

Degradation of Sputter-Deposited Nanocomposite MoS₂ Coatings for NIRCам during Storage in Air

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Abstract

The Focus and Alignment Mechanism (FAM) in NIRCам on the James Webb Space Telescope will be lubricated with nanocomposite sputter-deposited MoS₂ coatings. To respond to concerns regarding how exposure to humid air during storage would affect performance, a study was conducted involving real-time (i.e., unaccelerated) storage of coatings in air at 59% RH for over two years. Pin-on-disk friction testing showed that the endurance of the coatings dropped significantly during storage, but still provided acceptable margin for FAM. The endurance results correlated well with X-ray Photoelectron Spectroscopy results that measured the conversion of MoS₂ to nonlubricating MoO₃ during storage.

NIRCам Background

Nanocomposite sputter-deposited MoS₂ coatings are being used to lubricate sliding surfaces within the Focus and Alignment Mechanism (FAM) in the Near Infrared Camera (NIRCам); NASA chose NIRCам as one of four science instruments for the James Webb Space Telescope (JWST) (See Figure 1).¹ The three FAMs are linear actuators required to provide micron level positioning in tip, tilt and piston to the Pickoff Mirror that reflects the starlight into the rest of the NIRCам instrument. The FAM, along with the other NIRCам mechanisms such as the filter wheel assembly and pupil imaging assembly, are required to operate at approximately 37K for near infrared imaging during the 5-year JWST mission.²

The FAM consists of a fine pitch lead screw driven by 3-phase stepper motor through a high-ratio Harmonic Drive. It was required to pass a cryogenic 2X life test of 200,000 revolutions with repeatable position accuracy of less than 4 microns and with less than a 30% increase in threshold motor current. These demanding requirements and the need to operate at cryogenic temperatures put a high premium on selecting durable solid lubricant films. Sputter-deposited nanocomposite MoS₂-based coatings manufactured by Hohman Plating, Inc. were chosen for this application.

Because of the high precision nature of the FAM, the plan was to store the flight article in either a vacuum or a dry nitrogen purged environment during ground processing after delivery. This represented a conservative position due to the known sensitivity of the MoS₂ lubricant to humidity. However, providing such an environment proved to be impractical after integration with the next higher assembly, where it will be stored in air with 30 to 60% RH. Although non-reversible degradation of MoS₂ in the coatings to oxides is expected in poorly controlled storage environments, the specific amount of degradation over long periods of time has not been quantified.

Sputter-deposited MoS₂-based coatings are increasingly being used in spacecraft applications where solid lubricant formulations based on MoS₂ powders are precluded.³ Sputter-deposited coatings differ from such coatings in that they are thin (i.e., ~0.5–1 μm thick), have smaller crystallite sizes, higher crystalline defect levels, and do not use bonding agents. In their pure form, sputtered coatings exhibit significant sensitivity to oxidation in humid atmospheres. However, improvements in wear life have been achieved by co-sputtering MoS₂ with various species⁴⁻⁷ to form nanocomposites (as are used in the FAM), or forming multilayer coatings by alternating deposition of a metal with MoS₂.⁸ These mixed coatings should exhibit

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better resistance to oxidation than conventional sputter-deposited coatings, because the metals increase the density of the coatings, and also "seal" the reactive edges of the MoS₂ crystallites.^{8,9} However, quantitative data on the extent of oxidation and its consequent effect on performance is lacking.

The present study was initiated to address the risk of the FAM not being able to perform as required over its mission cycle life due to potential exposure to relative humidity levels up to 60% for extended periods of time. The study was conducted in real-time. We did not accelerate by increasing the temperature or humidity because that would give non-quantitative results that could not be readily applied to real systems. We investigated the effects of storing three types of sputter-deposited MoS₂-based coatings in air at 59% RH, all manufactured by Hohman Plating, Inc.: Ni-MoS₂, Au-Sb₂O₃-MoS₂, and Sb₂O₃-MoS₂. Hohman Plating supplies many of the spacecraft contractors in the U.S., including the coatings for the FAM: the Sb₂O₃-MoS₂ coating was chosen for the FAM, while the other two coating versions were tested for comparison purposes. Most of the FAM operation (both ground and on-orbit) will occur in inert environments (i.e., N₂ or vacuum); a relatively small amount of testing will occur in air. The testing was conducted in an inert environment (gaseous N₂) at exceptionally low humidity levels (<0.08% RH) to model these conditions. Although the absolute endurance values may vary slightly from that obtained in vacuum, we are most interested in measuring the relative amount of endurance degradation, which should be valid while testing in N₂.

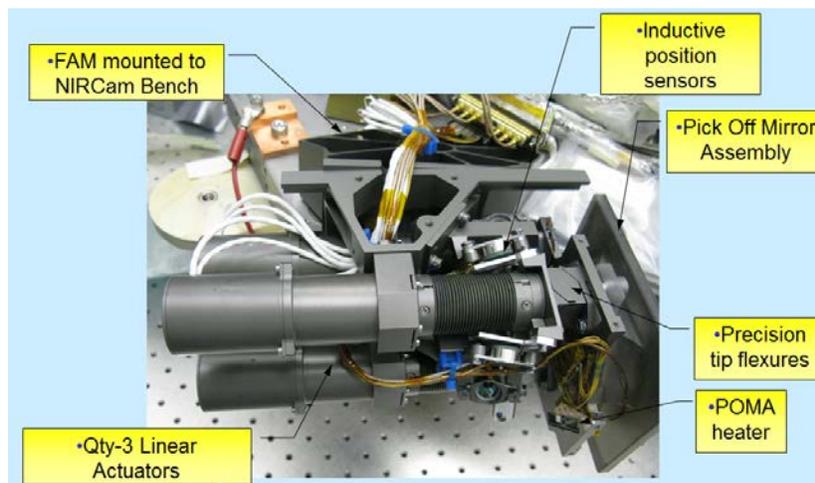


Figure 1. The Focus and Alignment Mechanism (FAM) provides tip, tilt and piston for NIRCams Pick Off Mirror (POM)

