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Aging Effects on the Transient Frictional Behavior of MoS_2-Based Solid Lubricants for Use in Extreme Environments

Chemistry and Physics of Tribology

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NNSA National Nuclear Security Administration

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Outline

Background

Motivation

- Extreme Environments
- Long Duration Storage

Solid Lubricant Materials of Interest

Experimental Plan

- Characterization and Environmental Exposure

Tribological Performance and Surface Composition

Aging-Resistant Structures

Conclusions

Background

In the early 1990’s NASA provided an opportunity to investigate interaction of materials with atomic oxygen

- an existing project was maturing sputtered MoS_2 coatings for solid lubrication of satellite gimbal bearings
- locations for project materials were made available on shuttle mission EOIM-3 (Effects of Oxygen Interaction with Materials)

Ultimately 5 sputtered solid lubricant coatings were flown on EOIM-3 and exposed to atomic oxygen

- the project ended before the shuttle flight was completed
- NASA supported post-flight analysis of 3 coatings and compilation of data in a JPL report
- a subset of the data was published in a Klewer book chapter

25 years later, revisit all materials and publish complete data in the open literature

MoS_2 Characteristics

Sputtered MoS_2 films have several desirable properties

- Ultra-low friction coefficient (below 0.04) in vacuum
- No migration or outgassing
- Shear stress is virtually independent of temperature and pressure
- Eliminates need for lubricant containment and delivery systems

However…oxidation increases friction coefficient and wear rate

- MoS_2 oxidizes after exposure to water vapor or atomic oxygen (AO)
- Low earth orbit (LEO) environment is primarily atomic oxygen
- Film densification increases resistance to reactive species

Objectives

- Investigate effects of film morphology on reaction with atomic oxygen
- Obtain flight history for sputtered MoS_2 films
- Determine validity of laboratory atomic oxygen simulation techniques

Atomic Oxygen Effects on MoS_2

J. Martin, J. Cross and L. Pope, *MRS Symp. Proc.* 140 (1989) 271-276

- dissociative chemisorption bypassed (unlike oxidation by water vapor)
- oxide thickness independent of crystallographic orientation
- primarily MoO_3, with small amount of MoO_2

J. Cross, J. Martin, L. Pope and S. Koontz, *Surf. Coat. Technol.* 42 (1990) 41-48

- SO_2 evolved during exposure
- no translational activation energy barrier (thermal reacts as readily as 1.5 eV/atom)

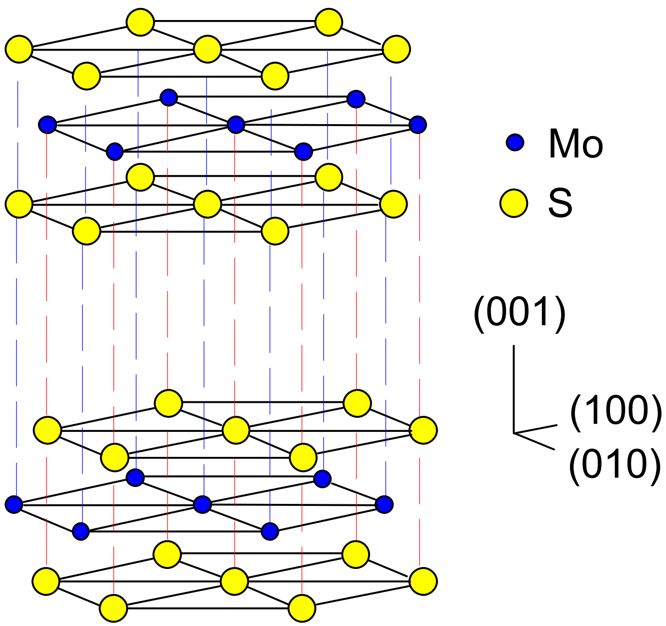
M. Arita, Y. Yasuda, K. Kishi and N. Ohmae, *Trib. Trans.* 35 (1992) 374-380

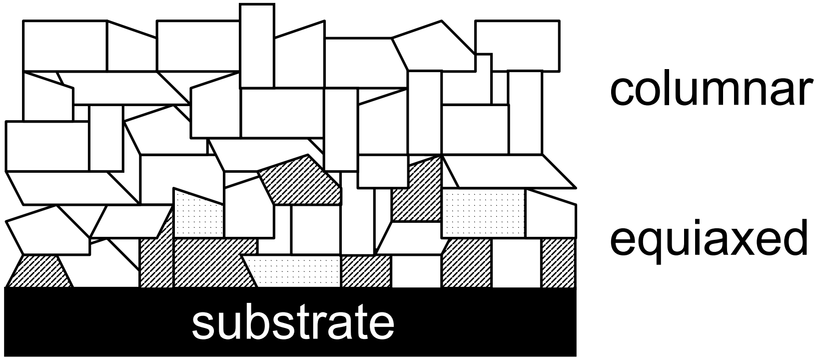
- 20-30% increase in initial friction
- depth profile suggests ~6 nm oxide thickness

