lose selectively a diamine which has the lower boiling point and (2) the thiocyanates deaminate in considerably lower temperature ranges than the corresponding chlorides, which is parallel to the fact that MSCN have much lower melting points as compared with MCl (M is ammonium or alkali-metal ion). In the next stage, the complexes (II) evolve a diamine (aa) to form transient *cis*-$[CrX_2(aa)_2]X$ (III). Whether or not the transient cis form undergoes isomerization upon further heating is largely dependent upon the combination of members in chelate rings of $(aa)_2$ and the size of the anions (X^-). Table IV shows the relationships between the isomerization of the transient cis form and the combination of members in chelate rings. In the case of X = Cl^-, if the transient cis form has two five-membered or five- and six-membered chelate rings, it does not isomerize, whereas if it contains two six-membered chelate rings, it isomerizes to the trans form, which coincides with the observation that only cis-to-trans isomerization takes place in the bis(diamine) complexes $[CrX_2(\text{tn or ptn})_2]X$ in which tn and ptn form a six-membered chelate ring with chromium(III) ion.[20-22] On the other hand, in the case of X = SCN^-, the transient cis form is considered to isomerize to the trans form in an indeterminably rapid period of time irrespective of the combination of members in the chelate rings probably because of the greater size of SCN^- (1.95 Å) as compared to Cl^- (1.67 Å). The idea is also supported by the fact that $[Cr(tn)_3]Br_3 \cdot H_2O$, which contains Br^- having an intermediate ionic size (1.87 Å), deaminates to form the unstable cis form which extremely rapidly isomerizes to the trans form. Therefore, it may be reasonable to conclude that the combination of members in chelate rings and anion sizes have important effects on the final geometry of the bis(diamine) complexes obtained by the deamination.

Registry No. $[Cr(en)_3]Cl_3$, 14023-00-8; $[Cr(pn)_3]Cl_3$, 14949-95-2; $[Cr(tn)_3]Cl_3$, 17978-78-8; $[Cr(tn)_3]Br_3$, 17631-72-0; $[Cr(en)_3](SCN)_3$, 14176-00-2; $[Cr(pn)_3](SCN)_3$, 22754-50-3; $[Cr(tn)_3](SCN)_3$, 17978-79-9; $[Cr(en)_2(pn)]Cl_3$, 81194-26-5; $[Cr(en)(pn)_2]Cl_3$, 81194-25-4; $[Cr(en)(tn)_2]Cl_3$, 41101-31-9; $[Cr(pn)(tn)_2]Cl_3$, 81194-24-3; $[Cr(en)_2(tn)]Cl_3$, 41101-32-0; $[Cr(pn)_2(tn)]Cl_3$, 81194-23-2; $[Cr(en)_2(pn)](SCN)_3$, 81194-22-1; $[Cr(en)(pn)_2](SCN)_3$, 81194-21-0; $[Cr(en)(tn)_2](SCN)_3$, 81194-20-9; $[Cr(pn)(tn)_2](SCN)_3$, 81194-19-6; $[Cr(en)_2(tn)](SCN)_3$, 81194-09-4; $[Cr(pn)_2(tn)](SCN)_3$, 81194-17-4; $[Cr(en)(pn)(tn)]Cl_3$, 81194-15-2; $[Cr(en)(pn)(tn)](SCN)_3$, 81194-14-1; *cis*-$[CrCl_2(en)_2]Cl$, 14240-29-0; *cis*-$[CrCl_2(pn)_2]Cl$, 18251-59-7; *cis*-$[CrCl_2(tn)_2]Cl$, 17632-36-9; *trans*-$[Cr(NCS)_2(en)_2]SCN$, 15654-67-8; *trans*-$[Cr(NCS)_2(pn)_2]SCN$, 17632-32-5; *trans*-$[Cr(NCS)_2(tn)_2]SCN$, 72982-94-6; *cis*-$[CrCl_2(en)(pn)]Cl$, 71884-67-8; *cis*-$[CrCl_2(en)(tn)]Cl$, 71884-68-9; *cis*-$[CrCl_2(pn)(tn)]Cl$, 81244-80-6; *trans*-$[CrCl_2(en)(pn)]Cl$, 71861-01-3; *trans*-$[CrCl_2(pn)(tn)]Cl$, 71861-02-4; *trans*-$[CrCl_2(en)(tn)]Cl$, 81194-12-9; *trans*-$[Cr(NCS)_2(en)(pn)]SCN$, 81194-11-8; *trans*-$[Cr(NCS)_2(en)(tn)]SCN$, 81205-62-1; *trans*-$[Cr(NCS)_2(pn)(tn)]SCN$, 81255-39-2; *trans*-$[CrCl_2(tn)_2]Cl$, 26186-25-4; *trans*-$[CrBr_2(tn)_2]Br$, 30862-87-4; *cis*-$[CrBr_2(tn)_2]Br$, 18251-60-0; tn·2HCl, 10517-44-9; en·2HCl, 333-18-6.

