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# The Effects of Environmental Water and Oxygen on the Temperature-Dependent Friction of Sputtered Molybdenum Disulfide

H. S. Khare · D. L. Burris

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Abstract Molybdenum disulfide  $(MoS_2)$  is well known for exceptional friction and wear properties in inert and high vacuum environments. However, these tribological properties degrade in humid and high temperature environments for reasons that are not fully understood. A prevailing hypothesis suggests that moisture and thermal energy facilitate oxidation, which increases the shear strength of the sliding interface. The purpose of this study is to elucidate the contributions of water, oxygen, and temperature to the tribological degradation of MoS<sub>2</sub>. Generally speaking, we found a minimum friction coefficient that occurred at a temperature we defined as the transition temperature. This transition temperature ranged from 100 to 250 °C and was a strong function of the MoS<sub>2</sub> preparation and thermal sliding history. Below the transition temperature, friction increased with increased water, but was insensitive to oxygen. Above the transition, friction increased with increased oxygen, but decreased to a limited extent with increased water. These results are generally consistent with prior results, but clarify some inconsistencies in the literature discussions. Contrary to the prevailing hypothesis, the results suggest that water does not promote oxidation near room temperature, but directly interferes with lamellar shear through physical bonding. Increased temperatures drive off water and thereby reduce friction up to the transition temperature. The results suggest that oxidation causes increased friction with increased temperature above the transition temperature. The data also suggest that water helps mitigate high temperature oxidation by displacing the environmental oxygen or by preferentially adsorbing to the surface.

H. S. Khare · D. L. Burris (⊠)
Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, USA
e-mail: dlburris@udel.edu 

#### **1** Introduction

Molybdenum disulfide (MoS<sub>2</sub>) is a ubiquitous lamellar solid lubricant and is often regarded as the gold standard in space lubrication. In hard vacuum and ambient temperature conditions, MoS<sub>2</sub> provides exceptional solid lubrication, with reported friction coefficients being as low as 0.002 [1, 2]. This unusual tribological performance is widely believed to result from easy shear between two or more MoS<sub>2</sub> lamellae (inter-lamellar shear), which are separated by weak Van der Waals forces of attraction. Conversely, the system performs relatively poorly at high temperatures and in reactive terrestrial environments, presumably due to the introduction of impediments to shear between lamellae [2, 3].

Most of the literature has targeted the room temperature lubrication behavior of MoS<sub>2</sub>. Fusaro [4] investigated rubbed MoS<sub>2</sub> films in dry argon, dry air, and moist air, and measured friction coefficients of 0.02, 0.02, and 0.08, respectively. Wear rates were also highest in moist air, thus implicating water, not oxygen, in the deterioration of lubricity. Stewart and Fleischauer [5] noted reduced wearlife of sputtered coatings when stored in humid environments over vacuum environments. Donnet et al. [2] measured friction of sputtered MoS<sub>2</sub> in ultra-high vacuum (UHV), high vacuum (HV), dry nitrogen, and ambient air and found that friction coefficient increased in that order, varying between 0.002 and 0.15. Dudder et al. [6] measured friction of a MoS<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-C coating in air, vacuum, and partial pressures of oxygen and water alone, and found friction coefficients of 0.06 for oxygen and vacuum and

0.15 for air and water. The literature consistently indicates that water increases friction at room temperature, while oxygen does not. Numerous hypotheses have been proposed to explain the increase in friction due to environmental moisture and include water adsorption, water-initiated oxidation, film softening, and increased shear strength due to physical bonding at the edge sites [2, 7–13]. To date, however, the underlying mechanisms remain uncertain.