F. Kustas, SBIR-92-1 Phase 1 Final Report, Contract NAS8-39800, CERL, Fort Collins, CO (1993)

- continuous exposure during wear increased wear rate

MoS_2 Sputter Deposition Growth Morphologies





Low Power, High Pressure

Structural Variants of MoS_2

Columnar Reference

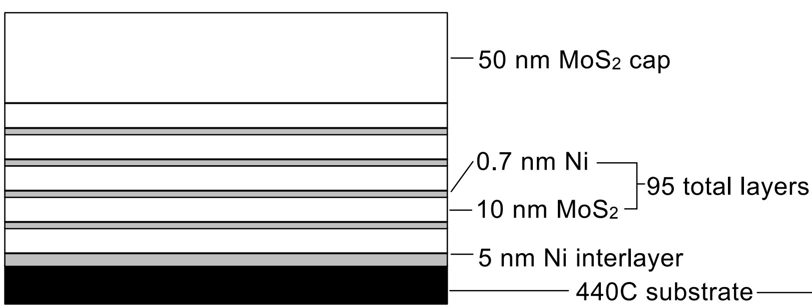
- DC diode sputtering process at low power, high gas pressure
- 1 μm total film thickness
- Designated AT

Cosputtered

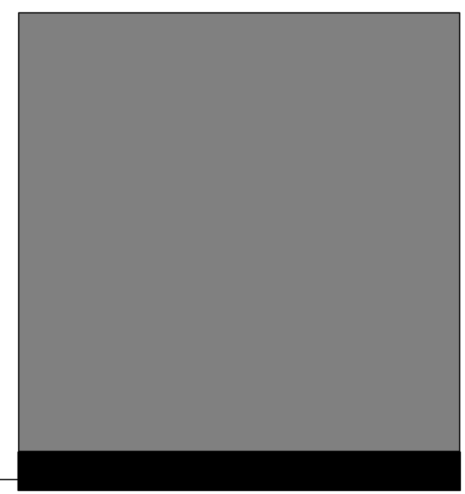
- DC triode sputtering process
- Composite target, MoS_2 + 20% Sb_2O_3
- 2 mm total film thickness
- Designated MoS_2+ SbO_x

Multilayer

- RF magnetron sputtering process
- 1 mm total film thickness
- Designated Ni/MoS_2



Ni/MoS2 multilayer

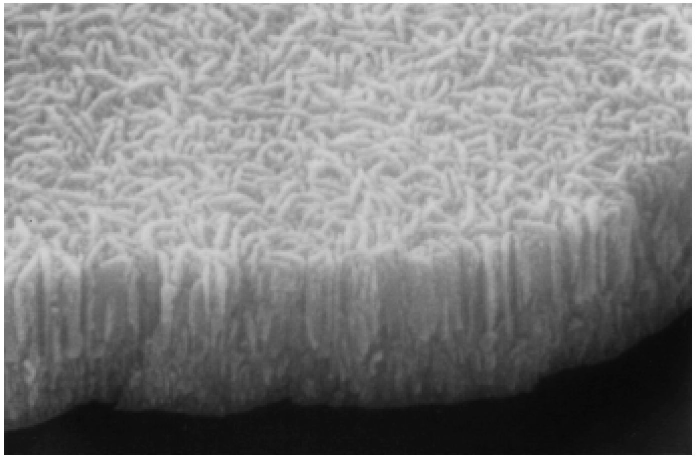


MoS2 + SbOx cosputter

Modification of Sputtered MoS_2 Film Growth Morphology

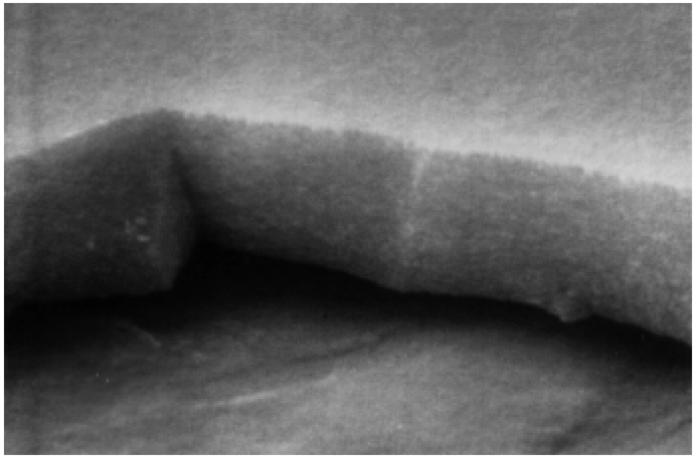
- Incoming atoms add to edges of basal planes
- Passivation of edge sites suppresses columnar morphology
- Equiaxed films have reduced porosity between columns

columnar



1 µm

equiaxed



Techniques to Assess Performance and Oxidative Degradation

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Films sputtered on 440C disks (25 mm diameter, 1 mm thick)

Pre-flight characterization

- Pin-on-disk friction test against 440C pin, 1 GPa peak Hertzian stress, in air (35-55% humidity) and vacuum (< 10^{-6} Pa), 1000 cycles
- In situ Auger Electron Spectroscopy (AES), worn and unworn regions

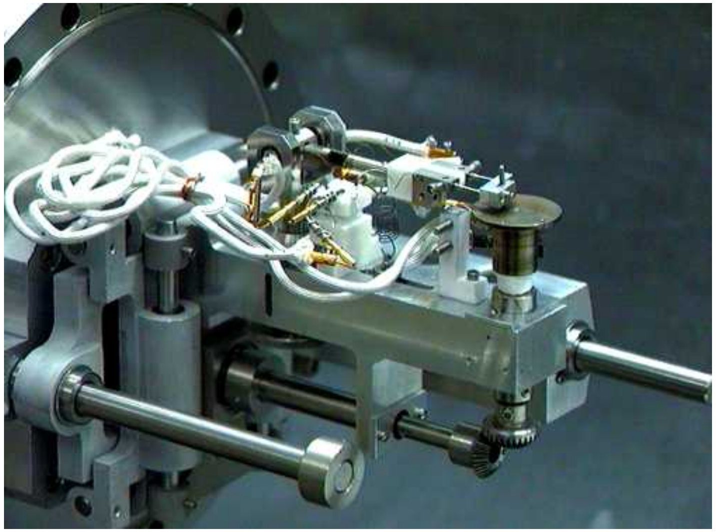
Environmental exposure

- Atomic oxygen in LEO aboard the United States space shuttle
  - select samples had a portion of their surface shielded from atomic oxygen
- Laboratory simulation of the LEO atomic oxygen environment
- Desiccated storage