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Chemistry of Sputtered Molybdenum Disulfide Films

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Radio-frequency- (rf) sputtered molybdenum disulfide films are being used increasingly as lubricants for spacecraft applications. The stoichiometry of such films has been tied to sputtering parameters; however, the change in stoichiometry and chemistry of these films after preparation has not been examined. In this study the room-temperature oxidation of rf-sputtered molybdenum disulfide has been investigated. Films were stored in various environments such as dry air, 100% relative humidity, and vacuum for a minimum of 2 weeks. The chemical states were examined by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Results of XPS analysis of films stored in 100% relative humidity show complete oxidation of Mo(IV) to Mo(VI) at the molybdenum disulfide surface. Both XPS and AES results show that sulfur is removed from the surface when oxidation occurs. The Auger results indicate that sulfur is removed from samples to a depth of at least 45 Å, which indicates that oxidation has occurred at this depth. XPS analysis shows that the retained sulfur is in the form of sulfide or elemental sulfur. There is no oxidation of sulfur to sulfite or sulfate. Wear-test measurements show that oxidation of films causes substantial degradation of the lubricating properties of the films. Also, Auger analyses reveal a degradation of molybdenum disulfide films as a result of wear even for unoxidized films.

I. Introduction

Solid-film lubricants such as molybdenum disulfide (MoS_2) have received much attention in the past decade for spacecraft applications because they maintain their lubricating properties over extreme temperature ranges, high and low bearing velocities, and unidirectional or oscillatory motion and under various loads. Sputtered MoS_2 films ~2000 Å thick have been found to have much longer wear life and better overall performance than films applied by other commonly accepted techniques such as burnishing or electroplating or with the use of binders.[1,2] Although sputtered films offer superior overall lubricating performance compared with that of films prepared by other techniques, the lubricating properties of such films can be greatly altered by varying the sputtering conditions during film preparation.[3-6] Wheeler used photoelectron spectroscopy as a surface diagnostic tool to show that the stoichiometries of films were altered greatly as a result of variation in sputtering conditions.[5] He found that the coefficient of friction increased with a decrease in sulfur in the sputtered films. Much work has been done on the effect of sputtering conditions on the initial chemical and lubricating properties of sputtered MoS_2 films, but no work has been reported on the chemical behavior of these films after preparation (i.e., during storage or use as lubricants). In this paper, we present findings on the room-temperature oxidation of MoS_2 films stored in various environments and on the effects

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[1] Spalvins, T. *ASLE Trans.* **1971**, *14* (4), 267–274.

[2] Ito, T.; Nakajima, K. *Philos. Mag.* [*Part*] *B* **1978**, *37* (6), 773–775.

[3] Christy, R. I.; Ludwig, H. R. *Thin Solid Films* **1979**, *64*, 223–229.

[4] Spalvins, T. *NASA Tech. Memo.* **1978**, *NASA TM-78914*.

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[6] Nishimura, M.; Nosaka, M.; Suzuki, M.; Miyadkawa, Y. *ASLE Proc. Int. Conf. Solid Lubr., 2nd* **1978**, 128.

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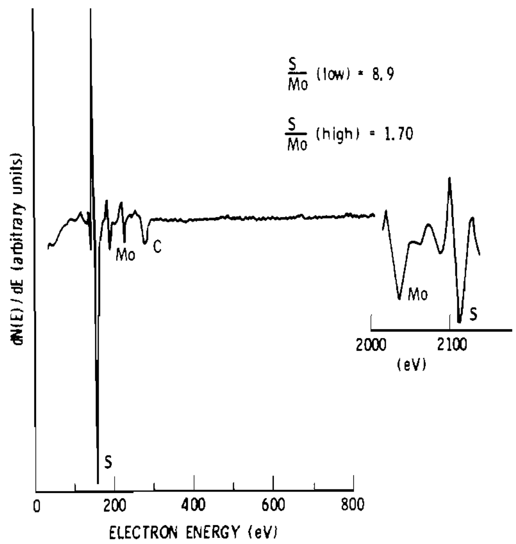

Figure 1. Auger spectrum of MoS_2 powder.

of this oxidation on the lubricating and wear properties on the films. We also report our findings on the spectroscopic examination of wear tracks produced during testing for the purpose of understanding the chemical changes that occur in the films during the wear process.

II. Experimental Section

Films of MoS_2 were prepared with an rf diode sputtering apparatus operating at 2 kW with a frequency of 13.56 MHz at an argon pressure of 1×10^{-2} torr. The sputtering target obtained from the Material Research Corp. was made from hot-pressed MoS_2 powder (99.9 pure); it was 25.4 cm in diameter and was bonded to a copper plate. The specimens to be coated were located 2.54 cm below the target on a grounded block. A 5 kV A dc power supply was used to sputter etch–clean the samples prior to coating. The specimens were coated to a thickness of 2000 Å. Two sets of specimen types were used for film characterization and wear testing. Initial work was performed on films sputtered onto sheets of C1018 steel. Wear-test specimens were made from 440 C steel hardened to Rockwell C-60.