Previous Studies into MoS₂ Aging and Oxidation

This section reviews previous work concerning oxidation of MoS₂ solid lubricants due to humid air exposure. MoS₂ can oxidize during exposure to water vapor alone, to oxygen alone, and to water and oxygen together. In general, at ambient storage temperatures, appreciable oxidation is unlikely with water or oxygen alone. For pure oxygen reacting with MoS₂, oxidation only occurs at temperatures >300°C.¹⁰ The reaction of pure water reacting with MoS₂ has been shown to proceed for temperatures above 780°C,¹¹ and would probably proceed negligibly at room temperature. However, wear of the films while they are under a partial pressure of H₂O can accelerate the reaction process. One study showed that H₂S was produced when rubbing supported MoS₂ films under an atmosphere containing dry nitrogen (N₂) and H₂O gases at ambient temperature.¹² As such, either elevated temperature or mechanical wear is required to oxidize MoS₂ in a humid atmosphere without oxygen present.

Oxidation of MoS₂ at ambient temperature is more likely when both water and oxygen are present. In most oxidation scenarios related to storage, both H₂O and O₂ are present to some degree. There are two reactions that have been proposed to occur:



In one study, H₂S was detected during wear tests of dry MoS₂ powders in a humid atmosphere.¹³ In another study, no detectable sulfates at the surface region of sputter-deposited MoS₂ coatings were found after considerable oxidation of the surface in humid air.¹⁴ The observation of H₂S production and the lack of sulfates in humid atmospheres indicate that Eq. (1) was active in these cases.

In another study, oxidation in a humid atmosphere was shown to produce sulfate ion and MoO₃ in an approximately 2:1 ratio, and acid was detected after washing the reaction products in water.¹⁵ This suggests that Eq. (2) was occurring. However, no analysis of evolved gases was conducted, so that Eq. (1) might also have been operative, with some production of H₂S gas.

The presence of H₂SO₄ is of concern because it can corrode the surfaces of metals such as aluminum and steel. In fact, the production of the acid H₂SO₄ has caused the establishment of pH limits of aqueous extracts of MoS₂ powders in several specifications.¹⁶

The presence of H₂O appears to accelerate the oxidation of MoS₂ in air. The study in Ref. 15 revealed that the rate of oxidation of MoS₂ (as measured by the rate of MoO₃ production) was two to three times higher in an air atmosphere that was saturated with H₂O compared to a dry air atmosphere. (This experiment was conducted at temperatures of 85°C to 100°C at 1 atm pressure, so that negligible condensation of the H₂O from the gas phase would be expected.)

Increased humidity has also been shown to degrade tribological properties. Ref. 14 demonstrated decreasing wear life of coatings treated with increasingly humid atmospheres. Ref. 17 showed that the friction coefficient of burnished MoS₂ coatings increased as the humidity increased.

A study was previously conducted at The Aerospace Corporation to better quantify the effects of oxygen and humidity exposure – as well as storage time – on the oxidation of MoS₂.¹⁸ The study used polycrystalline MoS₂ powders, which are used in fabricating burnished and bonded MoS₂ coatings, and also composites like bearing retainers and slip-ring brushes. The average particle size was 0.7 μm. After washing the powders in aqueous ammonium hydroxide (NH₄OH) to remove residual MoO₃, samples were placed into one of three storage environments: air with 4% RH, air with 33% RH, and air with 53% RH. Samples were placed in the bottom of small beakers, forming piles of MoS₂ powder ~1 mm thick. Oxidation of MoS₂ samples was analyzed after 1–3 years of storage by dissolving any MoO₃ present in aqueous NH₄OH and measuring the resultant Mo content in solution using atomic absorption (AA) spectroscopy.

Analysis gave the fractional amount of MoS₂ that was oxidized to MoO₃. These values are shown in Figure 2 for each storage atmosphere and storage time. The results for 4% and 33% RH are the same within the error limits, but the amount of oxidation for 53% RH is considerably greater than that for 0% or 33% RH. In addition, the amount of oxidation continues to increase for 53% RH after one year of storage, while the corresponding values for 4% and 33% RH do not.

The similarity of the 4% and 33% curves, and the rapid increase in oxidation between 33% and 53% RH, could indicate a two-step oxidation mechanism: the first step proceeds to completion without requiring substantial H₂O in the storage ambient, while the second step only proceeds at an appreciable rate for humidities greater than some threshold RH value between 33% and 53%.

As discussed above, the total magnitude of oxidation of the samples to MoO₃ at 53% RH is ~3%. However, this percentage represents the entire sample, and does not take into account the likelihood that a higher amount of oxidation occurs near the surfaces of the piles of powders. In fact, a whitish color indicative of MoO₃ was visible on the surfaces of MoS₂ piles samples stored at 53% RH for 1½ and 3 years, which was not apparent in the region below the surface of the piles.

