SAND2022-8489C

Quality over Quantity: Meaningful Metrics for Qualifying MoS_2 Coatings

Tomas F. Babuska[1,2,3], John F. Curry[1], Michael T. Dugger[1], Morgan R. Jones[1], Frank W. DelRio[1], Ping Lu[1], Yan Xin[4], Tomas Grejtak[2,3], Robert Chrostowski[5], FIlippo Mangolini[5], Nicholas C. Strandwitz[3], Md. Istiaque Chowdhury[3], Ryan Thorpe[3], Gary Doll[6] and Brandon A. Krick[2]

[1]Material, Physical and Chemical Sciences Center, Sandia National Laboratories, Albuquerque, NM
[2]FAMU-FSU College of Engineering, Florida State University, Tallahassee, FL
[3]Department of Materials Science, Lehigh University, Bethlehem, PA
[4]National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL
[5]Walker Department of Mechanical Engineering, University of Texas at Austin, Austin, TX
[6]College of Engineering and Polymer Science, University of Akron, Akron, OH

FAMU-FSU Engineering

SURFACE INTERFACES & MATERIALS TRIBOLOGY LABORATORY

Introduction

Sputter deposited MoS_2 coatings *without dopants* (i.e., pure) have been limited in use due to highly variable tribological properties between deposition runs (i.e., batch to batch variation) driven by *uncontrolled* changes in coating morphology

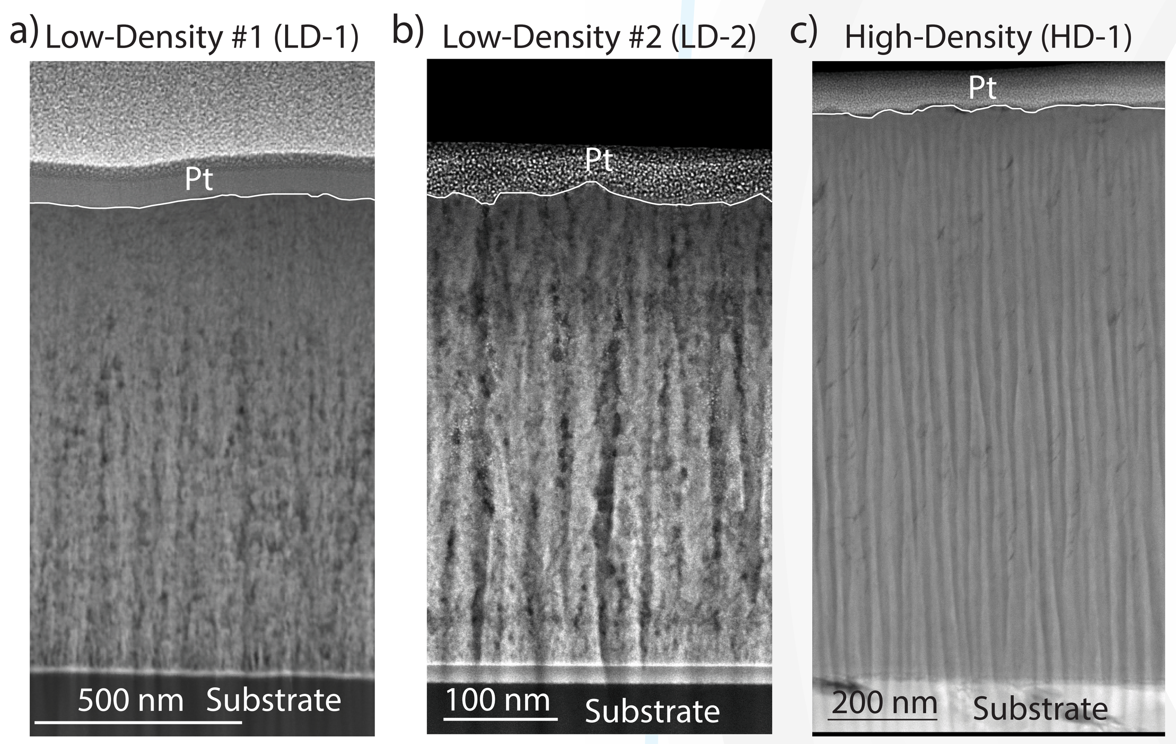

Figure 1: Transmission electron micrographs (TEM) of 3 pure MoS_2 coatings deposited with identical deposition parameters in the same chamber on different days showing a varying degree of void formation. (A) The low-density coating batch #1 (LD-1) and (B) the low-density #2 coating batch (LD-2). (C) The high-density coating batch (HD-1)

