CHEMICAL EFFECTS ON MoS₂ LUBRICANT TRANSFER FILM FORMATION – WEAR LIFE IMPLICATIONS

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SUMMARY
The friction and wear properties of sputter-deposited, MoS₂, lubricant films have been studied extensively, but significant questions persist concerning the mechanism of endurance and the effects of test environment. The general mechanism of lubrication is believed to involve the intercrystalline slip of nanometer-sized, platelet crystals, where sliding on the low energy basal surfaces provides for very low friction forces, but the chemical and mechano-physical factors that determine endurance are not understood. The recirculation of lubricant debris and the formation of transfer films are determining factors in establishing wear life. In this work we investigated the influence of test environment on the efficiency of transfer-film formation with emphasis on chemical effects on the bonding of films to steel substrates. We conclude that environmental oxygen provides “bridge” bonding from substrate to lubricant by substitution into the MoS₂ structure resulting in uniform robust films. We surmise that during recirculation of MoS₂ nanocrystals continuous bonding occurs in the oxygen environment but that in the presence of water vapour oxidation can lead to uneven and less-effective films.

Keywords: Solid lubrication, wear-life, transfer films, chemical effects

1 INTRODUCTION
Results of friction, wear, and ball bearing tests of sputter-deposited MoS₂ lubricant coatings exhibit wide performance differences among films and test environments. For most conventional (undoped) films the coefficients of friction (COFs) are increased and the wear lives decreased from optimum values by oxidation of the film material or by testing in a humid environment. [1] Pure MoS₂ films, produced under ultrahigh vacuum conditions and not exposed to air before testing, exhibit the lowest COFs. [2] Introduction of one to two per cent substitutional oxygen into films increases COF, but then additional oxygen substitution decreases COF as long as the original crystal structure is maintained. Ball bearing tests conducted under N₂ at atmospheric pressure (~1 kPa) outlast tests of identically prepared bearings tested in high vacuum (~1x10⁻⁶ Pa) by a factor of 20. [3] Pin-on-disk tests conducted in different atmospheres exhibit maxima in endurance as a function of ambient pressure. [4] Some of the wear life data have been correlated to film microstructure, including density effects; and a model based on recirculation of lubricant debris into the contact zone to provide increased life has been proposed [5].

In this paper we present results of measurements of lubricant transfer-film formation for MoS₂ coatings under different test environments from high vacuum (~1x10⁻⁶ Pa) to one atmosphere of different test gases. The results show that there is chemical specificity among gases for the efficiency of transfer of lubricant from a coated, steel surface to an uncoated pin and on to an uncoated, steel surface. Since these conditions are analogous to those in referenced bearing tests, [3] we use them to explain the wide variation in test life observed.

2 EXPERIMENTAL
A UHV tribometer was used for the experiments reported here. It consists of a pin-on-disk apparatus with the capability of conducting x-ray photoelectron spectroscopy of the pin and/or disk surfaces, upon interruption of the test, while maintaining the specimens under UHV conditions. A schematic diagram of the test configuration is shown in Figure 1. The “pins” consist of 3/16” 440C steel balls. The load on the pin was 0.6 N, and the rotational speed of the 440C-steel disk was 120 rpm, (sliding velocity = ~6.3 cm/s) with the diameter of the pin track being 1 cm. Tests in this tribometer were conducted with variable pressures of residual gases in the chamber.

Disks for the tribometer were masked so that only half of the disk was coated with MoS₂ to evaluate the properties of lubricant-transfer films on the uncoated pins (balls) or the uncoated portions of the disks.[6] A new multiple-target deposition facility was used to prepare films for the UHV tribometer experiments. A single MoS₂ target was used under conditions that produce AT-type films with 2 to 3 at % oxygen substitution. The vacuum chamber for this facility has a base pressure of ~3 x 10⁻⁷ Pa and a load-lock mechanism for substrate entry and removal. As-deposited films had various quantities of substitutional oxygen, but in general the amount was not specifically analysed. For most film batches the degree of oxidation,
crystallinity, and morphology were determined, but not necessarily on the specimens tested.

3 RESULTS AND DISCUSSION

In a typical experiment the COF on the coated portion of the disk is low (0.04 -0.1) while that on the uncoated portion is high (up to 1). Data for the initial twenty cycles of test for three environments are shown in Figure 2. The curves oscillate from relatively low COF in the oxygen containing environment. The minimum values of COF are lowest for the oxygen environment and highest in water vapour, and the approach to a steady-state value requires many more cycles in water vapour. The higher value of COF on the MoS2 coated surface (Figure 2c) may be related to adsorption of H2O on the edge planes of the nanocrystals, but there was no XPS evidence of oxidation to Mo(VI).