After preparation, films were stored for 2 weeks under various conditions such as vacuum, dry air ($CaSO_4$), and 100% relative humidity. X-ray photolelectron spectra were taken with a GCA/McPherson ESCA-36 spectrometer equipped with an electrostatic analyzer and a position-sensitive detector. The X-ray source was the Mg Kα radiation at 1254 eV. Binding energies were corrected for surface charging by reference to the C 1s peak at 285.0 eV. Auger spectra were taken on a Physical Electronic Industries Model 590 scanning Auger microprobe. Normal operating conditions were as follows: (1) primary beam energy of 5.00 kV, (2) current of 3.0×10^{-6} A, and (3) beam diameter of 3 μm. A powder sample of MoS_2 (ultrapure acid washed) was analyzed by both techniques for reference purposes.

Wear-test measurements were made with samples of the flat-thrust-washer type loaded against each other. The specimens were polished optically flat to a mirror finish. Wear-test measurements were performed at a normal force of 4.5 kg rotating at 40 rpm under a nitrogen atmosphere. A ball-in-socket self-aligning feature of the test machine ensured even contact between specimens during each test. One sample was run immediately after preparation to serve as a calibration point. Wear life was defined arbitrarily as the time to reach an operating torque of 0.8 in. lb after motion was begun.

III. Results

A. Electron Spectroscopy. A representative Auger spectrum of powdered MoS_2 is shown in Figure 1. The main features of the spectrum, which were used in the analyses of these films, are the sulfur *LMM*(*LVV*) and *KLL* peaks at 151 and 2117 eV, respectively, and the molybdenum *MNN* and *LMM* peaks at 186 and 2044 eV, respectively. Figure 2 is an X-ray photoelectron spectrum of MoS_2 powder with the Mo $3d_{5/2}$ peak at a binding energy of 229.4 eV and Mo $3d_{3/2}$ at 232.8 eV. The small shoulder at 227 eV is the sulfur 2s peak, but it is not nearly as useful for distinguishing S^{2-} from SO_x^{2-} as are the peaks in the 160–170 eV region.

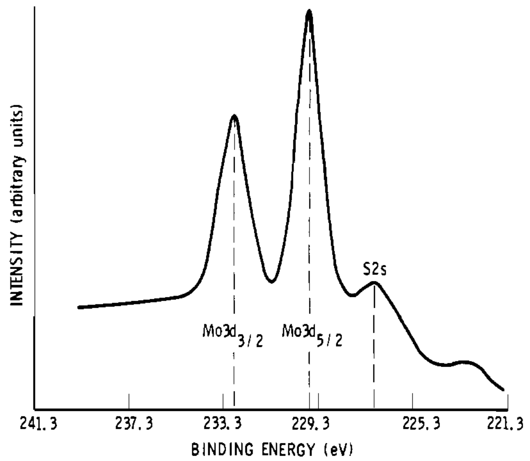

Figure 2. Photoelectron spectrum of MoS_2 powder.

Table I. Inelastic Mean Free Path of Electrons in Inorganic Solids (MoS_2)

element	process	kinetic energy, eV	λ, Å[a]
Mo	ESCA	1020	31
Mo	Auger	186	13
Mo	Auger	2044	43
S	ESCA	1080	32
S	Auger	151	12
S	Auger	2117	44

[a] Based on the expression λ (Å) = $0.96E^{1/2}$.[7]

Our initial findings from the XPS analysis of MoS_2 films stored in humid atmospheres indicated oxidation of molybdenum from +4 to +6 with an accompanying loss of sulfur. The results of Auger analysis of these films also indicated a loss of sulfur with an increase of oxygen. We have assumed on the basis of these observations that the loss of sulfur can be a measure of oxidation, and we have used this assumption to measure the degree and depth of oxidation of MoS_2.

The large energy difference between the sets of Auger electrons of sulfur and molybdenum affords an opportunity to use the resultant difference in the inelastic mean free path (IMFP) of the electrons to measure the sulfur loss (or the oxidation gradient) from the surface and from the bulk. The IMFP of both Auger and X-ray photoelectrons is a function of the kinetic energy of the respective electrons. For example, Auger electrons with energies of 2117 or 2044 eV will escape the surface from a much greater depth (~43 Å) than the 151- or 186-eV electrons (~12 Å). The IMFP values for both Auger and X-ray photoelectrons are provided in Table I. These values were computed from the expression

$$\lambda = 0.96E^{1/2} \qquad (1)$$

which was empirically derived by Seah for inorganic solids;[7] λ is the IMFP in angstrom units for electrons of energy E in eV. The above expression applies to electron energies greater than 150 eV.

The ratios of the peak-to-peak heights for the sulfur and molybdenum Auger spectra (S/Mo at 151/186 and 2117/2044 eV) were used to measure the degree of nonstoichiometry of films and relate this information to oxidation. One must be cautious when using peak-to-peak height as a semiquantitative measure of the elements present because the derivative spectrum is very sensitive to possible peak shape changes and such changes can have a profound effect on peak height in-

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(7) Seah, M. P.; Dench, W. A. *SIA, Surf. Interface Anal.* **1979**, *1*, 2.