The most widely discussed hypothesis for the environmental sensitivity of MoS<sub>2</sub> suggests that moist environments cause oxidation, which impedes lamellar shear [4-6, 14–22]. In one of the earliest efforts to correlate humidity with oxidation at near-ambient temperatures, Ross and Sussman [22] showed that pulverized  $MoS_2$  readily forms a native surface layer of MoO<sub>3</sub>. The rate of oxidation was slow at room temperature, but increased proportionally with increasing humidity. In sliding tests of resin-bonded  $MoS_2$ , Pardee [18] suggested that oxidation at rubbed surfaces in moist room temperature air was responsible for increased friction. Similar observations have also been made for sputter-deposited MoS<sub>2</sub> films, where storage or operation in humid environments caused an increase in friction and a corresponding increase in oxidation [4, 5, 15, 17, 19, 21]. This oxidation hypothesis was supported by Dudder et al. [6] who found that water was more likely than oxygen to cause oxidation of sputtered MoS<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-C at room temperature. These results support the general consensus that the presence of water increases the room temperature friction of  $MoS_2$  by promoting oxidation [1].

The literature on the high temperature friction and wear of MoS<sub>2</sub> is comparatively less abundant and makes fewer distinctions between constituents of ambient air (water and oxygen). Generally, increased friction of MoS<sub>2</sub> due to increased temperature is also believed to be driven by oxidation [1, 3, 23-25]. Godfrey and Nelson [25] noted that MoS<sub>2</sub> oxidation is a function of temperature, exposure time, and oxygen concentration, though the rates of oxidation for resin-bonded MoS<sub>2</sub> coatings were low below 400 °C in air and 540 °C in vacuum. Similarly, Sliney showed that friction coefficients of resin-bonded MoS<sub>2</sub> only increased above 400 °C in air and 600 °C in argon [3, 26]. Muratore et al. [27] made in situ Raman spectroscopy measurements of a sputtered MoS<sub>2</sub> coating during sliding in air and observed the appearance of an MoO<sub>3</sub> Raman intensity peak with an abrupt increase in friction at 350 °C. These results suggest a direct relationship between friction and oxidation.

Although there is strong evidence to support the hypothesis that water and temperature promote oxidation, which impedes inter-lamellar shear, the overall body of work in this field raises important fundamental questions. The room temperature studies suggest that water promotes oxidation, which causes increased friction, but high temperature friction and oxidation studies report that oxidation only occurs above a transition temperature that ranges from 100 to 500  $^{\circ}C$  [1, 3, 24, 25, 27, 28]; Windom et al. [28] showed, for example, that oxidation only appeared at temperatures above 100 °C in a humid environment which is consistent with the temperature associated with increased friction from Kubart et al. [24]. Furthermore, they found no evidence that water preferentially oxidizes MoS<sub>2</sub> at any temperature. Both sets of results are unexpected based on the hypothesis that moisture preferentially promotes the oxidation of MoS<sub>2</sub> at room temperature [1, 29]. The coupled effects of moisture, oxygen, and temperature on MoS<sub>2</sub> oxidation and friction have important scientific and practical implications. However, these effects and the responsible mechanisms remain unclear to date. The goal of this study is to elucidate the effects of water and oxygen on the friction of MoS<sub>2</sub> as a function of temperature.

## 2 Methods

#### 2.1 Materials

A molybdenum disulfide (MoS<sub>2</sub>) coating was commercially sputter-deposited (Tribologix Inc.) to a nominal thickness of 1 µm on a 440C stainless steel coupon. Only one coating was used to minimize potential variations in material properties. The coupon coating area measured 25 mm by 38 mm and was polished to an average surface finish  $R_a = 30 \pm 5$  nm prior to sputter deposition. A control coating of virgin MoS<sub>2</sub> powder was prepared by approximating the 'excess layers' preparation method from Deacon and Goodman [30]; this coating is referred to as 'mechanically deposited' hereafter. This mechanically deposited coating was prepared from 98 % pure MoS<sub>2</sub> powder (McLube Co.), with nominal particle diameters ranging between 1 µm and 30 µm. A solution of MoS<sub>2</sub> powder was dispersed in ethanol by ultrasonication. The solution was then dripped onto a polished 440C steel substrate, and evaporation of the ethanol left a 20 µm thick MoS<sub>2</sub> coating as measured with interferometry. The coating was consolidated to a thickness of approximately 1 µm after the initial sliding pass. The tribological contact in all tests consisted of MoS<sub>2</sub> sliding against a 6.4 mm diameter spherical counter surface. Commercial 440C steel ball bearings with average surface roughness  $R_a = 110 \text{ nm}$ were used as the counter surface for all tests.