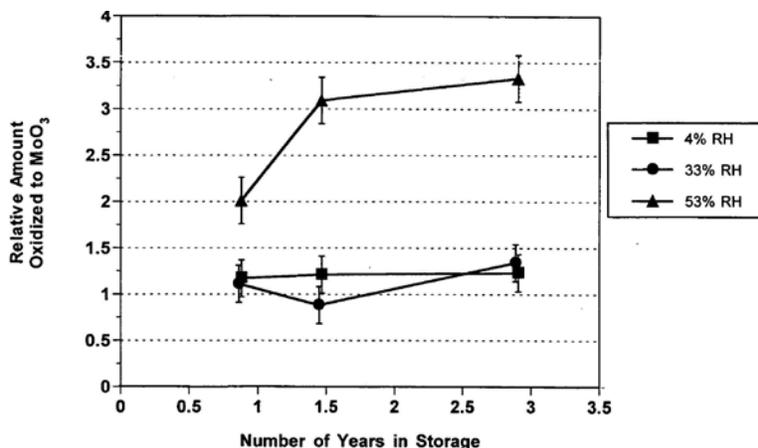


Figure 2. Relative amount (in percent) of powder MoS₂ samples that were oxidized to MoO₃ by exposure to air. Results are shown over 3 years storage for samples stored at three humidities.

MoS₂ solid lubricant coatings used on spacecraft include burnished films, sputter-deposited coatings, and pressure-sprayed coatings that are considerably thinner than the macroscopic samples evaluated in this earlier study (i.e., 1–10 µm thick). As such, the amount of oxidation *relative to the lubricant thickness* for thin coatings is potentially much greater compared to the more macroscopic samples in the MoS₂ powder study. In fact, for very thin or porous coatings, a previous study showed that oxidation could be as high as 40–100% throughout the depth of the coating.¹⁸ In less porous coatings, the amount of oxidation might be lower. However, the amount of oxidation would be significant in either case because the oxidation is enhanced at the surface of the coatings, where tribological interactions in lubricated devices occur.

Whether lubricant degradation due to MoS₂ oxidation adversely affects device performance depends on the application, the type of coating, and the tribological requirements, such as friction/torque and number of duty cycles. Applications involving low numbers of duty cycles and wide friction margins are more robust with respect to such degradation. For example, latches and other release mechanisms will only operate once on orbit (including a few cycles during ground test), and the dominant concern is to ensure that a maximum coefficient of friction (COF) is not reached and to prevent metal-to-metal contact that would cause galling or cold-welding. In such cases, the increase in friction due to partial conversion of the MoS₂ to MoO₃ may not be enough to significantly affect deployment. In contrast, scanner and gimbal bearings involve higher contact stresses and must operate for millions of cycles. Also, excessive MoO₃ production could prevent the bearings from meeting requirements for low torque noise. For these applications, even a small amount of degradation could be significant. For bearings containing self-lubricating retainers, a film of MoO₃ on the bearing race surfaces could affect the rate of formation and uniformity of transfer films. Poor transfer film formation could result in the appearance of torque noise and lowered lifetime.

The oxidation of MoS₂ is believed to be many times higher at the more chemically reactive edge plane surfaces of a MoS₂ crystallite, rather than the relatively unreactive basal plane surfaces.¹⁴ In resin-bonded coatings (containing powdered MoS₂ as the lubricant), these reactive edge sites are protected significantly from moisture by the surrounding binder matrix. As such, bonded coatings are generally less sensitive to humid air exposure. However, even for these coatings, a thin film of pure MoS₂ forms on the surface of a burnished/run-in coating, which is then susceptible to oxidation. The result is that there will be initially increased friction until this oxidized surface layer is worn off.

Long term storage life test data for sputter deposited MoS₂ coatings are uncommon. The data available generally involve pure MoS₂ coatings. For example, results reported in the 1980's in Ref. 14 showed that storage of pure sputter-deposited MoS₂ coatings in humid atmospheres (i.e., 84% relative humidity [RH]) resulted in considerably greater oxidation than in dry atmospheres for storage times of 2 weeks to 1 year. Some oxidation increase was even seen for storage in 52% RH compared to dry atmosphere.

Panitz et al. evaluated the friction and wear properties of RF-sputtered MoS₂ coatings after being stored for 150 days in 35%-45% relative humidity followed by over 75 days in either a 2% or 98% relative humidity environment.¹⁹ Two types of coatings were studied, one that was deposited on a heated substrate and subsequently annealed, and another that was deposited on a substrate at ambient temperature and not annealed. The heat-treated coating was more crystalline than the ambient-grown coating as measured by Raman peak intensity (this agrees with X-ray Diffraction results on RF-sputtered MoS₂ coatings that had similar heat-treatment in our laboratory²⁰). The coefficient of friction for the MoS₂ coating having a more crystalline structure increased from its initial air tested level of 0.085 to 0.10 after being stored in 98% RH. Its wear life decreased by a factor of 3 when stored the 2% dry environment but dropped by a factor of 10 when stored in the wet environment. The authors point out that this result was consistent with the observation of others that water vapor promotes the conversion of MoS₂ to MoO₃. On the other hand the less crystalline MoS₂ sample's wear life increased when stored in the wet environment, so microstructure clearly plays a role in oxidation.