Deposition of highly-dense pure MoS_2 is challenging (Figure 1), requiring the use of dopants (i.e., Ti, Au, Sb_2O_3) to densify coatings (Figure 2). Densification from dopants is a leading hypothesis for improved wear rates (~1 x 10^{-7} mm^3/Nm for $MoS_2/Sb_2O_3/Au$) in humid and inert environments

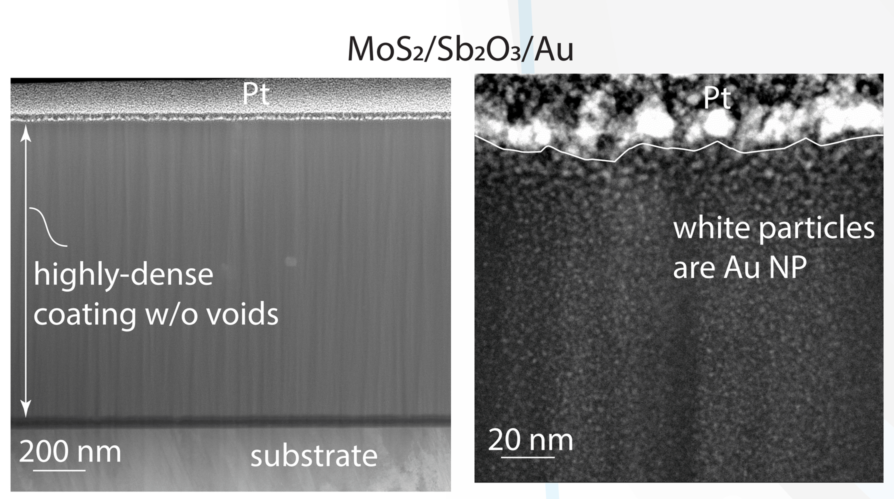

Figure 2: Transmission electron micrographs (TEM) of 3 pure MoS_2 coatings deposited with identical deposition parameters in the same chamber on different days showing a varying degree of void formation

Hypothesis: Density is a key characteristic influencing wear and aging for sputter deposited MoS_2 coatings.

1) Can pure MoS_2 coatings attain similar performance (i.e., low wear in humid and inert environments) to doped coatings if highly dense?

2) Are dense coatings more resistant to oxidation from prolonged storage in water and oxygen (i.e., aging)?

Results - Tribology

Three batches of sputter deposited pure MoS_2 coatings with identical parameters, but on different days, were deposited and tested in humid (30% and 60% RH) and inert environments (dry air and N_2)