## 2.2 Friction Measurement

Sliding tests were conducted on the custom-built, pin-onflat reciprocating tribometer illustrated in Fig. 1. The linear reciprocating stage of the tribometer is driven along the



**Fig. 1 a** Schematic illustration of the custom high temperature tribometer with a reciprocating pin-on-flat contact. A stepper motor drives the reciprocating motion in the *x*-axis for a given track length and siding frequency. Contact forces are measured by two strain-gage-based transducers connected to a manual vertical stage, used for loading the contact. A heater block with cartridge heater inserts is connected to a PID temperature controller; the tribometer and data

acquisition hardware are housed in a glove box for environmental control. **b** Friction coefficients were calculated using values from the final 30 sliding cycles (*grey markers*), where variations in friction between sliding cycles were observed to be below 20 % (*grey error bars*). **c** Friction coefficients at elevated temperatures also showed a steady-state behavior toward the last 30 of 50 sliding cycles

x-axis by a stepper motor (via a lead screw and flexure assembly) interfaced to a computer running LabView<sup>TM</sup> for motion control. MoS<sub>2</sub> samples were mounted to a copper heater block containing cartridge heater inserts. A surface-mounted thermocouple provided feedback to a PID temperature controller. MoS<sub>2</sub> coatings were mounted directly to the heater. The heater block was attached to the linear stage via two C-section brackets that were designed to minimize conduction into the stage. Two strain-gage load cells (strain measurement devices) measured the normal and friction force and were rigidly attached to a manual dovetail linear stage which was used for loading and unloading the contact in the z-direction. The load cells were calibrated with a Mettler mass balance with an uncertainty of 50  $\mu$ g; the overall force uncertainty in the calibration of the load cells was 0.1 mN. A thin aluminum cantilever separated the load cell assembly from the tribological contact, which enabled the load cell assembly to remain at  $27 \pm 3$  °C under all thermal conditions.

The normal load was maintained at 1 N, which corresponds to a mean contact pressures of approximately 100 MPa based on measurements of wear track width. Wear tracks of 5 mm were created for the coatings, and the sliding frequency was maintained at 0.5 Hz (5 mm/s sliding velocity). Real-time force, position, and temperature data were collected via a data acquisition system and custom LabView<sup>TM</sup> software. Single-cycle friction coefficients were evaluated using the method of reversals described previously [31] to minimize uncertainties in friction measurement due to angular misalignment between the contact and the transducer assembly. Repeat measurements were made with different wear tracks on the same sample. New test locations were obtained by indexing the manual translation stage shown in Fig. 1a.

Temperature-dependent friction measurements were made by heating the substrate from 25 to 250 °C at approximately 25 °C/min. During ramp-ups, friction coefficients were measured at 30, 50, 110, 150, 200, and 250 °C. A representative plot of friction coefficient as a function of sliding cycles is shown in Fig. 1c. Each friction measurement consisted of 50 sliding cycles. We employ a definition from the literature to identify transient behavior, which occurs when friction coefficient deviations exceed 20 % the nominal value [32]. In every condition, the last 30 cycles satisfied this definition for steady-state behavior; this period was used to determine the characteristic frictional behavior at each condition. Typical variations during testing are illustrated in Fig. 1b, c.

Two wear track conditions were considered to study the effect of thermal run-in. 'Unconditioned tracks' were exposed to thermal cycling from 25 to 250 to 25 °C, but were never exposed to sliding contact prior to testing. 'Conditioned tracks' had experienced sliding contact during thermal cycling from 25 to 250 to 25 °C prior to testing.

