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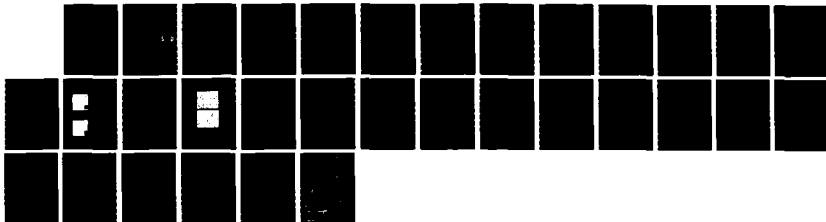
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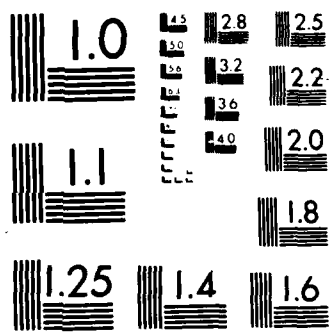
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The Influence of Surface Chemistry on MoS₂ Transfer Film Formation

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25 July 1986

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<p>A variety of MoS₂ films having different initial surface compositions and different degrees of reaction in oxidizing atmospheres have been prepared by sputter deposition onto 440 C steel substrates. The compositions of these films, including their degree of oxidation and their molybdenum-sulfur stoichiometry, have been determined by x-ray photoelectron and Auger electron spectroscopy immediately before the films were subjected to sliding wear tests. These tests, which used an in-house, "ring-on-disk" apparatus operating in an inert atmosphere, involved rubbing coated specimens against</p>								

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20. ABSTRACT (Continued)

Initially uncoated, polished 440 C steel countersurfaces. Films that had approximately 30 to 40% of their surface layers oxidized to MoO_3 gave the best wear results. In addition, the presence of elemental sulfur in the film surface layers appears to enhance wear life. These data are interpreted to mean that much better adhesion between the transfer film and the initially bare steel surface is obtained through chemical bonding of the transferred MoS_2 when its surface layers are disrupted by chemical modification. Keywords: Solid Lubrication

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PREFACE

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I. INTRODUCTION

Solid lubricant films of MoS_2 are prepared by numerous procedures that include burnishing the powder onto appropriate surfaces, bonding it with polymeric or inorganic hosts, sputter depositing it, and transferring the lubricant from a matrix (e.g., a bearing retainer) onto the contacting surfaces during their operation. In all applications the adhesion of the lubricant to the substrate surface is an important parameter in determining the performance, in particular the wear life, of the system. In a previous study of MoS_2 films, we proposed that the best lubrication performance would be obtained for layered solid lubricants if the basal planes of the lubricant crystallites were oriented parallel with the plane of the substrate.¹ Such orientation would be facilitated by the formation of chemical bonds between the substrate and the chalcogen atoms within the basal plane of the lubricant.

The low friction of certain layered transition-metal dichalcogenide (LTMD) materials is commonly believed to result from the fact that only Van der Waals forces hold the layers of the crystals together, leaving these layers to slide easily across each other. However, low friction is not sufficient to make a thin solid film a good lubricant. As already mentioned, the film must adhere to the contacting surfaces so that it will remain in the contact zone for the longest possible time. The low-shear planes of LTMDs are the same basal planes that we propose must be chemically bonded to their appropriate substrates if they are to adhere well to those substrates. Therefore, if one accepts the premise that good adhesion promotes good lubrication performance and that chemical bonds improve adhesion, there appears to be a contradiction between good adhesion and low friction.

Experimental results are presented in this report that relate lubricant-substrate interfacial chemistry to the wear properties (lifetimes) of MoS_2 transfer films (i.e., films formed on initially bare steel after the steel is rubbed with a coated countersurface). On the basis of these results, a model is presented that attributes friction behavior to bulk film properties and film adhesion to interfacial chemical interactions. Furthermore, for films

thicker than a few tens of nanometers it is suggested that the strength of adhesion can be altered independently of the value of the coefficient of friction, and that this adhesive strength is the primary determinant of wear lifetime for nominally pure MoS₂-type films.

II. EXPERIMENTAL PROCEDURE

Films of MoS_2 were prepared by rf sputtering onto polished 440 C stainless-steel substrates according to procedures described previously.¹⁻³ Some of the sputtered films were prepared with the substrate table intentionally heated to a temperature of approximately 230°C, while other films were prepared with the substrates initially at ambient temperature, although the temperature can get as high as 70°C during deposition. Films were also stored in air atmospheres of different relative humidity to achieve varying degrees of oxidation of their surfaces.²⁻⁴

Wear measurements were made with a test fixture that was designed and constructed in-house (Fig. 1). For all measurements the entire apparatus, including the sample, was within a closed chamber that was flushed with prepurified, extra-dry nitrogen gas. A gas purge of approximately 30 min was used before the sliding motion was initiated. Desiccant was contained inside the chamber and a relative humidity gauge read 0% after purging. The dead-weight load on the samples was 3.18 kg, and the speed of rotation was 123 rpm (for a mean sliding velocity of 33 mm/s). The area of contact between the rider and the stationary member was approximately 45.2 mm². This large contact area was used in order to provide a wear track larger than the x-ray photoelectron spectrometer (XPS) analysis beam. The wear measurements were made with the rotating member initially coated with the appropriate " MoS_2 " film and the stationary countersurface initially bare, polished 440 C steel (final polishing grit was 300 nm alumina). Strip-chart recorder traces of the output from the load cell (reaction torque) were obtained, and failure was defined as the point at which the torque exceeded approximately 0.07 N m.

