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TOWARDS AN OPTIMISED SPUTTERED MoS_2 LUBRICANT FILM

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It is shown that the tribological quality of MoS_2 lubricant films formed by magnetron sputtering is determined by the choice of sputtering conditions. By selecting the appropriate conditions, films of extremely high lubricity and endurance (in vacuum), which are well suited to many space applications, are obtained. Such MoS_2 films, when applied to precision ball bearings, give rise to the lowest torques (for the given test conditions) yet seen in our laboratory. Whilst a remarkably good performance is obtained in vacuum, tests in air show a marked deterioration in lubricating qualities. It is demonstrated that this is attributable to the adsorption of water vapour on MoS_2 surfaces and that the degree of deterioration is related to the partial pressure of water vapour present. Analysis of results indicates that the factors relevant to obtaining optimum films are deposition rate and film composition.

INTRODUCTION

Molybdenum disulphide's efficacy as a lubricant, particularly in high vacuum, is well established. However its application to surfaces by the technique of sputter deposition has only recently come into consideration as a viable process. Interest has grown in this method of application as it offers several advantages over the more conventional techniques of burnishing (of powders) and spray coating (of bonded lubricants). These advantages include:

a) Control over thickness: because the deposition rate is known, thin (sub-micron) films of the required thickness are readily produced. The process is therefore particularly suited to the coating of precision components.

b) Reproducibility: film reproducibility is high provided strict process control is applied.

c) Strong film to substrate adherence: good adherence which is necessary for effective, high endurance lubrication is a characteristic of sputtered films.

d) Coherent films: the lubricant film produced by sputtering is a continuous layer of high coherence.

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e) Intrinsic films: that is, the coatings are free of materials (such as bonding agents) which are extraneous to the lubricating process.

Though offering these advantages, sputtering is a complex process involving many variables. The conditions necessary to achieve lubricant films having the above qualities must be sought experimentally: this was the aim of the present study. The task was undertaken by sputter-depositing MoS_2 films under various conditions of gas pressure and RF power and evaluating the resultant films in air and vacuum using a pin-on-disc apparatus. The sputtering conditions necessary to give the best film (tribologically), once determined, were applied to coatings on ball bearings whose performance was then evaluated.

MAGNETRON SPUTTERING

Radio frequency sputtering (Ref.1) is brought about by applying RF power between a target (manufactured from the coating material, in our case MoS_2) and a substrate (the component to be coated), both target and substrate being located in a low pressure, argon environment. In these circumstances an Ar^+ plasma forms and there occurs a build up of charge on the target which gives rise to a negative bias. As a result, argon ions are accelerated towards the target, this bombardment resulting in the emission of target atoms/ions some of which transfer to the substrate. The process is depicted in Fig. 1. The target, in addition to ejecting target atoms, emits secondary electrons which help sustain the plasma but which also bombard the substrate and cause heating. Despite this, sputtering is, in relation to many other deposition techniques, a low temperature process. This is desirable, indeed mandatory, where the temper (i.e annealed condition) of the substrate material must be preserved.

In the present study, film deposition was by means of RF magnetron sputtering. This is an extension of the RF sputtering process described above which offers the additional advantages of:

a) High deposition rates.

b) The virtual elimination of secondary electron bombardment of the substrate and thus lower substrate temperatures.

These are achieved by confining the plasma to an area lying close to the target by means of permanent magnets located behind the target (the actual shape of the plasma is governed by the nature of the electrical and magnetic fields set up within the chamber). An improved ionisation efficiency results which increases the rate of target bombardment and thus gives rise to enhanced rates of deposition. The paths of secondary electrons are constrained by the electromagnetic fields and thus remain in the vicinity of the target.

A disadvantage, however, is that magnetron sputtering gives rise to films of less uniform thickness because the effective source area is smaller than the target area. A restriction is therefore placed on the size of component that can be coated uniformly.

RATIONALE OF TESTING

Although simple in concept, sputtering is, as noted earlier, a technically-complex process. This complexity arises as a result of the large number of parameters that collectively determine the conditions of sputtering. These parameters include applied power, gas pressure, target area, target to substrate distance, substrate temperature and substrate bias. Each parameter can influence the quality, in terms of structure, orientation, stoichiometry and adhesion, of the sputtered film (Refs. 2 to 6). Adding to this complexity is the interdependency of several of these parameters.