## 2.3 Environment Control

Temperature dependence of MoS<sub>2</sub> friction was evaluated in four background environments-dry nitrogen (N<sub>2</sub>), humid nitrogen  $(N_2 + H_2O)$ , dry air  $(N_2 + O_2)$ , and humid air  $(N_2 + O_2 + H_2O)$ . The nitrogen environment was established by purging the glovebox with 99.998 % pure nitrogen, and subsequently removing impurities by recirculating the gas through an environmental purifier. The humid nitrogen environment was established by passing nitrogen gas through a water bubbler and into the cleaned glovebox. The dry air environment was established by channeling standard lab air through a desiccant filter (rated for -80 °C dewpoint) and into the glovebox. Humid air environments of variable humidity were established using controlled flow rates of desiccated laboratory air and humidified laboratory air. Following gas infiltration, the glovebox was sealed and allowed to equilibrate prior to testing. The tribometer, data acquisition hardware, and computer were placed within the glovebox for tribological testing. Low-humidity conditions were measured with a trace moisture analyzer (GE Veridri) with a range from 0 to 1,000 ppm ( $\pm 4$  %). High-humidity conditions were measured with a hygrometer with a range from 10 to 90 % RH (Omega RH411). In dry conditions, the water content was always below 300 ppm.

#### 2.4 Energy-Dispersive X-Ray (EDS) Spectroscopy

The extent of oxidation of  $MoS_2$  in different environments was quantified by energy-dispersive X-ray spectroscopy (EDS). EDS measurements on the  $MoS_2$  coating were performed on a Zeiss Auriga 60 scanning electron microscope. A wear track was created on the coating with 50 sliding cycles in a dry nitrogen environment to 'wear off' any native oxides and provide the datum for the unoxidized coating. Six distinct locations within the wear track and four on the unworn coating were measured immediately after sliding. The coating was then annealed in a dry nitrogen environment for 20 min at 250 °C, and a second set of EDS measurements were collected for the same six locations within the track and four new locations outside the wear track. The measurements were repeated for humid nitrogen and dry air. All EDS maps were integrated over 20 frames at 1.5 keV accelerating voltage, which was found to give the best combination of signal and surface sensitivity.

# **3** Results

The friction coefficient of the conditioned track is plotted versus sliding temperature in each environment in Fig. 2. In dry nitrogen, friction increased weakly with temperature up to 250 °C; friction coefficient increased from 0.027 to 0.050 when temperature increased from 27 to 250 °C. The addition of oxygen to nitrogen (i.e., dry air) did not significantly affect the room temperature friction coefficient which is consistent with the previous findings [4, 6]. However, this environment did significantly increase the friction coefficient at high temperatures; at 250 °C, the friction coefficient was 100 % higher than at room temperature. The addition of water to nitrogen (humid  $N_2$ ) significantly increased the room temperature friction coefficient, but did not significantly affect the high temperature friction coefficient; at 30 °C, the friction coefficient increased from 0.027 to 0.09 with the addition of water to nitrogen. The addition of water and oxygen to nitrogen significantly increased friction at low and high temperatures; we call the temperature at which friction minimized the transition temperature. Interestingly, all four environmental conditions produced nominally identical friction coefficients at the transition temperature. In this case, the transition temperature occurred at 100 °C, which corresponds to the temperature at which Windom et al. [28] first observed increased oxidation and Kubart et al. [24] first observed increased friction. These results suggest that water drives increased friction coefficients below the transition temperature and oxygen drives increased friction coefficients above the transition temperature.



Fig. 2 Friction of conditioned sputtered  $MoS_2$  coatings in dry nitrogen, dry air, humid nitrogen, and humid air as a function of temperature. Water increases friction at low temperatures with or without oxygen. Oxygen increases friction at high temperature with or without water



Fig. 3 Friction coefficient plotted as a function of temperature during heating for varying humidity in air for **a** conditioned and **b** unconditioned interfaces. The transition temperature occurs at 100  $^{\circ}$ C for

the conditioned coating and 200 °C for the unconditioned coating. At low temperature, friction increased with increased humidity. At high temperature, friction decreased with increased humidity



Friction coefficient is plotted versus sliding temperature during heating as a function of humidity in air  $(N_2 + O_2 + H_2O)$  for conditioned and unconditioned tracks in Fig. 3. Conditioned and unconditioned tracks exhibit minimum friction coefficients near 0.04. In all humidity conditions, conditioned tracks (thermally and tribologically cycled) transitioned at 100 °C, which is consistent with the results in Fig. 2. Unconditioned tracks (thermal cycling only), on the other hand, transitioned at 200 °C. In every case, friction increased with increased humidity below the transition temperature and decreased with increased humidity above the transition temperature. The completely dry environment was the only exception to the rule; in this case, the friction coefficient increased monotonically with temperature for conditioned and unconditioned tracks. Water appears to prevent the transition to high friction at high temperatures, an observation that conflicts with the conventional wisdom of the role of water.