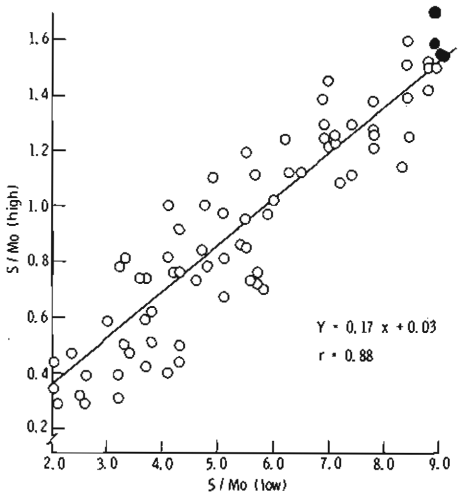


Figure 3. Plot of ratios of Auger peak-to-peak heights of sulfur and molybdenum. *Y* is the S/Mo peak-to-peak height ratio for the high-energy peaks, *X* the low-energy peak ratio, and *r* the correlation coefficient for the linear regression fit to the data.

tensities. Such chemical shifts have not been observed for molybdenum but have been observed for sulfur.[13] We have carefully examined chemical shifts in MoS_2 and have found that the effects of such shifts on the peak height intensities were much less than the uncertainty in measuring peak-to-peak heights. This technique of using intensity ratios at the appropriate energies, which is in effect using molybdenum as an internal standard, permits elimination of surface and instrumental effects that normally contribute to large uncertainties in Auger measurements. Because the energies of sulfur and molybdenum are closely matched, any surface anomalies will affect each peak nearly equally. The peak-to-peak height ratios (S/Mo) for MoS_2 powder are 8.9 and 1.7 for the low- and high-energy electrons, respectively. There is an 8% difference in IMFP for the 151-eV sulfur and the 186-eV molybdenum Auger electrons; therefore, the measured ratio is 8% lower than the actual ratio, because the sampling volume is larger for molybdenum. This variation will not affect our results since we are observing changes in the ratio. The preceding ratios are close to what is expected for stoichiometric MoS_2.

A plot of the high-energy S/Mo peak ratio against the low-energy peak ratio was made to provide some understanding as to the extent of change in the stoichiometry of the sample surface, as compared with the composition of the bulk. Since we have found that a loss of sulfur indicates oxidation, the plot would also indicate the extent of surface and bulk oxidation. Figure 3 is such a plot made from the results of many measurements of various samples stored under vacuum and in ambient air, dry air, and humid air for arbitrary time periods. Data for samples of films that are stoichiometric (that is, MoS_2 indicated by dark circles) will be located at the upper right of the plot, whereas data for nonstoichiometric (sulfur-deficient) films will tend to fall along the curve to the lower left. The correlation coefficient *r* computed from a linear regression of the data indicates that surface oxidation does not occur without simultaneous bulk oxidation. This observation is confirmed by XPS measurements, which show no MoS_2 for oxidized samples to a depth of λ (31 Å).

The possibility of beam damage to the surface was carefully examined by stepping the electron beam across the surface and monitoring for instantaneous changes in the oxygen signal. We found about a 10–15% reduction in the oxygen signal, which would make the apparent oxygen concentration less than what is actually present on the surface. We conclude that the desorbed oxygen is removed from the surface and not from the bulk. These findings were corroborated by the XPS results.

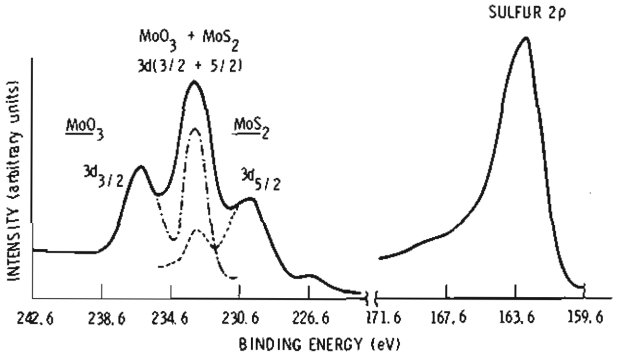
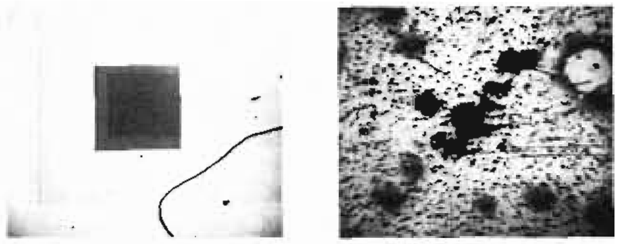


Figure 4. Photoelectron spectrum showing molybdenum and sulfur peaks for films exposed to laboratory environment (30–40% relative humidity).


AH11B
61 X

WH11B
61 X

Figure 5. Moisture effects on film structure (dark square in left photo is an electron beam effect from high-magnification photos; the secondary electron yield but not the Auger yield was changed in this region).

Additional chemical information was obtained from the photoelectron spectra of MoS_2 samples. Films prepared by rf sputtering were partially oxidized when stored for 1 week or more in room air, as shown by the spectrum of Figure 4. The spectrum is a composite of two underlying spectra: one attributed to MoS_2 and the other to a Mo(VI) compound, which is probably MoO_3. The peak at a binding energy of 230.0 eV is the Mo $3d_{5/2}$ electron of MoS_2. The peak at a binding energy of 235.5 eV is the Mo $3d_{3/2}$ electron of MoO_3. The large central peak is a combination of the Mo $3d_{3/2}$ of the sulfide and Mo $3d_{5/2}$ of the oxide.[8] The relative positions of the oxide and sulfide are indicated by the dashed lines under the main spectrum. Clearly, the film surface has been partially oxidized.