Auger electron spectroscopy (AES) was performed with a Perkin-Elmer PHI model 590 scanning Auger microprobe, using the same operating conditions as previously described.² X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA-36 spectrometer that has been described in detail.³

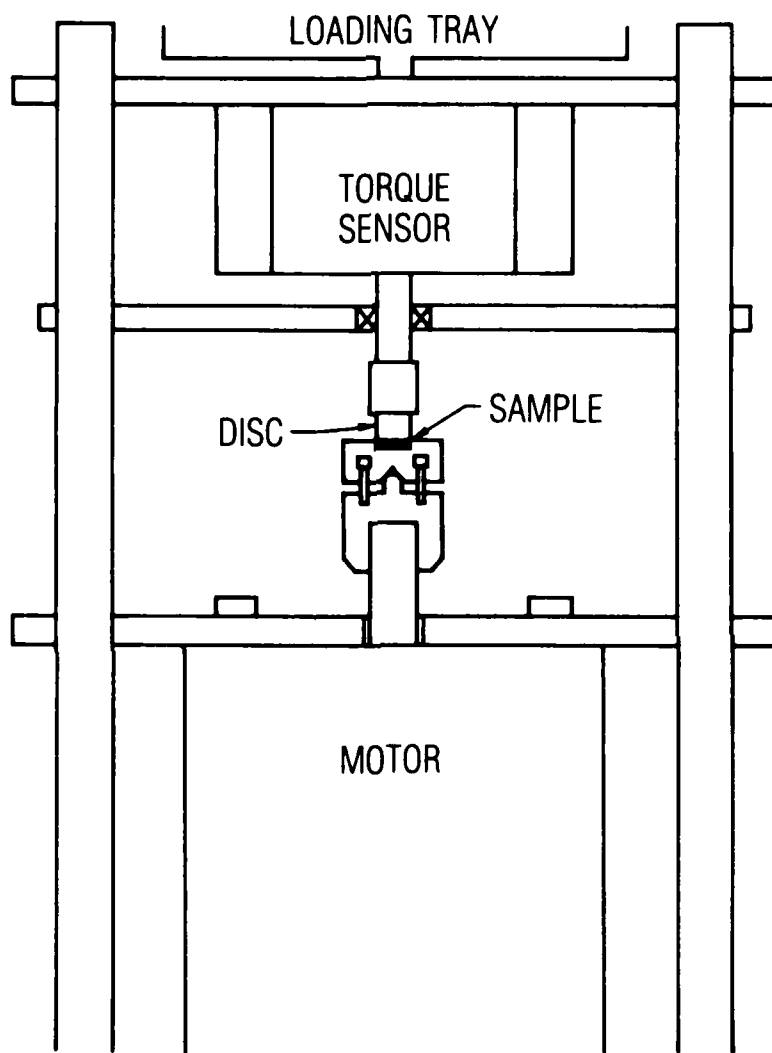


Fig. 1. Sliding Wear Test Apparatus

III. SURFACE CHEMICAL CHARACTERIZATION

A. CRYSTALLITE ORIENTATION

Typical XPS and AES spectra of MoS_2 are shown in Fig. 2. The interpretation of similar spectra for MoS_2 films after storage in various environments for various time periods has provided a basic framework of information on the films' chemistries, structures, and oxidation reactivities, as well as on the relationship of these properties to the films' wear behavior under sliding loads. These spectroscopic results have shown that sputtered films can be produced with two fundamentally different crystallite orientations that have drastically different oxidative reactivities and significantly different wear lifetimes.¹

XPS measurements at various angles of emission from the film surfaces, combined with electron scattering calculations on the XPS and AES data, showed that, under controlled relative humidity, one type of film is oxidized deeply into its bulk regions, while the second type reacts only within the outer two or three surface layers.^{3,4} These results are summarized in Fig. 3, which is a combination of electron microscope results and a schematic interpretation of both the micrographs and the electron spectroscopy results.

For Type I films, if the crystallites are oriented in the same direction as the particles shown in the micrographs, then their basal planes are random to the surface plane; the Type II films, on the other hand, have coplanar orientation. It was proposed that the planar orientation of lubricant film crystallites on substrate surfaces would provide optimum lubrication performance; however, it is not sufficient for only the outer film layers to be oriented as in a burnishing experiment. The orientation of the lubricant layers must extend from the initial film-substrate interface throughout the entire bulk film structure.¹

B. CRYSTALLITE SIZE

A problem with the interpretation of the results for Type I and Type II films has been our lack of understanding of the specific preparation condi-