To simplify the determination of optimum sputtering conditions only the effects of changes in argon pressure and R.F power were examined in the present study: all other parameters being kept constant.

Sputter depositions were carried out at argon pressures of 5, 12.5 and 20 microns (0.67, 1.67 and 2.67 Pa. respectively) and at applied powers of 0.3, 0.6 and 0.9 kW. Thus, in total, nine sputtering conditions were studied.

The values of the remaining parameters were fixed as follows.

Target diameter: 152.4 mm
Target to substrate distance: 56 mm
Substrate bias: zero volts
Substrate temperature: ambient

No bias was applied to the substrate although its potential during deposition would rise naturally to that of the plasma potential. The main intention was to avoid a negatively-biased substrate as this is known to repel sulphur ions and lead to sulphur-deficient films (Ref. 4).

The substrate was water-cooled during etching and film deposition. However substrate temperature rose above ambient (though probably remaining below 70 deg.C) due to heat dissipated by depositing atoms.

APPARATUS AND TEST SAMPLES

Sample preparation and sputtering conditions

Depositions of MoS_2 were carried out in a Nordiko Vacuum System equipped with NM 2000 Sputtering Modules and an N6-1400 pumping system. High vacuum was achieved by means of an oil diffusion pump. A liquid nitrogen trap, located above the pump, ensured negligible transfer of oil vapour to the sputter chamber.

Coatings were produced, at each of the nine chosen sputtering conditions, on steel (EN31) discs (thrust washers) for pin-on-disc evaluation (see below) and on aluminium stubs for film analysis by EPMA (electron probe micro-analysis). Deposition rates had been measured previously and are reproduced in Fig. 2. Samples were also prepared on glass slides and subjected to freeze fracture so that film morphology could be examined by scanning electron microscopy.

Disc samples were initially cleaned by wiping with cloth soaked in Arklone P solvent followed by three separate ultrasonic cleans in fresh solvent. Prior to sputter deposition the steel discs were sputter etched for 15 mins. at a sputter power of 100 W and at the pressure at which the subsequent deposition was to be carried out (5 to 20 microns Ar) so as to remove loosely bound surface contaminants. The target material was cleaned by sputtering for at least 30 minutes under the intended sputtering conditions of the test.

Tribological assessment-sliding wear tests

Steel discs were coated to a thickness of 1 micron and assessed in high vacuum and air by means of a pin-on-disc apparatus.

The discs had the following specification:

Type: shaft locating thrust washers
Material: EN31 ball bearing steel (52100 AISI)
Hardness: Diamond microhardness 860 ± 10 Vickers
(HRC 58-65)
Surface Finish: Radial 0.15 micron CLA
Circumferential 0.10 micron CLA

The coated discs were spring-loaded to 10 N against three, equispaced, uncoated, EN31 steel balls. A rotational speed of 100 rpm (0.3 m/sec.) was employed for vacuum testing and 10rpm for air tests. The speed was reduced in air so as to reduce rig instabilities which arose as a result of the higher and noisier torque which characterised in-air performance. The apparatus was set to trip when the friction coefficient exceeded 0.3 for 0.5 seconds. Film endurance was defined as the number of disc revolutions completed (or distance travelled) at trip activation. Where film failure did not occur within about 4.5×10^6 revs. the test was stopped so as to enable completion of the remaining tests within an acceptable timespan. Wear rate calculations were made from measurements of the diameters of the ball wear scars.

RESULTS

In-vacuo performance

The performance of sputtered MoS_2 in vacuum was assessed through measurement of endurance, mean friction coefficient and, where failure did not occur, specific wear rate.

TABLE 1(a) ENDURANCE (x 10^6 REVS.)