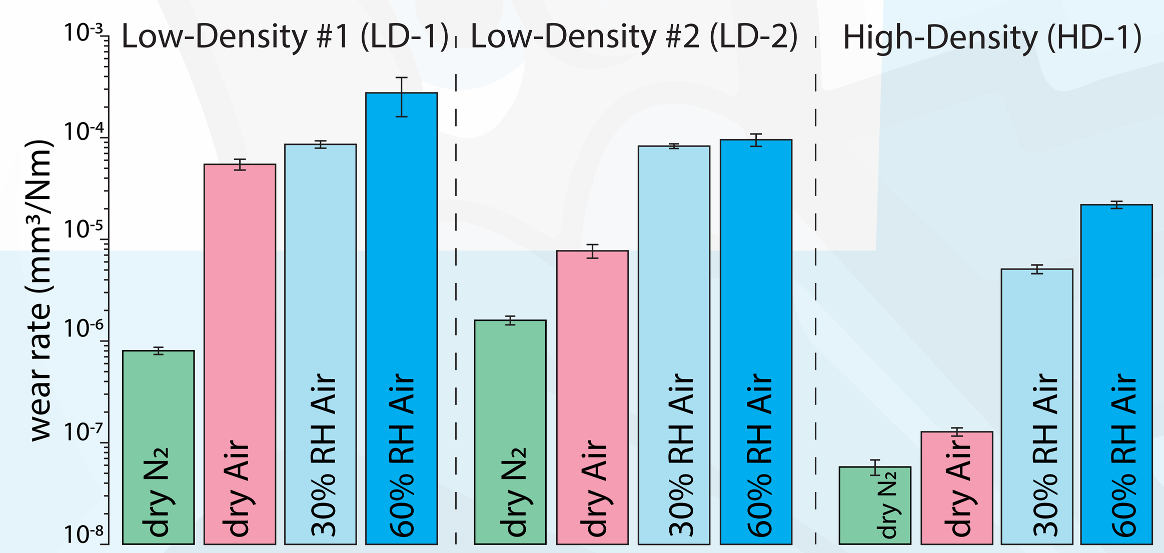

Figure 3: Wear rates of the low-density #1 (LD-1), low-density #2 (LD-2), and high-density (HD-1) coatings in dry N_2, dry air, 30% RH air and 60% RH Air.

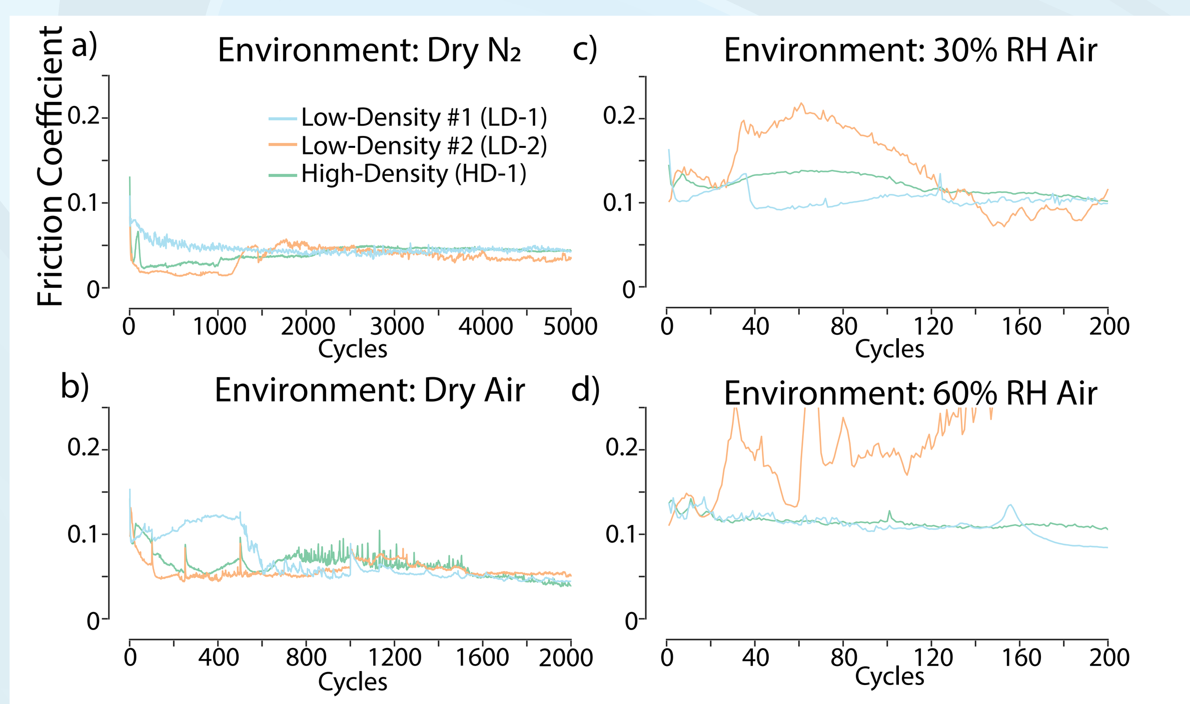

Figure 4: Coefficients of friction for the low-density #1 (LD-1), low-density #2 (LD-2), and high-density (HD-1) coating batches in (A) dry N_2, (B) dry air, (C) 30% RH air, and (D) 60% RH air