Post-flight analysis

In Situ Tribology and Surface Analysis System

Scanning Auger Microprobe



Pin-on-Disk Friction/Wear Tester

Sliding experiments to 10^{-9} Torr

Analysis of worn surfaces:

- electron microscopy (40 nm spot size)
- Auger Electron Spectroscopy (100 nm spot size)

Atomic oxygen exposure was performed in low earth orbit and in the laboratory

Aboard the U.S. space shuttle Atlantis, in a 230 km orbit

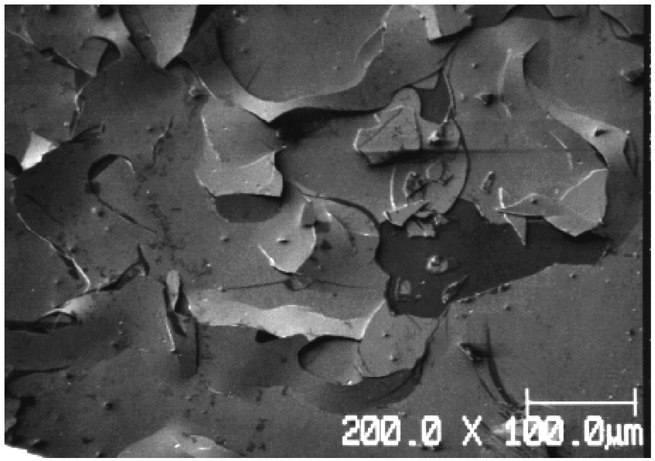
- orbital velocity of 8 km/s creates hyperthermal (~5eV/atom) impacts
- fluence 2.2 to 2.5x10^{20} O-atoms/cm^2, created by UV photon-induced dissociation of O_2 in the upper atmosphere
- 42.25 hours duration
- ~22 equivalent solar hours UV exposure
- tray cycled between 5 and 20^{o}C, at orbital frequency

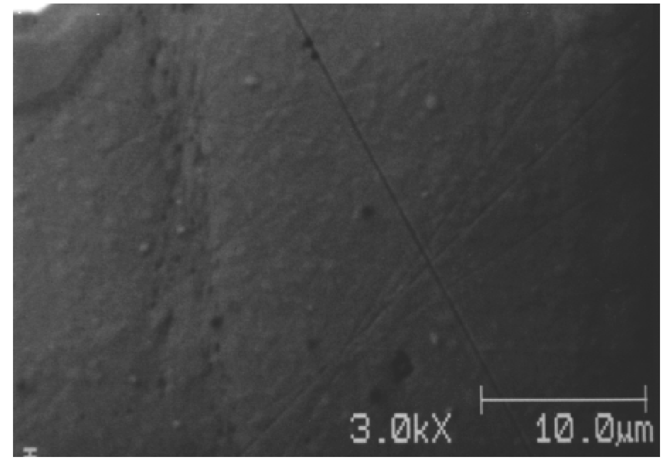
At a laboratory atomic oxygen simulation facility

- Physical Sciences, Inc. (Andover, MA)
- pulsed molecular beam valve coupled to a 14 J/pulse CO_2 laser
- fluence of 1.97x10^{20} O-atoms/cm^2 (mean velocity of 7.8 km/s)
- 25.28 hours duration
- negligible UV radiance
- isothermal, near room temperature

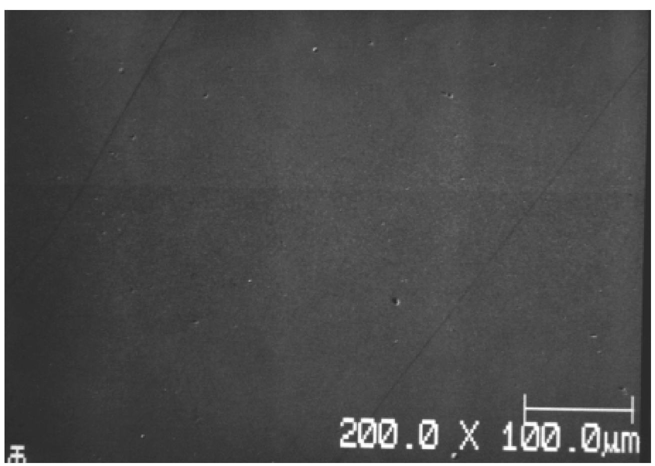
Ni/MoS_2 films exhibited delamination after space flight