Friction coefficients are plotted versus sliding temperature for heating and cooling in air of varying humidity in Fig. 4a. The width of the hysteresis loop depends on humidity and is highlighted by the shaded region. The room temperature friction increases with increased humidity. The high temperature (250 °C) friction coefficient and the width of the hysteresis loop decrease with increased humidity. Figure 4b illustrates the effect of the frictional transition on the hysteresis. The friction coefficient is plotted for two heat cycles on two different tracks in 45 % RH air. The friction coefficient increased upon cooling from 250 °C, but decreased upon cooling from 150 °C.

The normalized friction coefficient is plotted versus sliding temperature during heating for different surface conditions in Fig. 5. The conditioned and unconditioned tracks on the sputtered coating had a room temperature friction coefficient of  $\mu = 0.05$ ; the powdered MoS<sub>2</sub> coating had a slightly higher initial friction coefficient of 0.07. Friction for each coating initially decreased with increased temperature. The conditioned sputtered coating transitioned at 110 °C, the unconditioned sputtered coating transitioned at 200 °C, and the powdered coating remained low up to 250 °C. The results demonstrate that the transition behavior of MoS<sub>2</sub> bearings strongly depends on sliding conditions and method of deposition.

EDS measurements of oxygen content (O K $\alpha$ ) were made to assess the possible role of oxidation in determining frictional transitions in varying environmental conditions. The coating was worn for 50 cycles at 25 °C in N<sub>2</sub> to remove surface contaminants (including oxides), and the worn track was treated as the reference datum for oxidation. Following wear, the coating was exposed to 25 °C air for 20 min prior to EDS measurement at 10<sup>-8</sup> torr, a condition that helps remove any adsorbed oxygen-containing species. Measurements collected at six-fixed locations served as the control for each annealing treatment.



Fig. 5 Friction coefficient normalized by corresponding room temperature values for a conditioned coating, an unconditioned coating, and a mechanically deposited coating in humid air (RH = 15 %). The results demonstrate that each system provides a unique threshold temperature that can vary from 100 °C (conditioned sputtered coating) to >250 °C (pure MoS<sub>2</sub>)

The coating was then heated to 250 °C in  $N_2$ , exposed to air for 20 min, and measured with EDS at the same six locations. The procedure was repeated for humid  $N_2$  and dry air within different tracks. In each case, four measurements were made outside the wear track to assess the effect of sliding on oxygen removal from sliding.

The EDS results for oxygen content relative to the control (worn) condition are shown in Fig. 6. Annealing the coating at 250 °C in dry N<sub>2</sub> did not increase oxygen content in the wear track; in fact, there was a statistically significant reduction in oxygen content that may be due to additional water desorption. Annealing in humid N<sub>2</sub> had no significant effect on oxygen content. In contrast, exposing the wear track to 250 °C in dry air significantly increased O K $\alpha$  at every measurement location. We attribute this increase to chemically bound oxygen (oxidation) since high temperature annealing would encourage desorption of physically bound species.

Interestingly, the unworn areas had much higher oxygen content, averaging 800 counts above the mean (not shown), suggesting that wear normalization does remove a significant amount of oxidation. We propose that the surface was heavily oxidized by exposure to many cycles of annealing. The annealing step had no effect on oxygen content in unworn regions for any environment, suggesting that this is a sort of equilibrium state for temperatures below 250 °C. Annealing to temperatures above 250 °C in air would likely increase oxidation and oxygen content above this limit.