We observe from the tribological testing (Figures 3 and 4) that porous coating batches (LD-1 and LD-2) due to void formation (Figure 1) have 10-100x higher wear rates than the high-density coating (HD-1)

Results - X-ray diffraction (XRD)

X-ray diffraction (XRD) shows differences in orientation: LD-1 is vertically-oriented (i.e., columnar), LD-2 is weakly basally-oriented, and HD-1 is randomly oriented

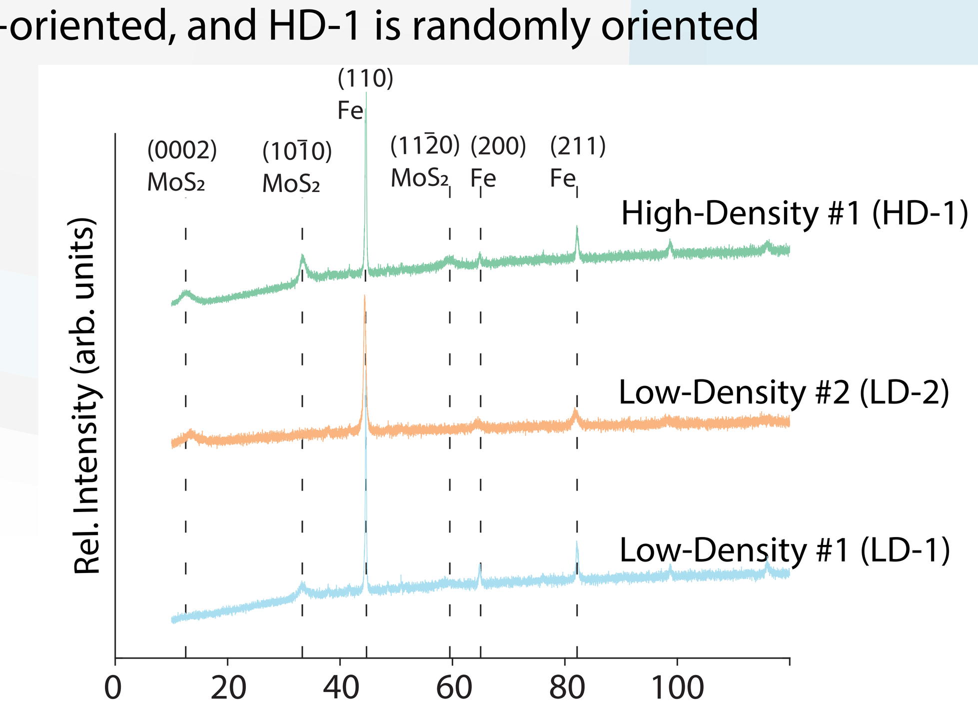

Figure 5: XRD of the low-density #1 (LD-1), low-density #2 (LD-2) and high-density (HD-1) coatings showing differences in orientation

Results - Density and Hardness

- Rutherford backscattering spectroscopy (RBS) can be used to quantify coating density
- Combined with hardness from nanoindentation, a relationship between hardness and density can be developed