Storage tests were conducted by Iwaki et al. on sputter deposited MoS₂ at 40%, 60% and 80% relative humidity for up to 24 months of storage.²¹ Wear lives of samples stored for 6 months were relatively unchanged within the scatter of the data except for samples stored at 60% RH which showed improvement. However tests at 1, 1.5 and 2 years showed mixed results with some 60% RH readings showing lower life while others showing essentially no change.

For use in current spacecraft mechanisms, it has been found that greatly improved tribological properties are obtained from cosputtered coatings that consist of MoS₂ mixed with species like Ni and Sb₂O₃ to form nanocomposites. The higher densities and altered crystalline structure of these cosputtered coatings imply that their sensitivity to storage in humid air should be different also. Storage sensitivity of these mixed coatings is the focus of our study.

Experimental Approach

Ni-MoS₂, Au-Sb₂O₃-MoS₂, and Sb₂O₃-MoS₂ coatings were deposited onto a series of polished 440C steel disks to a thickness of 400±100 nm. Several of each type of coating were stored in a closed container containing air with humidity controlled to 59% RH by using a saturated solution of NaBr. Samples were periodically removed for testing. Samples not being exposed to humid air were stored in dry, flowing N₂ gas.

Friction/wear testing was conducted using a CSEM Pin-on-Disk Tribometer. The upper specimens for the tests were uncoated 6-mm 440C steel balls (grade 3, R_a=0.01 μm), cleaned with IPA prior to testing. For all tests, a 3N load was used, and the sliding speed was 20 cm/s. The nominal maximum Hertzian contact stress was calculated as 938 MPa (136 ksi) based on the properties of 440C steel substrate.

Prior to starting the friction/wear tests, the tribometer enclosure was purged with nitrogen gas (99.999% nominal purity, passed through an Aeronex Gatekeeper® getter, which is advertised to reduce oxygen, water, and other impurities to less than 1 ppb) for four hours, and until the relative humidity was reduced to below 0.08% RH. The tests were started, and were run until failure, which is defined as when the COF rose above 0.5. Three tests were conducted on each sample to determine the data uncertainty, but different radii were chosen to ensure that each test was conducted on virgin material; new balls were used for each test.

X-ray Photoelectron Spectroscopy (XPS) was used to aid in understanding the chemical changes occurring in the coatings that gave rise to changes in friction and endurance. Our main interest was in the oxidation

state of Mo since the most significant result of storage in humid air is to oxidize the lubricating MoS₂ to nonlubricating MoO₃, as discussed above. For this study, a Physical Electronics Versaprobe II instrument was used.

In order to determine the composition variation with depth into the coatings, Ar⁺ sputtering depth profiles were obtained using a 1 kV accelerating voltage. Ion bombardment has an unpredictable effect on chemical state, and so it is difficult to quantitatively determine relative elemental amounts as well as chemical state with depth. However, it is useful in providing semi-quantitative comparisons between materials.

Friction and Endurance Results

A typical friction trace for a Hohman Plating Ni-MoS₂ coating tested before storing in humid air is shown in Figure 3. The mean endurance for the Hohman Plating Ni-MoS₂ coating prior to humid air storage was 125,000 cycles. In contrast, the endurance for the Au-Sb₂O₃-MoS₂, and Sb₂O₃-MoS₂ coatings were 2.2 million and 3.3 million cycles, respectively, or 18 and 26 times the endurance for the Ni-MoS₂ coating. It has previously been shown that the Sb₂O₃-containing coatings performed better than the Ni-MoS₂ coating when tested in an air environment.⁶ (In that study, tests conducted in dry N₂ were stopped prior to failure for all coatings, so relative lifetimes in an inert environment were not obtained.)

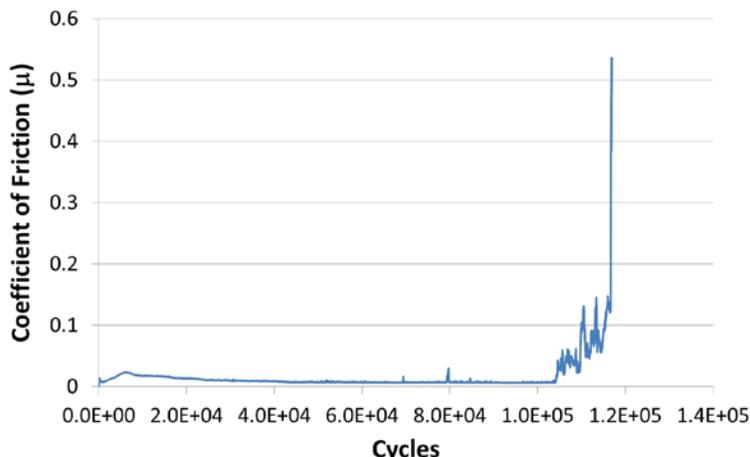


Figure 3. A typical friction trace for a Hohman Plating Ni-MoS₂ coating tested before storing in humid air. Data were obtained during pin-on-disk testing in a dry N₂ environment.

Figure 4 shows endurance data for the Ni-MoS₂ coating for various storage times. Even considering the large scatter of the data in the first 200 days, there is a clear reduction in endurance with storage time. The endurance continues to drop for longer storage times up to 827 days (2.3 years), although the rate of decrease appears to slow with increasing storage time. The total reduction over 2.3 years is about 55%, which represents a significant degradation in the performance of this coating.

