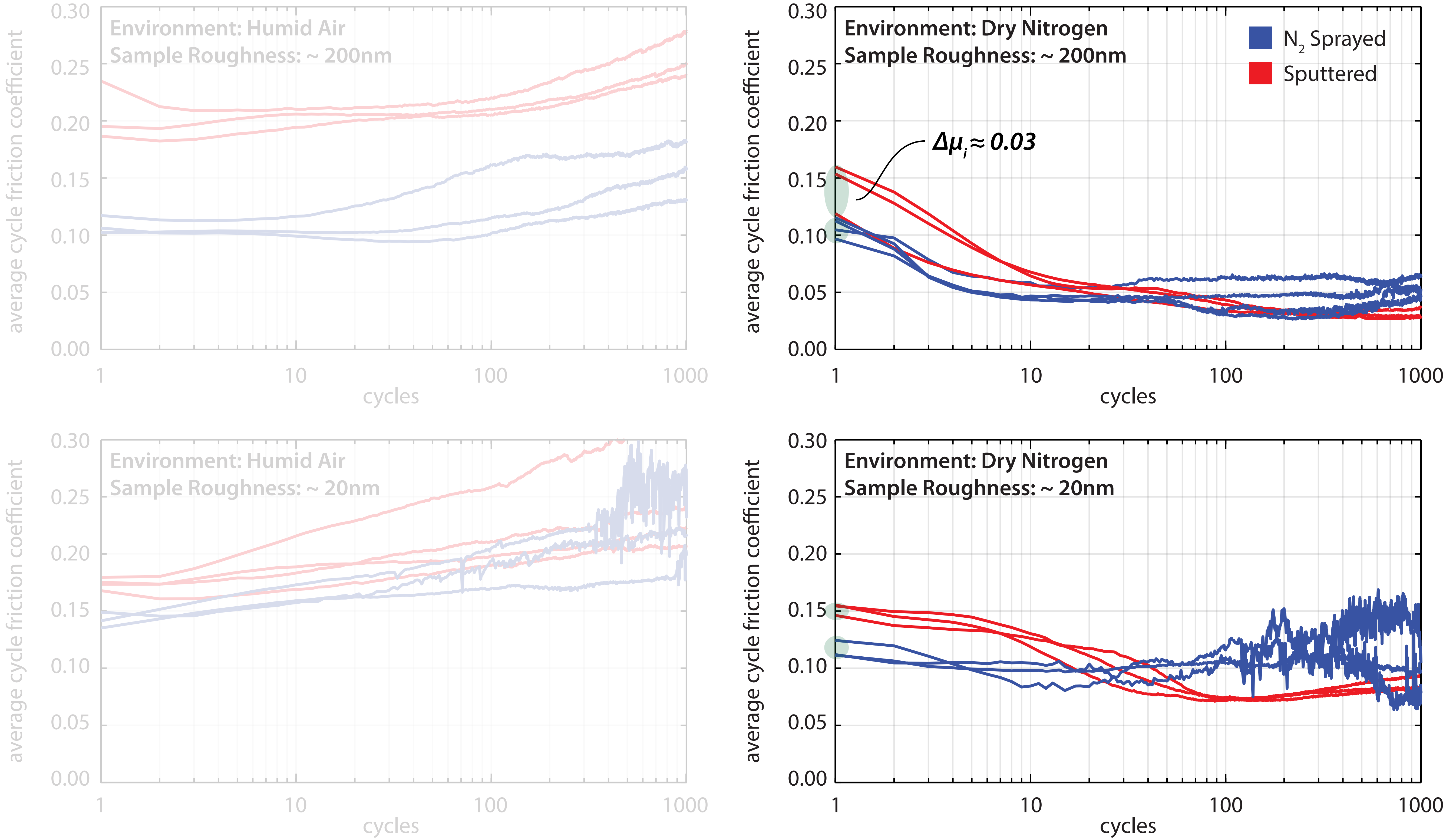


Artist's Renderings



Cross sectional TEM showing the nucleation of edge defects that cause growth of the columnar structure [6].

Tribological Testing

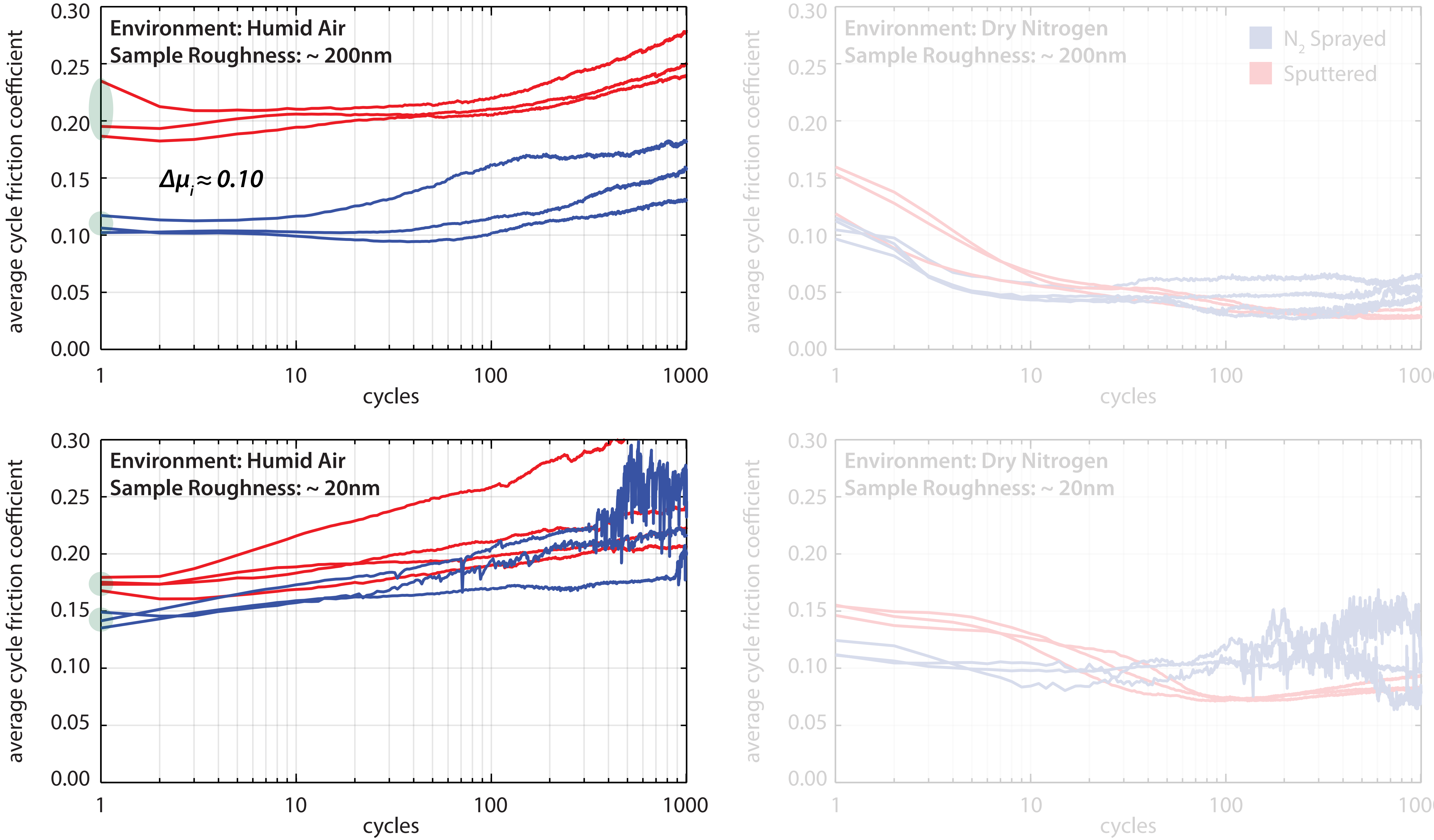


Test Parameters

Contact Geometry:	Pin on Disc
Sliding Mode:	linear bi-directional
Speed:	1 mm/s
Stroke:	1 mm
Normal Load:	100 mN

Experiment Conditions

Substrates:	17-8 PH Steel (Coupon - 1” disc)
	440C SS (Pin - 1/8” diameter)
Roughness:	“smooth” (R_a ~ 20 nm)
	“rough” (R_a ~ 200 nm)



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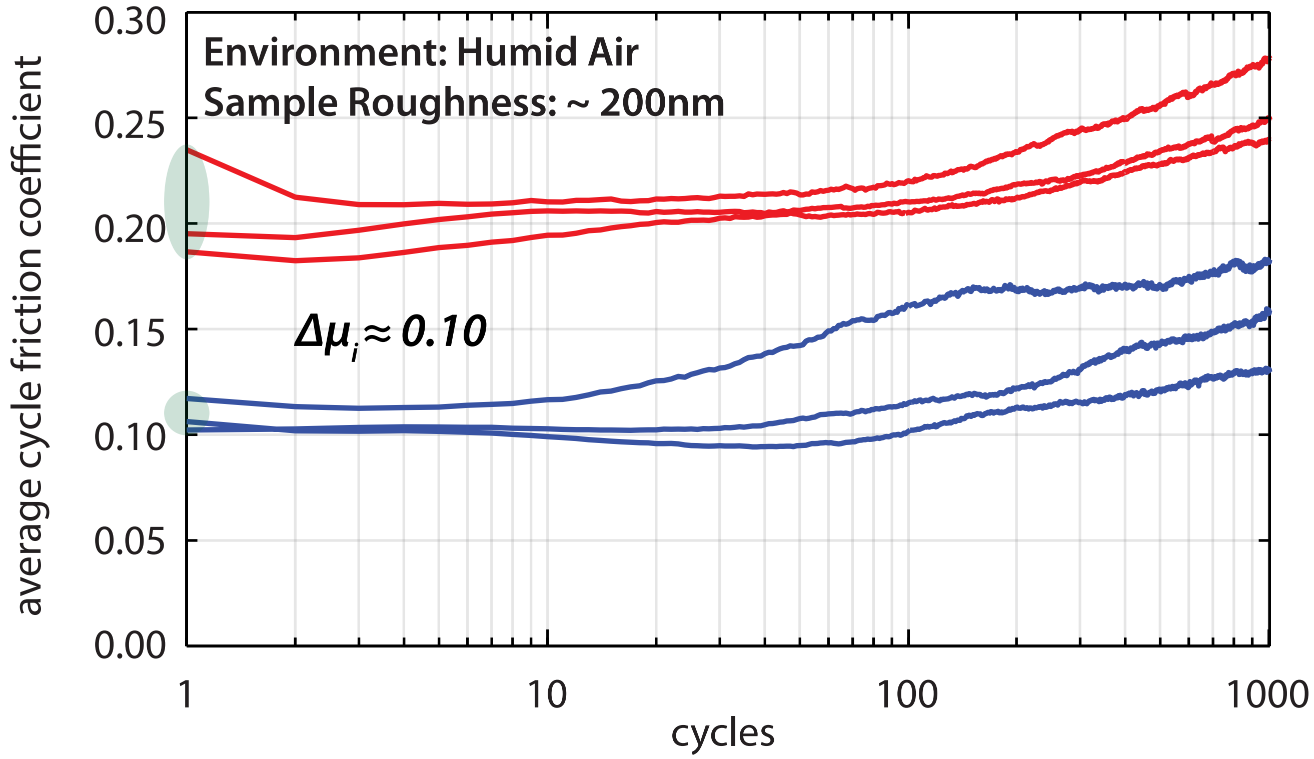