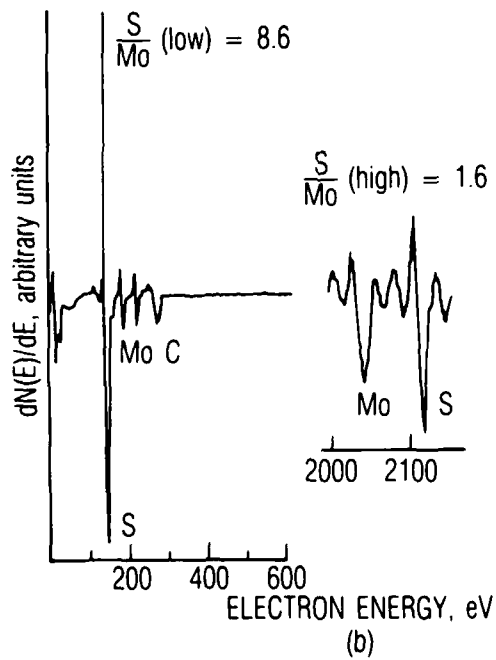
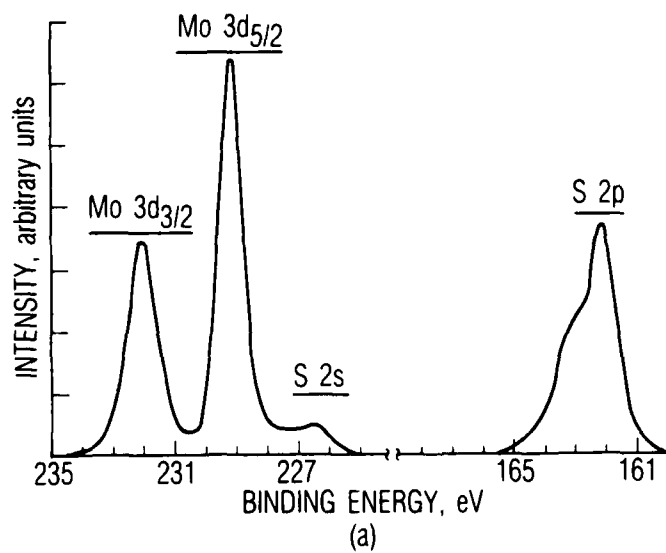
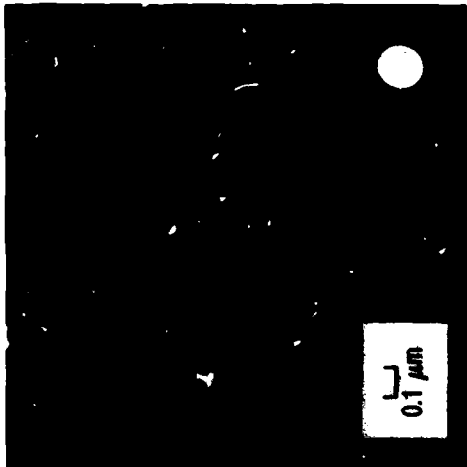
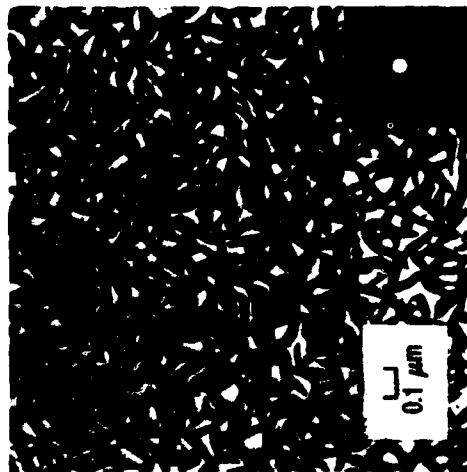
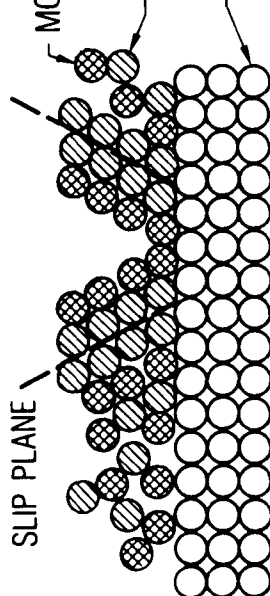


Fig. 2. X-Ray Photoelectron and Auger Electron Spectra of Molybdenite Crystal

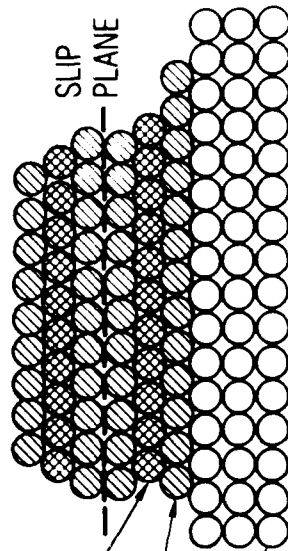
TOP VIEW



SIDE VIEW



TYPE I FILMS HAVE SLIP PLANES RANDOMLY ORIENTED WITH RESPECT TO THE SURFACE, ALLOWING PENETRATION OF ENVIRONMENTAL ELEMENTS AND DEGRADATION OF THE FILMS.



TYPE II FILMS HAVE SLIP PLANES ORIENTED PARALLEL TO THE SURFACE, PROVIDING GOOD LUBRICATION AND RESISTANCE TO ENVIRONMENTAL ATTACK.

Fig. 3. Crystallite Orientation of Sputtered MoS₂ Films

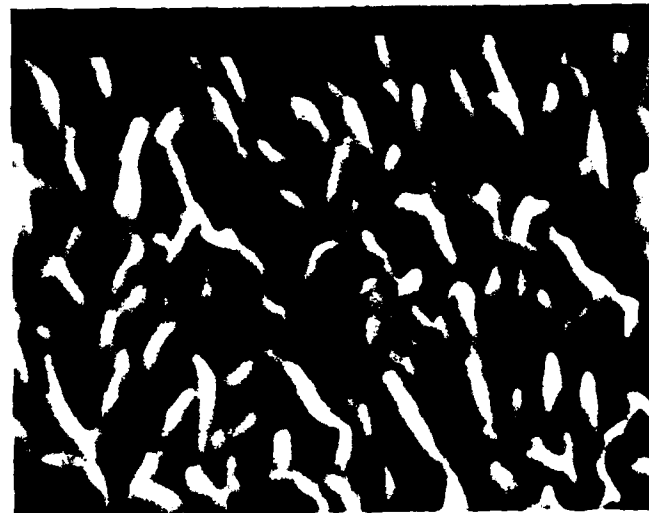
tions that produce each film type. Recent results on film composition, morphology, and reactivity as a function of substrate temperature during deposition provide some insight into this question. They show that the previous observations for different film types may have been the result of inadvertent deposition at different temperatures. Figure 4 shows scanning electron micrographs of films deposited with the substrates at ambient or elevated temperatures. The particles in the films deposited at high temperature are in the form of large platelets having a relatively high ratio of face to edge area, while those for the room-temperature films are much smaller platelets or more needle-like particles.