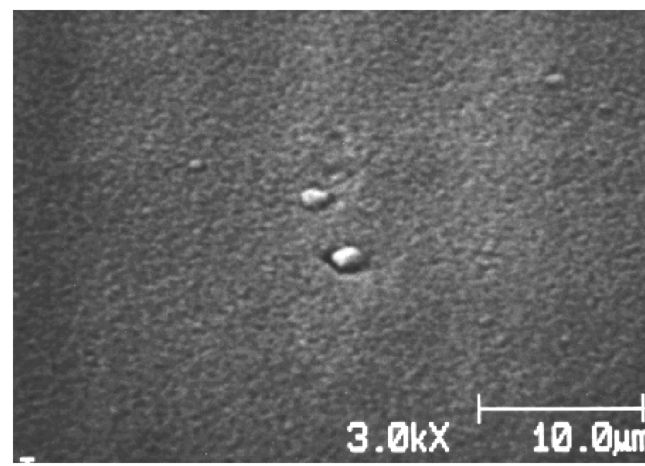
Ni/MoS_2



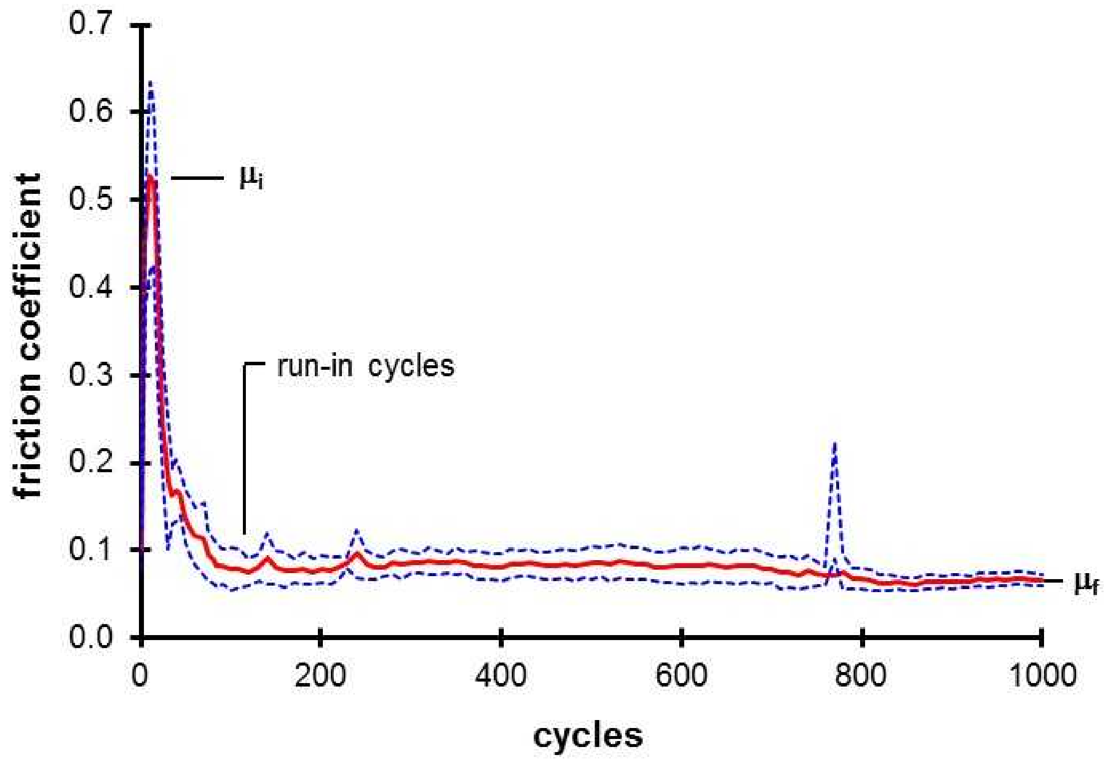


MoS_2 + SbO_x





Initial run-in period on oxidized specimens

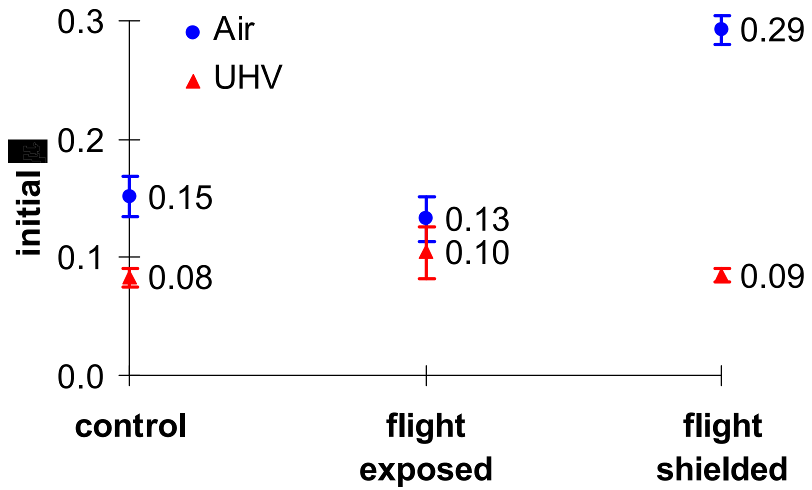


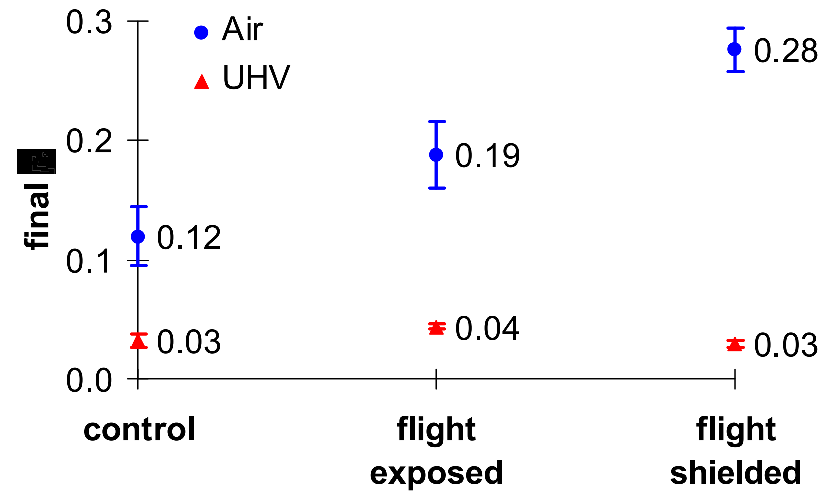
- Startup friction coefficient is >5x steady state value (air example)
- Mechanisms susceptible to film oxidation before use must accommodate higher startup energy losses than in normal operation