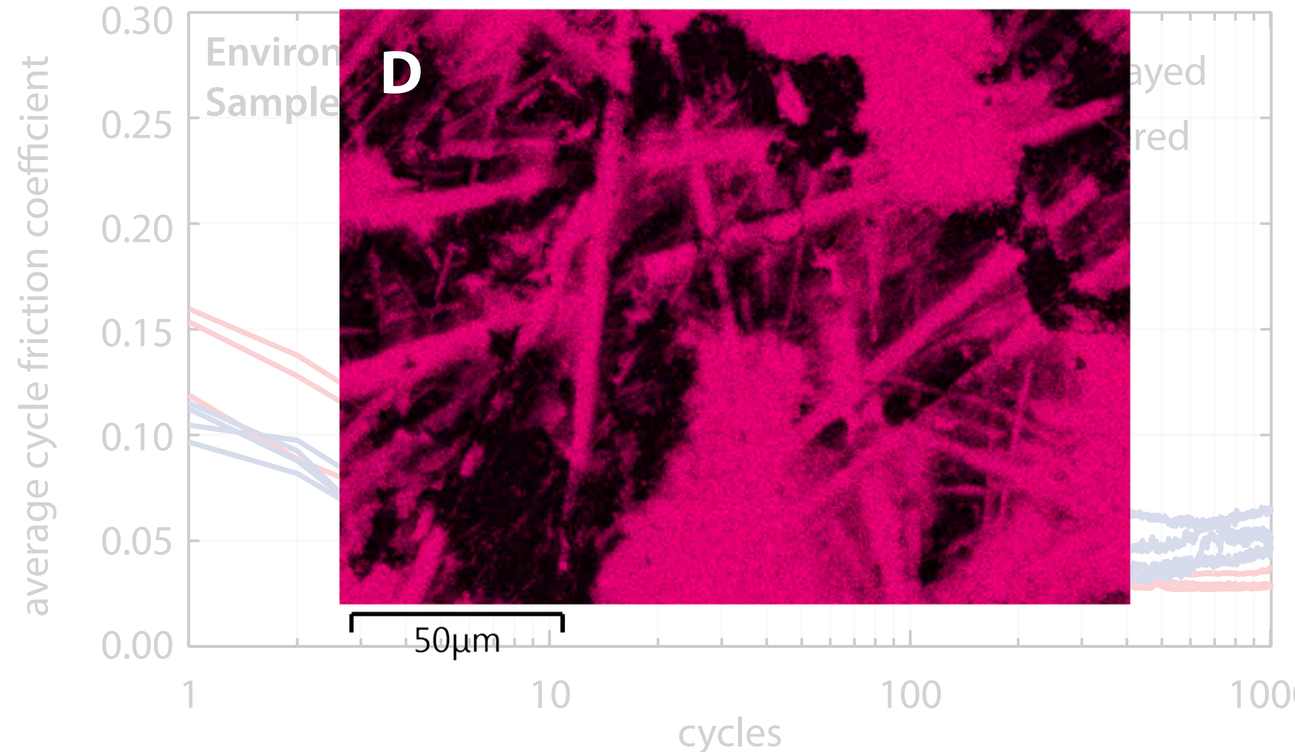

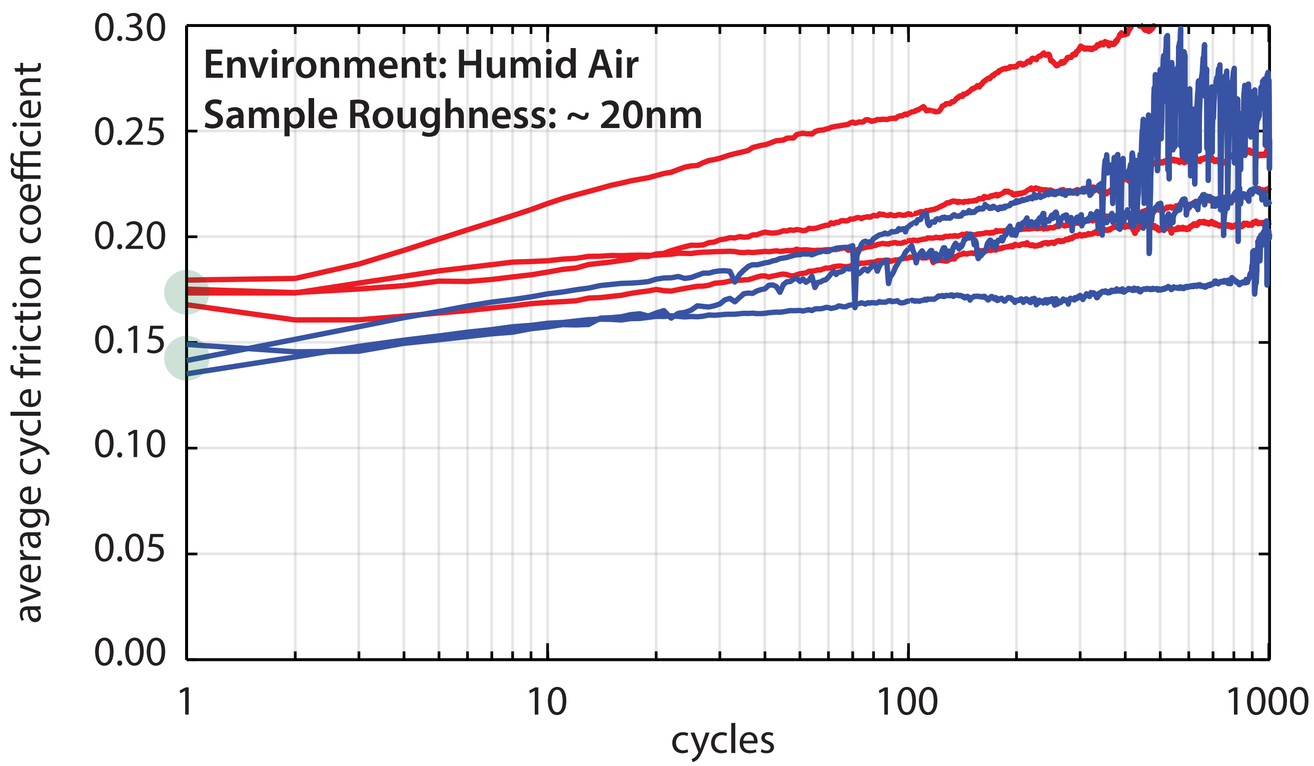

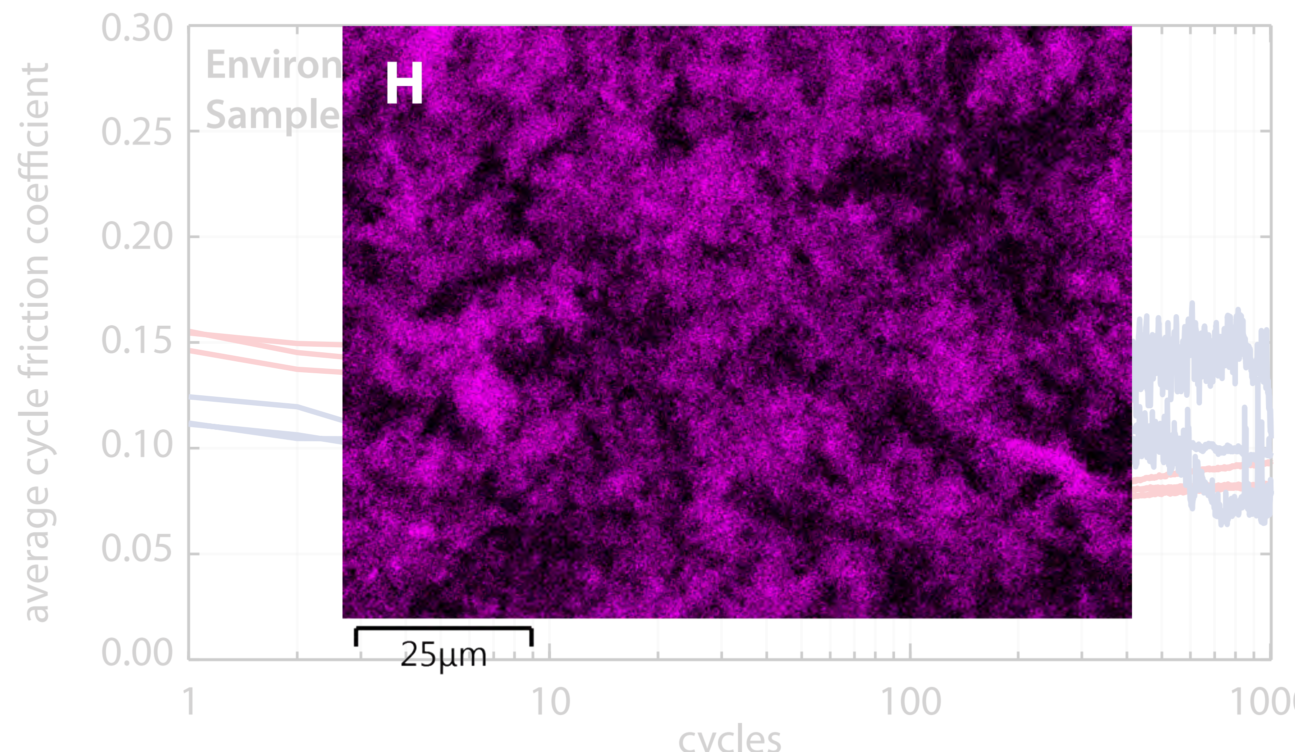

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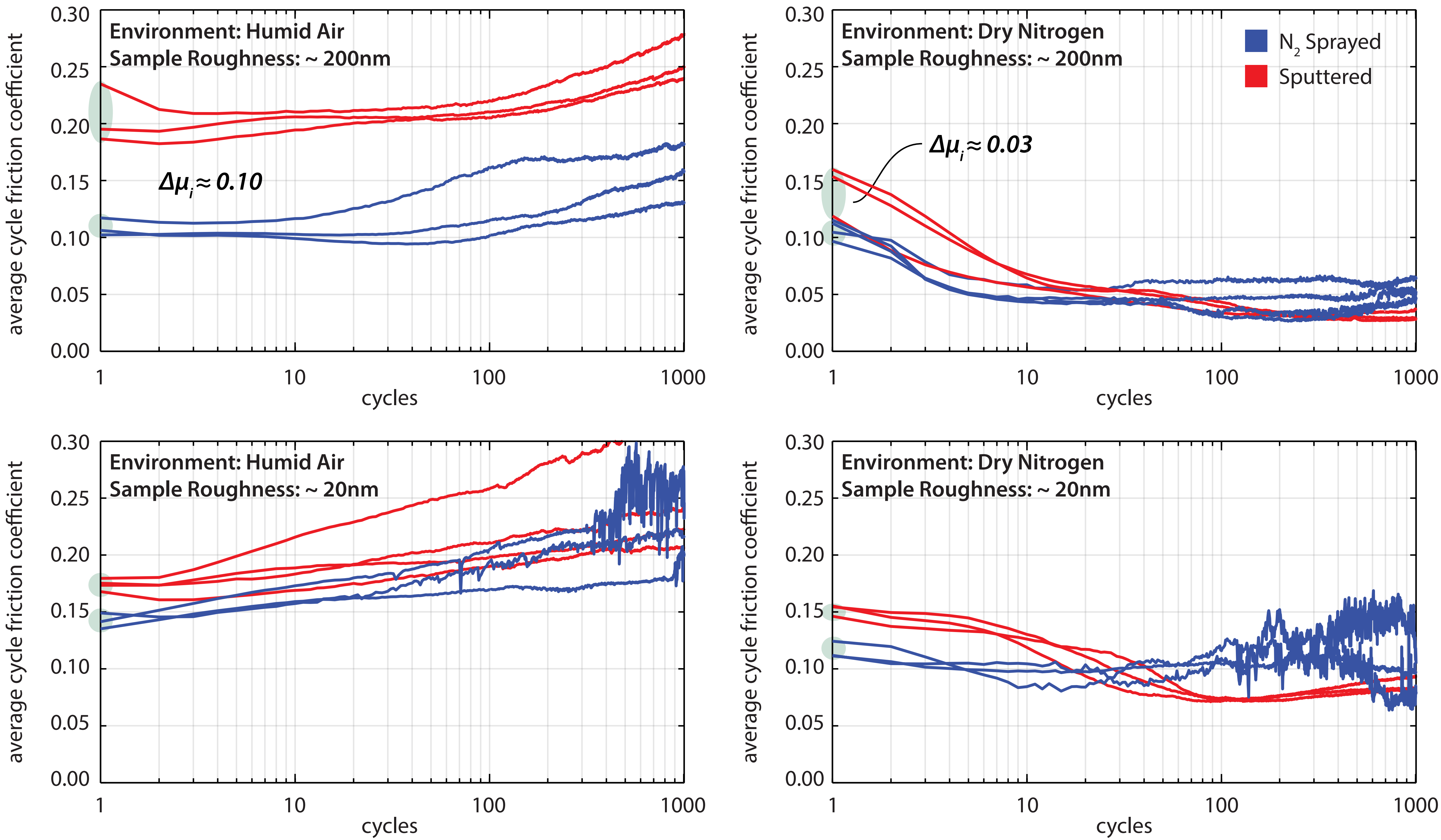

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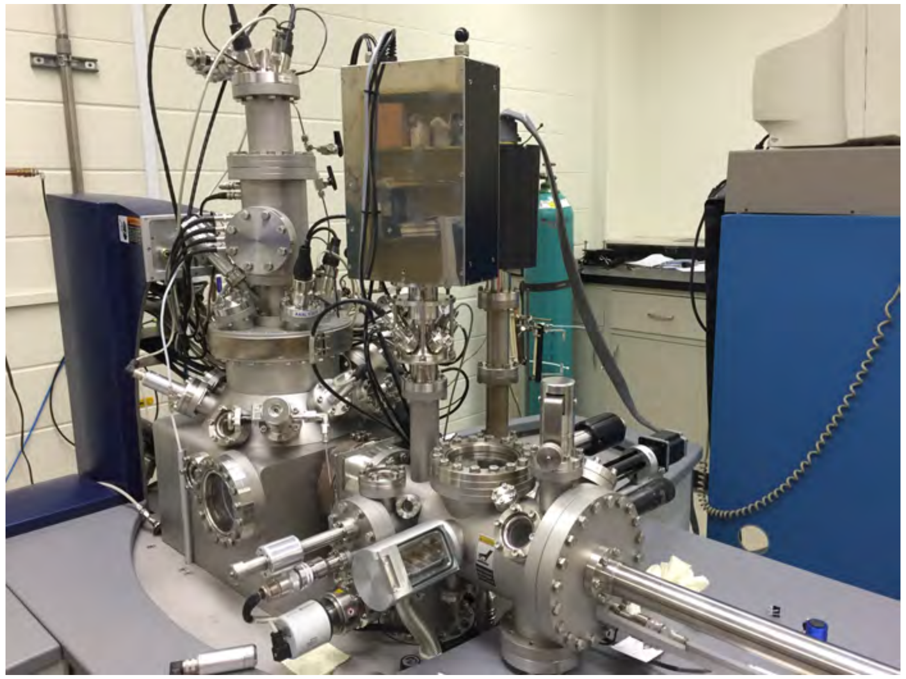
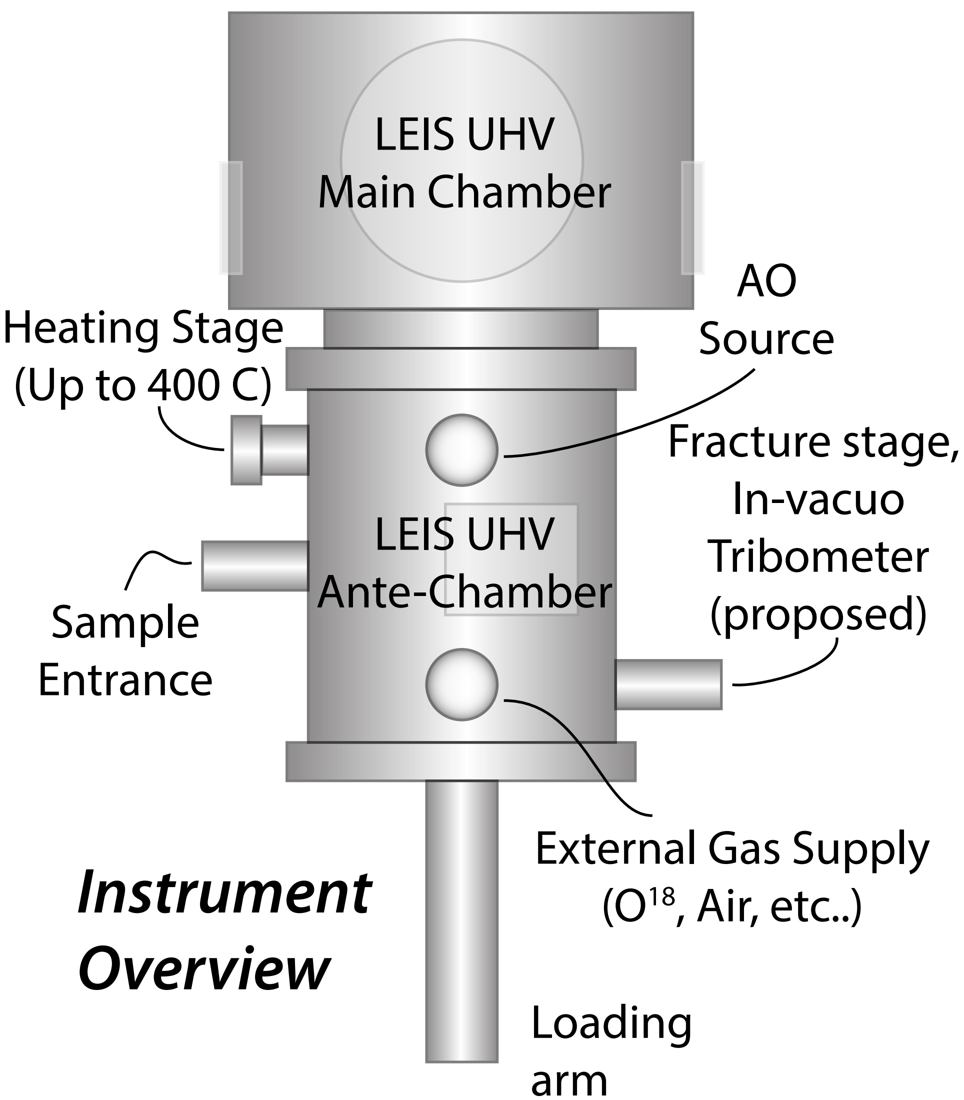
High Sensitivity Low Energy Ion Scattering (HS-LEIS)





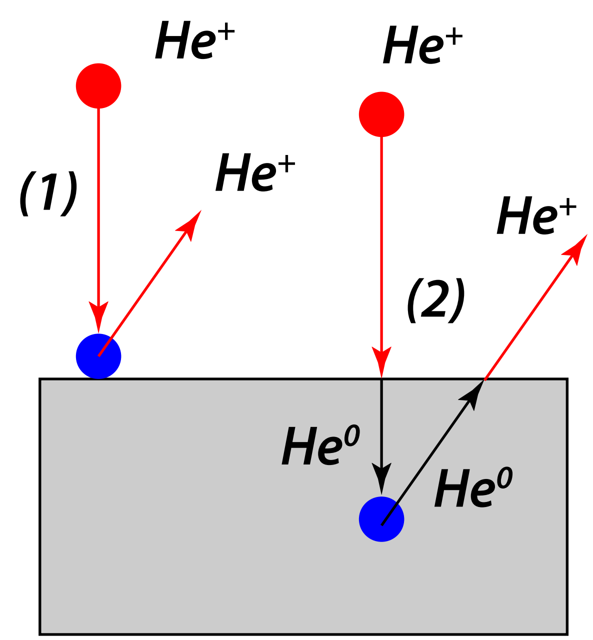
Instrument Overview

Key Features

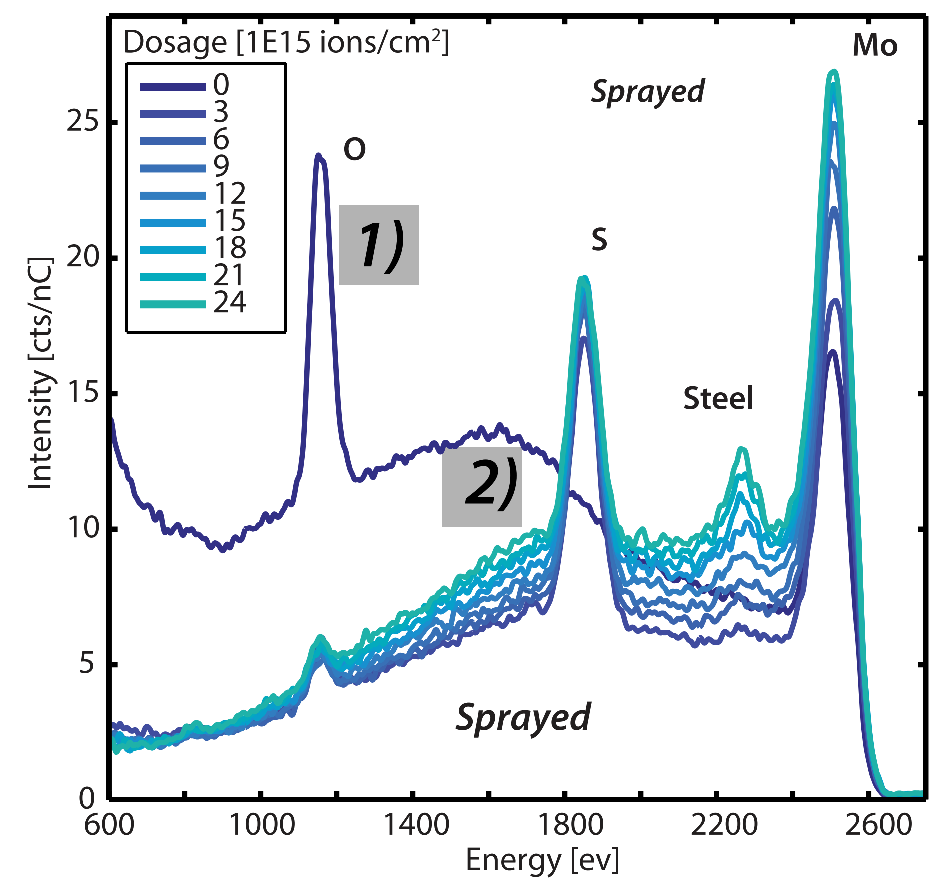
- Gives atomic composition of outermost layer
- non-destructive depth distribution of elements within 0-10 nm
- Little to influence of surface roughness
- Can use ToF filtering as well to reduce background

Why LEIS?