Typical XPS spectra for ambient and high-temperature films are shown in Fig. 5; they show that the films prepared at different temperatures also have substantially different surface compositions and reactivities. Those prepared at high temperature have compositions much closer to that of molybdenite crystals and are oxidized to a much lesser extent in humid atmospheres than are the lower-temperature films. For the high-temperature films, both the molybdenum and sulfur peaks are well resolved and "clean," like those of the crystal. Conversely, the Mo and S peaks of the room-temperature films are broad and poorly resolved, and they show substantial oxidation to MoO_3 upon storage at 84% relative humidity.

The large platelets in the high-temperature films are not oriented with their faces parallel to the substrate as were the Type II films, but the differences in reactivity between room-temperature and high-temperature films are similar to the differences between Type I and Type II films. These reactivity differences may be attributed to particle (crystallite) size differences, or more specifically to differences in the relative surface-area ratios (i.e., face to edge areas) independent of orientation with respect to the substrate, although crystallite orientation is still a significant variable with regard to lubrication performance.

C. SULFUR PEAK-SHAPE CHANGES

Changes in the XPS peaks during oxidation are greater for Mo and hence easier to resolve, but those for S may be equally important. The S peaks for



A



B

Fig. 4. Scanning Electron Micrographs for Films Deposited by rf Sputtering onto 440 C Steel Substrates at (a) Ambient and (b) Elevated (220°C) temperature

the molybdenite crystal (Fig. 2) and those for the high-temperature films consist of a partially resolved doublet ($2p_{3/2}$, $2p_{1/2}$) that is a primary peak with a lower-intensity shoulder on the high-binding-energy side. The splitting of this doublet would be from 1 to 1.5 eV if it were resolved. As shown in Fig. 5, the S peak for the room-temperature films is more symmetrical, with the peak maximum shifted slightly toward higher binding energy. Upon oxidation there is very little change in the peaks (Mo or S) for the high-temperature films, but there are measurable shifts in both sets of peaks for the low-temperature films.

The broadening of the S peak is probably due to the formation of sulfur species other than S^{2-} in MoS_2 . It could represent a difference in the bonding environment between basal-plane S and edge-plane S, but we think it is more likely due to elemental sulfur or polysulfide ions formed in the two-electron oxidation of S^{2-} from MoS_2 .

Figure 6 shows a graphical procedure we have used to evaluate the extent of change in the S peaks. The measured S peak is divided by first drawing a vertical line at the binding energy corresponding to the peak maximum and then a horizontal line representing the full width at half maximum. The "peak shape factor" is then calculated as shown in the figure. The larger the value of the peak shape factor, the greater is the contribution to the total peak made by the oxidized S species (presumably elemental sulfur or S_n^{2-}).

Figure 7 shows a plot of this peak shape factor for a number of different films versus the fraction of molybdenum disulfide (compared to molybdenum trioxide) in the films. The various points in this plot are for films that were stored for various lengths of time under the conditions specified. The general trend in the plot shows that the peak shape factor increases (i.e., the relative amount of oxidized sulfur species increases) as the fraction of molybdenum oxide in the film increases.

The variations in oxidation behavior for room- and high-temperature films and for Type I and Type II films, respectively, are quite analogous. The differences can be attributed to differences in crystallite size and resultant surface area variations. Oxidation occurs at edge planes or dislocations in