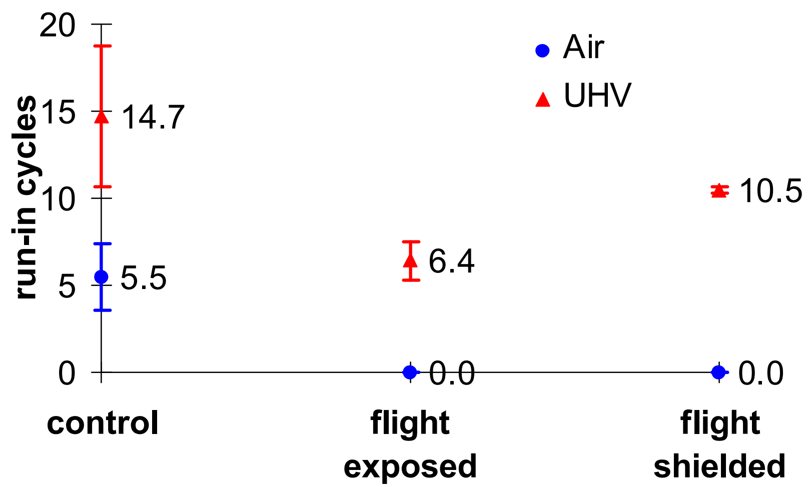
Friction and Wear of Columnar Reference (AT) Films

A portion of the sample surface was shielded from direct atomic oxygen impact

High Start-up Friction was Observed on Columnar Films

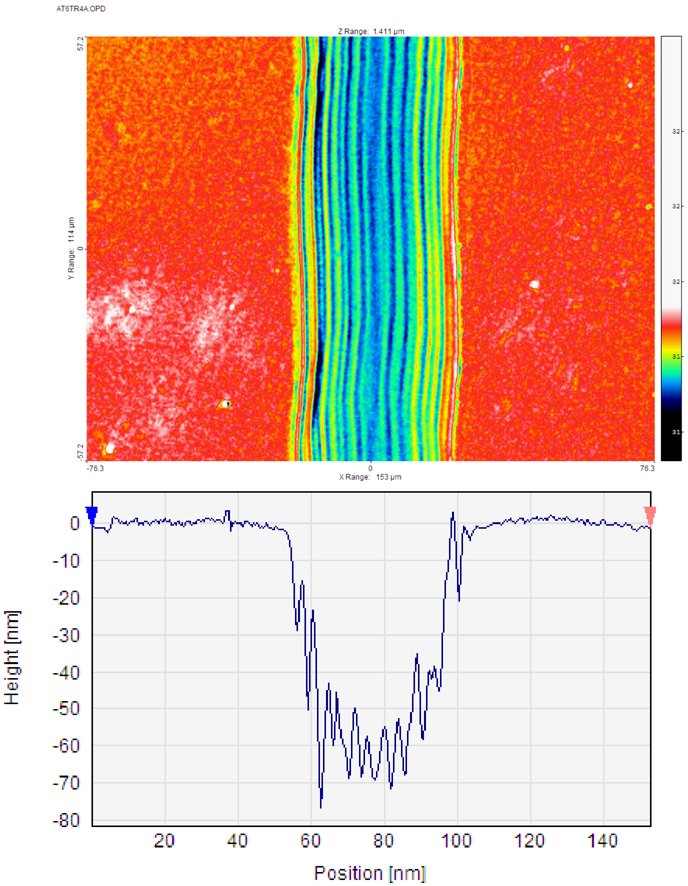


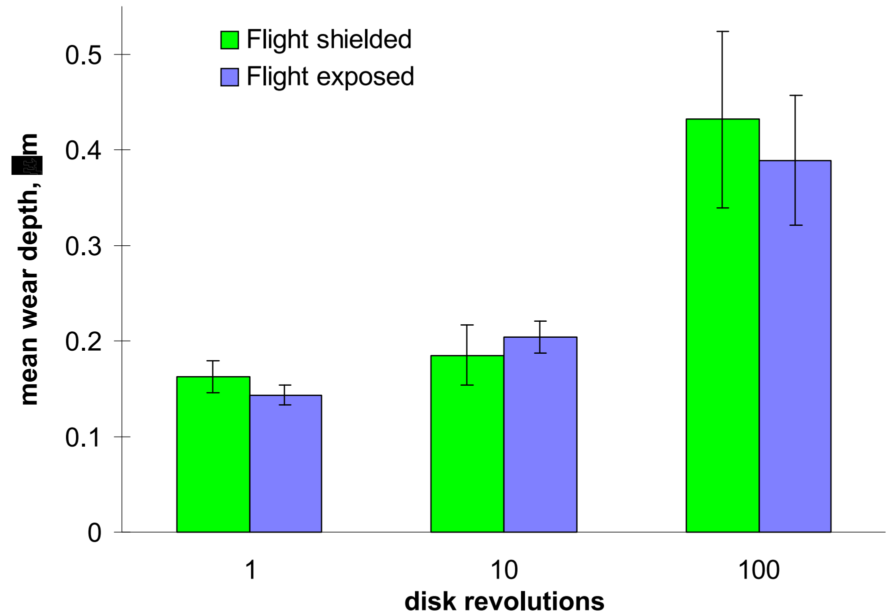




- starting friction higher than steady-state due to oxidation
- atomic oxygen did not increase steady-state friction in vacuum
- atomic oxygen exposure did not increase run-in time