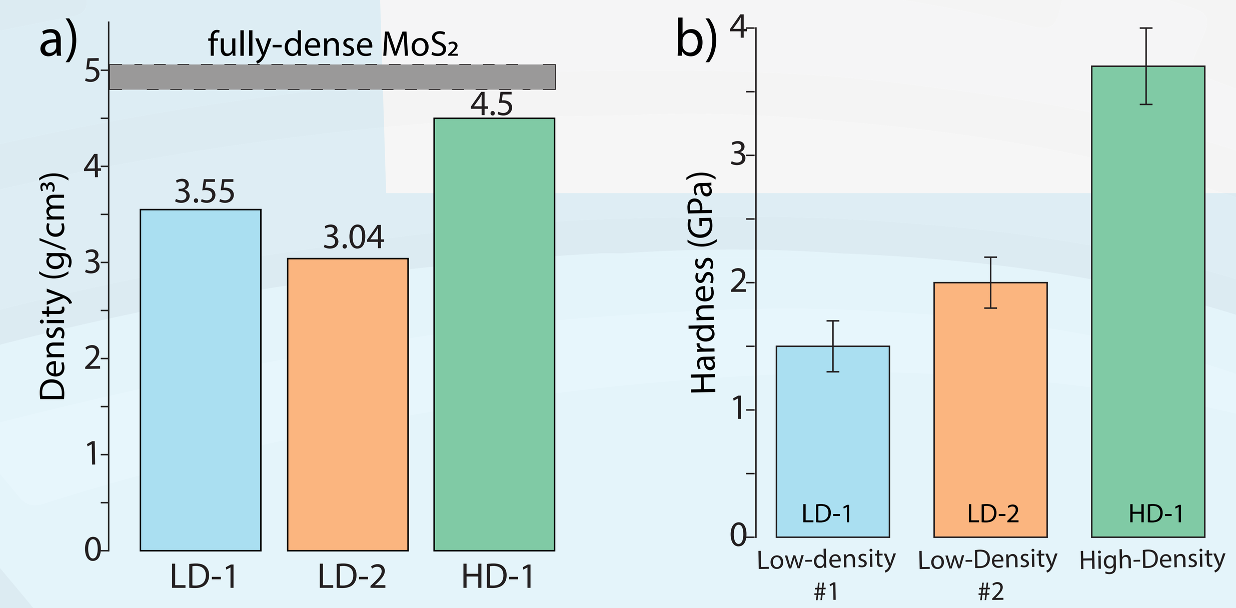

Figure 6: (A) Coating density measured via RBS for the low-density #1 (LD-1), low-density #2 (LD-2), and high-density coating batches. (B) Hardness of LD-1, LD-2 and HD-2 measured via nanoindentation showing higher hardness values for denser coating batches

Key Findings:

- Hardness is dependent on density - pure MoS_2 coatings have a ~2x higher hardness than porous coatings
- Hardness is dependent on coating orientation with columnar films having a lower measured hardness than basally-oriented films
- Hardness can be used as an indicator to distinguish coating batches that are not high quality (i.e., low-density or columnar)

Results - Accelerated Aging and Depth profiling using HS-LEIS

- Accelerated aging was performed on a low-density coating (LD-1) and a high-density (HD-1) coating using high-temperature O_2
- High-sensitivity low energy ion spectroscopy (HS-LEIS) depth profiles were perfomed to probe surface oxidation and penetration of oxygen into the coatings

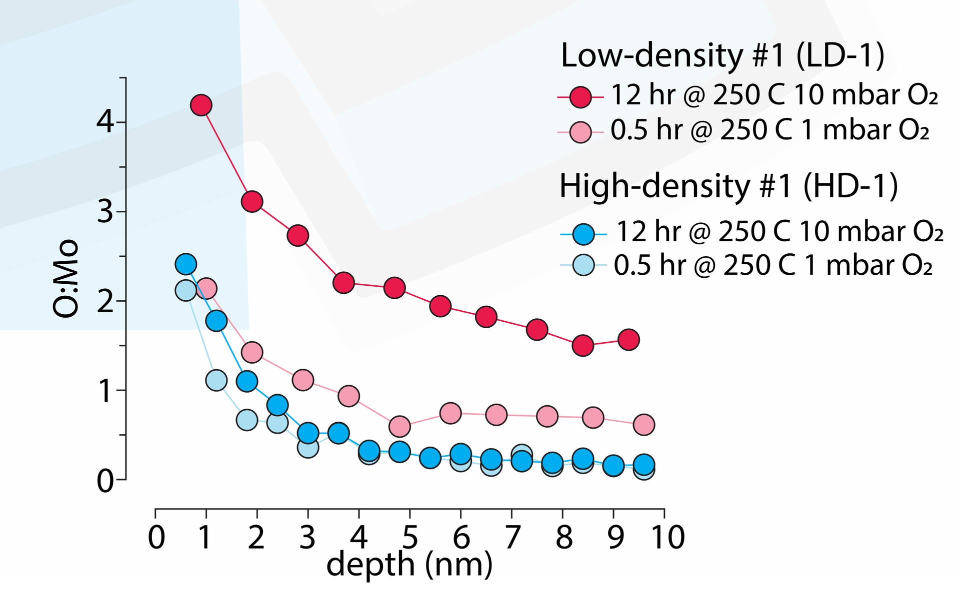

Figure 7: HS-LEIS depth profiles of the oxygen to molybdenum ratio (O:Mo) for the low-density #1 (LD-1) and high-density (HD-1) coatings after two high-temperature oxygen exposures of varying severity

