Environmental Sensitivity and Aging of Composite Solid Lubricant Coatings

M.T Dugger¹, B.L. Nation¹, J.F. Curry¹, N. Argibay¹, M.E. Chandross¹, A. Hinkle¹ and A. Korenyi-Both²

¹Sandia National Laboratories, Albuquerque NM
²Tribologix Inc., Golden, CO
mtdugge@sandia.gov

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Outline

• Lubrication Mechanism and Aging
  ◦ shear accommodation in lamellar solids
  ◦ effects of aging on performance
  ◦ evidence of lattice orientation effects in pure MoS$_2$

• Mitigation of Environmental Effects

• Accelerated Aging of Select Lubricant Films
  ◦ experimental approach
  ◦ performance and surface chemistry
  ◦ implications

• Conclusions
Extreme Environments

Space:
- operate in vacuum (+atomic oxygen in low earth orbit)
- store months – years before use; generally non-serviceable
- operating temperatures from 50 – 300K, depending on location
- large investments of time and money

Precision Mechanisms:
- inert gas near $P_{atm}$, trace $O_2$, $H_2O$, outgassing species
- store for decades; non-serviceable
- operating temperatures 200 – 350K
- large investments of time and money
- consequences (political, societal) of failure are unacceptable
Costly Lubrication Failures

Failure - August 1981 - Sci platform seized due to migration of lubricant out of motor gear shaft.

Cost - Delayed use for 16 months. All future experiments ran at 0.083°/sec scan speed instead of 1°/sec. [1]

Failure - 2013-2014 - 2/4 reaction wheel seized due to uneven lubrication of mechanical bearings leading to galling.

Cost - Prolonged mission delays. Similar to Voyager 2, combination of heat and radiation pressure from the sun was used to redeposit lubricant [2]

Failure - April 1991 - Sticking of 3/18 antenna ribs in stowed position due to high friction between standoff pins and sockets.

Cost - Over 100 personnel involved in testing, simulation, analysis, consultation and review. [3]

Report - “The use of dry lubricant, specifically molybdenum disulfide, on a mechanism that is going to be operated in an atmosphere should be carefully evaluated.”

MoS₂ Lubrication Mechanism

*molybdenum disulfide*

\[ \mu = 0.02 - 0.06 \text{ (inert gas/vacuum)} \]

\[ \mu = 0.15 - 0.25 \text{ (humid air)} \]

- View along basal planes
- View down c-axis

The shear accommodation mechanism of these materials is inter-lamellar sliding.

**Run-In Processes:**

1) *Transfer Film Formation*

2) *Shear-induced re-orientation and coalescence*

*Sliding occurs between weakly bonded basal planes*
Model of MoS$_2$ Shear Strength

\[ S_0 = 55.3 \pm 3.1 \text{ MPa} \]

simple model prediction \[ S(T) = S_0 \left(1 - \exp\left(-\frac{\Delta E_i + \Delta E_r}{k_B T}\right)\right) \]

zero kelvin shear strength, \( S_0(T=0K) \)

- successfully rotate; slide incommensurately
- failure to rotate; slide commensurately

MoS\textsubscript{2} Environmental Effects

- Water vapor in the operating atmosphere increases friction coefficient
  - water absorption into structure
  - friction increase due to alteration of transfer film adhesion and dynamics

- Steady-state friction coefficient at 30°C of sputtered MoS\textsubscript{2}
  - friction increases with water vapor content
  - friction is far less sensitive to oxygen

\[ H. \text{Khare and D. Burris, Tribology Letters 53 (2014) p.329-336} \]

\( \text{O}_2 \) has little influence on dynamic friction, while \( \text{H}_2\text{O} \) in the atmosphere significantly increases friction
MoS₂ Aging Effects

- Surface oxidation can dramatically increase the initial friction coefficient.
- In this example, atomic oxygen reacted with top 100 nm of film.

Some aerospace mechanisms “live” in run-in:
- Dormant for months/decades, then operate once/few cycles.

Mitigation of Environmental Effects

Strategies
- dopants (Ni, Ti, Au, ...)
- compositing - multilayers, multiple phases (Sb$_2$O$_3$, Ni, AuPd, ...)
- ion bombardment during growth

Proposed Mechanisms
- densification
- increased hardness
- preferential orientation
- sacrificial oxidation of dopants
- passivation of MoS$_2$ edge sites
- crack arresting

How do dopants/composite phases influence interaction with the environment?
Experimental Setup

Run In
- coated disk
- run in patch 4x8 mm
- 13-8PH or 440C stainless steel disks
- run in at 530 MPa, 50 passes, overlapping areas

Accelerated Age
- 200°C, dry (DP < -60°C) air, 5 SCFH
- 12 hours

Friction (Stripe) Test
- 440C ball, 3.2 mm dia.
- 1 mm/s sliding speed
- Hertz contact pressures of 275, 530 and 785 MPa

Materials Investigated:
- N₂ (pure MoS₂ sprayed with N₂)
- DC (pure DC sputtered MoS₂)
- Ti (RF sputtered MoS₂, Ti-doped)
- Sb₂O₃/Au (RF sputtered Sb₂O₃+Au-doped MoS₂)
Run-In Area