Wear rate for Flight Shielded and RAM AO Exposed Surfaces





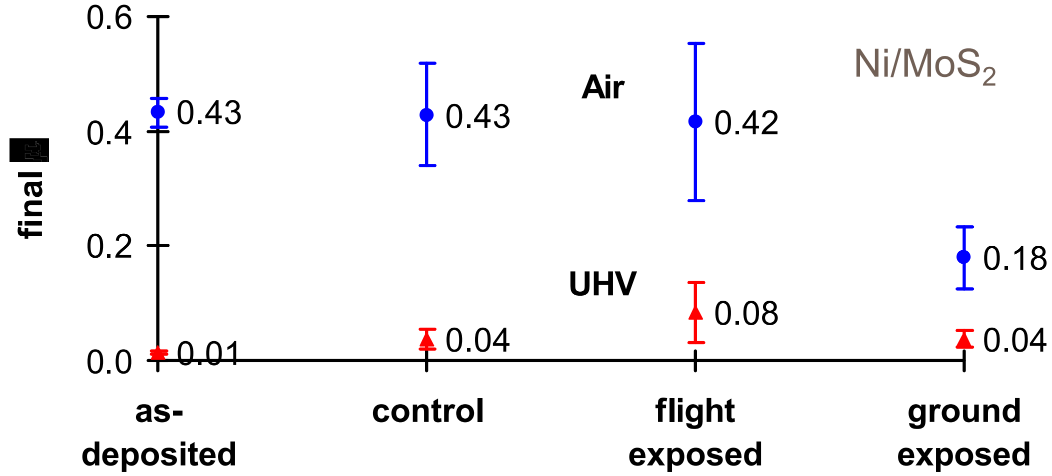
- Hyperthermal atomic oxygen did not increase the initial wear rate of columnar coatings over that due to non-RAM AO flight exposure

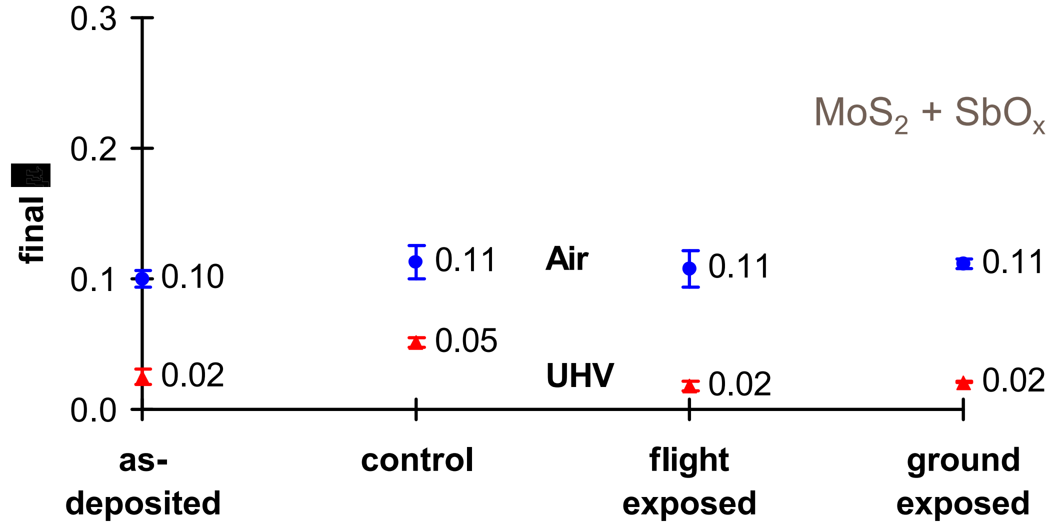
Friction of Densified Films

Identical samples were exposed to atomic oxygen in a laboratory facility

Steady-state Friction for Dense MoS_2 Films

- High friction of Ni/MoS_2 films in air is due to partial film delamination
- $MoS_2 + SbO_x$ films also produce consistently low friction in air
- Friction coefficient in vacuum is similar to that for AT films