Examination of the sulfur 2p region (160–170 eV) of the photoelectron spectrum (Figure 4) shows a slight shift to higher binding energy and a moderate broadening of the S^{2-} peak. There is no evidence for sulfite or sulfate peaks, indicating that the Mo(IV) and not the S^{2-} is the primary reductant in the surface oxidation process.

B. MoS_2 Film Chemistry. Water vapor is known to accelerate the oxidation of MoS_2 power.[9] So that the mode and mechanism of oxidation of the thin film might be understood, samples were stored in different environments: 100% relative humidity, dry air, ($CaSO_4$), and vacuum ($\sim$1 torr) for a 2-week period. Two electron micrographs of identical samples stored in extreme environments are shown in Figure 5. The left photograph is a specimen stored in dry air, and the right photograph is a specimen stored in 100% relative humidity. Sample WH11B from the humid atmosphere shows the formation of particles and a considerable roughening of the

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(8) "Handbook of X-ray Photoelectron Spectroscopy"; Perkin-Elmer Corp., Physical Electronic Division: Eden Prairie, MN, 1979.

(9) Ross, S.; Sussman, A. *J. Phys. Chem.* **1955**, *59*, 889.

(10) King, D. A.; Tompkins, F. C. *Trans. Faraday Soc.* **1968**, *64*, 496.

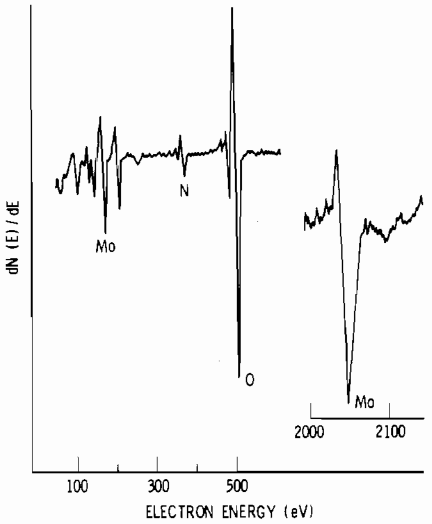

Figure 6. Auger spectrum of a particle on WH11B.

Table II. Auger Results of Oxidized Films

sample	location	S/Mo low energy	S/Mo high energy
WH11B	plane area	2.6	0.39
WH11B	particle	0.7	0.08
WH11B	plane area	2.5	0.32
WH11B[a]	particle	...	...
AH11B		6.0	

[a] No sulfur found on this particle.

surface compared with that of the sample stored dry. Figure 6 is an Auger spectrum of a particle on the surface of the reacted sample (right photograph of Figure 5). The high-energy sulfur peak is not present, indicating a complete loss of sulfur to depth of ~43 Å. The particle appears to be MoO_3 with some nitrogen present. (We have found that all oxidized films contain nitrogen.) The analyses of films stored in different environments indicate that the presence of water vapor accelerates or catalyzes the oxidation of MoS_2 films at room temperature.

The results of Auger analyses of particles and areas adjacent to particles are tabulated in Table II. The areas adjacent to particles indicate relatively low S/Mo ratios for low- and high-energy peaks, which indicate a decrease in sulfur concentration with oxidation. The results of Auger analysis of samples stored in dry air (AH11B) provide a low-energy S/Mo peak ratio of 6.0. This ratio is somewhat lower than the expected value of approximately 8.9. The reduced value may be a result of the sputtering process that is used to prepare the films. The XPS spectrum of AH11B did not indicate any oxidation. We have observed significant variations in the S/Mo ratios for sputtered films, and future work will be directed toward determining the extent to which sputtering parameters affect film stoichiometry.

Table III. Auger Peak Ratios and Wear Data for MoS_2 Films

sample	storage	S/Mo low energy	S/Mo high energy	wear life, h[a,b]
WT-1	immediate	7.7	1.26	4.26
WT-2	2 weeks under vacuum	8.9	1.3	2.2
WT-3	2 weeks under vacuum	7.9	1.29	5.6
WT-4	2 weeks 100% RH	3.1	0.32	0.1
WT-5	2 weeks 100% RH	3.4	0.44	0.1
bulk MoS_2		8.9	1.7	

[a] Test conditions: (1) 10 lb (4.5 kg) normal force, (2) 40 rpm. [b] Wear life defined as time to reach an operating torque of 0.8 in. lb.