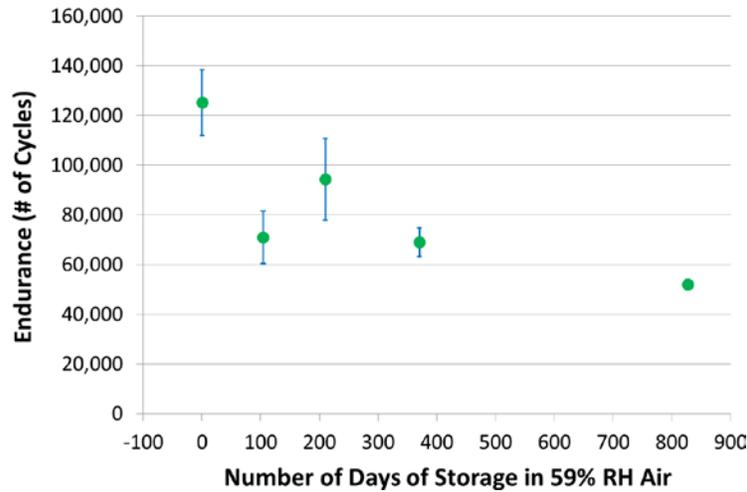


Figure 4. Endurance of Hohman Plating Ni-MoS₂ coatings as a function of days stored in 59% RH air. The endurance is defined as the number of cycles for which the COF is below 0.5. Each data point represents the mean of three tribometer runs on one sample; the error bars represent the scatter of the three runs. There is a reduction in endurance of about 55% for a storage time of 2.3 years.

The endurance data for the stored Au-Sb₂O₃-MoS₂ coating is shown in Figure 5. For the early storage data (i.e., ≤200 days), the trend in endurance with storage time is not clear; it is obscured by the scatter in the data. However, over longer storage times (i.e., 1 and 2.3 years), the endurance is clearly lower than the unstored coating. Furthermore, the endurance at 1 year and 2.3 year are comparable, suggesting there is a reduction in the degradation rate of the coatings after 1 year but more data would be needed to confirm this. The total reduction over 2.3 years is about 20%, considerably smaller than for the Ni-MoS₂ coatings. Figure 6 shows corresponding data for the Sb₂O₃-MoS₂ coatings. As for the similar Au-containing coating, it also shows a reduction in endurance with storage time, i.e., by 17% over 419 days of storage (1.1 years; this coating was placed into storage later than the other two, and so longer storage times are not available at the time of this writing). Again the data suggests that the endurance may have stabilized.

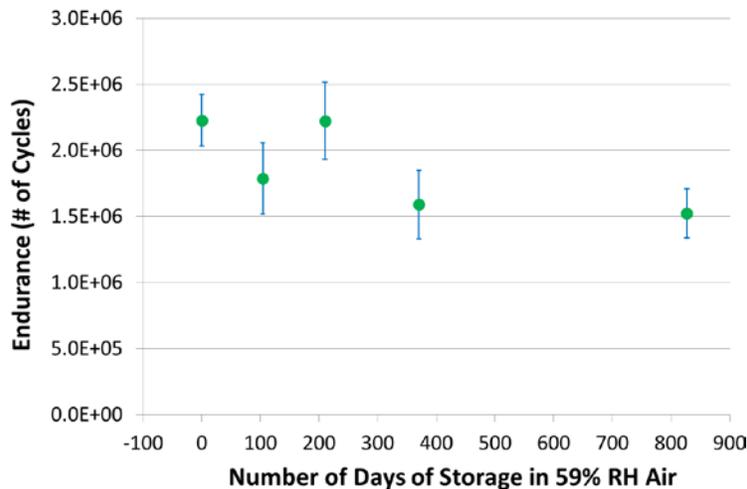


Figure 5. Endurance of Hohman Plating Au-Sb₂O₃-MoS₂ coatings as a function of days stored in 59% RH air. (See Figure 4 caption.) The endurance has reduced by about 30% for a storage time of 2.3 years.

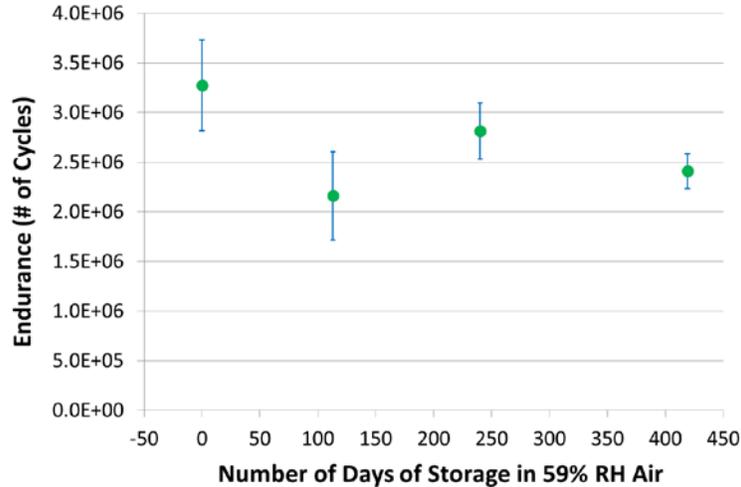


Figure 6. Endurance of Hohman Plating $\text{Sb}_2\text{O}_3\text{-MoS}_2$ coatings as a function of days stored in 59% RH air. (See Figure 4 caption.) The endurance has reduced by about 27% for a storage time of 1.1 years.