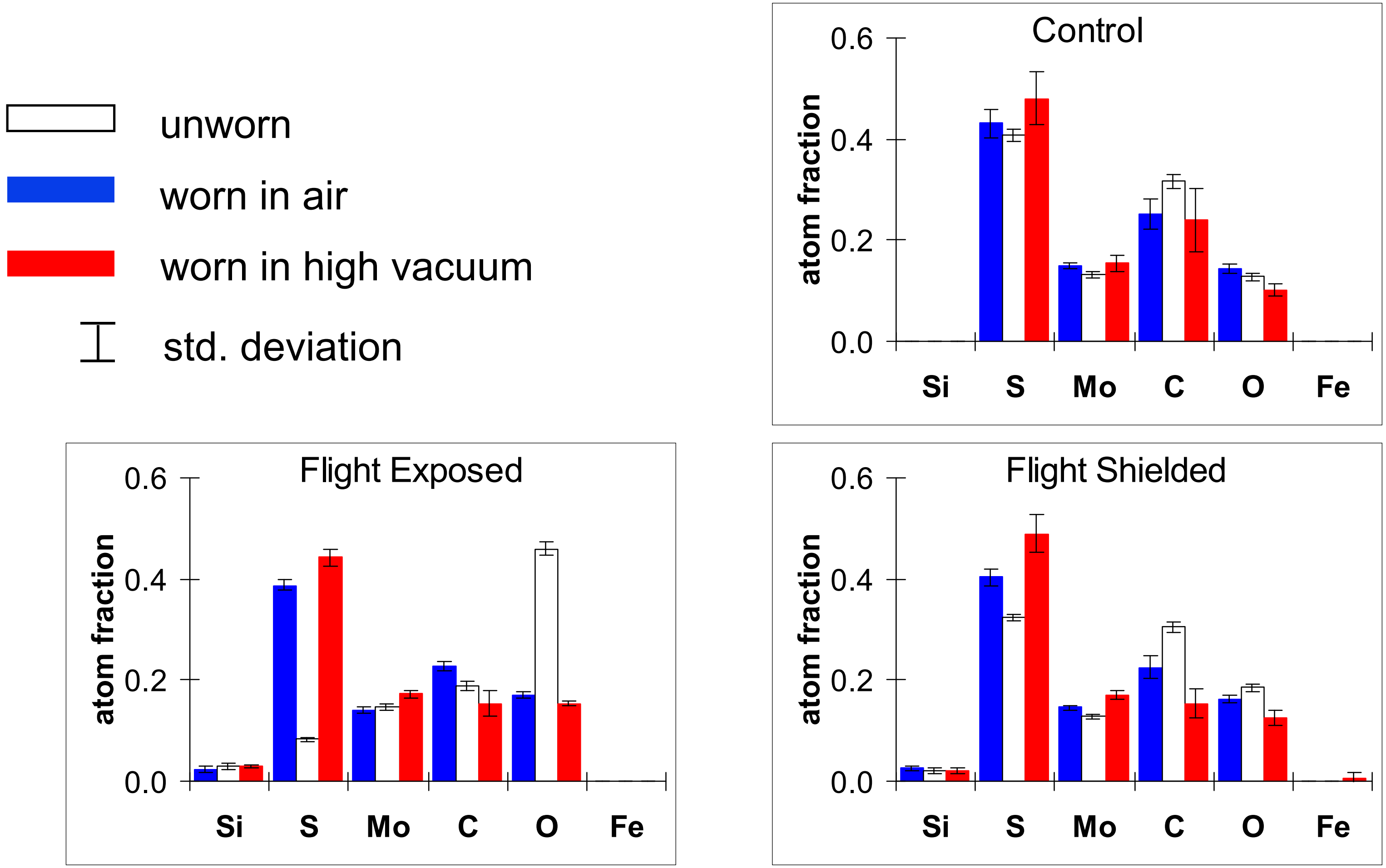
Friction and Wear Summary

- Initial high friction on oxidized surfaces returns to pre-exposure levels when reacted layer is worn through
- The number of cycles required to achieve a stable friction coefficient do not increase after exposure to atomic oxygen
  - high steady-state friction observed in air masks surface oxidation effects
- The steady-state friction of AT MoS_2 films in vacuum is insensitive to atomic oxygen exposure
- Similar topographical changes with sliding were observed for exposed and control surfaces of AT films
  - film compaction under load contributes to observed topography changes
- Ni/MoS_2 partially delaminated due to flight-exposure
  - inadequate or non-uniform adhesion of coating
  - despite delamination, friction in vacuum was similar to pre-exposure levels
- Friction of MoS_2 + SbO_x is insensitive to atomic oxygen exposure