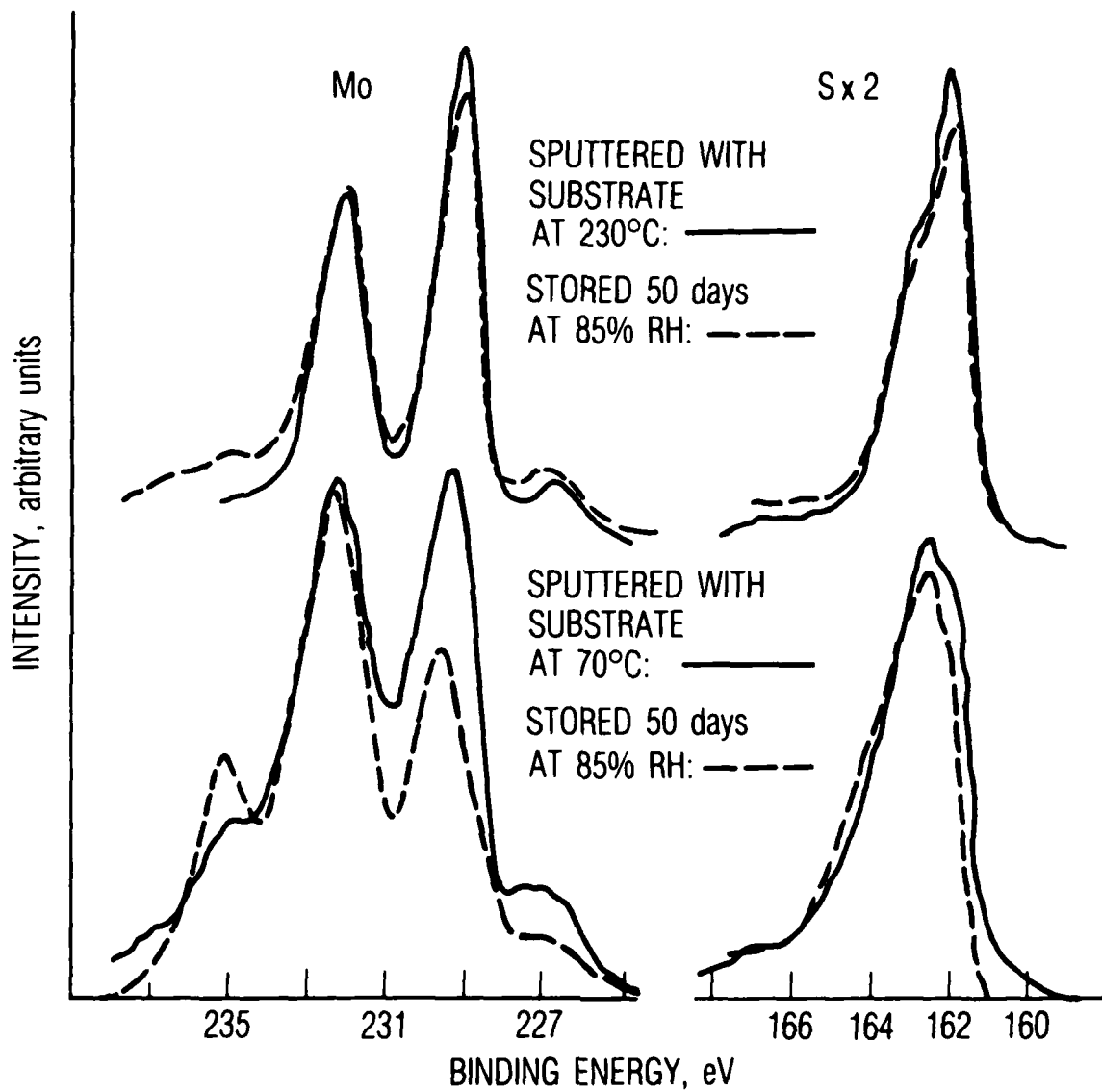


Fig. 5. X-Ray Photoelectron Spectra of Sputtered MoS₂ Films

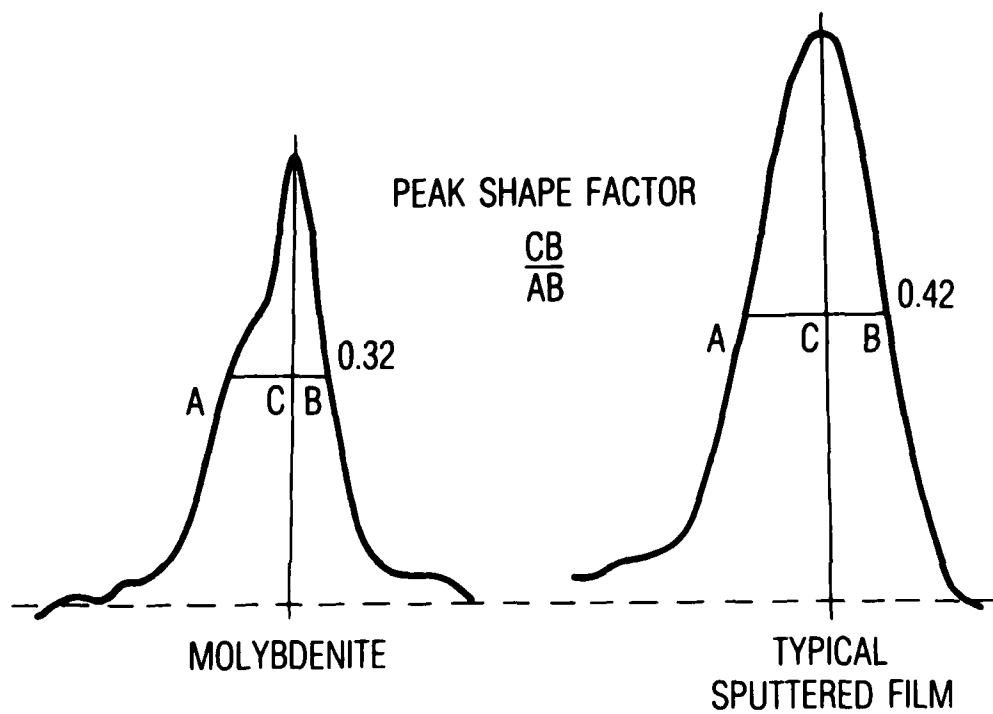


Fig. 6. XPS Evaluation of Multiple Sulfur Species

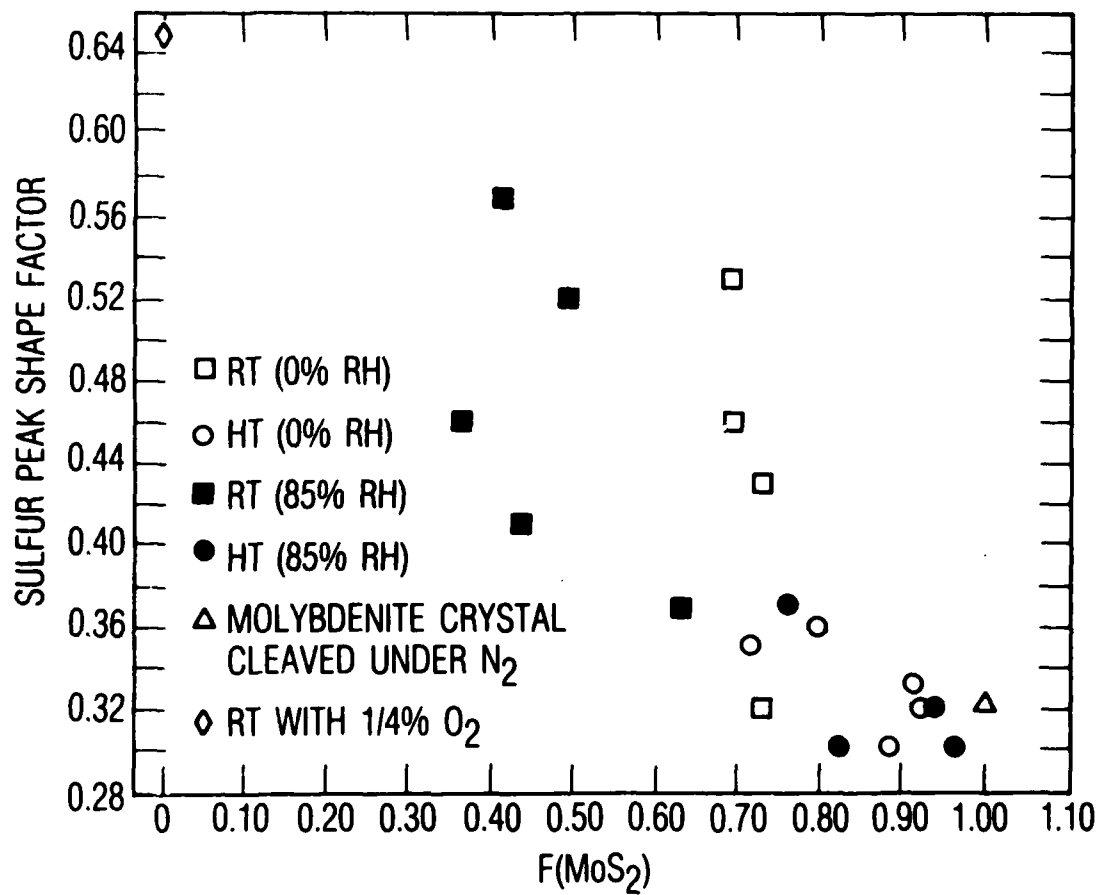


Fig. 7. Correlation between Sulfur and Molybdenum Oxidation. Point at upper left is for a film that was sputtered with 1/4% O₂ (compared to argon) in the chamber. Sulfur is detected on the surface, but the film is 100% MoO₃. RT (room temperature) and HT (high temperature) are defined in the text.

the basal planes of the MoS_2 crystals.⁵ Small, randomly oriented crystallites provide a much higher ratio of accessible reactive (edge plane) surface area to total exposed surface area than do large, especially oriented, crystallites.

IV. TRANSFER-FILM WEAR EXPERIMENTS

Initial results of wear experiments with the sputtered "MoS₂" films of variable surface composition rubbing against bare steel countersurfaces provide information on the influence of film-substrate interface composition on lubrication performance. The type of test performed involves sliding contact between initially coated and uncoated surfaces. During the very early stages of rubbing, lubricant material is transferred from the outer layers of the coated coupon to the bare disk. This type of film application process is analogous to that for a burnished film or one that is formed by contact between bearing balls and impregnated retainers. The quality of the film formed on the disk, its adhesion and morphology, will have major consequences on the lubrication performance of the sliding system. It