EDS results suggest that the chemistry, particularly oxidation, plays a major role in governing the friction of  $MoS_2$  at high temperature. Third bodies are often equally important to the tribology of solid lubricant systems. We did not observe marked changes in the wear track profile with temperature or sliding. However, the thickness of the transfer film varied significantly with sliding distance, environmental composition, and temperature. Transfer films formed by sliding in dry



Fig. 6 EDS O K $\alpha$  values above the control after annealing in different environments. The control is a wear track on sputtered MoS<sub>2</sub> that was formed in 25 °C N<sub>2</sub>. The control and all three treatment surfaces were exposed to room temperature air for 20 min prior to measurement. EDS measurements were made at 10<sup>-8</sup> torr. Only annealing in dry air caused a significant increase in the oxygen content in the wear track, suggesting that oxygen is more effective than water at oxidizing MoS<sub>2</sub>

air with varied temperature are illustrated in Fig. 7a–d. The film was undetectable after the first 50 cycles at room temperature, but reached a steady-state thickness of ~ 500 nm at 150 °C. For extended sliding distances in dry nitrogen at room temperature, low friction was retained despite thickening of the transfer film from <50 to ~ 150 nm (Fig. 7e); this suggests a lack of direct correspondence between transfer film thickness and friction coefficient. However, sliding at high temperature in dry air did cause significant thickening of the transfer film, while the opposite was observed for humid nitrogen.

#### 4 Discussion

Most generally, this study demonstrates that the friction of  $MoS_2$  exhibits two distinct regimes delineated by a transition temperature. Below the transition temperature, friction is controlled by water; above the transition, friction is controlled by oxygen. These findings are not inconsistent with any of the results in the literature that we know of. Room temperature studies have shown sensitivity to water and not oxygen, while high temperature studies generally show higher friction in air than in inert environments. To our knowledge, there has been no high temperature friction study of  $MoS_2$  to isolate contributions of water and oxygen as a function of temperature.

Our goal here was to better understand why  $MoS_2$  friction responds to environment as it does. A predominant hypothesis is that water, a constituent in air, causes oxidation, which increases inter-lamellar shear strength and friction. Our results in the high temperature regime were consistent with oxidation as the cause of increased friction, but high temperature oxidation was driven by environmental



Fig. 7 a–d Transfer film during variable temperature sliding of the unconditioned coating in dry air. Film coarsening coincides with an increase in friction. e–h Comparison of transfer films at low and high temperatures in dry air and humid nitrogen after 300 sliding cycles

oxygen not water; furthermore, we found evidence that water attenuates frictional sensitivity to temperature in air (Fig. 3). The EDS data showed direct evidence that only oxygen-containing environments cause significant oxidation. This is consistent with the variable temperature friction coefficient measurements in environments containing water and oxygen (Fig. 2). Friction increased with temperature above 100 °C in both oxygen rich environments, but did not increase significantly with temperature in oxygen-deficient environments, even when they contained water. This increase in friction at high temperature in oxygen rich environments coincided with a transition to thick transfer films. While transfer films were generally found to thicken during high friction conditions, increased sliding distances at room temperature in dry air also caused thickening without increasing friction. Additionally, because these films quickly wore away at room temperature to restore low friction, the data suggest that thick films are consequences of the interface conditions and not necessarily the cause of high friction.

Oxidation is an irreversible chemical processes. The high temperature oxidation hypothesis explains the hysteresis of heating and cooling (Fig. 4). The hysteresis is most pronounced at high temperatures and disappears at lower temperatures. Oxides formed at 250 °C remain upon cooling to 150 °C, for example, resulting in elevated friction coefficients compared to those during heating. Heating to 150 °C and then cooling did not cause oxidation, which

resulted in reduced friction during cooling than during heating. In the former, high temperature forms oxides, which increases friction; in the latter, high temperature removes water, which reduces friction. Following oxidation, sliding at lower temperatures physically removes the oxides, and at some point, the rate of removal exceeds the rate of formation; it is around this point that the hysteresis loop closes. The loop width decreases with increased humidity in air, which reinforces the notion that water mitigates high temperature oxidation.