Ar PRESSURE (microns)	SPUTTERING POWER (kW) 0.3	0.6	0.9
5	0.3	0.9	1.7
12.5	0.7	>4.5	>4.5
20	>4.5	>4.5	>4.5

TABLE 1(b) MEAN FRICTION COEFFICIENT

Ar PRESSURE (microns)	SPUTTERING POWER (kW) 0.3	0.6	0.9
5	0.021	0.024	0.017
12.5	0.02	0.01	0.01
20	0.019	0.013	0.01

TABLE 1 (c) SPECIFIC WEAR RATE (10^{-19} m^3/Nm) OF PINS

Ar PRESSURE (microns)	SPUTTERING POWER (kW) 0.3	0.6	0.9
5	-	-	-
12.5	-	3.7	2.2
20	12.1	5.3	3.3

<u>TABLES 1 (a)-(c) PERFORMANCE OF SPUTTERED MoS_2 IN VACUUM</u>

Pin-on-disc tests were continuously monitored by recording the torque output as a function of time. Typically, torque traces were as shown in Fig. 3, curve A. The curve is characterised by a brief running-in period followed by a period of stable performance. Film failure, when it occurred, was seen to be catastrophic, in that it happened suddenly over a relatively small number of disc rotations (Fig. 3, curve A). Because pin wear became rapid in the failure regime, meaningful measurements of wear rates could not be made in those cases where failure occurred within the time available for testing.

Measurements of endurance, friction coefficient and specific wear rates are summarised in Tables 1 (a), (b) and (c). Endurance (Table 1(a)) is observed to be strongly dependent on sputtering conditions with the best films lasting at least fifteen times longer than the worst. It is apparent that film endurance improves with increasing argon pressure and increasing RF power. Friction coefficient, however, is less sensitive to sputtering conditions but nevertheless a similar trend of improved lubricity with increasing pressure and power is discernible. Note that all the films examined gave rise to very low values of friction coefficient (<0.03).

Wear rates of the balls (pins), where measurable, were extremely low, lying in the range 2 to 13×10^{-19} m^3/Nm.

<u>Selection of Optimum Sputtering Conditions</u>

From the above performance data the sputtering conditions, within the range examined, necessary to produce the best tribological film in vacuum can be determined. In the power/pressure matrix of Table 2 the regions

TABLE 2 OPTIMISATION MATRIX FOR MOS_2

SPUTTERING POWER (kW)

Ar PRESSURE (microns)	0.3	0.6	0.9
5	*	*	*
12.5	*	B *	A *
20	* C	* D	* E

corresponding to films of highest observed endurance (area ABCE) and lowest friction coefficient/wear rate (ABDE), within experimental error, are shaded. The area where overlap between these two regions exists, and thus the area in which the optimum sputtering conditions lie, is bounded by ABDE. Since films produced under the conditions designated A, B, D and E are of equally high quality then it follows that any combination of R.F power and Ar pressure which lies within the area ABDE will give rise to the best MoS_2 film. Based on this reasoning we have chosen as our sputtering conditions for subsequent tribological assessment those values of R.F power and Ar pressure lying at the centre of the area ABDE, that is, 0.75 kW and 16 microns respectively.

Performance of Optimised Film in Air

An MoS_2 layer of nominal thickness 1 micron was sputter deposited under the above conditions and assessed on the pin-on-disc apparatus in both air and vacuum. Fig. 4 indicates the changes in friction coefficient that occur on cycling the chamber pressure between high vacuum (10^{-6} torr) and atmospheric pressure. It is apparent from Fig. 4 that on admitting air into the chamber there is a corresponding rise in friction coefficient to about 0.18. On re-establishing high vacuum the friction coefficient decreases to its initially-low value. Thus the effect of pressure on friction coefficient is reversible for brief periods of air-running. If the film is run continuously in air then failure occurs after some 15000 disc revolutions i.e. film endurance is much inferior to that in high vacuum (see, for example, curve B, Fig.3).