Solid lubricant coatings typically exhibit increased friction at the beginning of testing due to the initial coating surface chemical state, morphology, and crystallinity. After steady-state conditions have been reached (i.e., post run-in), the friction is generally at a minimum. Early-life friction was measured during separate (higher data rate) scans for the Ni-MoS₂ and Au-Sb₂O₃-MoS₂ coatings stored in N₂ and for storage in air for 2.3 years (these were only run for a few hundred cycles, i.e., not to failure). Results are shown in Table 1. Also shown are the steady-state values obtained from the original endurance runs.

The early-life friction for the Au-Sb₂O₃-MoS₂ coating (without air storage) is slightly lower than that for the Ni-MoS₂ coating. After storage for 2.3 years, the early-life friction increases slightly for both types of coatings. For the steady-state values, the friction for the Au-Sb₂O₃-MoS₂ coating (without air storage) is lower than that for the Ni-MoS₂ coating. After storage, the steady-state friction does not change significantly for either coating.

Table 1. Friction Values Obtained from Sputter-Deposited MoS₂ Coatings Before and After Storage in 59% RH Air for 2.3 years (tested in dry N₂)

| Sample | Maximum COF measured at Start of Test | | Steady State/ Minimum COF | |
|---|---------------------------------------|---------------|---------------------------|---------------|
| | Stored in N ₂ | Stored in Air | Stored in N ₂ | Stored in Air |
| Ni-MoS ₂ | 0.22 ± .01 | 0.25 ± .005 | .008 ± .002 | .007 ± .002 |
| Au-Sb ₂ O ₃ -MoS ₂ | 0.18 ± .01 | 0.22 ± .01 | .005 ± .002 | .003 ± .001 |

Surface Chemical Results

In order to help understand the chemical changes occurring in the coatings that gave rise to the changes in friction and endurance, X-ray Photoelectron Spectroscopy (XPS) was used to study unworn areas of the coatings. Our main interest was in the oxidation state of Mo since the most significant result of storage in humid air is to oxidize the lubricating MoS₂ to nonlubricating MoO₃, as discussed above.

Figure 7 shows XPS spectra in the Mo 3d region of the Ni-MoS₂ coating that had been stored in dry N₂, along with one stored for 2.3 years in air with 59% RH. In the spectra, the Mo 3d doublet for MoS₂ overlaps

with that for MoO_3 , giving a structure that appears to be three peaks. This necessitated using linear least squares deconvolution to determine the molecular ratios of the two species. The ratio of the MoO_3 to MoS_2 spectrum indicates the amount of oxidation that has occurred through the detection depth. The two spectra in Figure 7 indicate that some of the MoS_2 has been oxidized to MoO_3 at the surface of the coating stored in dry N_2 . However, significantly more of the MoS_2 has been oxidized to MoO_3 for the coating stored in humid air.

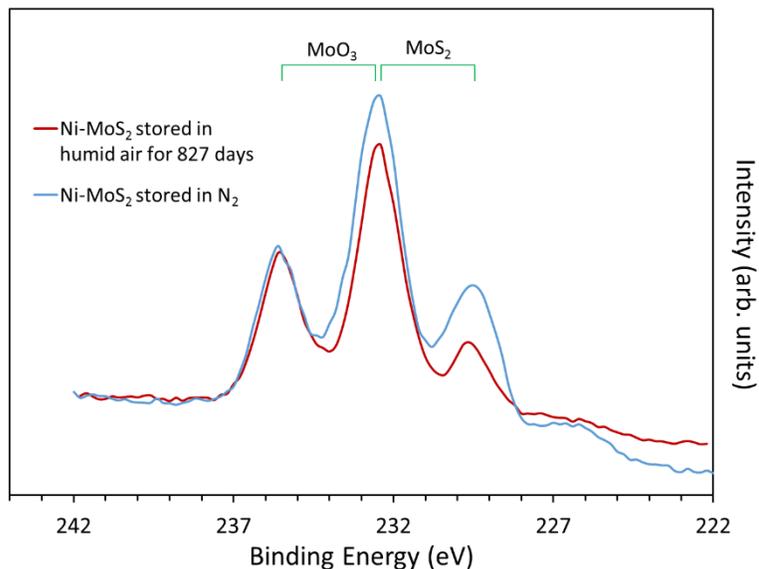


Figure 7. XPS spectra in the Mo 3d region for Hohman Plating Ni-MoS₂ coatings stored in dry N₂ and stored in 59% RH air for 2.3 years. In the spectra, the Mo 3d doublet for MoS₂ overlaps with that for MoO₃. The spectra are normalized so that they show equal contributions of MoO₃. The MoO₃:MoS₂ ratio is significantly higher for the coating stored in humid air.

Figure 8 shows corresponding spectra for the Au-Sb₂O₃-MoS₂ coating. The two spectra indicate that some of the MoS₂ has been oxidized to MoO₃ at the surface of the coating stored in dry N₂, although somewhat less than for the Ni-MoS₂ coating. In addition, although some of the MoS₂ in the Au-Sb₂O₃-MoS₂ coating has been further oxidized to MoO₃ after storing in humid air, the change is considerably less pronounced than for the Ni-MoS₂ coating.