Our results suggest that the transition temperature is associated with the onset of oxidation in oxygen-containing environments. While the magnitude of this transition temperature is extremely important for specifying design thresholds, the reported temperatures in the literature vary over a huge range from 100 °C [24] to more than 450 °C [3]. Within this single study, we found similar variations due entirely to variations in sliding history and coating deposition method (Fig. 5). The variations in the literature likely reflect differences in materials rather than the experimental methods. The transition temperature was unexpectedly found to decrease by 50 % following a thermal sliding cycle (conditioning). This reduction was not observed when the sample was subjected to the thermal cycle alone or the sliding cycle (300 cycles) alone; the results suggest that conditioning requires thermal cycling during tribological contact. We did not observe a transition for the mechanically deposited coating. This is consistent with the literature, where, generally speaking, mechanically deposited coatings have demonstrated higher temperature transitions [3, 25] than sputtered coatings [24]. One key difference between sputtered and powdered  $MoS_2$  is grain size, which can be on the nanoscale in sputtered coatings. We have not studied the mechanism responsible, but finer grain structure would be expected to increase susceptibility to oxidation.

Water increases friction below the transition temperature independent of oxygen content. We found no chemical or tribological evidence that this increase is due to waterinduced oxidation as is often hypothesized in the literature [18]. The first piece of evidence against this hypothesis is the oxidation-mitigating effect of environmental moisture at high temperature (Figs. 3, 4). This effect is best illustrated by Fig. 3b, which shows dramatically reduced friction in the range from 30 to 200 °C for a 10 % humid air environment compared to a dry air environment. This result counters the general notion that dry air produces low friction comparable to vacuum conditions, which is only true at low temperatures. The second piece of evidence is the decrease in friction coefficient with increased temperature below the transition, a result consistent with thermally activated desorption not oxidation. The third comes from EDS measurements, which provided no evidence of oxidation after annealing in humid environments devoid of oxygen.

These observations are consistent with water desorption, which, like oxidation, is thermally activated. Deacon and Goodman proposed that water bonds to edge sites and impedes inter-lamellar shear of  $MoS_2$  [30]. The results of this study are consistent with this hypothesis for the subtransition friction regime. The marked reduction in friction with increased temperature in the vicinity of room temperature suggests physical bonding since chemisorbed water desorbs in the vicinity of 200 °C [33]. This hypothesis also explains why oxygen has no effect on room temperature friction even though it increases the likelihood for oxidation. Native oxides likely form at low temperatures, but their presence does not appear to markedly affect friction, especially after a brief period of run-in. In fact, aggressive oxidation during sliding at 250 °C in air had no adverse effect on the room temperature friction coefficient, presumably because rates of oxidation become uncompetitive with rates of removal at low temperature. We propose that oxides previously observed and suspected to have caused increased friction in humid environments were either native or activated by tribological energy. Similar tribological oxidation effects have been well documented for low-wear polytetrafluoroethylene, an extremely inert material [34]. We propose that water desorbs and friction decreases up to the transition point, when higher friction oxides begin to accumulate on the surface.

# **5** Closing Remarks

- 1. Two distinct frictional regimes were observed for  $MoS_2$  in air. At temperatures below the transition temperature, friction decreased with increased temperature. At temperatures above the transition temperature, friction increased with increased temperature.
- 2. The transition temperature exceeded 100 °C and depended on the nature of the material and the thermal sliding history (ease of oxidation). Coatings of mechanically deposited MoS<sub>2</sub> powder achieved the highest transition temperatures, which exceeded 250 °C. Unconditioned sputtered coatings (unworn) transitioned at 200 °C, while conditioned sputtered coatings (previously worn at 250 °C) transitioned at 100 °C; this reduction required both thermal and tribological energy.
- 3. Below the transition temperature, friction increased with increased moisture whether or not oxygen was present. Above the transition temperature, friction increased with increased oxygen and decreased moisture.
- 4. The results are consistent with the following hypothesis: The frictional sensitivity of  $MoS_2$  to environment at temperatures below the transition is due to water physically bonding to the near-surface and directly impeding inter-lamellar shear. Above the transition temperature, friction increases with environmental oxygen and temperature due to oxidation. Surprisingly, water was found to discourage the transition to high friction at high temperature.

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