Linking Density to Aging Resistance

- HS-LEIS depth profiles show that low-density, columnar coatings have more severe surface oxidation and allow oxygen to penetrate the coating through pathways formed by voids

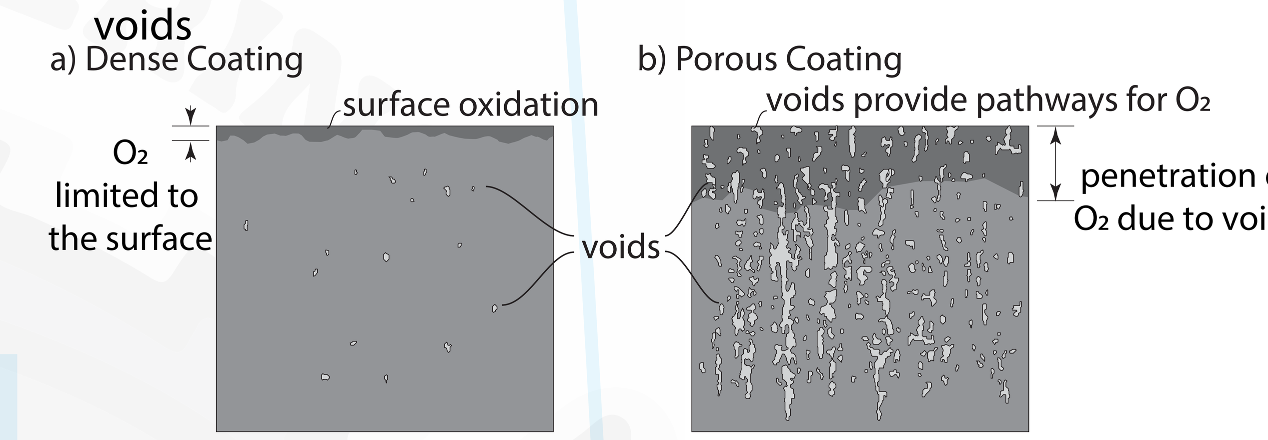

Figure 8: Mechanistic framework linking coating density and oxidation. Low-density columnar coatings are susceptible to aging as voids provide pathways for oxidative species into the coating and expose reactive edge sites that are easily oxidized.

We can reduce the effects of aging on low-density coatings by sliding before oxidation. Sliding results in a basally-oriented surface layer and compacts voids.