will be shown that initial chemical interactions during the formation of the transfer films have major consequences on the wear lives of the films, and it is proposed that such variations in performance result from the dependence of film adhesion and uniformity on interfacial chemical bonding.

Torque traces for three typical films are shown schematically in Fig. 8. These traces, reproductions of the actual data recorded on a strip chart recorder during the tests, show that the wear lives of various films can differ significantly, even when the friction properties of the films during their wear lifetimes are the same. The wear lifetimes, or cycles to failure, for a series of films are plotted against two different variables that describe film composition (Fig. 9). The data for all of the films tested are collected in Table 1. The x-axis (horizontal) in Fig. 9 represents the mole fraction of MoS₂ for a two-component mixture of MoS₂ and MoO₃ (as determined from the Mo peaks in the XPS spectra). Pure MoS₂ would be at the extreme right, and the fraction of MoO₃ increases toward the left. The y-axis is the S-to-Mo(IV) ratio from the XPS peak areas, where the Mo(VI) from the oxide is not included in the molybdenum concentration. This S:Mo ratio is related to the peak shape factor and represents the presence of the additional sulfur species referred to above. The z-axis (vertical) represents the wear lifetimes or cycles to failure for the films.

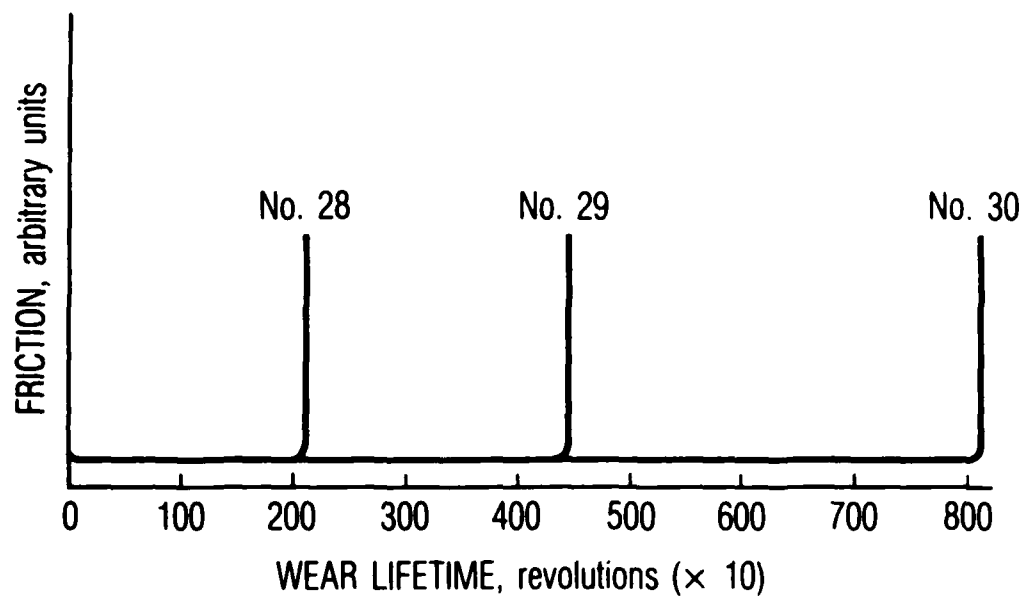


Fig. 8. Schematic Torque Traces for Three Different MoS₂ Films. See Table 1 for sample identification.