The shapes of these traces are indicative of the progression of the transfer-film process. In oxygen from very early in the test (after five cycles) the high-friction peaks become quite sharp and narrow, meaning that only a small portion of the bare-steel side remains uncoated. For the vacuum and water vapour environments (and also in the purified N2) the peaks remain broad for the initial 200 to 500 cycles, showing that transfer is less efficient.

In Figure 3 are shown compressed plots of COF versus number of cycles (running time) for four different test environments; vacuum, purified N2, “standard” N2, and O2.

![Figure 2a: Vacuum](image1)

![Figure 2b: 0.13 Pa Oxygen](image2)

![Figure 2c: 0.13 Pa Water Vapour](image3)

![Figure 3a: COF for ~1.33 x 10^-6 Pa vacuum](image4)

![Figure 3b: COF for Purified N2](image5)

![Figure 3c: Coefficient of friction for “Standard” N2](image6)
Depending on the environment the COF either remains high on the uncoated half of the disk, indicating inefficient lubricant transfer (vacuum and purified N₂), or it is reduced rapidly to a value very near to the initially coated part of the disk (standard N₂ and O₂).

For our high vacuum condition and for purified nitrogen at atmospheric pressure the COF remained high for 600 to 1300 cycles, and when it did decrease it was erratic. For 1 atm (~1 x 10⁵ Pa) “standard” N₂ and for ~1x10⁻¹ Pa O₂ the COF decreased to the nominal values of 0.06 and 0.03, respectively, within 300 to 400 cycles and remained stable for the remainder of the test. (Note: Standard N₂ refers to gas boiled off from a liquid N₂ tank; uncalibrated mass-spectral analysis indicates that it contains very little water but that the oxygen content is in excess of 1 ppm. Purified N₂ came from a lecture bottle and was passed through an Aeronex® getter, supposedly achieving ppb purity.)

XPS results for the wear tracks on the pins and disks showed evidence of a decrease in the sulphur to molybdenum ratios without oxidation to Mo(VI). This observation suggests that oxygen is being substituted into the MoS₂ lattice and that oxidation is not observed. Therefore the Mo(IV) oxidation state is preserved in the MoS₂−Oₓ – type species. Both XPS results and electron micrographs indicated that the transfer films formed in the oxygen environments were very smooth and continuous, while those formed in vacuum or purified nitrogen were clumpy and uneven.

We interpret these results to indicate the rapid and smooth formation of transfer films in molecular oxygen containing environments. We further interpret this relatively efficient transfer-film formation to be due to the effects of oxygen, not water, both intentionally added to the vacuum chamber (at 1x10⁻¹ Pa) and unintentionally present in the “standard” N₂ at about the same partial pressure. We speculate that the oxygen enhances the bonding of the MoS₂ to the uncoated pin and disk surfaces as it is rubbed off of the coated portions of the disks according to the following model. During early rubbing, as shown in Figure 2b, the uncoated steel is abraded to expose elemental Fe (and possibly Cr), and oxygen forms a bridge bond between the Fe and Mo through a sulphur defect in the MoS₂ basal surface. Such bonding provides for smooth, continuous film formation on the initially bare steel, which facilitates low-friction sliding of all contacting surfaces. During additional sliding, some material is worn away from the tracks, but debris can be recaptured as long as surface bonds can be formed. The low COF in oxygen may be due to the smooth, continuous nature of the transfer films formed in this environment.

We also measured transfer-film formation (COF traces) in environments of different pressures of oxygen and water vapour. At a water vapour pressure of approximately 133 Pa the friction trace resembled very closely that shown in Figure 3d for the lower pressure of oxygen. At higher pressures of oxygen the friction decreased to the steady-state value equally rapidly, but the stability of the COF was slightly more erratic with some noise spikes up to values of 0.2. If our model of transfer-film formation is correct, we have no immediate explanation for these high-pressure results for water other than that it must require higher pressures of water vapour to obtain dissociation of the water molecules to form the oxygen bridge bonds. We note that our results appear to be the inverse those of Suzuki [4], who observed maximum endurance lives for lower pressures of water than for oxygen. However, we also note that our operating conditions are substantially less severe; a factor of ten less pin load and 100 times slower sliding speed.

Finally, we submit that these results on the efficiency of lubricant transfer-film formation provide a plausible and consistent explanation of previous results of bearing tests in different atmospheres. [3, 7] Tests conducted in “standard” N₂ exhibited bearing lives up to 20 times longer than tests conducted in vacuum. Our interpretation is that contaminant oxygen in the N₂ test environment provides for effective transfer-film formation on the uncoated balls and retainers that lengthens the bearing life. We are in the process of conducting additional bearing tests in oxygen and purified N₂ environments to verify this conclusion.

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