The poor performance of sputtered MoS_2 in air prompted experiments aimed at determining the factors responsible for film degradation. To determine which of the main constituents of laboratory air (nitrogen, oxygen and water vapour) reduces the lubricity and endurance of MoS_2 the following tests were carried out. A test disc was coated with sputtered MoS_2 and mounted in the pin-on-disc apparatus. The disc was run-in under high vacuum, until the friction coefficient had become steady at a value of 0.01. The vacuum pump was then isolated and nitrogen bled slowly into the test chamber. The flow of gas was controlled in such a way that the pressure increased incrementally and, at each pressure rise, time was allowed for the torque to stabilise. In this manner it was possible to determine how the friction coefficient varied with changing gas pressure. A similar test was carried out using oxygen. The results of both tests are shown in Fig. 5(a). The introduction of nitrogen has but a small effect on the friction coefficient whilst the influence of an oxygen atmosphere is greater, increasing the friction coefficient from 0.01 to 0.02. A similar test was then conducted using laboratory air (RH=50%, temperature=20.5C) as the test gas. Fig. 5(b) indicates that, upon admission of air, there is a small increase in friction coefficient. This increase , which occurs as the pressure rises from 0.1 torr to 10 torr, corresponds to that seen in the previous tests using nitrogen and oxygen and is presumably attributable to the presence of these gases. Further increases in air pressure up to atmospheric pressure are accompanied by an emphatic increase in friction coefficient, which reaches a value of 0.16. This increase has two components. These can be resolved by differentiating the curve of Fig. 5(b) to obtain the rate of change of friction coefficient with gas pressure (Fig. 5(c)). Thus the first increase occurs at a pressure of 80 torr and the second, final increase at a pressure of 300 torr. It may be inferred that these two effects are due to the presence of water vapour. Note that these values (80 torr and 300 torr) correspond to partial pressures of water vapour of 0.9 and 3.4 torr (given that the air had a relative humidity of 50 % and a temperature of 20.5 deg.C). If present at these pressures in laboratory air these would give rise to relative humidities of 5% and 19% respectively. This implies that lubricity in air is determined by the dryness of the air: as a guide, best lubricity would be obtained at $RH < 5\%$, intermediate lubricity in the range $5\% < RH < 19\%$ and relatively poor lubricity at $RH > 19\%$.

On re-establishing a vacuum within the test chamber the friction coefficient immediately drops to 0.045. This decrease is the result of the evaporation of some, but not all, of the adsorbed water from the MoS_2 lattice. On rotating the disc at 60 rpm there is a further decrease in friction coefficient to about 0.02 resulting from desorption of the remaining water molecules.

Performance of sputter-coated ball bearings

Using optimised sputtering conditions, ball bearings (designation: ED20; type: angular contact) were coated with MoS_2 and assessed (at 100rpm) under high vacuum in a pre-loaded (40N) pair configuration. The bearings were fitted with steel (EN31) cages. Two types of test were undertaken. In the first of these all the bearing components with the exception of the balls were coated (i.e. both raceways and EN31 cage). In the second type of test all components of the ball bearing were coated (i.e. including the balls). The coating thickness was nominally 0.5 microns. In each test six bearings were run until the torque reached 8×10^{-3} Nm., this corresponding to a sliding (microslip and spin) friction of approximately 0.4.

The manner in which mean bearing torque varied with number of revolutions under vacuum is summarised in Fig. 6. Bearings having uncoated balls exhibited very low mean torque (typically 4×10^{-4} Nm) and failed following some one million revolutions. Bearings having all their component parts lubricated showed higher torques (about twice the level seen with bearings employing uncoated balls) though a significant improvement in endurance was observed (typically 4×10^{6} revs.).

Thus coating of the balls with MoS_2 in addition to raceways and cage brings about, on average, a fourfold increase in endurance though at the expense of a twofold increase in torque. The improvement in endurance may simply be a consequence of the increase in MoS_2 -coated area on surfaces which undergo rolling contact (it is proposed to test this notion by coating only the balls). The reason for the twofold increase in torque consequent upon coating balls is as yet unresolved.

Note that, in air, ball bearings with all components coated achieved a lifetime of only about 0.25×10^{6} revolutions.

Film Composition and Structure

Analysis of MoS_2 by EPMA indicated small deviations from stoichiometry (Table 3): films being either sulphur-rich or sulphur-deficient.