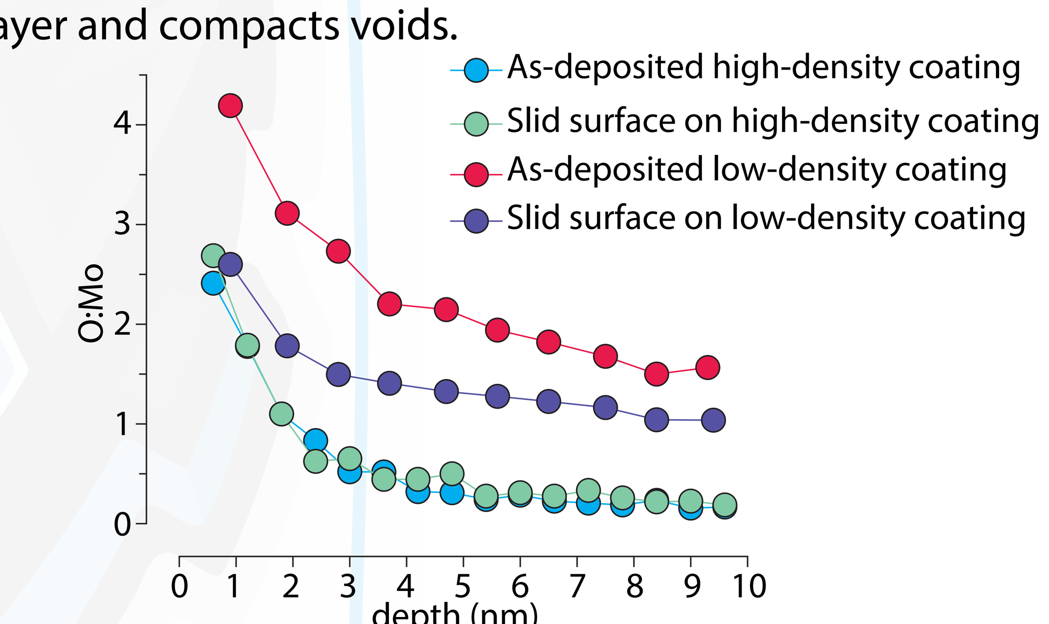

Figure 9: HS-LEIS depth profiles of the oxygen to molybdenum ratio (O:Mo) for the low-density #1 (LD-1) and high-density (HD-1) as-deposited coatings and slid regions after high-temperature oxygen exposures for 12 hours

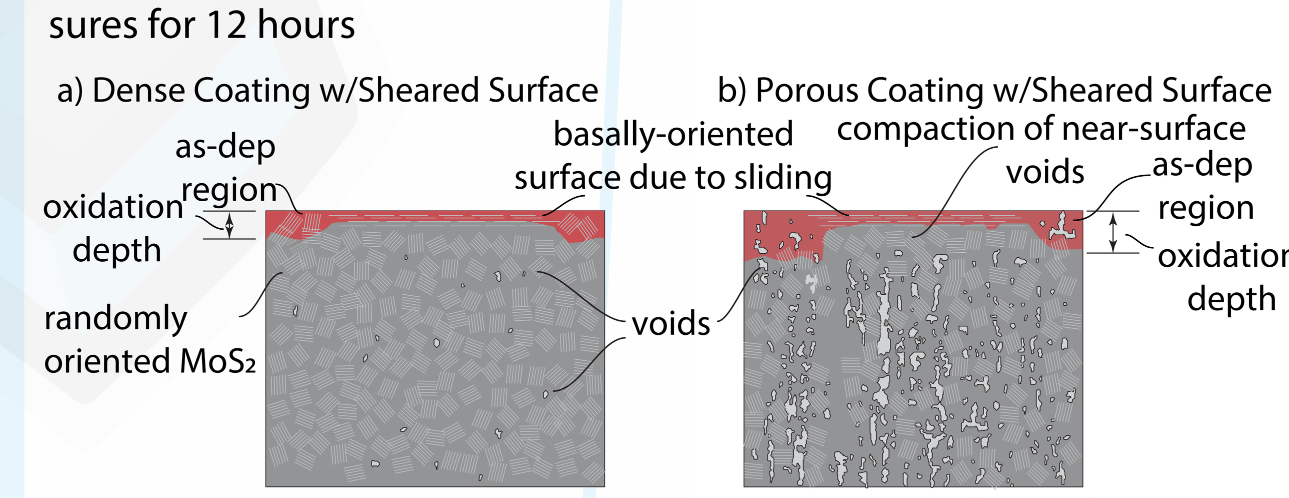

Figure 10: Mechanistic framework showing the benefits of sliding before oxidation for low-density coatings. Sliding orients the surface and elimates pathways into the coating improving aging resistance.

Questions to think about:

How can we determine coating batch "quality" without costly characterization?

1) What does "quality" mean for MoS_2 coatings?
- Resistant to oxidation from aging
- Low wear in inert environments
  - Will not fail when briefly tested in humid environments
- Low initial coefficient of friction
- Minimize cycles to achieve steady-state friction

2) Can we assign values to the above coating qualities with easily determined quantifyable metrics?

This material is based upon work supported by the National Science Foundation under Grant No. 2027029, 1826251, and NSF GRFP No. 1842163.This work was funded by the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525