- Detection limits and resolution optimized for MoS2 region of interest
- Other techniques do not approach in sensitivity... also average signal



Primary Ion Beams: He^+, Ne^+, Ar^+, Kr^+ (0.1 - 10 keV)



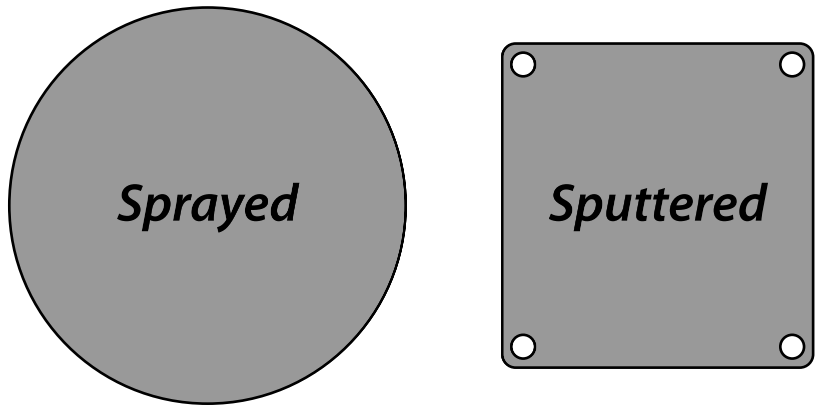
1) Peaks
elements detected on surface

2) Shoulders
subsurface signal

Brongersma, H.H.: Low-Energy Ion Scattering. Characterization of Materials. 2024–2044 (2012).

HS-LEIS Experimental Methods

Samples Tested



Material (SS):	13-8 PH	440C
Thickness (nm):	100-300	1500
Surface Finish:	~250 nm Ra	

Tribotest Parameters:

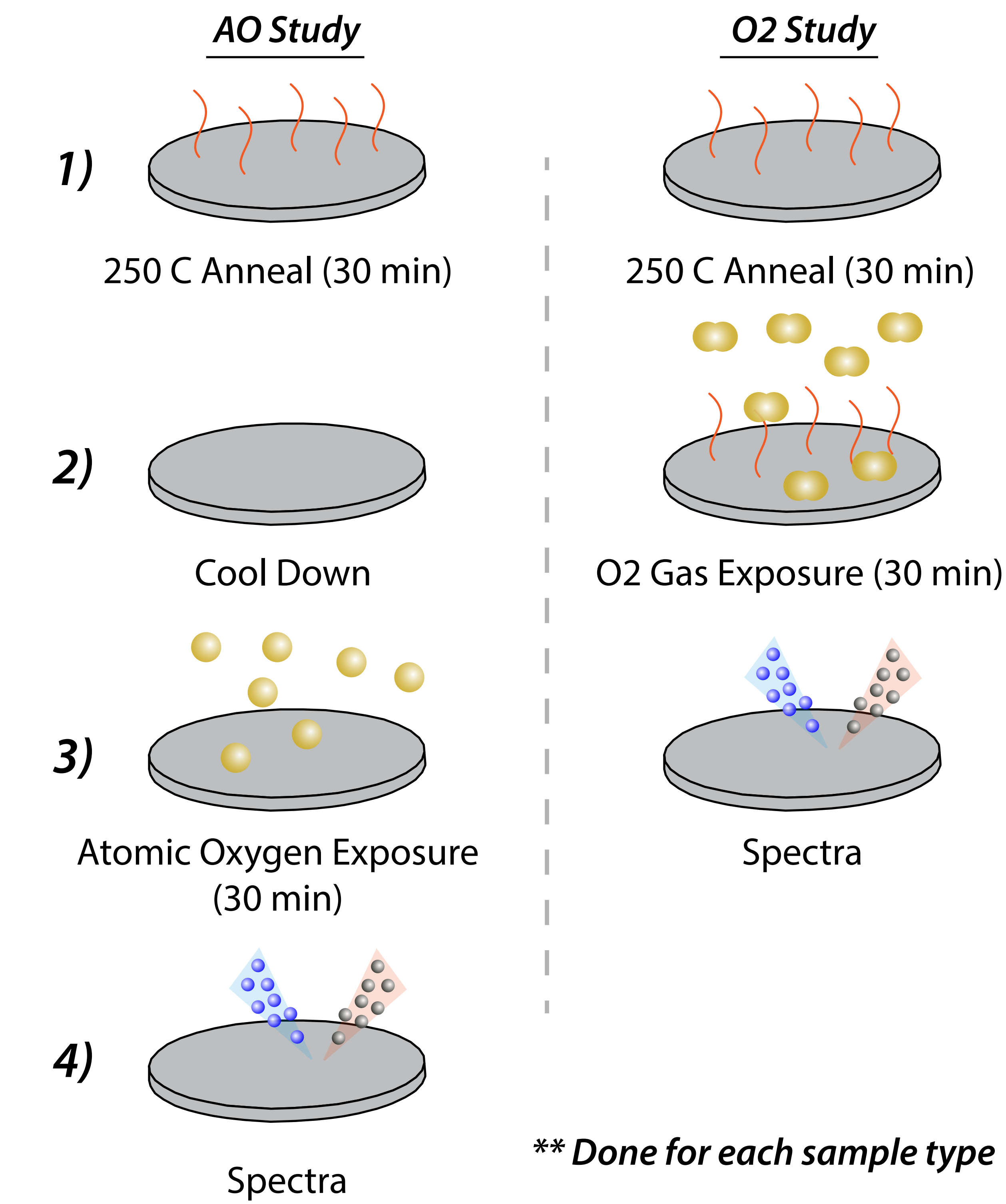
Contact Geometry:	Pin on Disc
Sliding Mode:	linear bi-directional
Speed:	1 mm/s
Stroke:	1 mm
Normal Load:	1 N
Environment:	dry N_2 (< 10 ppm O_2, dew point < -60°C)
Temperature:	20°C

HS-LEIS Parameters:

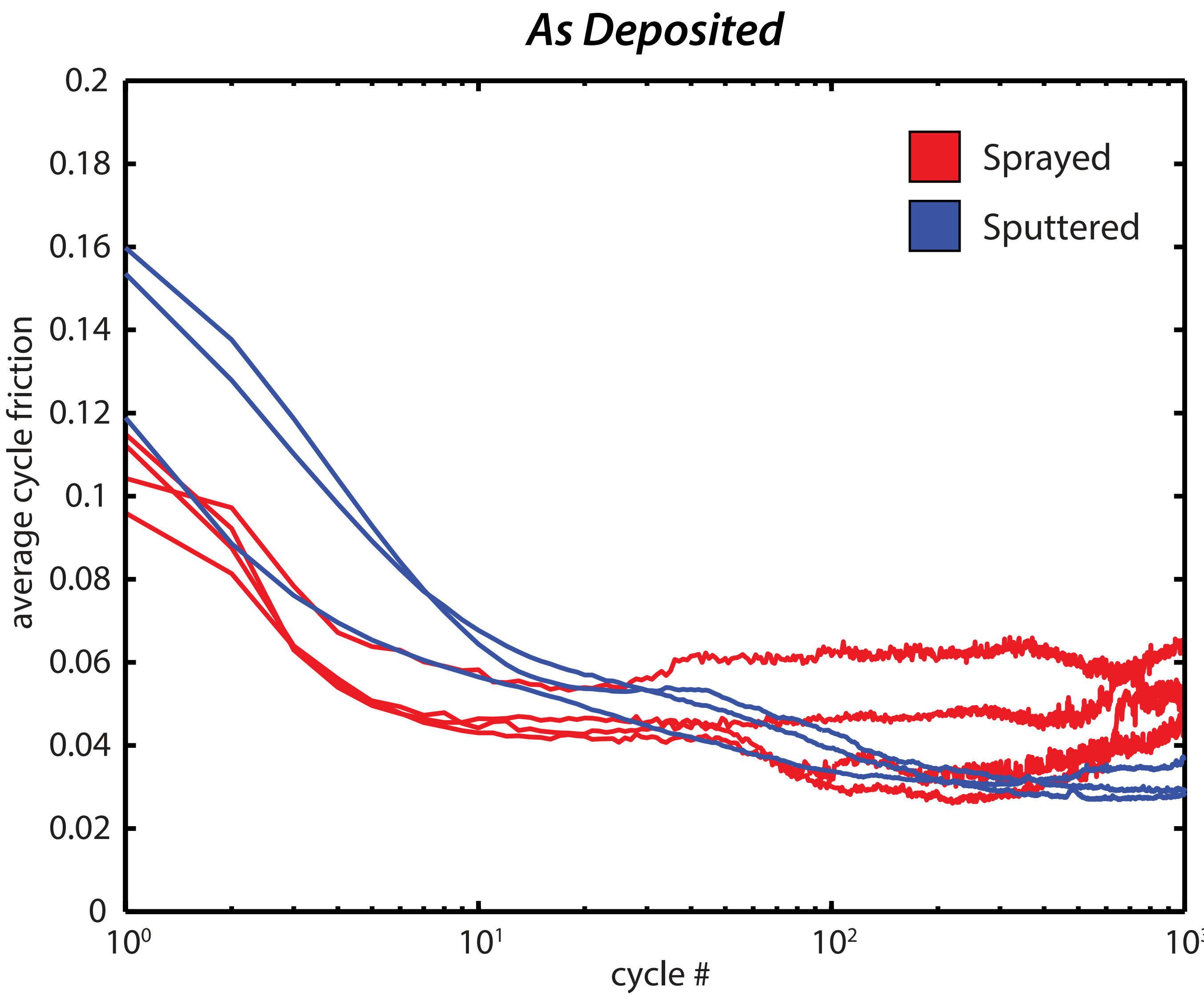
Primary Ion Beam:	He^+ 3 keV
Sputtering Ion Beam:	Ar^+ 1 keV
Deep Profile Fluence*:	3E15 ions/cm^2
Shallow Profile Fluence*:	1E15 ions/cm^2

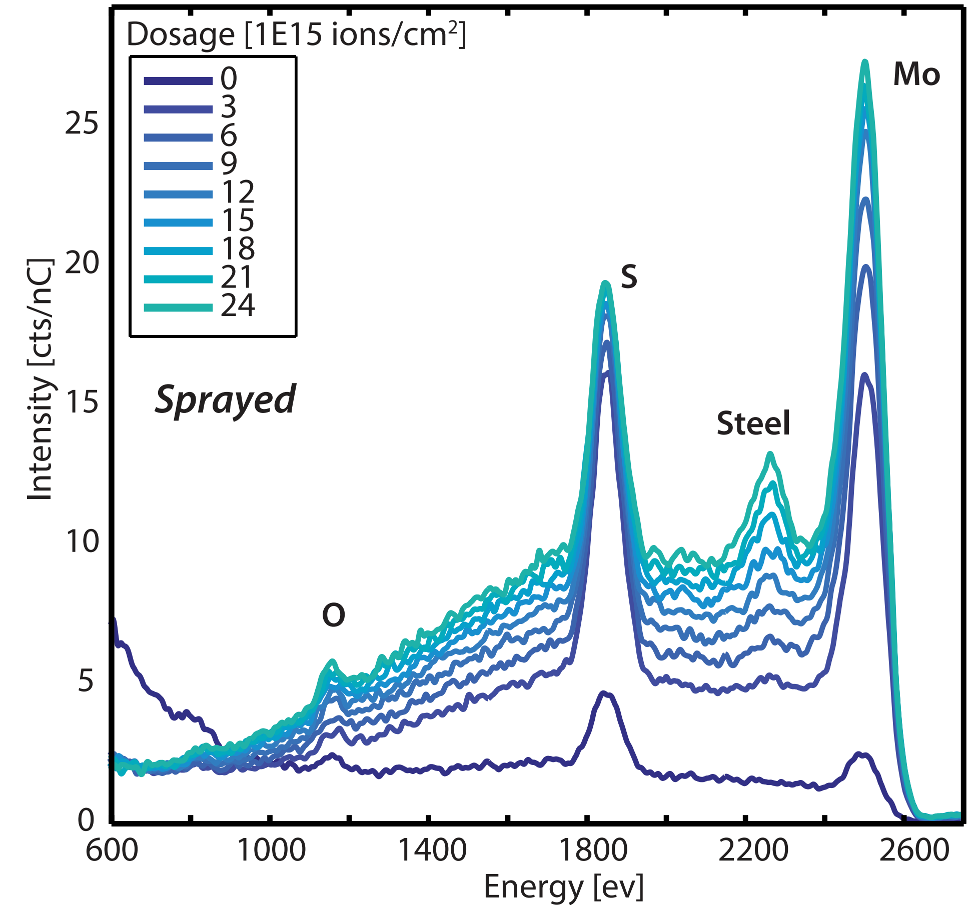
with 1E15 ions/cm^2 being approximately 0.35nm