TABLE 3 RATIO OF SULPHUR TO MOLYBDENUM ATOMS IN SPUTTERED MoS_2

Ar PRESSURE (microns)	SPUTTERING POWER (kW) 0.3	0.6	0.9
5	1.67	1.69	1.75
12.5	2.00	2.26	2.13
20	1.71	2.21	2.08

Observations of MoS_2 films by scanning electron microscopy revealed two types of film morphology. Micrographs of these morphologies which we term Type A and Type B are shown in Fig.7. Type A films are distinguished in section by a columnar structure which gives rise to their distinctive surface appearance whereas the structure of type B films appear more amorphous, their surfaces exhibiting a granular texture. Table 4 indicates the film morphologies resulting from the sputtering conditions examined.

TABLE 4 TYPES OF MoS_2 FILM STRUCTURE

Ar PRESSURE (microns)	SPUTTERING POWER (kW) 0.3	0.6	0.9
5	B	A	B
12.5	B	A	A
20	B	A	A

It is apparent from Tables 3 and 4 that the optimised MoS_2 film has a type A structure (columnar) and is, to a slight degree, sulphur enriched.

DISCUSSION

Examination of our results and observations indicates three features common to the best performance films. These are:

a) film compositions are near-stoichiometric and are, to a slight extent, sulphur rich.
b) the films are formed at relatively high deposition rates.
c) the films exhibit type A morphology.

Fig. 8 shows that, within the range of compositions observed, the lubricity of MoS_2 films increases with sulphur content. It further appears that deposition rate is a crucial parameter in obtaining the desired stoichiometric or sulphur-rich films. Thus as shown in Fig. 9 high sulphur content is a feature of films deposited at high deposition rates.

This observation is consistent with a view recently put forward by Buck (Ref.7) in which it is proposed that the composition and hence quality of sputtered MoS_2 films is governed largely by the level of water vapour in the sputtering chamber during deposition. He derives an equation relating, in effect, a film "quality factor" to the deposition rate of MoS_2 and the partial pressure of water vapour. In essence, higher quality films are obtained by maximising the MoS_2 deposition rate and minimising water vapour contamination. This is consistent with our observation that the best lubricating films are obtained at the higher deposition rates. Buck also observes that poor-quality MoS_2 films are depleted of sulphur. This also is consistent with our findings.

We observe that optimum films exhibit Type A structure. However a strong correlation between film structure and film performance is not proven since some observations were inconsistent with this e.g one film of poor endurance (0.6kW/5 microns) exhibited Type A structure and conversely one film of high endurance (0.3kW/20microns) had a Type B structure (Table 4). Further, these structures are of films deposited on glass substrates and the conditions giving rise to each film morphology on glass may differ from those conditions applying to depositions on steel. It might be expected, for example, that higher substrate temperatures would arise with glass (due to its lower thermal conductivity) and film morphology is known to be dependent on substrate temperatures (see for example Ref.8). Thus, at present, the relationship between film morphology and lubrication is not clearly established.

In air, particularly where motion is of a purely sliding kind, the lubricating properties of sputtered MoS_2 are much inferior to those observed in vacuo. Our studies confirm an earlier finding (Ref. 9) that this degradation is attributable to the presence of water vapour. However our observation that the degradation in lubricity is a two stage process which depends on the partial pressure of water vapour gives further insight into this phenomenon. In particular, these observations may indicate that water molecules are adsorbed at two types of surface site. Upon adsorption of water vapour at the first type of site the friction coefficient increases to about 0.05 and on filling the sites of the second type the coefficient of friction rises to 0.16. Since the second site is readily vacated on reducing the chamber pressure and desorption from the first site requires only a small increase in temperature above ambient (obtained by increasing disc speed), it may be surmised that the heat of adsorption associated with the first type of site is higher than that of the second, though both are low and correspond to heats of adsorption characterisic of physisorption rather than chemisorption. It remains a matter of conjecture as to which sites in the MoS_2 lattice correspond to the above. Clearly intercalation sites and edge sites are candidates since adsorption at each type of site would likely affect film lubricity. Indeed there is some evidence that water molecules can penetrate MoS_2 layers (intercalation) (Ref.10). However the precise mechanism responsible for lubricant degradation upon physisorption of water is not, as yet, fully understood.