- Perform XPS inside versus outside rubbed area
- Return to run-in area after aging for additional friction testing
Friction Measurements: “Stripe” Tests

<table>
<thead>
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<th>Load, mN</th>
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<td>484</td>
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<td>L3</td>
<td>1500</td>
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Permits performance assessment over a range of contact pressures
N$_2$ sprayed MoS$_2$ exhibits large crystals and basal orientation
Pure sputtered MoS$_2$ and MoS$_2$+Ti exhibit small crystals, some basal orientation
MoS$_2$+Sb$_2$O$_3$+Au is amorphous
Quantifying MoS$_2$ Oxidation

X-ray Photoelectron Spectroscopy (XPS) for surface chemical analysis
- survey scan for concentration of major elements present
- detailed scans of Mo3p, S2p spectral regions
- deconvolution of detailed scans to determine amount of Mo, S bonded to one another compared to oxidized species (MoO$_3$, sulfates, sulfites, etc.)
- surface sensitive – analyzing the top few nanometers

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![Graphs showing Mo 3p$^{3/2}$ and S 2p spectra for light and heavy oxidation of MoS$_2$.](image-url)
Steady-State Friction Response to Accelerated Aging

- the DC sputtered pure MoS$_2$ film failed at all but the lowest contact stress after aging
- N$_2$ sprayed and composite films fare well after aging
XPS of Aged Samples

As Deposited

200°C
12 hrs

Aged

Run In + Aged

Atomic Concentration

---

N2 DC

Sample

MoS2 MoO3

Atomic Concentration

---

N2 DC

Sample

MoS2 MoO3

Atomic Concentration

---

N2 DC

Sample

MoS2 MoO3
Pure MoS$_2$ films initially exhibit a majority of Mo present as sulfide.

DC MoS$_2$ exhibits significant oxidation as-deposited, but responds to aging similar to N$_2$ MoS$_2$ after run-in.

Doped films exhibit Mo primarily as sulfide before aging.

- Aging produces a majority of Mo-oxide.
- Previously run-in surfaces respond to aging similar to the as-deposited surfaces.
Run-In Behavior (First 10 Cycles)

- All as-deposited films except Ti-doped exhibit some degree of run-in relative to steady state, the Sb$_2$O$_3$+Au-doped film exhibits the largest change.
- All run-in and aged films except N$_2$ sprayed MoS$_2$ exhibit 15-100% increased initial friction compared to as-deposited behavior, with more variability.
Effect of Structure on Run-In

- run-in exposes S-terminated, oriented basal planes
- minimizes defects where oxidation initiates

- sputtering produces highly defective, small crystals
- doping densifies the films

Effects of Environment on Inter-Platelet Bonding

- Use reactive MD simulations to study chemical reactions of MoS$_2$ with environment
- Prepare system by allowing H$_2$O, O$_2$ or atomic O to diffuse into layers

Environmental species interrupt formation of larger flakes
- Hypothesize that dopants can similarly interrupt flake aggregation
Conclusions

- **Impingement MoS$_2$ coatings resist oxidation and changes in initial friction with aging**
  - deposition process results in basal planes oriented with the sliding direction
  - S-terminated basal planes present few reactive sites for interaction with environmental species

- **Pure sputtered MoS$_2$ becomes more resistant to oxidation after reorientation by sliding**
  - initially small crystals are formed during deposition
  - contact and shear reorients basal planes parallel to the sliding direction
  - the absence of dopants allows MoS$_2$ flakes to grow larger, behaving more like impingement coatings

- **Doped films resist aging effects on steady-state friction by sequestration of unreacted MoS$_2$**
  - disruption of crystal growth by dopants during deposition creates dense films
  - dopants also prevent aggregation of flakes during contact and shear
  - smaller crystallites on the run-in surface create many reactive sites for oxidation, but this is confined to the top few layers
Acknowledgments

- Mike Brumbach for XPS measurement of MoS$_2$ oxidation states
- Mark Rodriguez for XRD of coatings
- Morgan Jones and John Wellington-Johnson for tribology testing and coating aging

Backup
the DC sputtered pure MoS$_2$ film failed at all but the lowest contact stress after aging

N$_2$ sprayed and composite films fare well after aging
Future Work

- Include adsorption and oxidation effects in shear model for pure MoS$_2$
- Incorporate defects, dopants and composite phases in MD model for MoS$_2$ composites
- Use MoS$_2$ shear model to design environment- and aging-resistant PVD solid lubricant for electromechanical mechanisms
Friction vs Stress in Dry $N_2$

- Impingement pure MoS$_2$ exhibits steady-state friction $\leq 0.05$ at all stresses
- All doped MoS$_2$ composites exhibit lower friction coefficient than resin-bonded legacy coatings
  - several also exhibit lower friction than $N_2$ sprayed MoS$_2$ and DLC
XPS of Aged Samples

Pure MoS$_2$ films initially exhibit a majority of Mo present as sulfide.