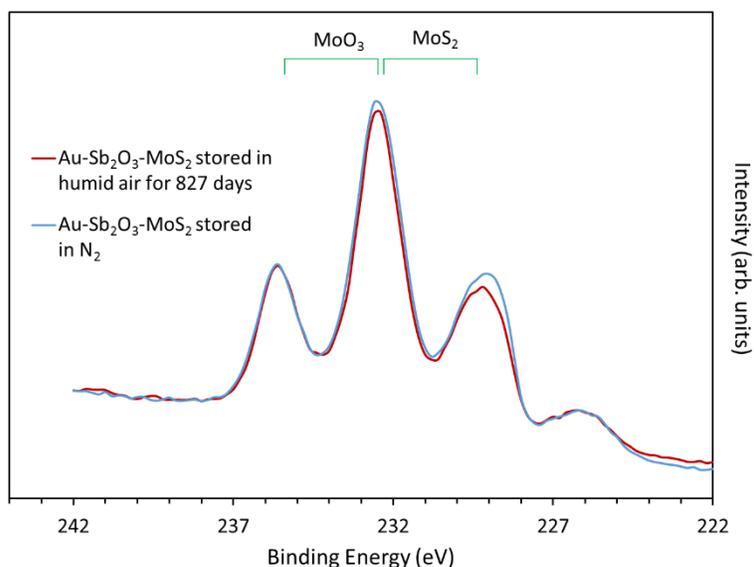


Figure 8. XPS spectra in the Mo 3d region for Hohman Plating Au-Sb₂O₃-MoS₂ coatings stored in dry N₂ and stored in 59% RH air for 2.3 years. In the spectra, the Mo 3d doublet for MoS₂ overlaps with that for MoO₃. The spectra are normalized so that they show equal contributions of MoO₃. The MoO₃:MoS₂ ratio is only slightly higher for the coating stored in humid air.

Table 2 gives the calculated ratios of MoO₃ to MoS₂ for the spectra shown in Figures 6 and 7. For the Ni-MoS₂ coating stored in N₂, there is slightly more oxidized material present in the surface region than non-oxidized material, as shown by a MoO₃:MoS₂ ratio of 1.15. However, after storing in humid air for 2.3 years, the ratio has almost doubled to 2.16, indicating considerable oxidation has occurred during humid air storage.

Table 2. MoO₃:MoS₂ Ratios Obtained from XPS Spectra of Sputter-Deposited MoS₂ Coatings

| Sample | Storage Condition | MoO ₃ :MoS ₂ |
|---|------------------------------------|------------------------------------|
| Ni-MoS ₂ | Stored in N ₂ | 1.15 |
| | Stored in 59% RH Air for 2.3 years | 2.16 |
| Au-Sb ₂ O ₃ -MoS ₂ | Stored in N ₂ | 1.02 |
| | Stored in 59% RH Air for 2.3 years | 1.14 |

For the Au-Sb₂O₃-MoS₂ coating stored in N₂, Table 2 shows that about the same amount of oxidized material is present in the surface region as non-oxidized material, as shown by a MoO₃:MoS₂ ratio of 1.02; this represents slightly less surface oxidation than for the Ni-MoS₂ coating stored in N₂. For the Au-Sb₂O₃-MoS₂ coating stored in 59% RH air for 2.3 years, the value of 1.14 indicates that only about 10% greater oxidation has occurred during humid air storage. Storage in air clearly has less of an effect on the Au-Sb₂O₃-MoS₂ coating than the Ni-MoS₂ coating.

To investigate oxidation throughout the bulk of the coatings, Ar⁺ ion sputter depth profiles were obtained. Figure 9a shows the early stages of the depth profile of the Ni-MoS₂ coating stored in N₂. At longer sputtering times, about 25 at% O is seen in the coating, indicating that significant oxygen was present in the coating as deposited. This is commonly due to residual water vapor in the chamber during the coating process, which results in the formation of a MoS_xO_{2-x} solid solution, rather than conversion of the Mo to a higher oxidation state.²² However, the surface of the coating shows that significantly more O is present (55

at%), which as shown in Figure 7, is due substantially to oxidation of the MoS_2 to MoO_3 . This probably occurred during brief exposure to the air when not being stored in N_2 . The region of surface oxidation appears to be about 0.5-nm thick (based on estimates of thickness vs. sputtering time). For the Ni- MoS_2 coating stored in air for 2.3 years, there is more O seen at the surface (65 at%) (see Figure 9b), and in addition, the oxidized layer is about three times thicker than that for the coating stored in N_2 .