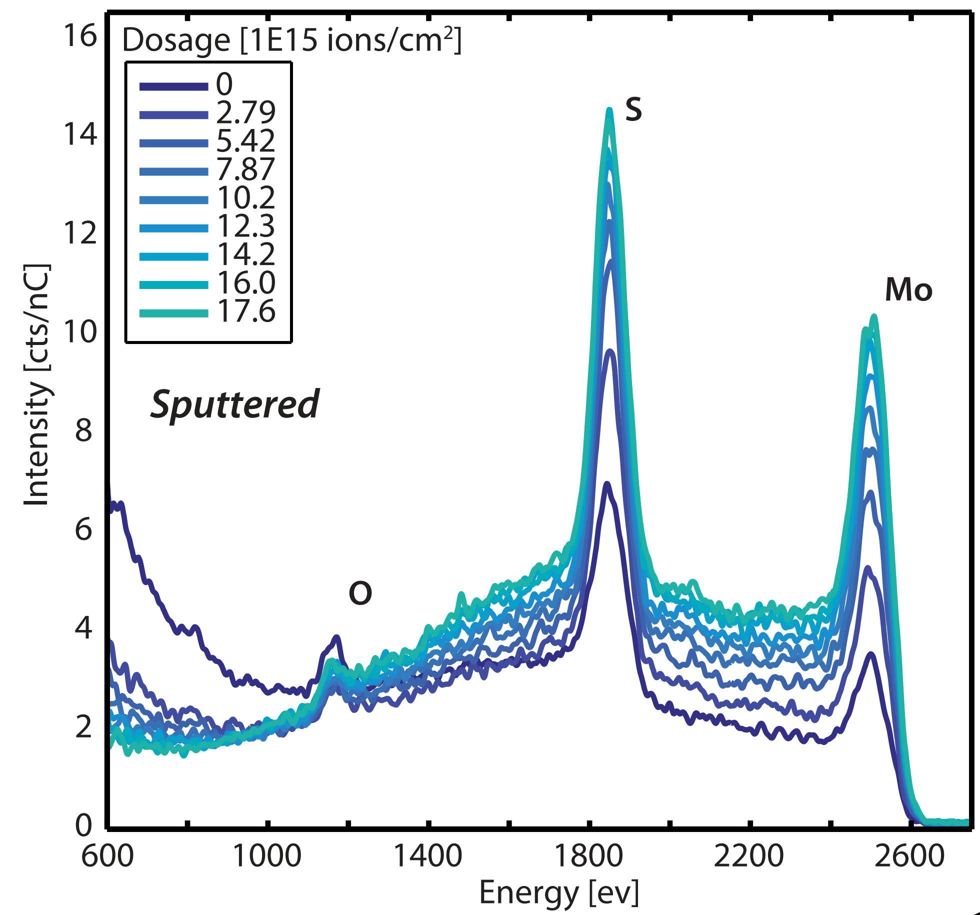
Methods



As Deposited







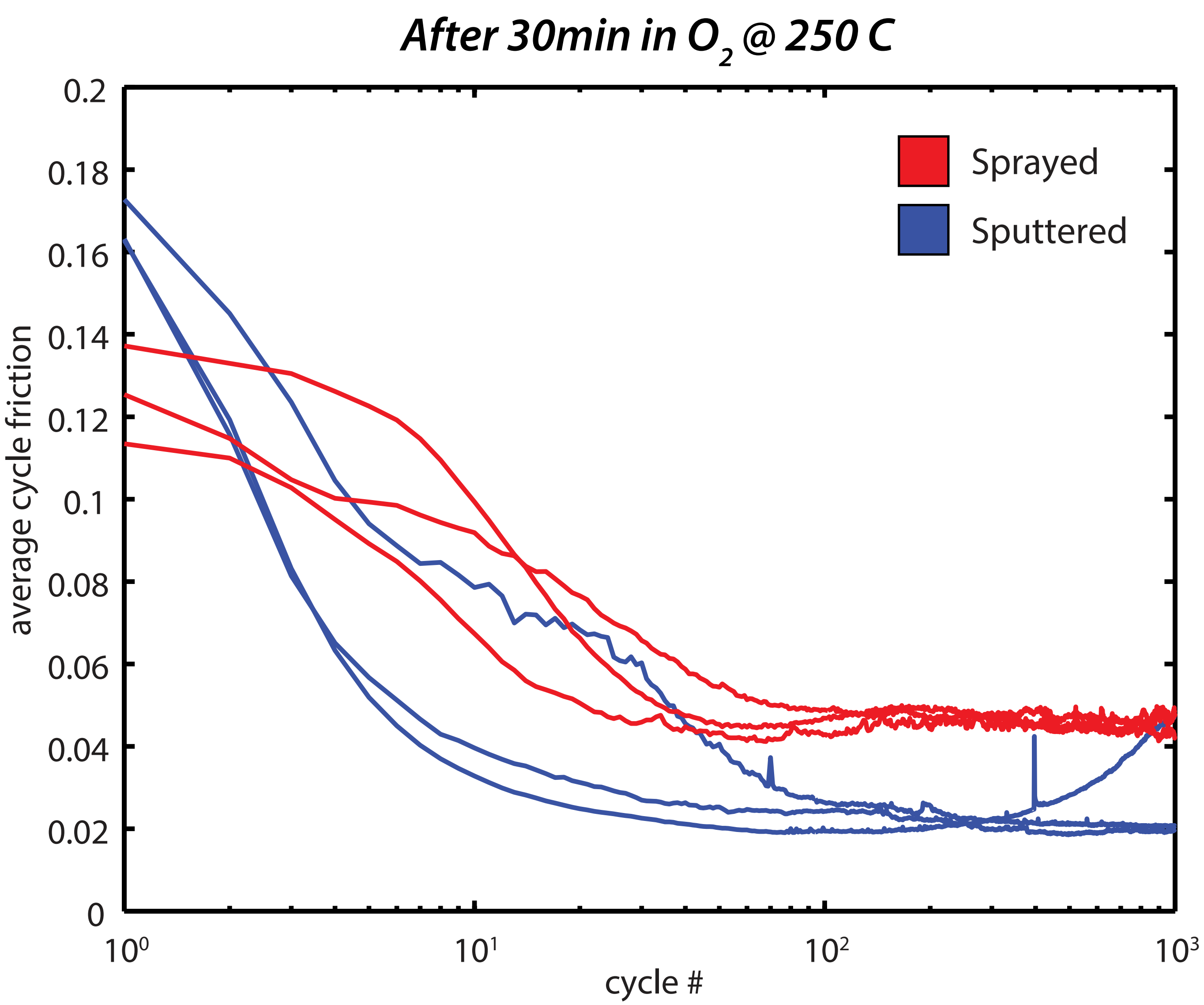
Tribological Testing

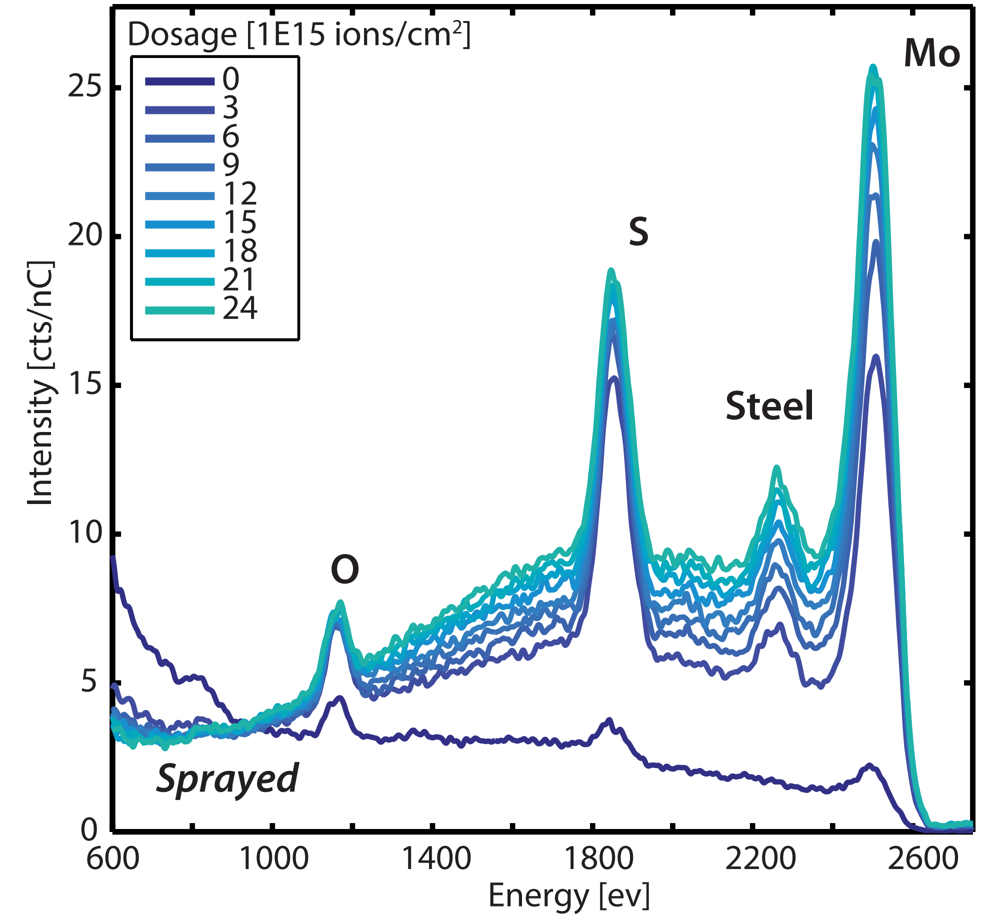
- Spray coatings generally lower (0.107) than sputtered (0.144) with exception of one sputtered sample
- Sprayed coatings begin to exhibit more erratic and higher friction than sputtered

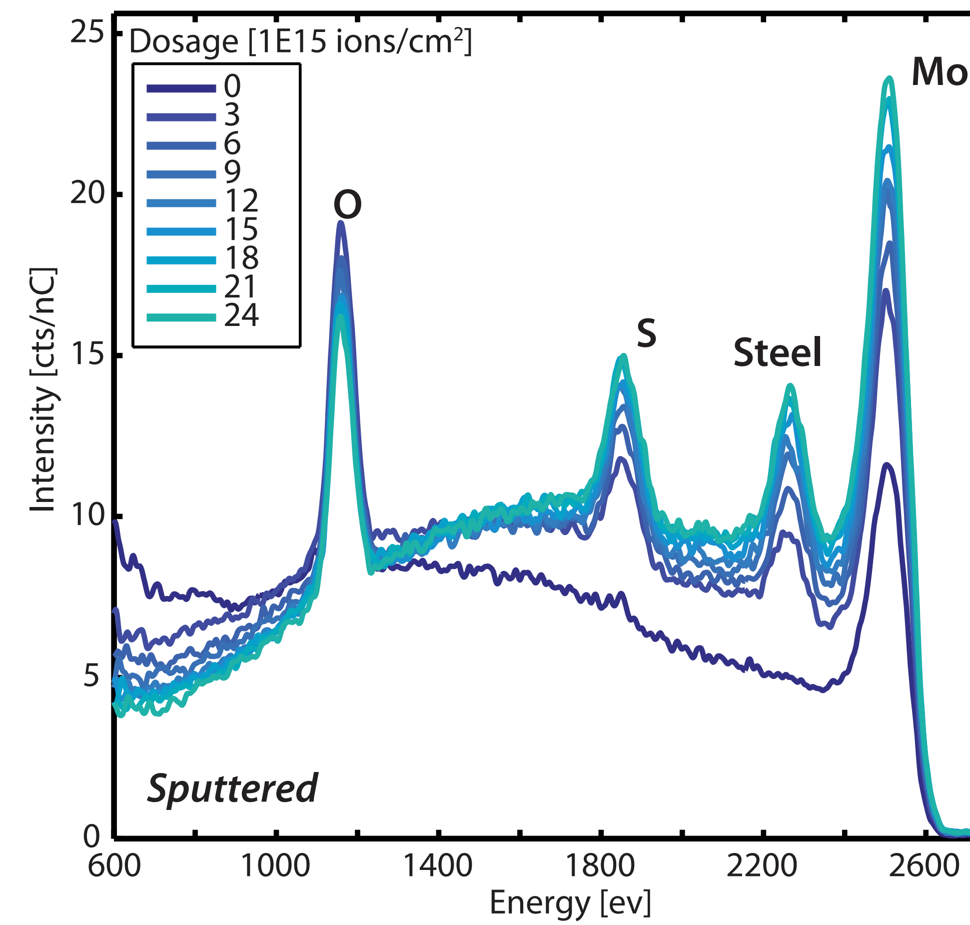
HS-LEIS Results

- Relatively similar profiles
- Higher low Z contamination (adventitious carbon) through depth of sputtered coating
- Adventitious carbon more uniformly covering sprayed surface

O_2 Artificial Aging







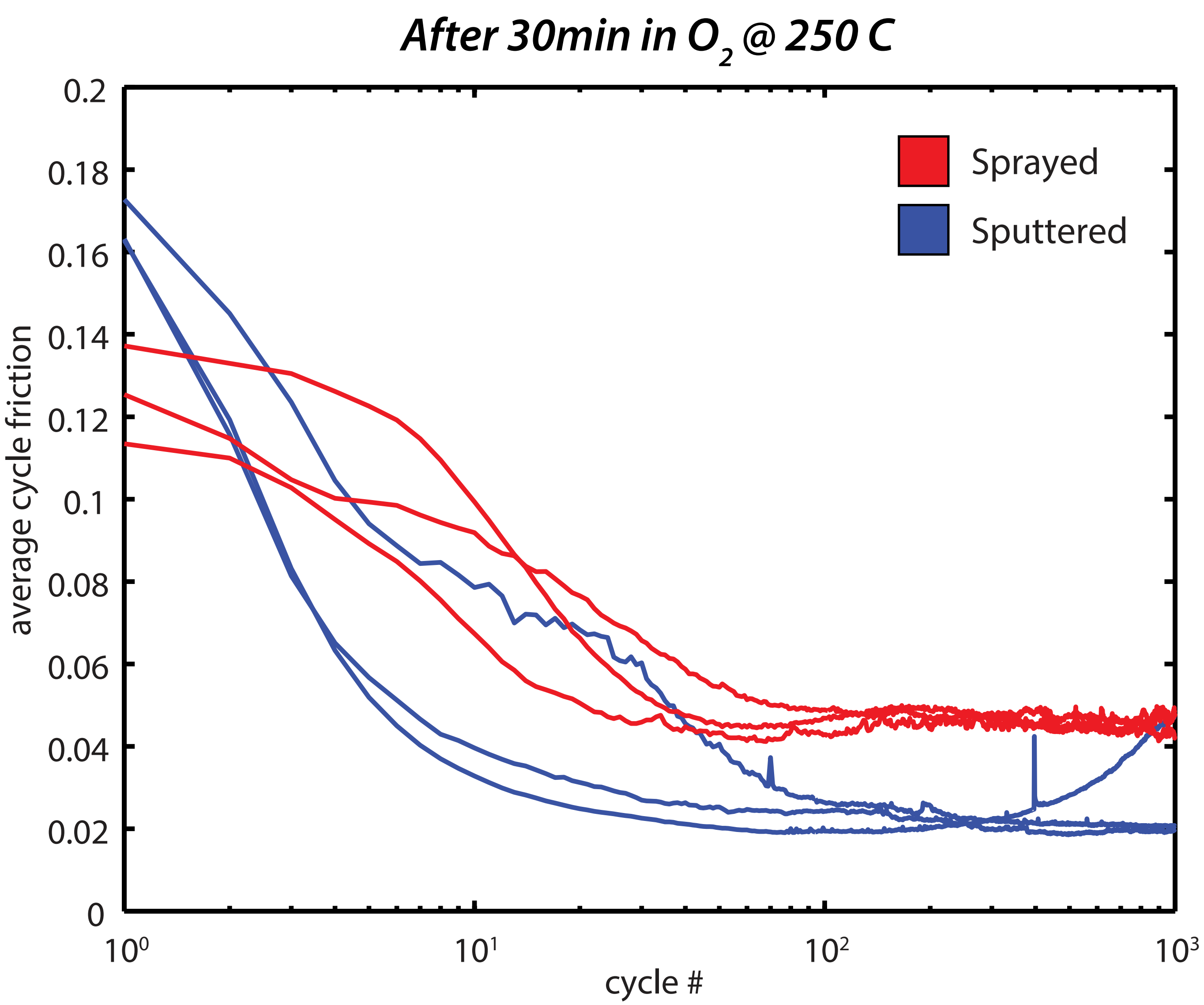
Tribological Testing

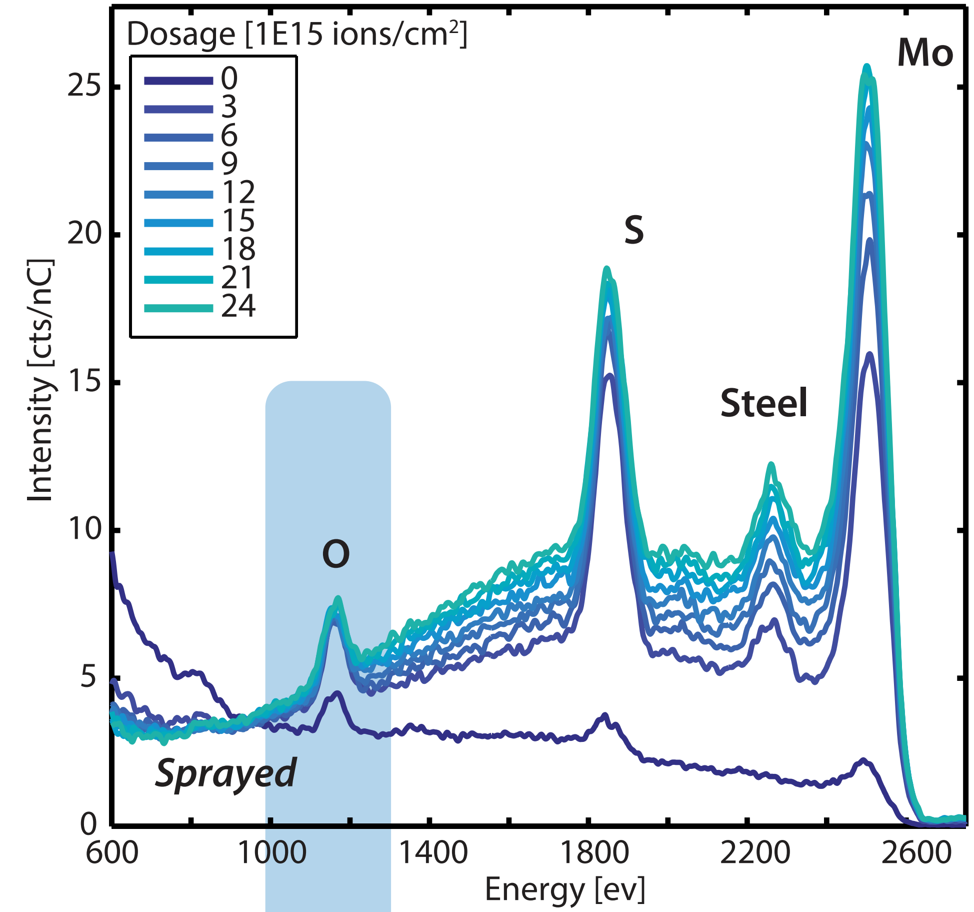
- Sprayed coatings show lower initial friction (0.126) than sputtered (0.164)
- Sputtered coatings attain lower steady state values (~0.02) than sprayed (~0.05) but reach them in a similar amount of cycles