Surface Composition Analysis

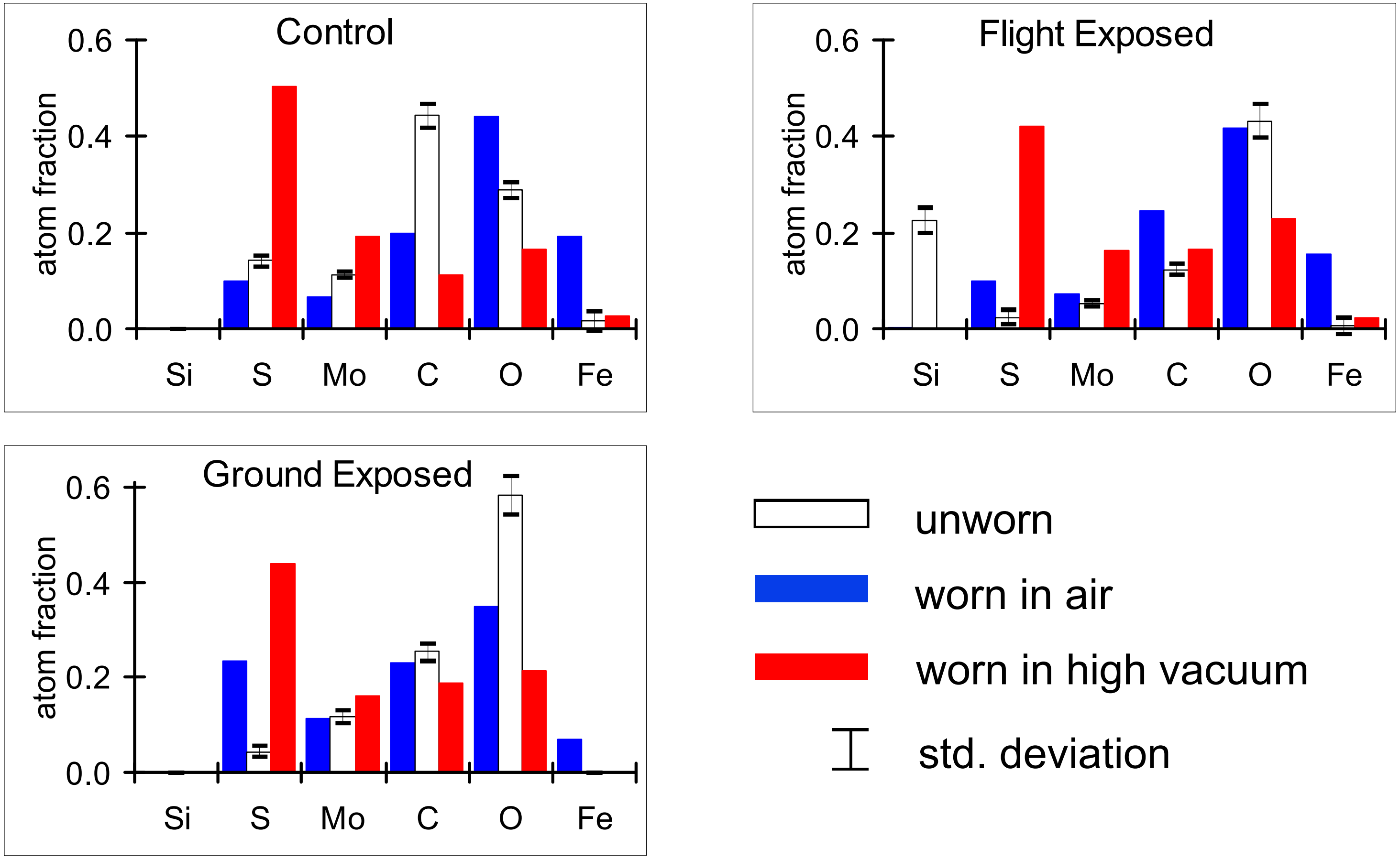
Columnar Reference (AT) and Dense Films

Composition of Columnar MoS_2 Surfaces



- Atomic oxygen exposure results in the loss of C and S from the unworn surface, and increase in oxygen content
- Sliding restores surface composition to pre-exposure levels

Composition of Dense Ni/MoS_2 Surfaces



- Flight exposure resulted in the loss of C and S, and the contamination of the surface with Si
- Si contamination from ablation of a thermal protection blanket

Estimated Depth of Reacted Layers on Columnar Films

AT films:

Specimen	S_{LVV}/Mo_{MNN}	S_{KLL}/Mo_{LMM}	O_{KLL}/Mo_{MNN}
	(152eV/186eV)	(2117eV/2044eV)	(510eV/186eV)
Flight exposed	2.25	0.94	3.89
Flight shielded	7.27	1.29	1.81

3x S reduction
95% of Auger electrons from top 2.6 nm

6% S reduction
95% of Auger electrons from top 8.8 nm

- Most of the sulfur depletion occurs in the top few nm of the surface

Lab exposed samples exhibit greater sulfur depletion than those exposed in orbit

Specimen	S_{LVV}/Mo_{MNN}	S_{KLL}/Mo_{LMM}	O_{KLL}/Mo_{MNN}
Ni/MoS_2	(152eV/186eV)	(2117eV/2044eV)	(510eV/186eV)
Control	3.20	1.03	3.98
LEO exposed	2.34	1.11	18.04
Lab exposed	1.38	0.73	5.61
MoS_2+SbO_x			
Control	8.32	1.27	4.80
LEO exposed	2.94	0.70	10.18
Lab exposed	1.58	0.81	9.19

The majority of sulfur depletion occurred within 10 nm of the surface

Surface Composition Summary

- Atomic oxygen reacts with near-surface species
  - forms volatile products with C, S
  - forms molybdenum oxide
- Wear returns surface S, Mo, O concentration to pre-exposure levels
- Silicon contamination was found on flight samples
  - other samples on EOIM-3 confirm source; erosion of insulating blanket
- Reacted layer thickness for AT, Ni/MoS_2 and MoS_2 + SbO_x are similar to literature reports for lab-exposed sputtered nanocrystalline and single crystal MoS_2
- SiO_2 from flight contamination reduced reaction layer thickness on LEO-exposed films

Conclusions

Failure of as-deposited Ni/MoS_2 in air indicates poor adhesion

- proper surface preparation is critical to ensure optimum performance from all sputtered MoS_2 lubricants

Adherent MoS_2 films retain their excellent tribological performance after atomic oxygen exposure

- morphological changes and oxidation in ambient air are significant contributors to “run-in” friction transients

Laboratory simulation of LEO atomic oxygen is a valid tool to qualify MoS_2 films for space service

A thin cover of SiO_2 could protect sputtered MoS_2 on exposed surfaces until ready for use

- design for higher starting friction until protective layer is displaced

Acknowledgments

- Lt. Col. Michael Obal (USAF) provided space flight opportunity
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- John Gregory (U. Alabama, Huntsville) made space available for samples on GAS (Get Away Special) can
- Useful conversations with Larry Pope (Sandia) and John Cross (Los Alamos).

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