Table IV. Sulfur 2p Photoelectron Results

sample	energy, eV	fwhm, eV	sample	energy, eV	fwhm, eV
MoS_2 (powder)	162.6	2.2	WT-2	162.8	2.7
AH11B	162.8	2.7	WT-5	164.0	3.8
WH11B	163.5	3.3			

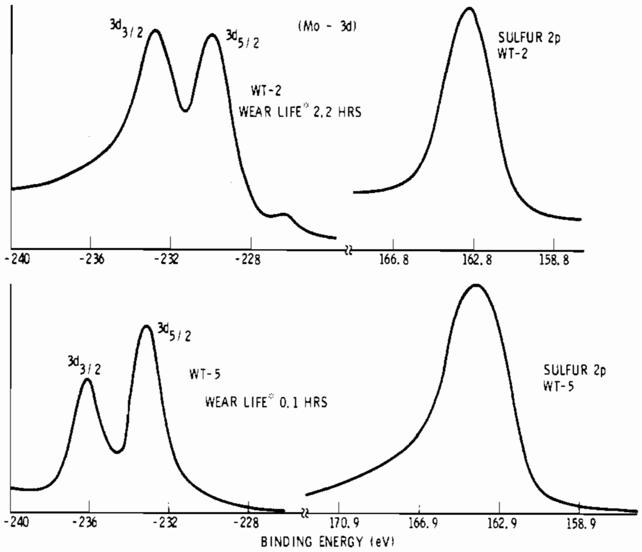

Figure 7. Photoelectron spectra of wear-test specimens: peak heights in arbitrary units, scale expansion of 5× for sulfur peaks of WT-5. See Table III for a definition of conditions.

C. Wear Properties of Films. The effect of film oxidation on wear life was measured after storage under vacuum and in 100% relative humidity. Wear-life measurements for samples stored in different environments are given in Table III. Sample WT-1 was run immediately after preparation and served as our standard. The results of wear-test measurements indicate that films stored in 100% relative humidity had dramatically lower wear life than films stored under vacuum. Variations in wear life for WT-1, -2, and -3 are indicative of the uncertainty in the measurements. WT-2 possessed a surface imperfection that shortened this film's wear life. The photoelectron spectrum of wear-test specimen WT-5 (Figure 7) indicates complete oxidation of Mo on the surface. In contrast, the photoelectron spectrum of WT-2 indicates very little or no oxide present, although the ratio of peak heights for the Mo 3d multiplets in WT-2 is not in the correct proportion for Mo $3d_{3/2}$ and $3d_{5/2}$ electrons. The ratio should be 4/6 or 2/3, which is not the case. The relatively large $^3/_2$ peak and the slight broadening of the peak on the high-binding-energy side may be indicative of the presence of some other oxidation states of molybdenum. The relative height and position of Mo peaks in WT-5 are what would be expected for MoO_3.

The photoelectron sulfur peaks indicate a decrease in surface sulfur concentration with a 0.6-eV shift of the peak to a higher binding energy and a 1.0-eV broadening of the peak. The intensity of the sulfur peak for WT-5 in Figure 7 has been expanded by a factor of 5 for illustrative purposes. The shift to a higher binding energy and broadening suggest that some form of oxidation of sulfur had occurred, but again the spectra do not indicate any sulfates or sulfites to be present on the surface. Atkinson and Swift, in studies on the tribochemical oxidation of MoS_2, found that some S^0 and S^{4+} species were

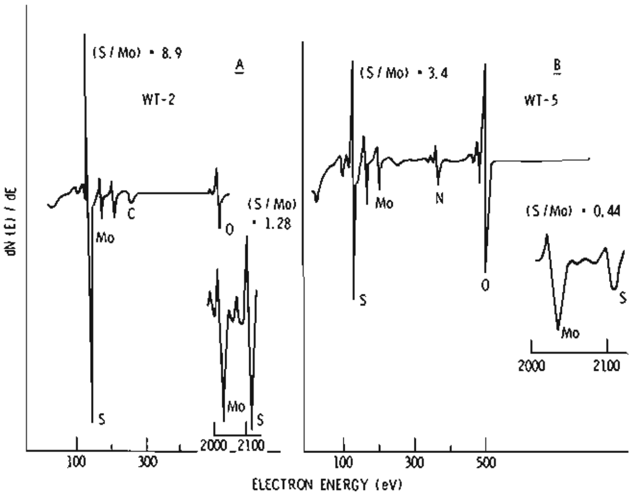

Figure 8. Auger spectra of wear-test specimens.

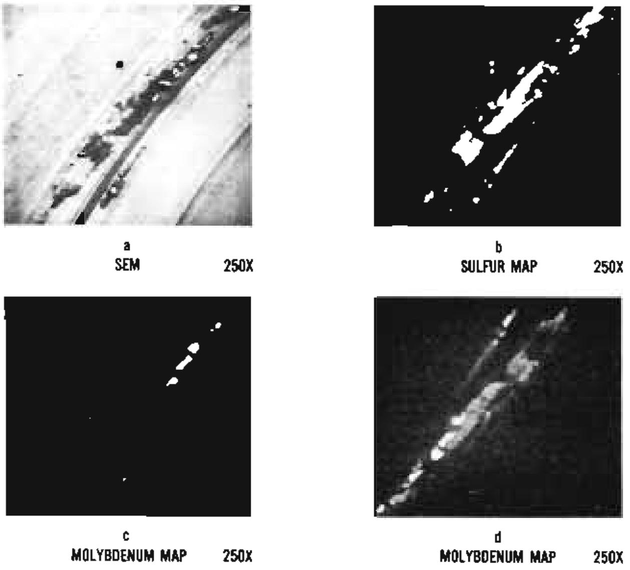

Figure 9. Wear track of WT-2: (a) SEM, (b) sulfur map, (c) molybdenum map, (d) molybdenum map, reduced contrast.

present in oxidized powders.[11] S^0 species broaden the photoelectron peak of S^{2-}.