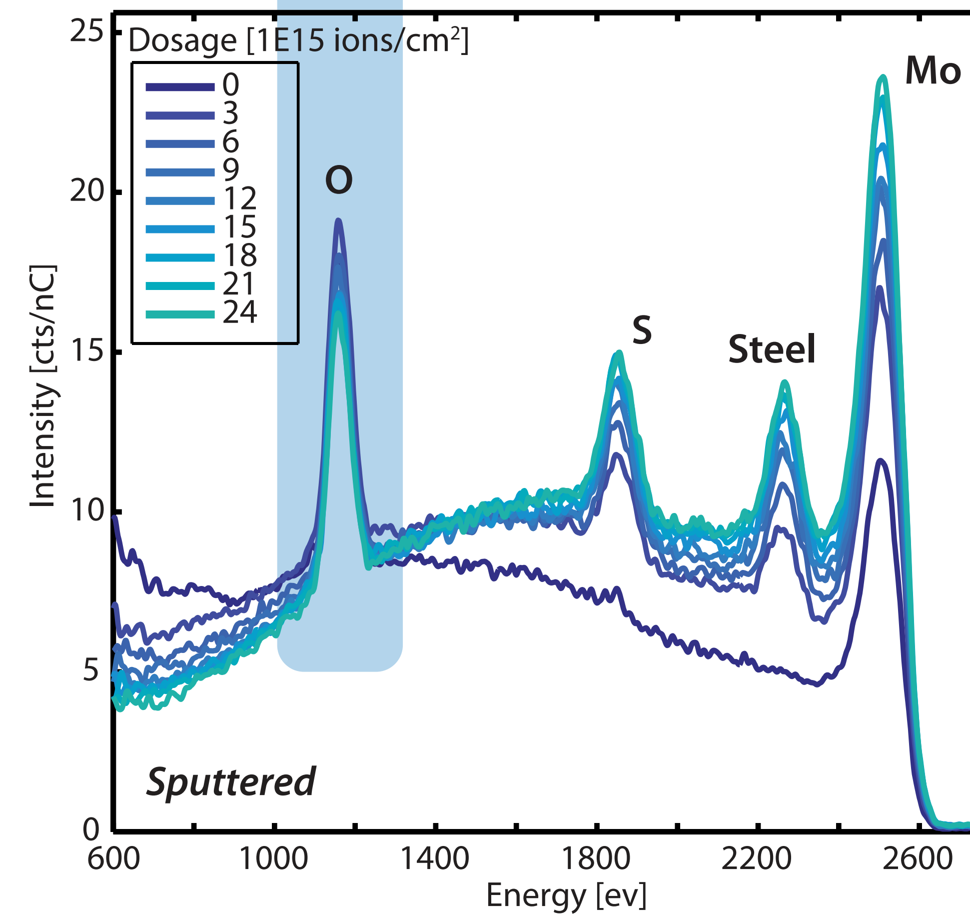
HS-LEIS Results

- Sprayed spectra similar to after anneal - marginally higher oxygen presenece
- Sputtered samples are largely affected by oxygen exposure, with complete loss of sulfure on surface
- Relative size (not necessarily ordering) of crystallites matters

O_2 Artificial Aging







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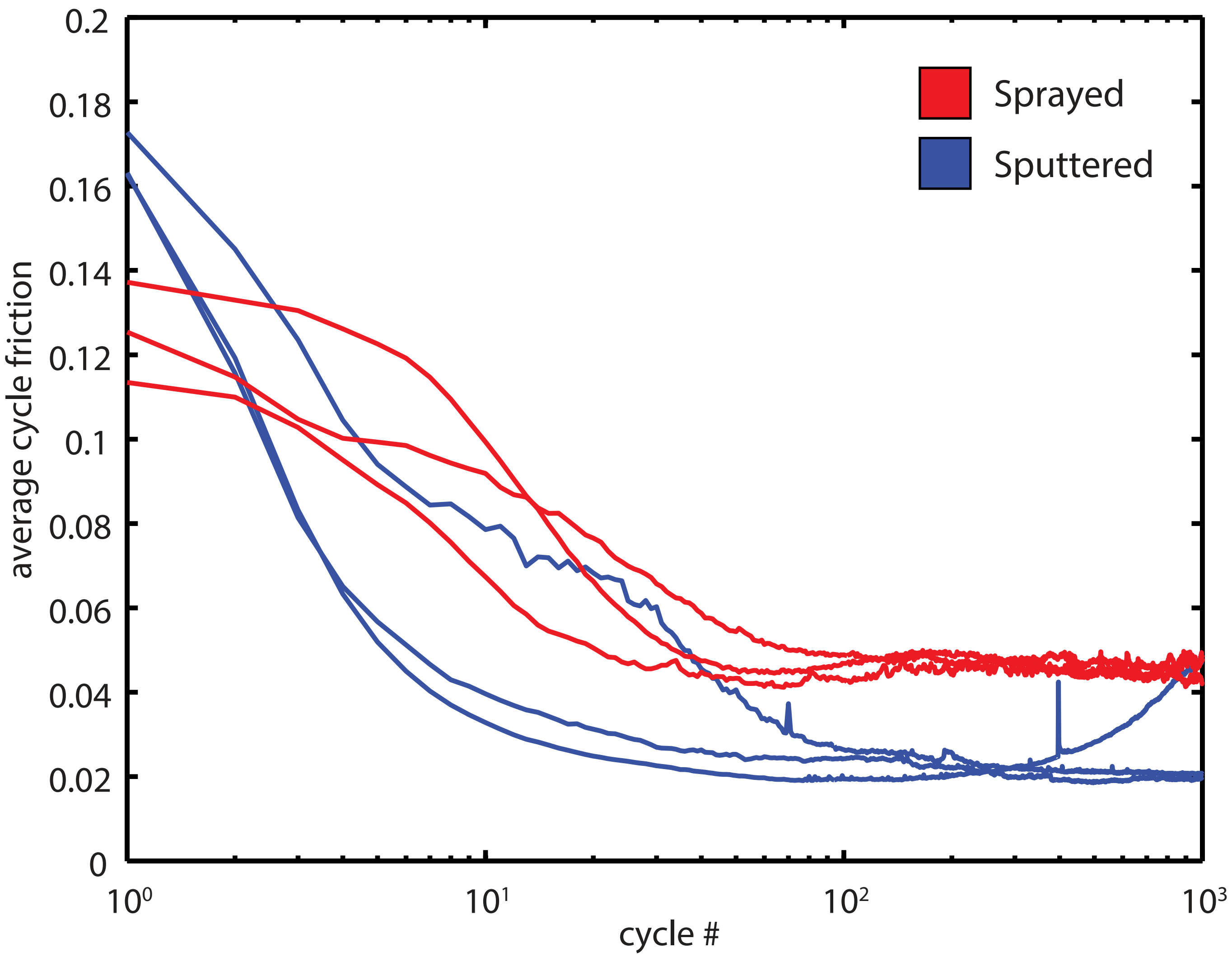
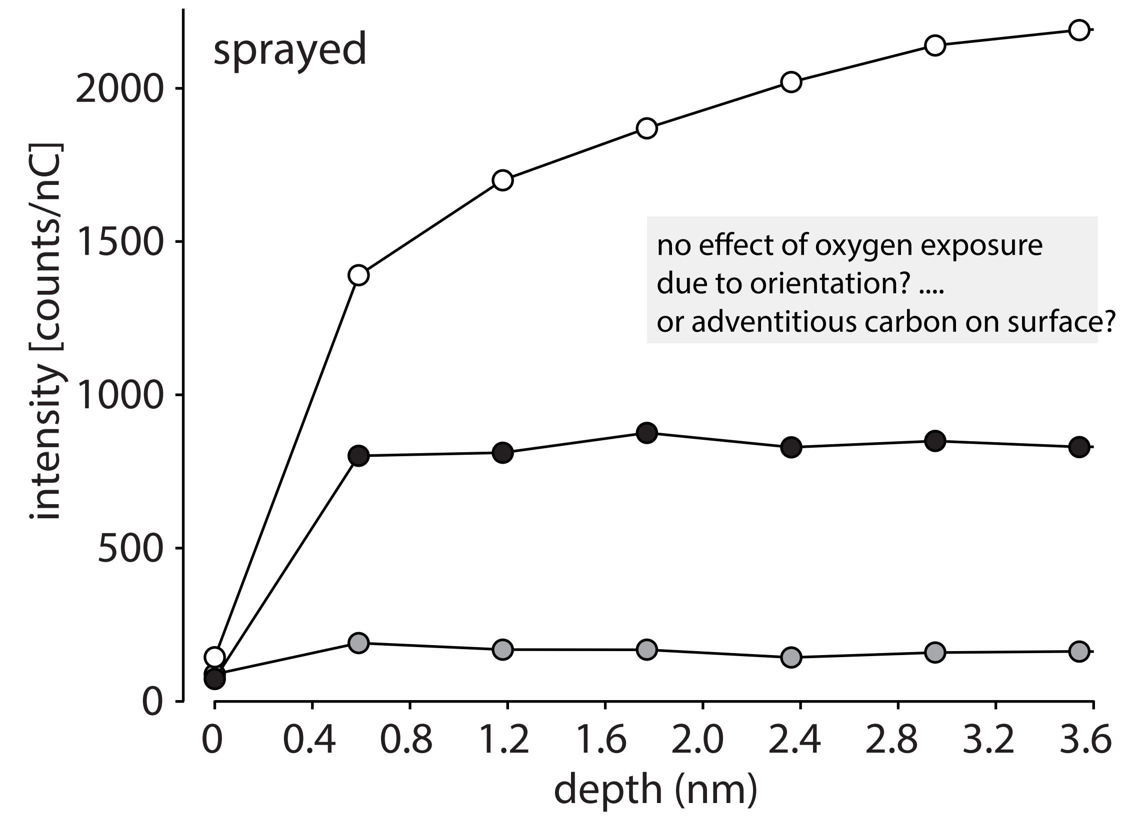
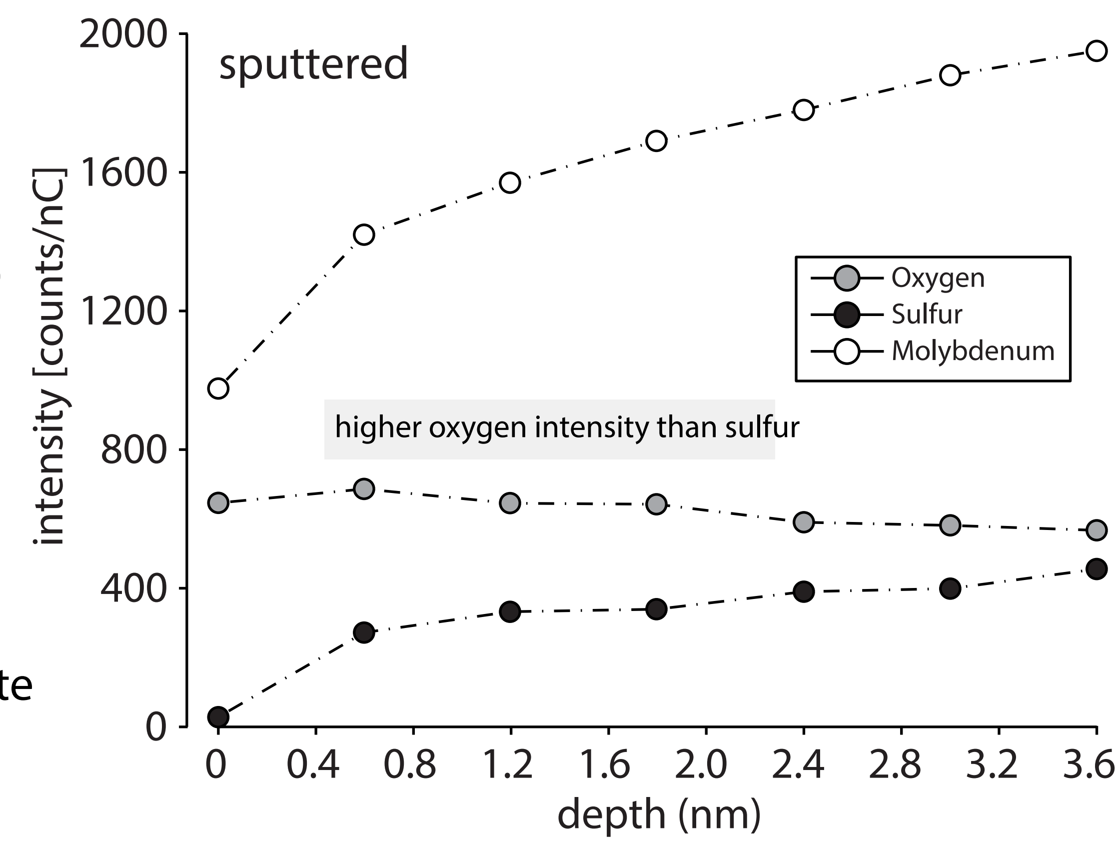
O_2 Artificial Aging

After 30min in O_2 @ 250 C







Tribological Testing

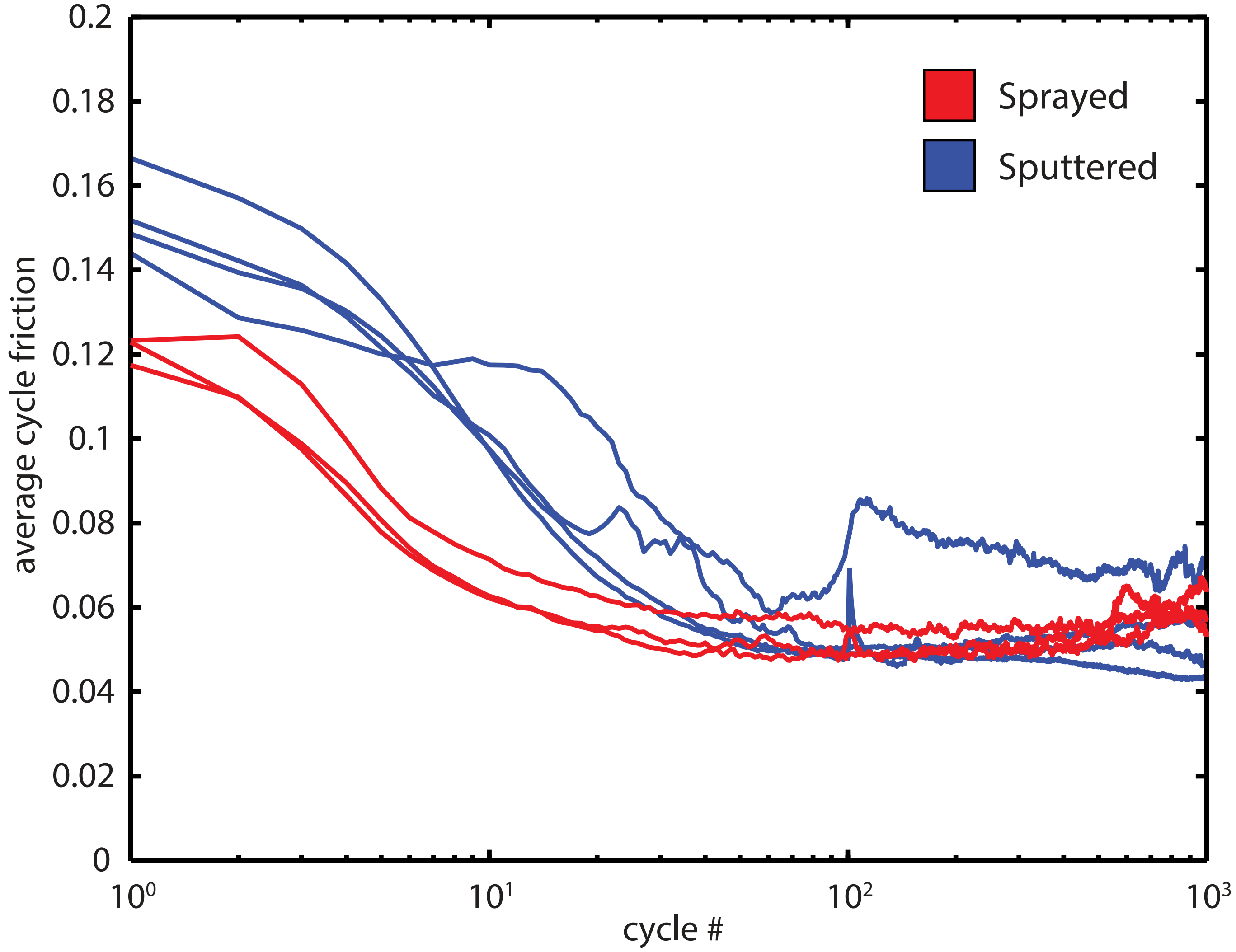
- Sprayed coatings show lower initial friction (0.126) than sputtered (0.164)
- Sputtered coatings attain lower steady state values (~0.02) than sprayed (~0.05) but reach them in a similar amount of cycles