CONCLUDING REMARKS

It has been shown that, to obtain high lubricity films, high deposition rates are required. Such deposition rates are afforded by RF magnetron sputtering under conditions of relatively high argon pressure and R.F power.

When deposited under optimum sputtering conditions MoS_2 films are observed to give rise to very low levels of friction (friction coefficient = 0.01) when measured under conditions of sliding motion (pin-on-disc) under vacuum. This same film, when tested under conditions where motion is principally of a rolling kind (i.e in ball bearings), gives rise to extremely low torque levels. Indeed, these results represent the lowest levels of torque hitherto seen at ESTL, regardless of the lubricant employed, for bearings of this type tested under identical conditions. As an illustration Fig. 10 compares the bearing torques (as a function of rotational speed) obtained in vacuum with various lubricants. These results show that the lubricity of sputtered MoS_2 in vacuum is second to none and that the lubricant is well suited to those bearing applications where very low torque and torque noise are required and where the finite film endurance is not a problem.

In air (RH = 50%) MoS_2 loses its high lubricity and endurance is reduced very significantly. However, lubricity is recovered on re-establishing vacuum provided operations in air are brief (when compared with endurance in air). The degree to which lubricity is lost is dependent on the partial pressure of water vapour present and occurs in two distinct stages as this pressure is increased. It is recommended that if in-air operation is unavoidable then, where possible, the humidity level should be kept below 5% RH or failing this, below 20% RH.

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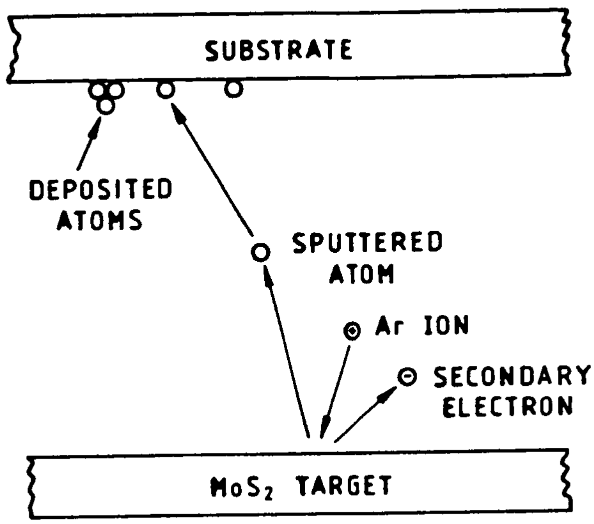

Figure 1. - Sputtering process.

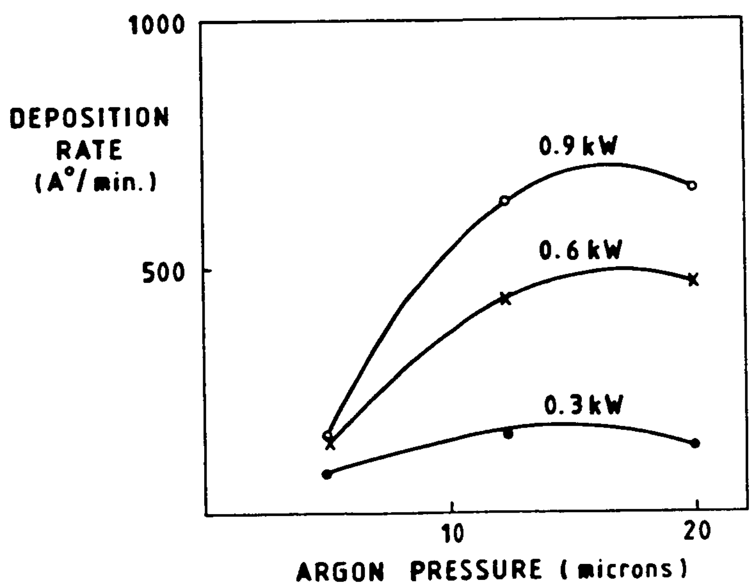

Figure 2. - Deposition rate of sputtered molybdenum disulphide as function of argon pressure.