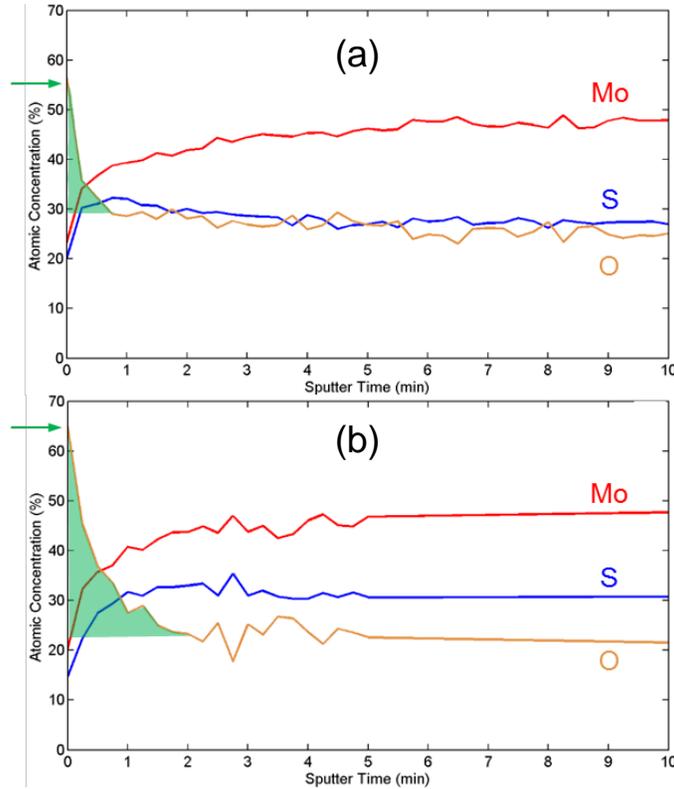


Figure 9. XPS sputter depth profiles for Hohman Plating Ni- MoS_2 coatings. Profiles are shown for (a) a coating stored in dry N_2 , and (b) a coating stored in 59% RH air for 2.3 years. (Ni is not shown because of its low intensity.) The profiles show an enhancement in oxygen near the surface (i.e., at low sputtering times) due to surface oxidation of the MoS_2 . The coating stored in humid air for 2.3 years shows a higher level of oxidation at the surface, and a thicker oxidized layer. (Measured atomic percentages after extended sputtering differ from actual bulk values due to preferential sputtering of one element over another.)

A corresponding depth profile for the Au- Sb_2O_3 - MoS_2 coating stored in dry N_2 (not shown) also indicates the presence of oxygen at the surface, but at a much lower level (12 at%) than for the corresponding Ni- MoS_2 coating. The Au- Sb_2O_3 - MoS_2 coating stored in air for 2.3 years shows increased oxygen at the surface (18 at%), but the thickness of the oxidized layers for the two Au- Sb_2O_3 - MoS_2 coatings appear similar.

The XPS results correlate with the endurance results during pin-on-disk testing. Specifically, both the Ni- MoS_2 and Au- Sb_2O_3 - MoS_2 coatings show increased oxidation at their surfaces after 2.3 years of storage in 59% RH air, and both show decreased endurance. The increase in oxidation due to air storage is significantly greater for the Ni- MoS_2 coating compared to the Au- Sb_2O_3 - MoS_2 coating, and the decrease in endurance is correspondingly greater for the Ni- MoS_2 coating.

Conclusions

The results of this study demonstrate that the endurance of nanocomposite, sputter-deposited MoS₂ coatings that are typically used on spacecraft can be significantly degraded after storage for two years under typical storage conditions (i.e., storage in air at 59% RH). Specifically, pin-on-disk friction testing showed that sputter-deposited Ni-MoS₂ coatings degrade by 55% over 2.3 years of storage, while Au-Sb₂O₃-MoS₂ coatings degrade by 20% over the same period. Sb₂O₃-MoS₂ coatings degrade by 17% over 1.1 years of storage.

The reduction in endurance was shown to result from oxidation of lubricating MoS₂ to non-lubricating MoO₃ at the surface of the coatings. This was demonstrated by XPS of the surfaces of the coatings, including Ar⁺ ion sputter depth profiles. All coatings exhibited a small amount of oxidation of their surfaces, even those stored in dry N₂ due to brief exposure of the coatings to air. After storage for 2.3 years, a Ni-MoS₂ coating stored in 59% RH air showed significantly greater surface oxidation than a coating stored in dry N₂, while Au-Sb₂O₃-MoS₂ coatings showed a relatively small increase in oxidation stored under the same conditions. These results demonstrate that the degree of oxidation correlates with a decrease in endurance.

Storage effects aside, Au-Sb₂O₃-MoS₂ and Sb₂O₃-MoS₂ coatings were shown to greatly outperform the Ni-MoS₂ coating, by 18x and 26x, respectively. This may be explained partly by the higher amount of cosputterant in the Sb₂O₃-containing coatings relative to the Ni-MoS₂ coating, since a major effect of forming the nanocomposite is to densify the coatings and reduce their crystallinity. Among other effects, this results in a harder, more fracture tough coating that resists wear.^{6,9} With respect to oxidation sensitivity, denser, more amorphous coatings would be more likely to resist intrusion of water and oxygen into the coatings, reducing the likelihood of oxidation to nonlubricating MoO₃.

The results of this study may be used as a guide to storing hardware lubricated with sputter-deposited MoS₂-based coatings. For devices that require a limited number of cycles (i.e., deployment or release devices), degradation at typical humidities (i.e., <60% RH) will not have a significant effect on performance. However, the degradation must be taken into account for high cycle mechanisms, as endurance can be lowered by 20 to 55% during storage for two years at typical humidities, depending on the type of coating. Storage in dry N₂ or if necessary in air at lower humidities (i.e., <30% RH) can significantly slow the endurance degradation rate.^{3,18}

Regarding the FAM storage question, we showed that although the MoS₂ coatings exhibited some degradation in friction performance after the first year of storage, the reduced cycle life of 1.5 million cycles for the Au-Sb₂O₃-MoS₂ coating and 2.4 million cycles for the Sb₂O₃-MoS₂ coating was more than adequate to meet the NIRCcam cycle life requirement.

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