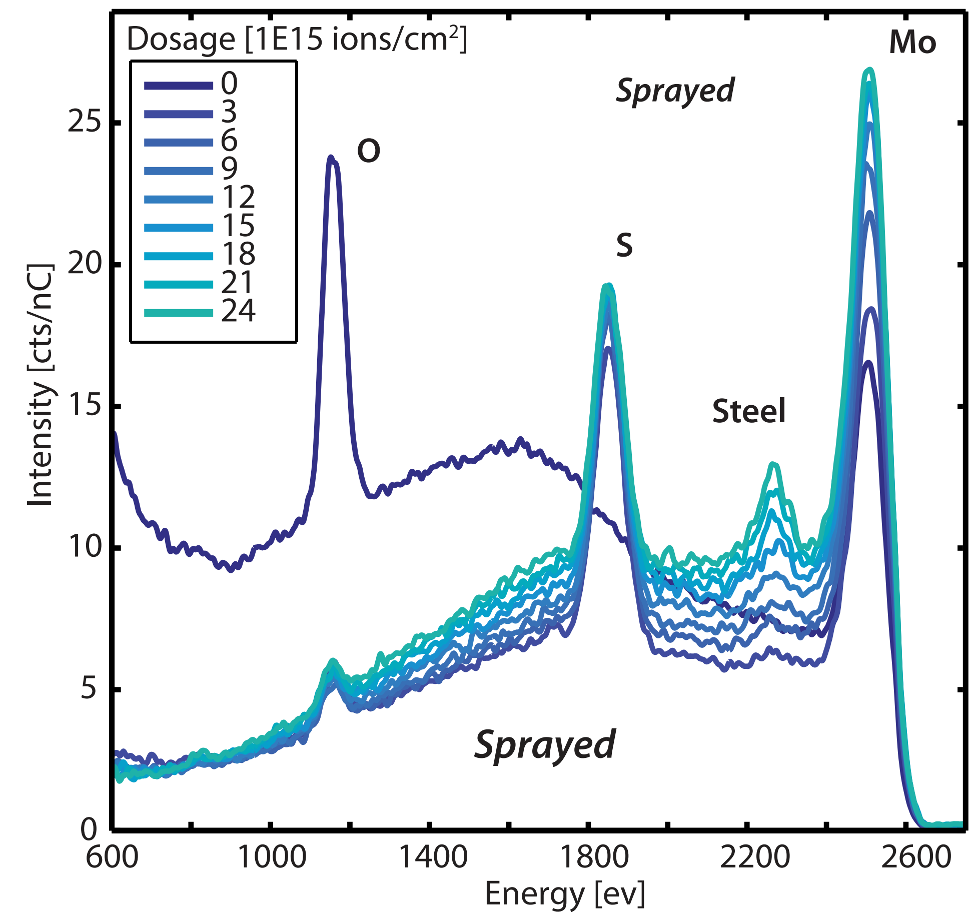
HS-LEIS Results

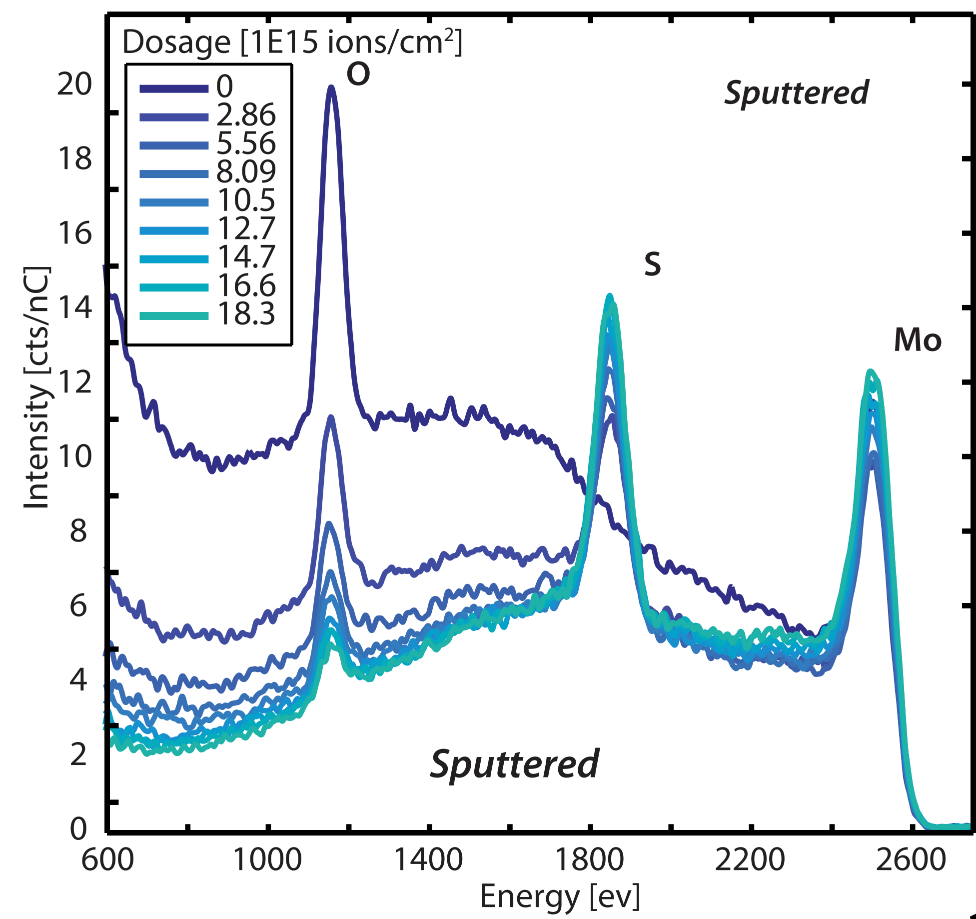
- Sprayed spectra similar to after anneal - marginally higher oxygen presenece
- Sputtered samples are largely affected by oxygen exposure, with complete loss of sulfure on surface
- Relative size (not necessarily ordering) of crystallites matters

Atomic Oxygen Artificial Aging

30 min Atomic Oxygen Exposure







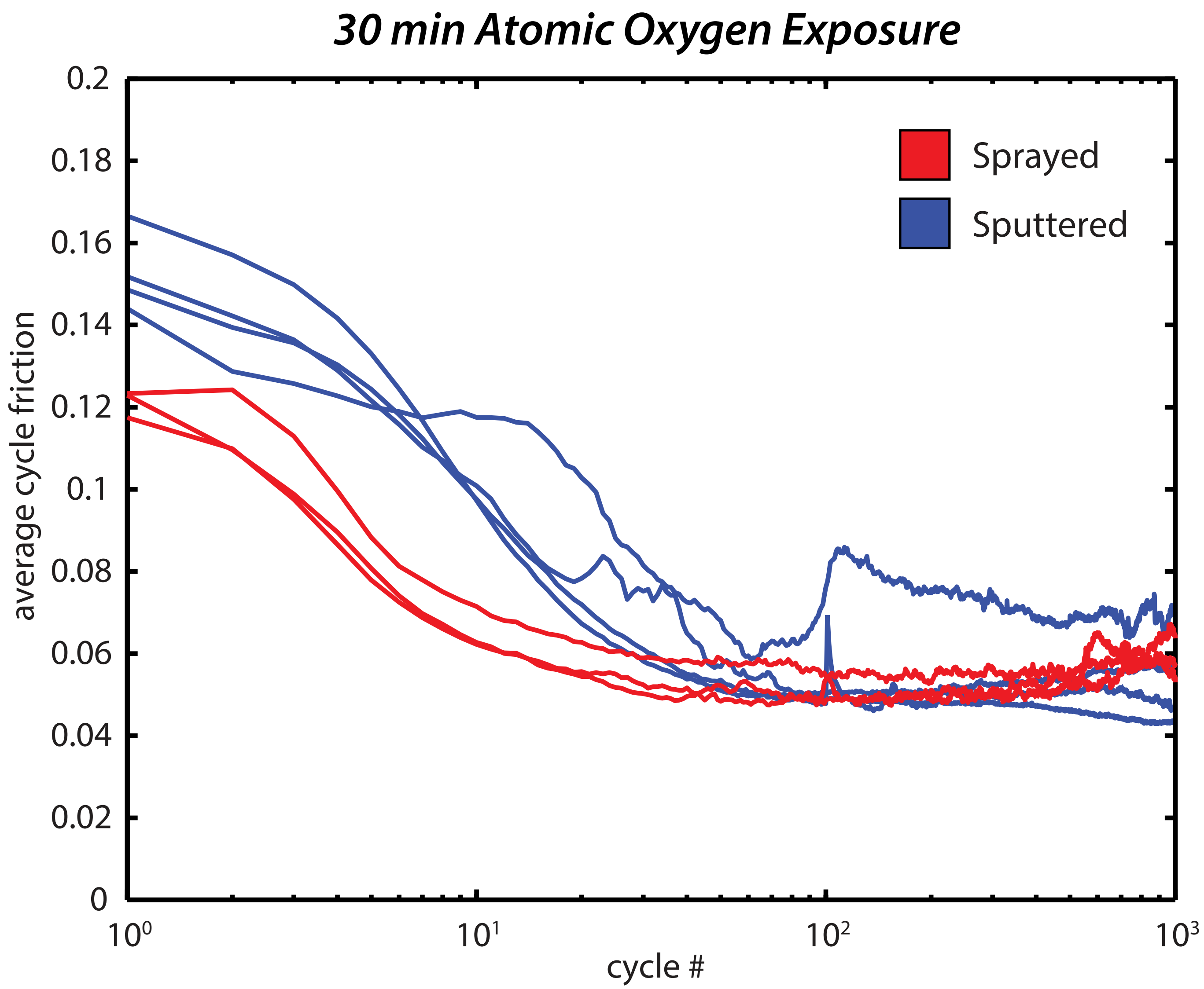
Tribological Testing

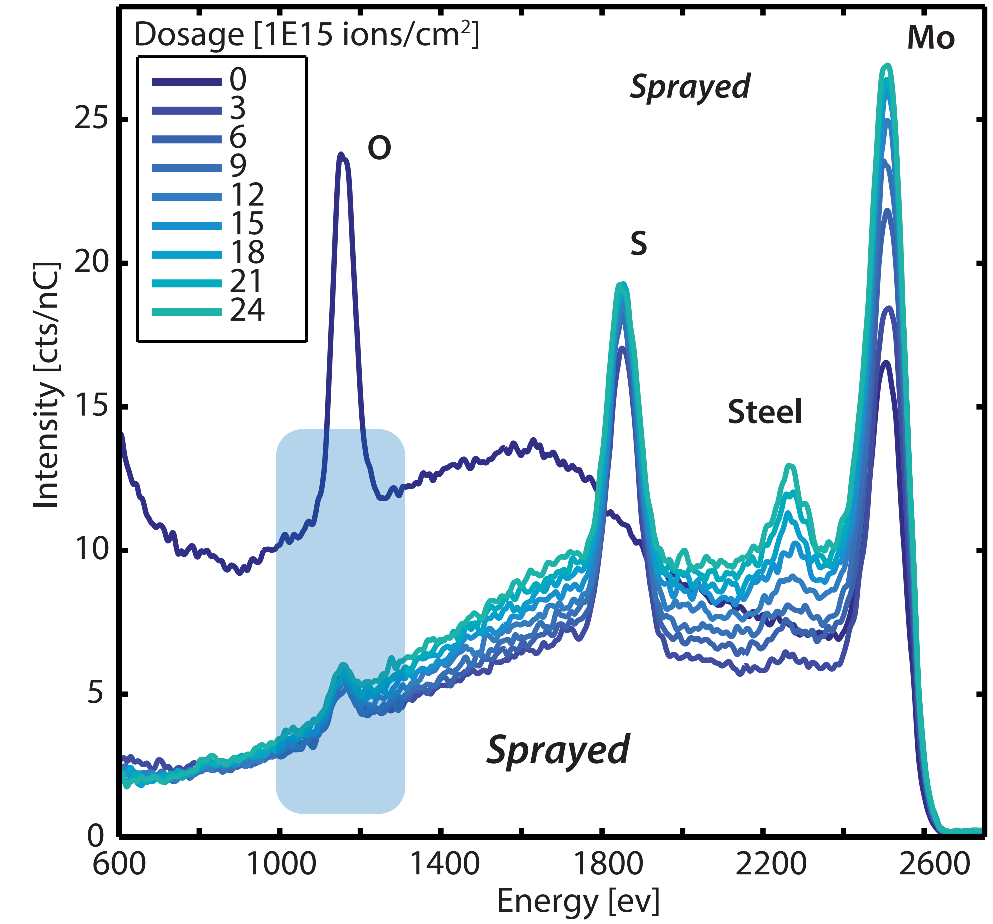
- Sprayed coatings show lower initial friction (0.123) than sputtered (0.153)
- Both coatings approach similar steady state values for friction

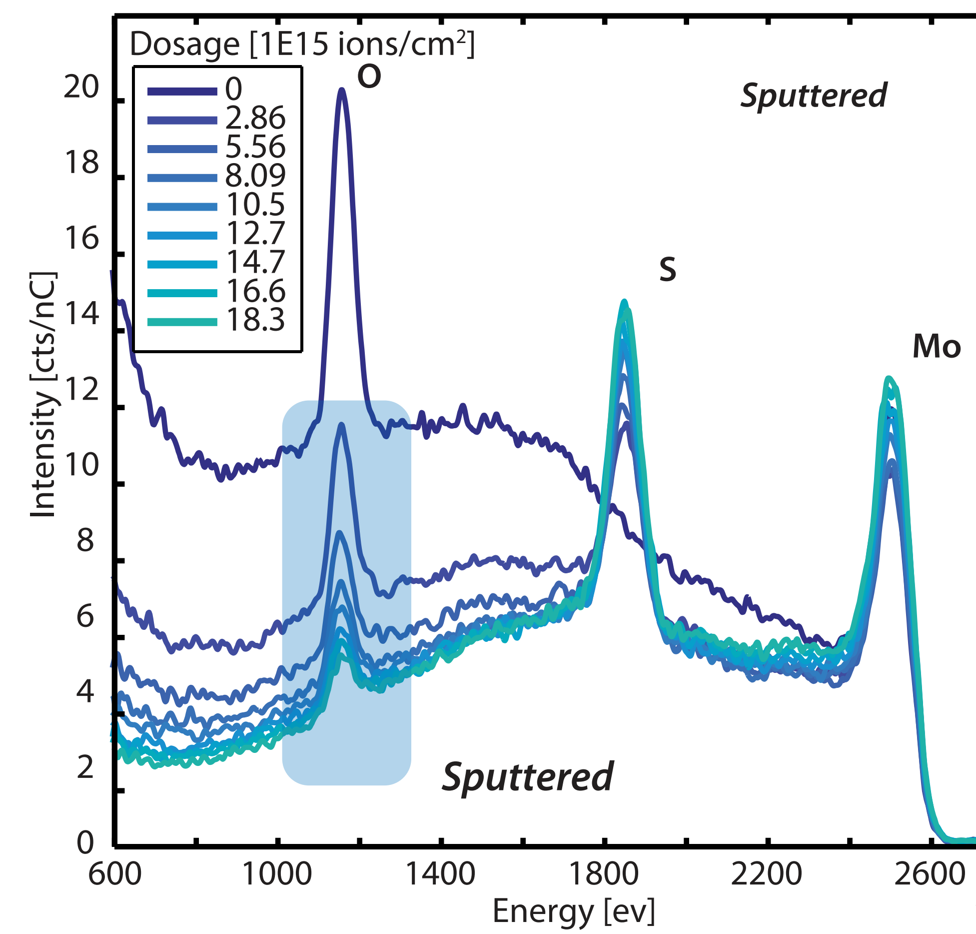
HS-LEIS Results

- Both coatings show complete loss of sulfur on surface... sprayed shows higher sulfur elbow (closer in subsurface)
- Sprayed coatings show lower intensity of oxygen through depth with steeper gradient