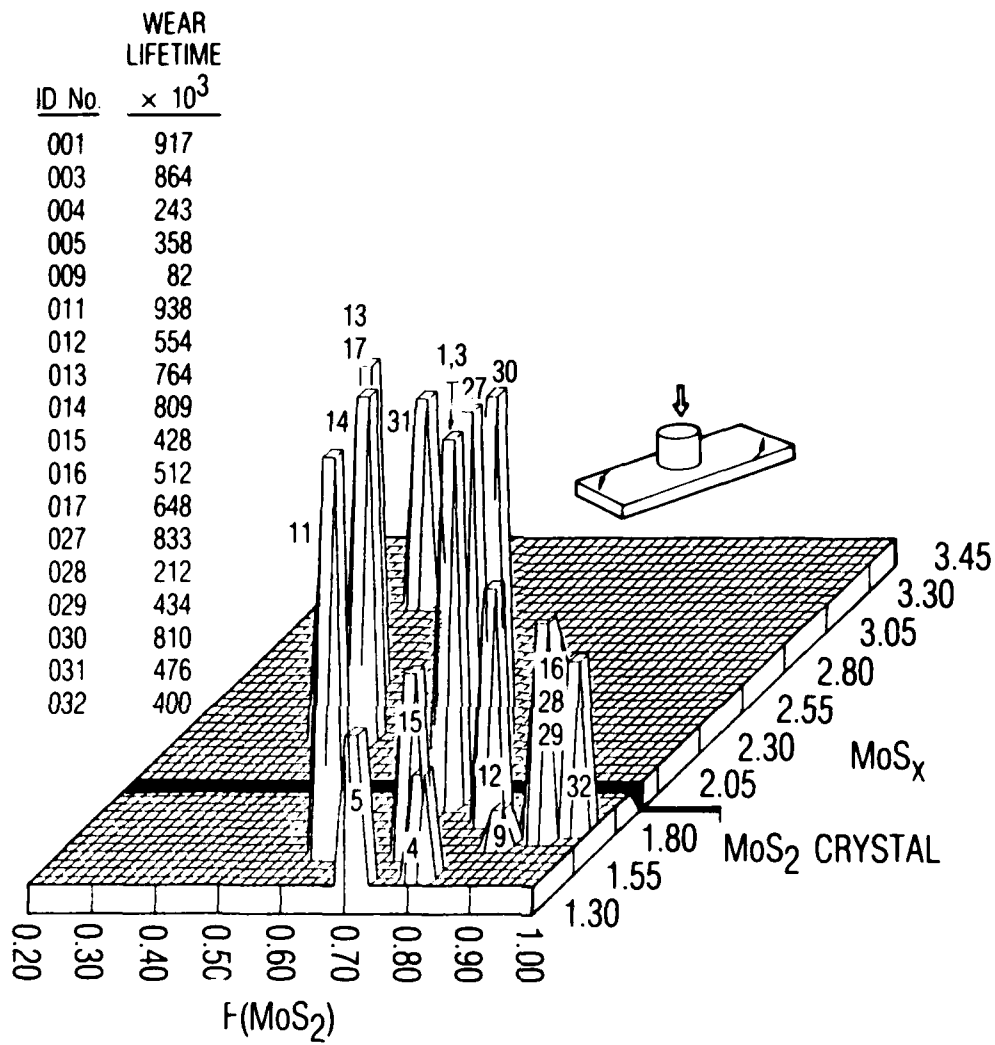


Fig. 9. Sliding Wear Life versus MoS_2 Film Composition. $F(\text{MoS}_2)$ Represents the Mole Fraction of Sulfide in a Sulfide-Oxide Mixture.

Table 1. Composition and Wear Data for Sputtered MoS₂ Films

Sample #	History ^a	F(MoS ₂)	MoS _x x=	Lifetime ^b	PSF ^c
001	RT; 2 mo. 0%RH	0.730	1.83	917	0.32
003	RT; 2 mo. 0%RH	0.726	1.83	864	0.43
004	HT; 2 mo. 0%RH	0.798	1.38	243	0.36
005	HT; 2 mo. 0%RH	0.715	1.34	358	0.35
009	HT; 2 mo. 0%RH	0.885	1.60	82	0.30
011	RT; 2 mo. 85%RH	0.627	1.53	938	0.37
012	HT; 2 mo. 85%RH	0.823	1.76	554	0.30
013	RT; 2 mo. 85%RH	0.411	2.54	764	0.57
014	RT; 2 mo. 85%RH	0.493	2.24	809	0.52
015	HT; 3 mo. 85%RH	0.758	1.54	428	0.37
016	HT; 3 mo. 85%RH	0.937	1.65	512	0.32
017	RT; 3 mo. 85%RH	0.432	2.26	648	0.41
027	RT; 5 mo. 0%RH	0.696	2.09	833	0.46
028	HT; 5 mo. 0%RH	0.923	1.69	212	0.32
029	HT; 5 mo. 0%RH	0.913	1.72	434	0.33
030	RT; 5 mo. 0%RH	0.689	2.23	810	0.53
031	RT; 6 mo. 85%RH	0.362	3.10	476	0.46
032	HT; 6 mo. 85%RH	0.967	1.66	400	0.30

^aRT = sputter at room temperature

HT = sputter at 240°C

mo. %RH = months stored at specified relative humidity

^bLifetime is given in 10³ cycles until failure.