The results of Auger analyses of films (Figure 8) also indicate a considerable difference in their composition. WT-2 has S/Mo peak ratios of 8.9 and 1.3, which are close to those of stoichiometric MoS_2. In contrast, the S/Mo ratios for WT-5 were 3.4 and 0.44, respectively. The fact that both the high- and the low-energy peak ratios are reduced indicates that oxidation has taken place below the first layer and beyond a depth of 45 Å. One interesting feature of the Auger spectrum of oxidized samples is the presence of nitrogen in relatively high concentration.

Wear data for the samples stored in different environments indicate that oxidation definitely and substantially degrades the lubricating properties of the sputter-deposited films. It is, however, also interesting to understand any chemistry involved in the wear process of good or unoxidized films. For this purpose the wear tracks of samples WT-1, -2, and -3 were examined with the scanning Auger microprobe. A scanning electron microscope (SEM) micrograph of the wear track of WT-2 is shown in Figure 9, which reveals a heavily scarred area with particles in the track. Detailed Auger analysis of the particles in this area indicates that they are composed of solid molybdenum with a trace of sulfur (Figure 9c). The dark areas adjacent to the particles appear to be remnants of the original MoS_2 film as indicated by their Auger spectrum, Figure 10A. Auger elemental maps of sulfur and molybdenum (Figure 9) indicate that the elements have segregated during the wear process.

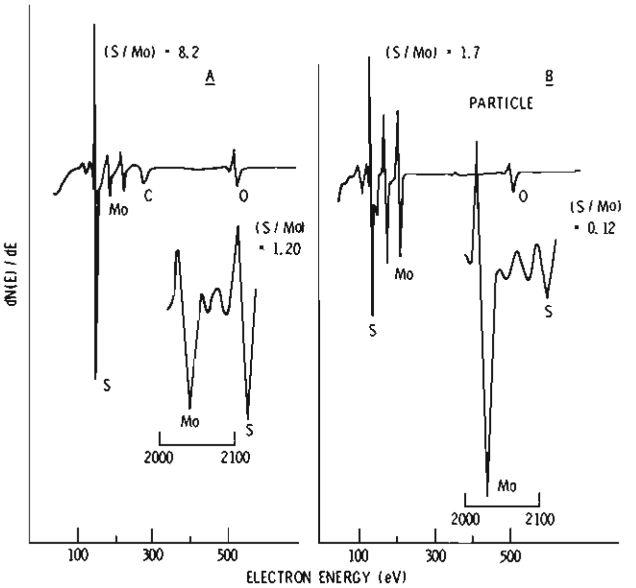

Figure 10. Auger spectra of regions in the wear track of sample WT-2: (A) spectrum of dark area adjacent to particle (see Figure 9); (B) spectrum of particle within the track.

IV. Discussion

A. MoS_2 Film Chemistry. Oxidation of MoS_2 films prepared by rf sputtering occurs readily at room temperature, at ambient relative humidity (25–35%), and it is accelerated considerably at 100% relative humidity. X-ray photoelectron spectra of film surfaces clearly indicate the formation of oxidized molybdenum, i.e., Mo(VI), and only minor changes in the sulfur. There is no evidence of any sulfite or sulfate on the film surface. The slight shift in binding energy and broadening of the sulfur peak could well be caused by the increased electrophilicity of the Mo(VI) compared with that of the Mo(IV) ions. Auger electron spectroscopy indicates that a substantial decrease in the sulfur to molybdenum ratio, both at the outermost surface and to a depth up to 50 Å within the film, accompanies the oxidation process. Electron micrographs show that the oxidized surface is very rough and sparsely covered with particles of MoO_3.

These results are similar in some respects but also different from results reported for the oxidation of MoS_2 powder.[9] In both cases, humidity accelerates the reaction; in fact little if any oxidation occurs on sputtered films at room temperature in the absence of water (vapor). Oxidation of the powder requires temperature in excess of 80 °C and results in the formation of some sulfate although oxide is apparently also formed.[9] It is reported that oxidation of the powder occurred on the outermost layer of the MoS_2 and that the resulting oxide protected the underlying layers from further reaction. In contrast to these reports, we find that oxidation of the thin films penetrates well below the outermost MoS_2 layer, as demonstrated by the reduction in the S/Mo peak height ratios at high energy. The surface defined in ref 9 may in fact be different from our surface,[9] which was defined on the basis of IMFP of electrons in Auger and X-ray photoelectron studies.