Atomic Oxygen Artificial Aging







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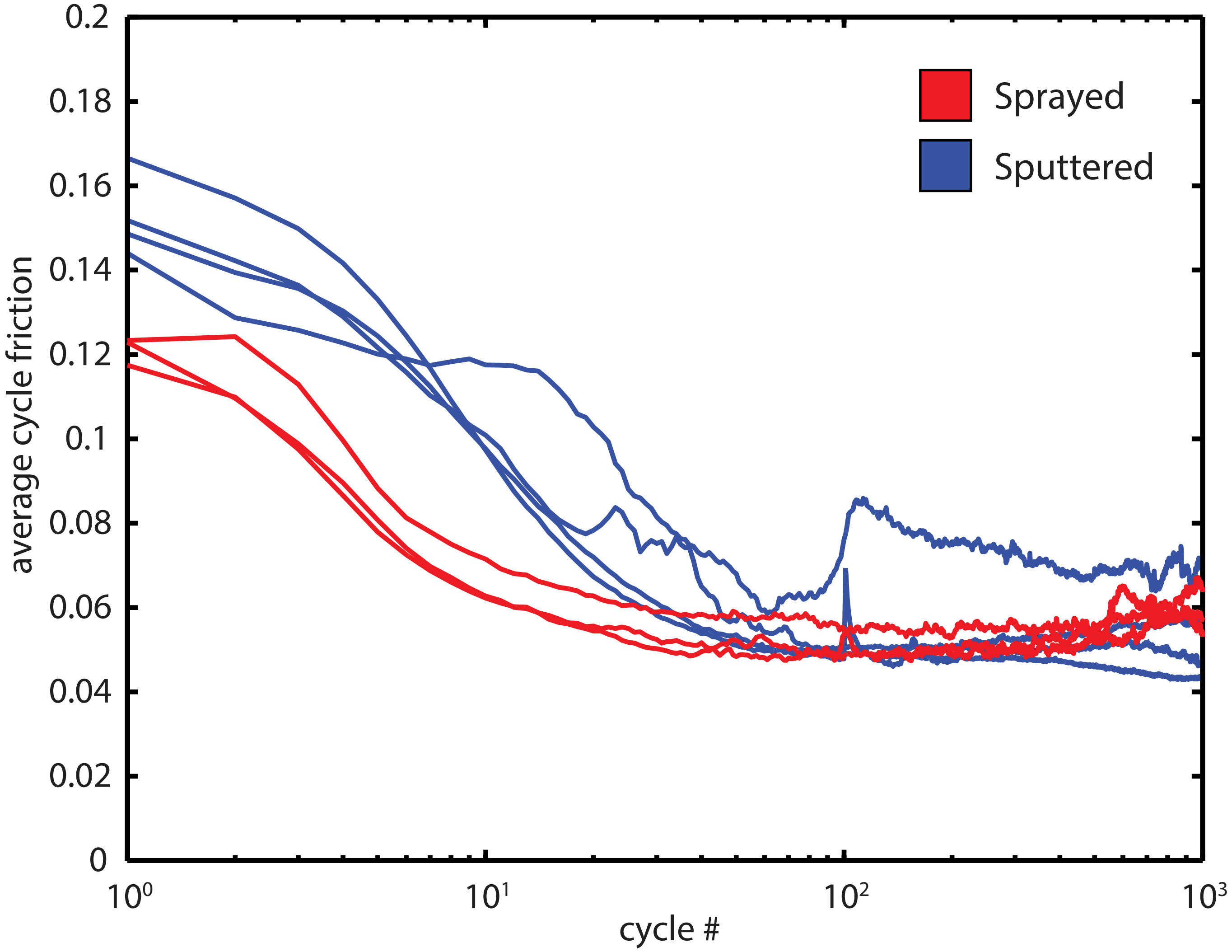

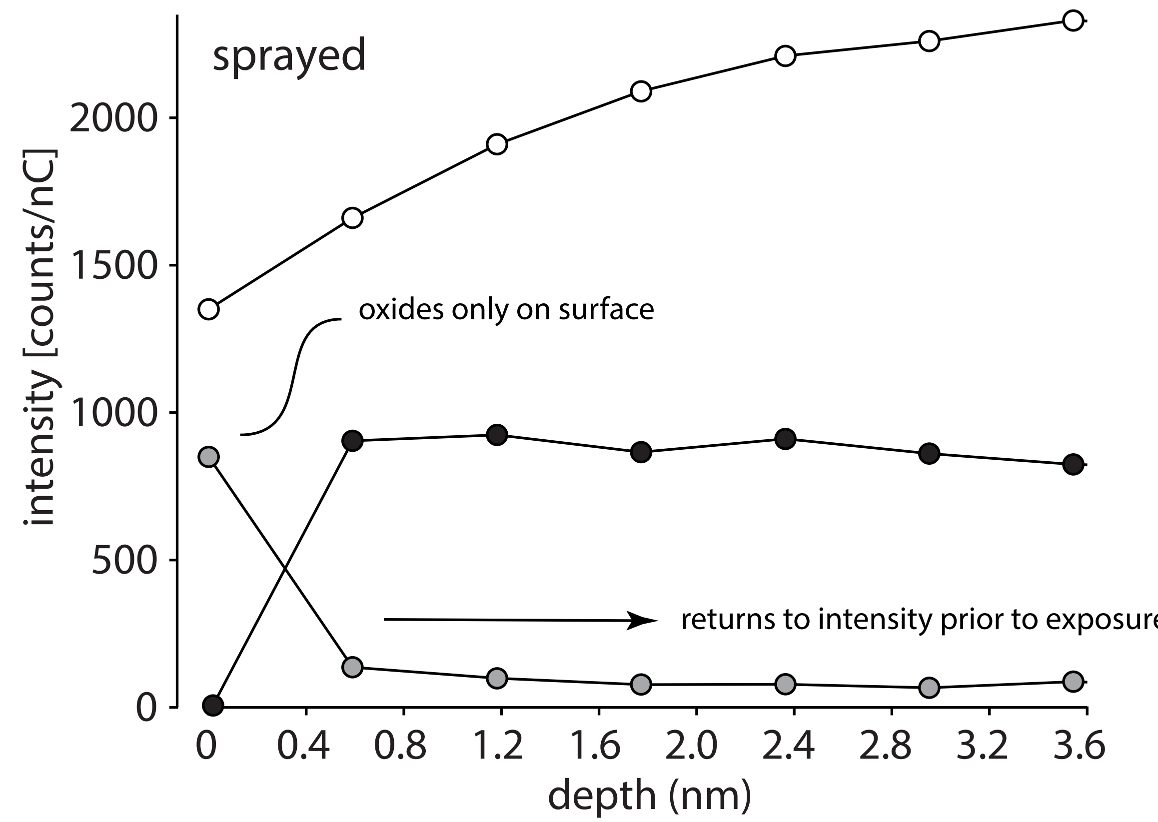

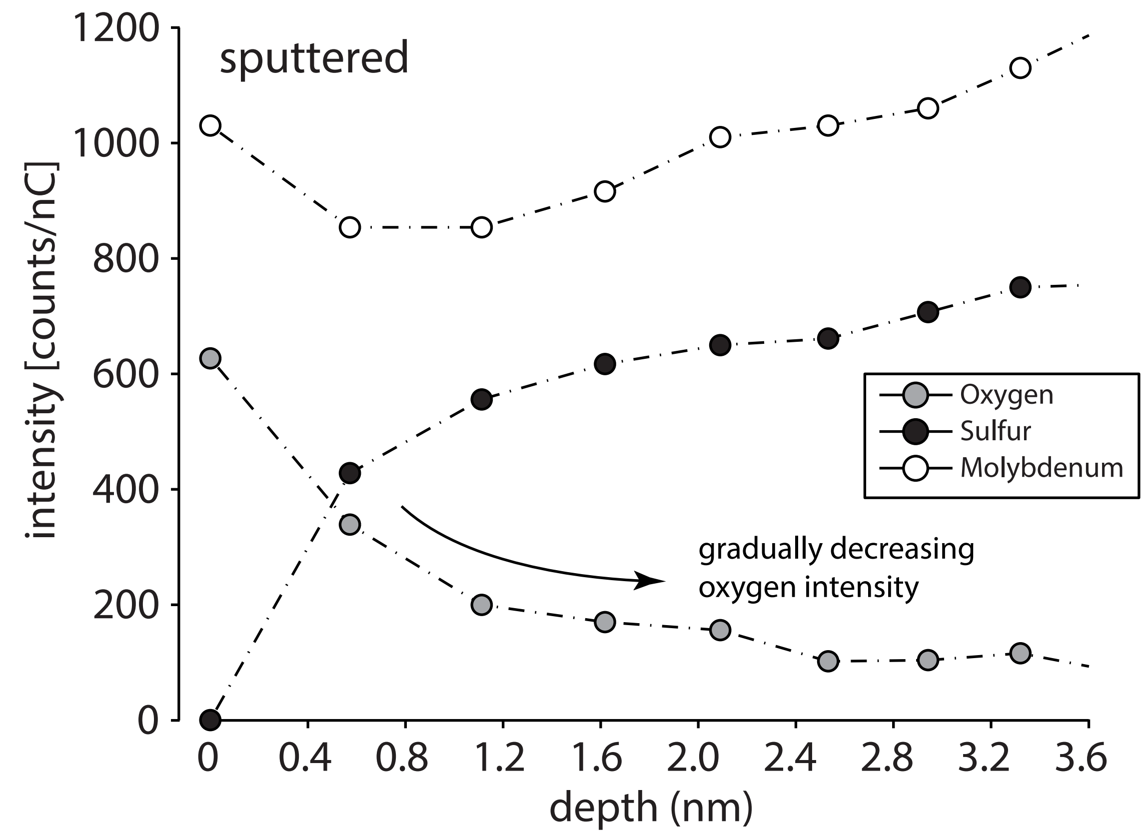

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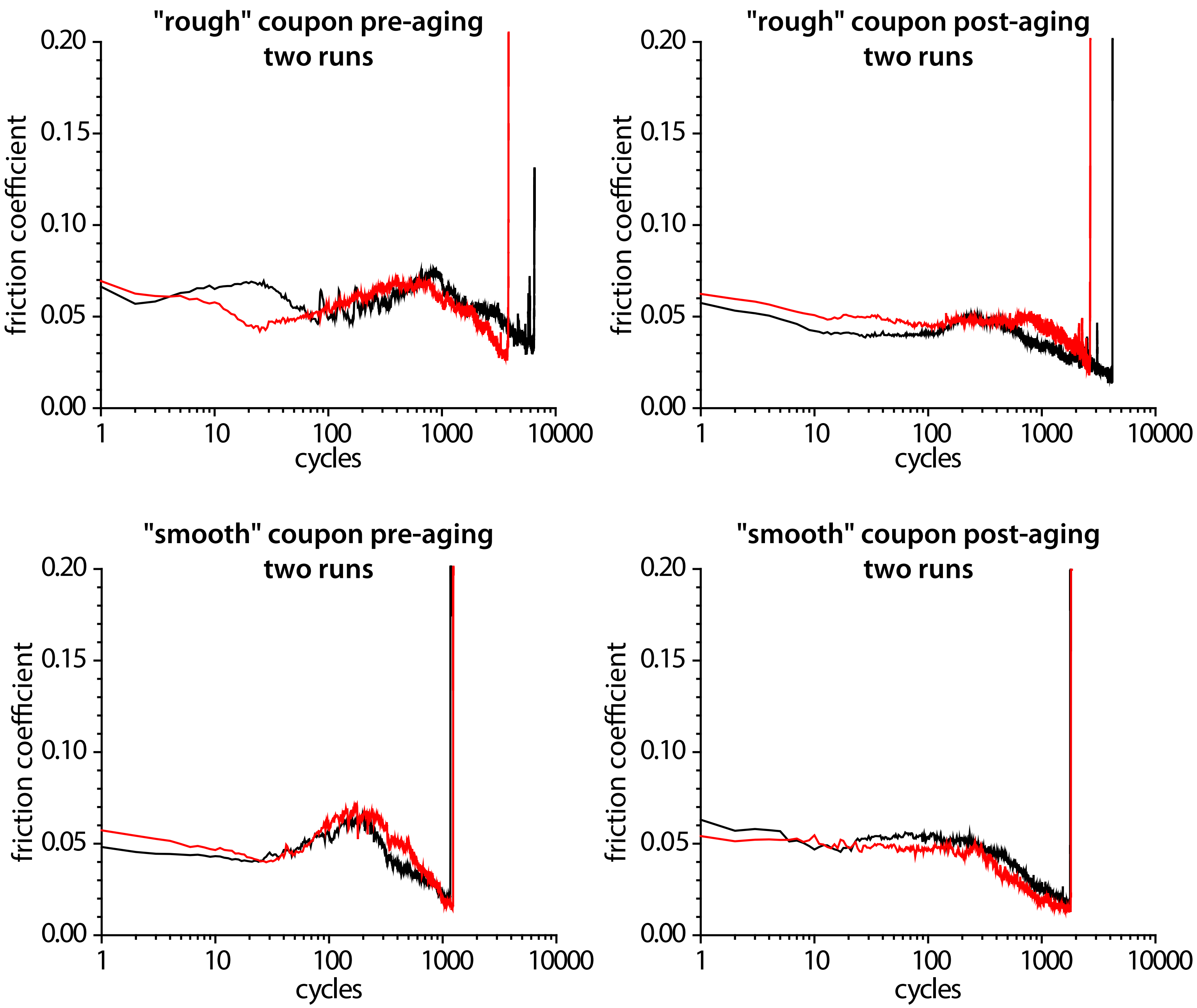
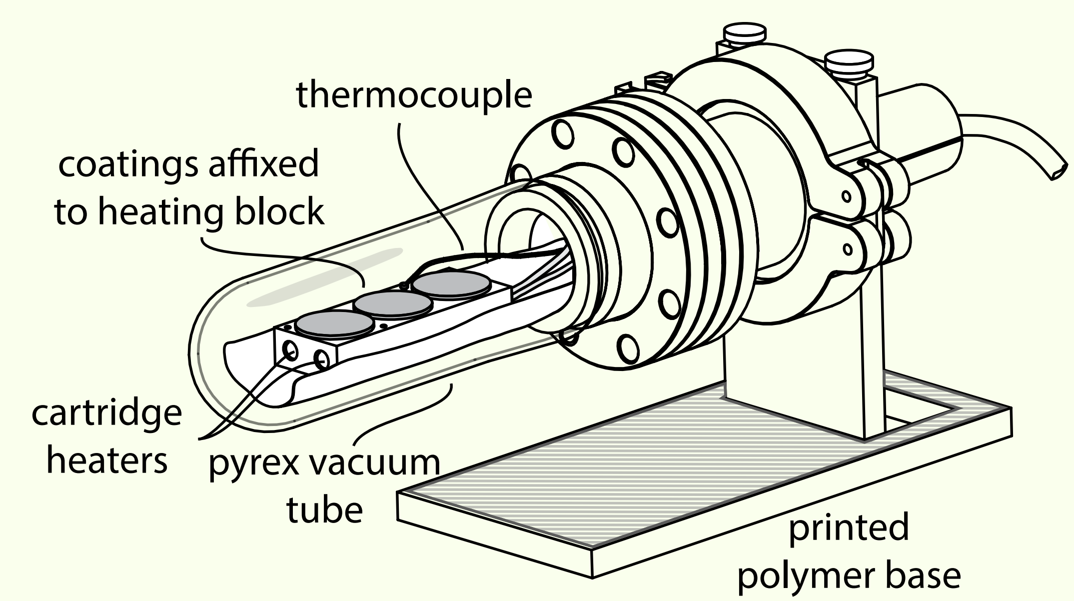
Aging Study in Humid Nitrogen





Annotated photograph of vacuum flange aging vessel

Aging Process

1) Sealed in 50% RH nitrogen environment at rooom temp
2) Heated to 150°C for 10 days
3) Chamber cooled and samples removed for testing in dry nitrogen environment

Notable Results

Coatings able to resist poisoning from extreme artificial aging procedure

No differences between testing before or after aging

Only factor affecting coating life in this case is the roughness of the substrate