^cPSF = peak shape factor

The results show that films whose surface layers have from 30 to 40% oxidized molybdenum have the longest wear lifetimes. However, the dependence of wear lifetime on the S:Mo ratio is much less obvious. In general, those films with the longest lifetimes also have the largest values of their peak shape factors, but the S:Mo ratios vary from approximately 1.5 to 2.3. These differences in lubricant performance reflect the influence of interfacial chemistry on the formation of the transfer film of lubricant on the initially bare steel disk. AES analyses of the lubricant films prior to wear testing show that the variations in S:Mo ratios occur within the outer 1 to 3 nm of the film.⁴ Analysis of the transfer film immediately prior to failure shows that its composition is very close to pure MoS₂, indicating that the bulk layers of the films are probably not significantly oxidized, nor do they contain excess sulfur.

V. INTERFACIAL CHEMISTRY AND LUBRICANT PERFORMANCE

It is proposed that the oxidation of some portion of the molybdenum disulfide in the interface region between the film and the substrate results in longer wear lifetimes because such oxidation promotes good adhesion of the transfer lubricant film. Although the evidence is less compelling, the presence of elemental sulfur is also believed to enhance bonding and film adhesion. The same conditions probably apply to the achievement of good adhesion of sputtered films to substrates, i.e., the interface region must be tailored to a particular composition.

There is empirical evidence of this chemical effect.⁶⁻⁸ The results of very early work on burnished MoS₂ and WS₂ films indicated that improved performance was obtained for films having metal sulfide additives or for films made on presulfided steel surfaces.⁶ More recently^{7,8} it was shown that sputtered MoS₂ films exhibited substantially longer wear lifetimes if the substrates were precoated with transition metals and these metals were sulfided prior to deposition of the MoS₂. The effect on wear lifetime was the greatest for rhodium and palladium interlayers, with the overall increase in time until failure being three orders of magnitude. The interpretation of this effect was that the adhesion of the lubricant film was substantially improved by the interlayer and that the improved adhesion provided the improvements in wear lifetime.

The ideal situation for MoS₂ lubricant films is to have a highly adherent film whose crystallites are oriented so that their basal planes are parallel to the plane of the substrate surface. Such adhesive strength should be facilitated by the formation of chemical bonds between film and substrate atoms, but the basal surface of MoS₂ is very inert.⁹ This lack of reactivity results from the fact that all of the valence electrons in the material are used to form strong covalent bonds within the S-Mo-S layers. The crystal symmetry is such that there are no accessible orbitals on the S or Mo atoms which can form bonds on the basal plane of the MoS₂ crystallites.¹⁰ Covalent bonds can be formed to the edge surfaces where all the orbitals are not fully utilized (although such bonding is unacceptable for optimum lubrication performance),

or by disruption of the trigonal prismatic symmetry of the basal plane contiguous with the substrate.

The present results can be interpreted as indicating that the oxidation of portions of MoS_2 to MoO_3 , combined with the incorporation of extra sulfur in the interfacial layer, provides the necessary disruption of the MoS_2 structure to form a chemically mixed region having strong substrate bonding. A graded interface is envisioned that consists of a transition from metal to mixed oxides and sulfides and, finally, to nominally pure MoS_2 . The mixed region may be only a few atomic layers thick, but it is nonetheless required for good adhesion and consequently long endurance of the film. It is emphasized that coplanar crystallite orientation is not required for strong film adhesion, but it is believed to be necessary for optimum lubricant performance.

VI. CONCLUSIONS

Lubricant films of MoS_2 must adhere to the contacting surfaces and provide low friction in order to exhibit good performance and long life. The results of this study show that (1) the best lubrication performance is obtained for MoS_2 transfer films when the bonding layers between the films and the steel substrates contain MoO_3 and probably excess elemental S compared to stoichiometric MoS_2 ; (2) the chemistry within the interfacial region between film and substrate is a primary determinant of the wear life of the lubricated system; (3) this chemistry can be manipulated without causing significant variations in the friction properties of the films (the friction being determined by the chemistry and structure within the bulk of the films, which presumably must be as close to stoichiometric MoS_2 as possible); and (4) the interfacial chemistry between substrates and MoS_2 films prepared by sputtering is probably equally important in determining the adhesion and wear behavior of these films. Therefore, in order to obtain the best performance for thin lubricant films of layered transition-metal dichalcogenides, it is necessary to develop techniques to control independently the chemistries of both the interface and bulk film regions, so that those regions can provide maximum adhesion and minimum friction.

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LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security projects, specializing in advanced military space systems. Providing research support, the corporation's Laboratory Operations conducts experimental and theoretical investigations that focus on the application of scientific and technical advances to such systems. Vital to the success of these investigations is the technical staff's wide-ranging expertise and its ability to stay current with new developments. This expertise is enhanced by a research program aimed at dealing with the many problems associated with rapidly evolving space systems. Contributing their capabilities to the research effort are these individual laboratories:

Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, chemical dynamics, environmental chemistry, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed chemical and excimer laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, sensor out-of-field-of-view rejection, applied laser spectroscopy, laser chemistry, laser optoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photo-sensitive materials and detectors, atomic frequency standards, and environmental chemistry.

Computer Science Laboratory: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, micro-electronics applications, communication protocols, and computer security.

Electronics Research Laboratory: Microelectronics, solid-state device physics, compound semiconductors, radiation hardening; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; microwave semiconductor devices, microwave/millimeter wave measurements, diagnostics and radiometry, microwave/millimeter wave thermionic devices; atomic time and frequency standards; antennas, rf systems, electromagnetic propagation phenomena, space communication systems.

Materials Sciences Laboratory: Development of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; non-destructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.

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