These results concerning the oxidation of MoS_2 films, specifically the necessity for water vapor and the loss of sulfur during reaction, can be explained by assuming the formation

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(11) Atkinson, I. B.; Swift, P. *Wear* **1974**, *29*, 129.

of H_2S according to the reaction

$$MoS_2 + {}^1/{}_2O_2 + 2H_2O \rightarrow MoO_3 + 2H_2S\uparrow \qquad \Delta G^\circ = -68.7 \text{ kcal mol}^{-1} \tag{2}$$

Such a reaction is consistent with the observed absence of any surface sulfates and is not without precedence in the literature. Salomon et al. have observed the formation of H_2S during wear tests on dry MoS_2 powders in humid atmosphere.[12] They found that moisture must be present for mechanochemical oxidation to occur and that powders that were run in dry air did not degrade. Their results are somewhat different from our findings because we observed oxidation during storage and not as a result of mechanochemical oxidation. Oxidation of MoS_2 powder films was also observed by Atkinson and Swift during tribochemical oxidation studies. Their photoelectron studies indicate that molybdenum was oxidized to MoO_3 and that sulfur was oxidized from S^{2-} to S^0 and S^{4+}. Note that their samples were prepared in air at 85% relative humidity and wear tested in humid atmospheres. These authors state that during high-temperature oxidation studies (nonwear) of MoS_2, no S^0 or S^{4+} was observed and that the formation of elemental sulfur may be humidity dependent. The formation of elemental sulfur may explain the slight broadening of the sulfur peak in our photoelectron spectra.

One observation that is not consistent with this reaction is that nitrogen is detected by Auger spectroscopy on all oxidized surfaces. The dissociative adsorption of N_2 on molybdenum metal is known,[10] but we are unaware of any reports of adsorption on or reaction with MoS_2, MoO_3, or any intermediates. Unfortunately, it is impossible to identify the oxidation states of surface nitrogen by means of the X-ray photoelectron spectrum because of interference with the molybdenum 3p electron peaks. The Auger peak height for N does not appear to scale with either that for oxygen or that for sulfur (compare Figures 6 and 8), which suggests that the N is simply adsorbed nitrogen on the oxidized surface.

B. Lubricating Properties of Films. The lubricating properties of layer lattice compounds such as MoS_2 depend on the facile slippage of intracrystalline planes that are composed of, for example, alternating molybdenum and sulfur layers. Planes of sulfur slide past each other, and any process such as adsorption of water or oxidation disrupts the planar structure and inhibits sliding. The net result is an increase in the coefficient of friction for MoS_2-lubricated surfaces. As the oxidation process progresses, the lubricating properties of the films further degrade. It is also known that changes in Mo–S stoichiometry independent of oxidation such as changes caused by MoS_2 decomposition change the effectiveness of the lubricant; the coefficient of friction increases as the S/Mo ratio decreases.[4,5]

Auger electron spectroscopy is an effective analytical tool for determining the degree of sulfur loss from MoS_2 films and for predicting the effectiveness of the films as lubricants. Plots such as that in Figure 3 can be used to determine film stoichiometry both at the immediate surface and to a depth of approximately 50 Å. We have not yet established a quantitative relationship between, for example, wear life or coefficient of friction and position on the line in Figure 3. However, we can have confidence in our conclusion concerning the minimum depth of oxidation. If oxidation and the resultant loss of sulfur were confined to the outer 12–13 Å of MoS_2 film, a drop in the high-energy S/Mo peak ratio of about 27% would be observed corresponding to the ratio of the respective escape depths for the low- and high-energy Auger electrons. Consequently, the slope and intercept of the line in Figure 3 would be 0.045 and 1.05, respectively, compared with the observed values of 0.17 and 0.03. The steepness of the line through our data constitutes verification of relatively deep oxidation of the film. Unquestionably, the oxidation of MoS_2 films results in poor lubricating properties, increased friction, and reduced wear life.

Although we are reporting bulk observations based on a 43-Å IMFP for the high-energy S and Mo Auger electrons, we are in fact sampling these elements well below their respective IMFP in these solids.[14] This is illustrated by considering the equation for attenuation of electrons by an overlayer

$$n = n_0 \exp(-Z/\lambda \cos \theta) \tag{3}$$

where n_0 is the total Auger current produced, Z is the overlayer thickness, λ is the IMFP, and θ is the acceptance angle of the electron analyzer. Since a signal of $n/n_0 \leq 0.01$ is easily detectable, a layer thickness that will produce $n/n_0 = 0.01$ will be

$$Z = -\lambda \cos \theta \ln 0.01 \tag{4}$$

or

$$Z = 3.4\lambda \tag{5}$$

Therefore Z will be ~144 Å for S and Mo high-energy electrons. These numbers indicate that we are observing a reduction in the sulfur signal well into the bulk.

The wear process of unoxidized films appears to involve the decomposition of MoS_2 during the sliding motion of the interacting parts. We conclude that the heat generated during such motion is enough to degrade the film and reduce the MoS_2 film to Mo metal. The wear track in Figure 9 shows the presence of Mo particles that were produced during the wear process. Once the particles were formed, the films would be destroyed by the abrasive action of the particles and wear would be further accelerated. Extensive examination of the wear tracks in other wear-test specimens also reveals a reduced S/Mo ratio. The wear process must involve the removal of sulfur with subsequent formation of molybdenum-enriched films. Once the stoichiometry of the film is altered, the alternating planes of sulfur and molybdenum atoms do not slide past each other as effectively, and friction increases. The increase in friction produces more heat that breaks sulfur and molybdenum bonds. Future work will be directed toward understanding the wear process and the prevention of film breakdown.

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