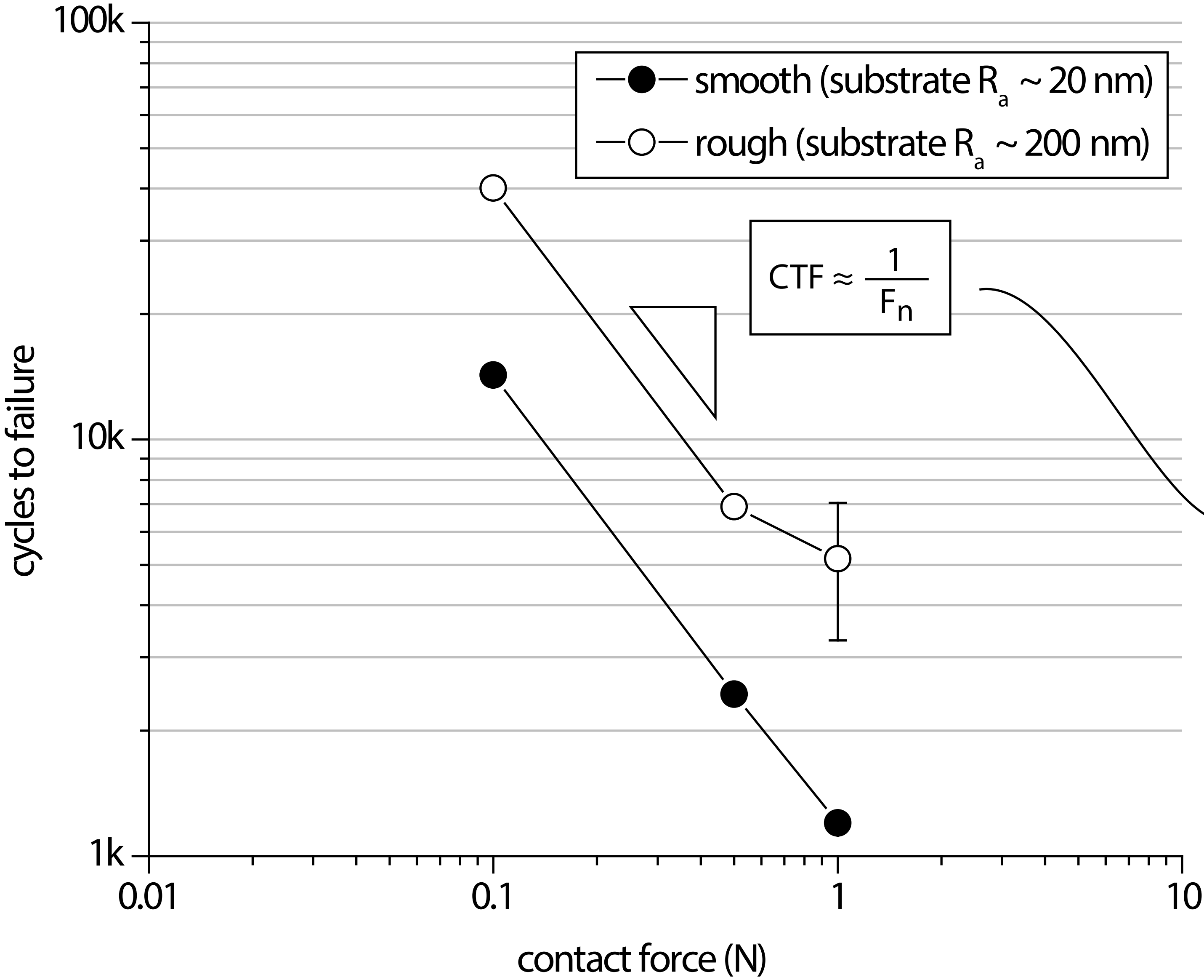
Experiment Conditions

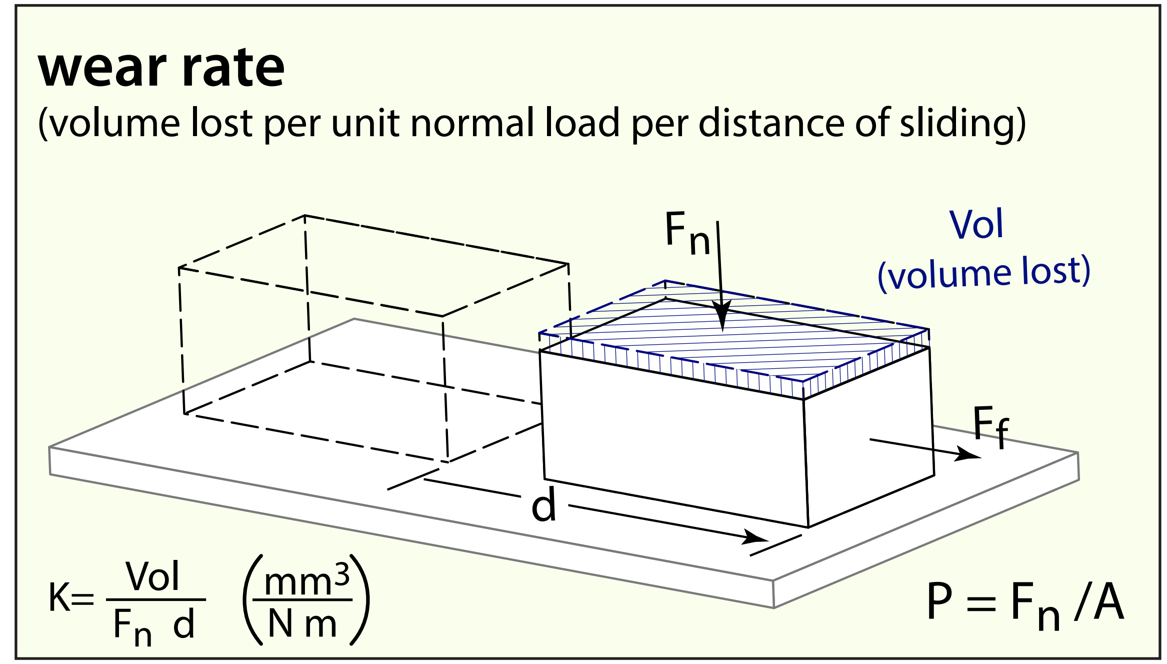
Substrates:	17-8 PH Steel (Coupon - 1" disc)
	440C SS (Pin - 1/8" diameter)
Roughness:	"smooth" (R_a ~ 20 nm)
	"rough" (R_a ~ 200 nm)
Deposition:	N_2 sprayed MoS_2 coupons
Environment:	dry N_2 (< 10 ppm O_2, dew point < -60°C)
Temperature:	20°C

Test Parameters

Contact Geometry:	Pin on Disc
Sliding Mode:	linear bi-directional
Speed:	1 mm/s
Stroke:	1 mm
Normal Load:	**1 N**

Wear of N_2 Sprayed MoS_2





Coating life measured by evidence of a sharp transition in friction coefficient associated with metal-on-metal contact

Only rough coupon showed significant variability in cycles-to-failure at 1 N normal force, error bars represent standard deviation for six separate experiments.

Slopes of linear regression best fit lines to both data sets suggest that the wear rate is inversely proportional to contact force, in agreement with the Archard wear theory

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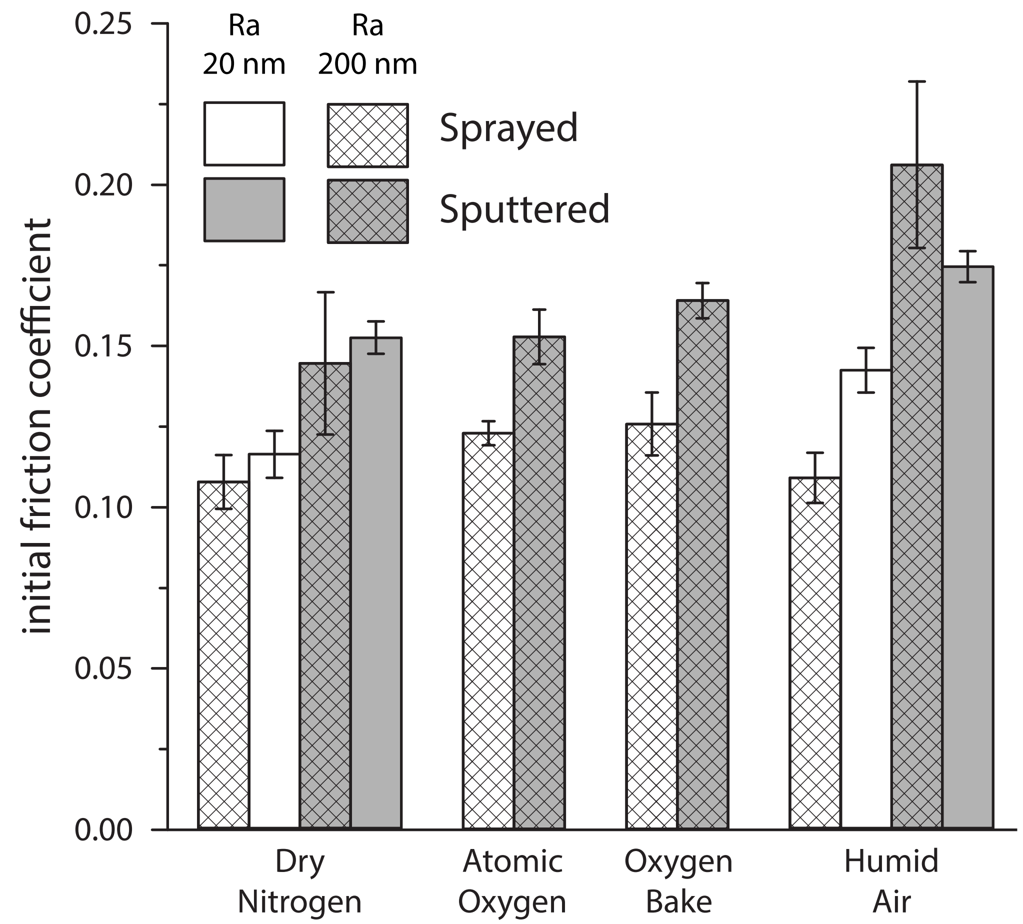
Results Summary & Conclusion

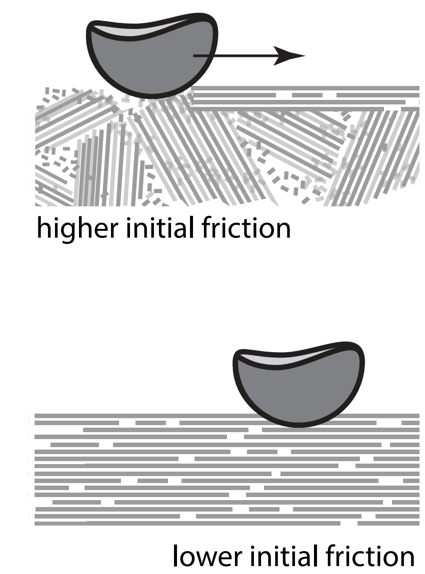
- ***Tribological tests*** show spray coatings reduce initial friction, likely from greater basal plane orientation showed via ***XRD***

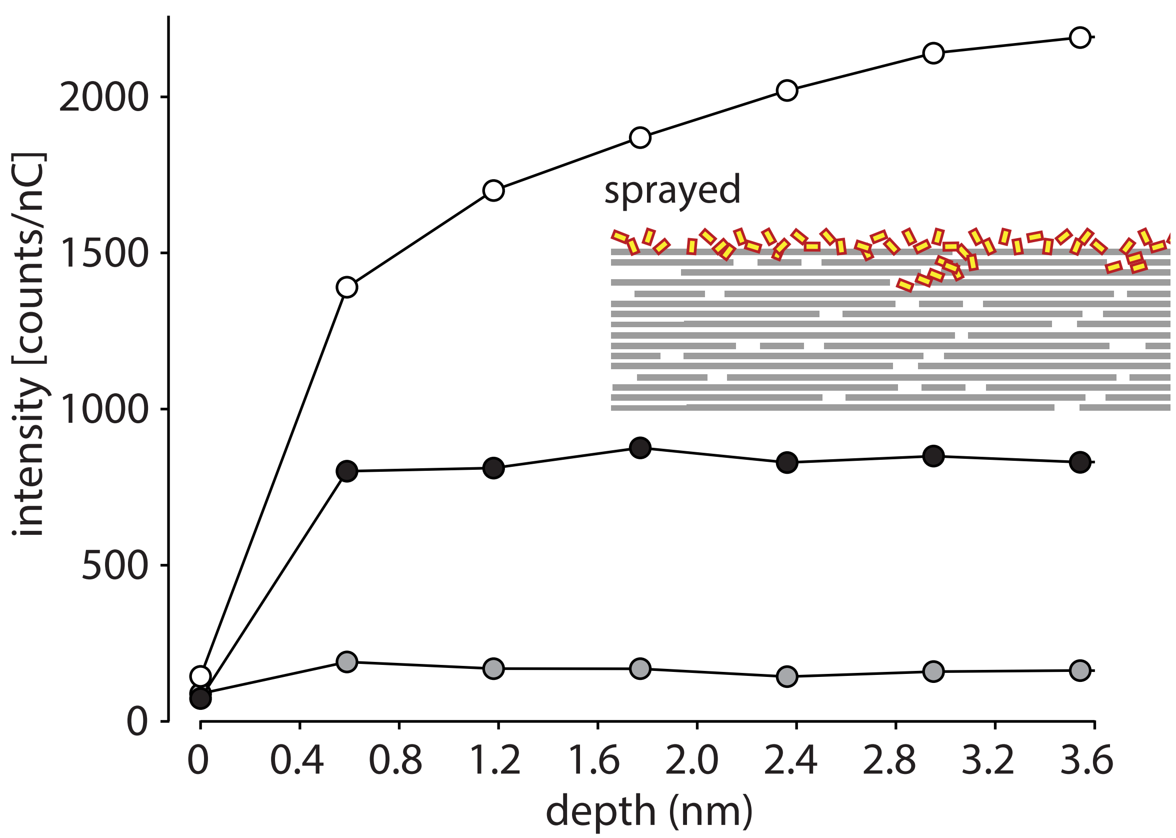
- ***HS-LEIS*** shows less % intensity of oxygen presence for sprayed coatings throughout depth

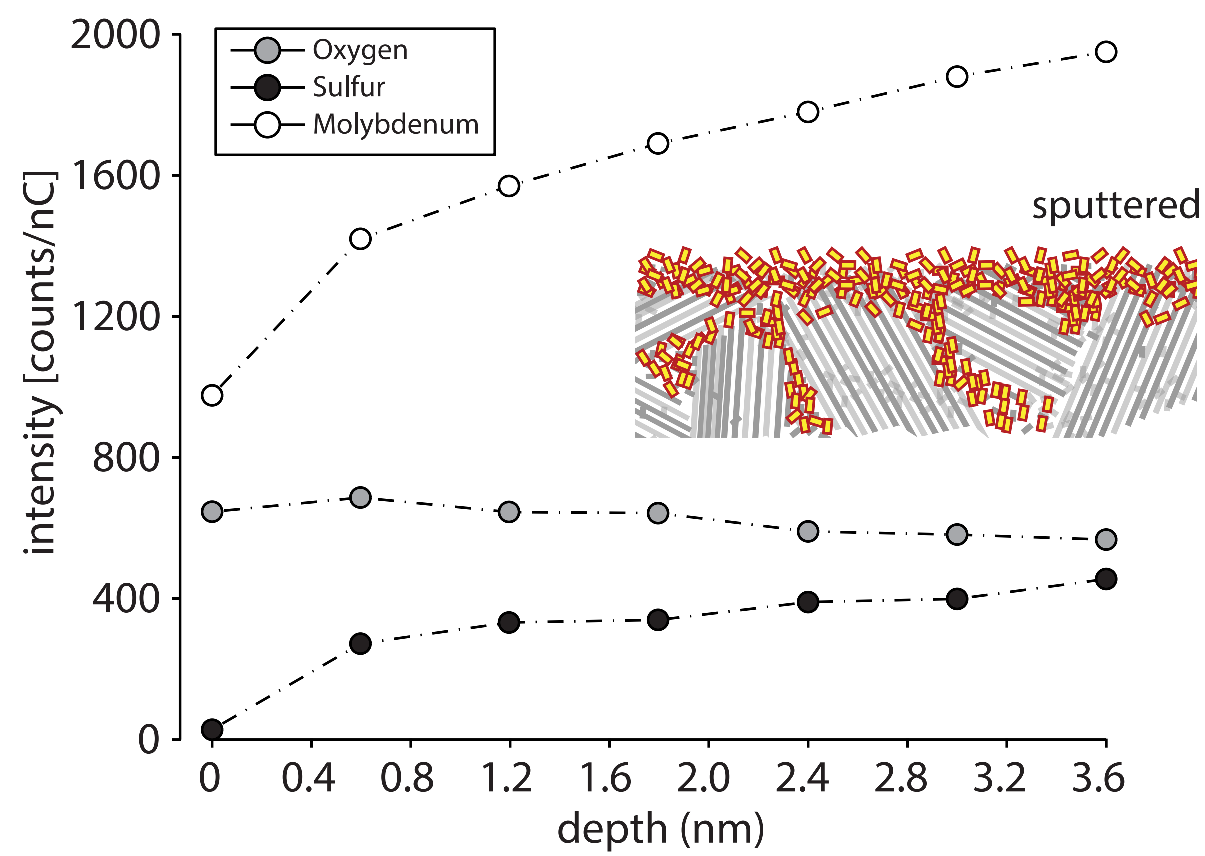
- Ratio of basal surface to open edge sites is likely the cause

- Great for single actuation mechanisms requiring reliably low initial friction









Acknowledgements

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Ashlie Martini (Tribological Testing)

Tribologix

Andras Korenyi-Both (Sputtered Samples)

Questions?