DC MoS$_2$ exhibits significant oxidation as-deposited, but responds to aging similar to N$_2$ MoS$_2$ after run-in.

Doped films exhibit Mo primarily as sulfide before aging.
  - Aging produces a majority of Mo-oxide; previously run-in surfaces respond similar to the as-deposited surfaces.
Friction vs Stress in 50% RH Air

- All films exhibit increased friction compared to that in inert gas
  - the resin-bonded legacy film is the least impacted
- Several PVD coatings (MoS$_2$+Sb$_2$O$_3$+C) exhibit friction coefficient comparable to that of the legacy coatings
Legacy Solid Lubricants and Processes

Resin-bonded films
- blast surface with Al₂O₃
- clean, mask, spray, cure, burnish, clean
- few parts at a time
- high volatile organic solvent use; carcinogens
- 2.5 µm minimum thickness

N₂ Sprayed MoS₂
- clean, mask, spray, clean
- one to few parts at a time
- 150 nm maximum thickness

Harperized MoS₂
- clean, mask, tumble, clean
- batch process
- 150 nm maximum thickness
Friction Measurements: “Stripe” Tests

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each segment at a different contact force

L1  L2  L3  L2  L1

Test parameters:
- 440C ball, 3.2 mm diameter
- 1 mm/s sliding speed
- Controlled atmospheres:
  - dry N₂ (<10 ppm O₂, <50 ppm H₂O)
  - 50% RH air

Permits performance assessment over a range of contact pressures
Friction Coefficient Traces from “Stripe” Tests

**N₂ Sprayed MoS₂**

- 275 MPa
- 530 MPa
- 785 MPa

**MoS₂-Sb₂O₃-C Composite**

- Run-in
- Steady-state behavior

Friction coefficient decreases as stress increases, typical of solid lubricant behavior.

Consider steady-state performance at each stress.
The DC magnetron sputtered pure MoS₂ responds to aging similar to N₂ sprayed films after run-in.

Oxidation of the N₂ sprayed and doped-MoS₂ surfaces are minimally impacted by run-in prior to aging.
NEB Calculation of Energy Barriers

- Flakes of increasing size forced to translate/rotate and calculated required energies
- Energy barriers converge at larger flake sizes
- Commensurate sliding most energetically expensive route; incommensurate sliding $28\times$ less expensive
Converged Barriers & Analytical Model

The probability ($p_n$) and failure ($f_n$) to overcome a barrier:

$$p_n = A \exp \left( \frac{-\Delta E_n}{k_B T} \right)$$

$$f_n = 1 - p_n$$

The probability to slide and fail to slide (friction):

$$p_{\text{slide}} = p_r p_i + f_r p_c$$

$$f_{\text{slide}} = 1 - p_{\text{slide}} = 1 - \left( p_r p_i + f_r p_c \right)$$

- Model based on probability to overcome energy barriers to translation & rotation (Arrhenius)
- Expressed as inverse (1-exp) due to failure to thermally diffuse and slide under shear
Experimental Setup

Run In
- 13-8PH or 440C stainless steel disks
- Run in at 530 MPa, 50 passes, overlapping areas

Accelerated Age
- 200°C, dry (DP < -60°C) air, 5 SCFH
- 12 hours

Friction (Stripe Test)
- 440C ball, 3.2 mm dia.
- 1 mm/s sliding speed
- Hertz contact pressures of 275, 530 and 785 MPa

Samples were run-in prior to aging to examine the effects of accelerated aging on the structurally modified lubricant surfaces.
Film Compositions Investigated

- N$_2$ Sprayed MoS$_2$
- DC Magnetron Sputtered MoS$_2$ (Tribologix)
- RF Magnetron Sputtered MoS$_2$ + Sb$_2$O$_3$ + Au (Tribologix)
- RF Magnetron Sputtered MoS$_2$ + Ti by (Teer)

### Pure MoS$_2$

### Doped MoS$_2$

Red = Ti
Green = Mo-S
Blue = Sb-O
Yellow = Fe, Cr, Si, O

800 nm by 1600 nm field of view

X-ray Energy [kV]
Highly Ordered MoS$_2$ Coatings

Nitrogen Spray Deposited MoS$_2$

- Deliver MoS$_2$ powder to surface in dry N$_2$ gas
- High kinetic energy imparted shears MoS$_2$ onto surface to produce a higher orientation of basal planes.
- Similar to burnishing, large continuous crystallites will form, reducing presence of surface defects

deposition process

micro-abrasion spray nozzle

Nitrogen Spray & MoS$_2$ Powder

steel substrate
Doping in MoS$_2$ Films Increases Density

- Tailored film structures improve performance in a range of atmospheres
- Wear rates are improved by densification and inclusion of hard, load-supporting phases


Run-In Behavior

- $\text{N}_2$ sprayed MoS$_2$ and MoS$_2$+Ti exhibit no run-in during as-deposited tests.

- Aging increases initial friction coefficient in all except $\text{N}_2$ sprayed and MoS$_2$+Sb$_2$O$_3$+Au.