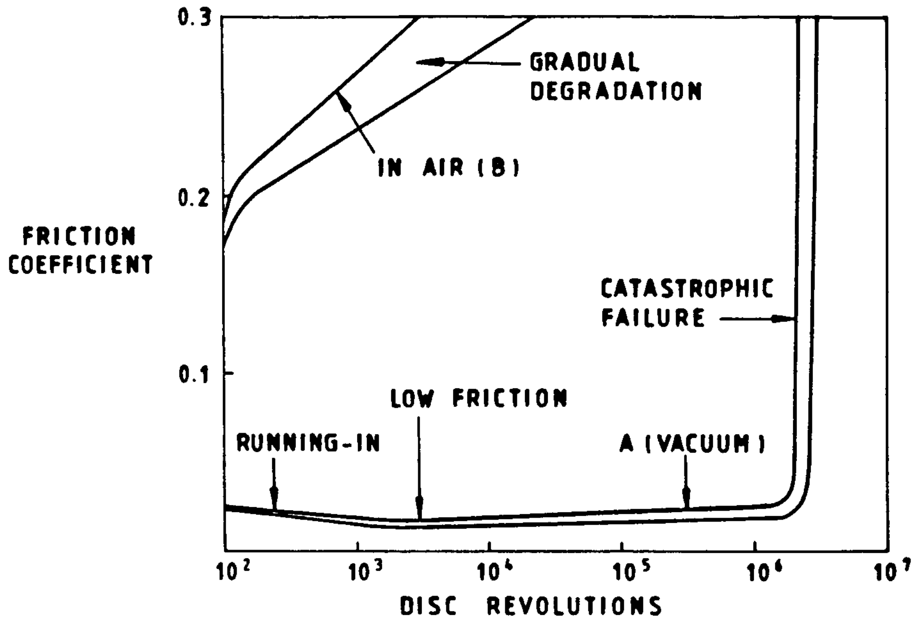

Figure 3. - Failure modes of sputtered MoS_2 under sliding motion.

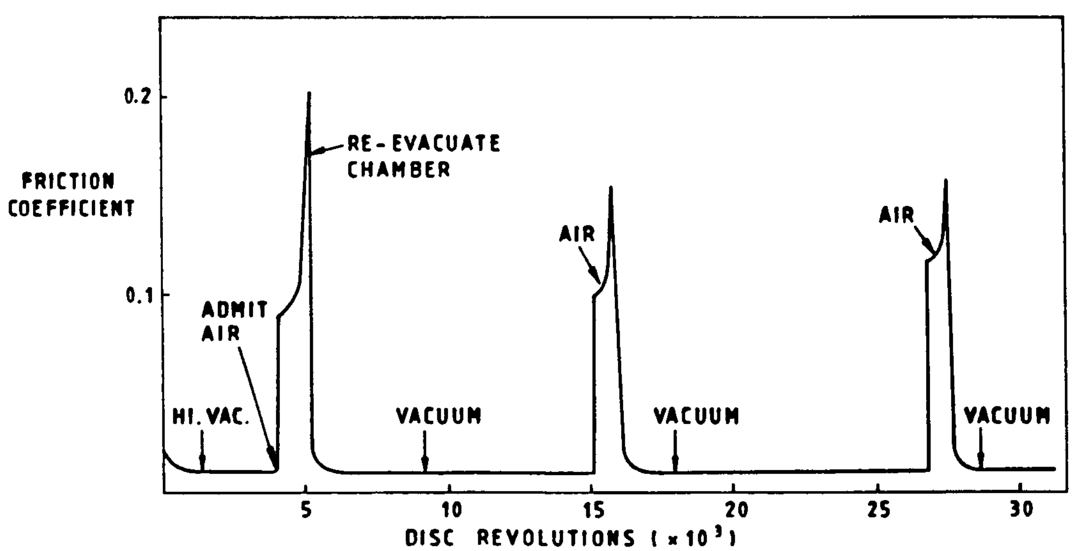

Figure 4. - Effect on MoS_2 lubricity on alternating environment between high vacuum and laboratory air (RH = 50 %, T = 20.5 °C).

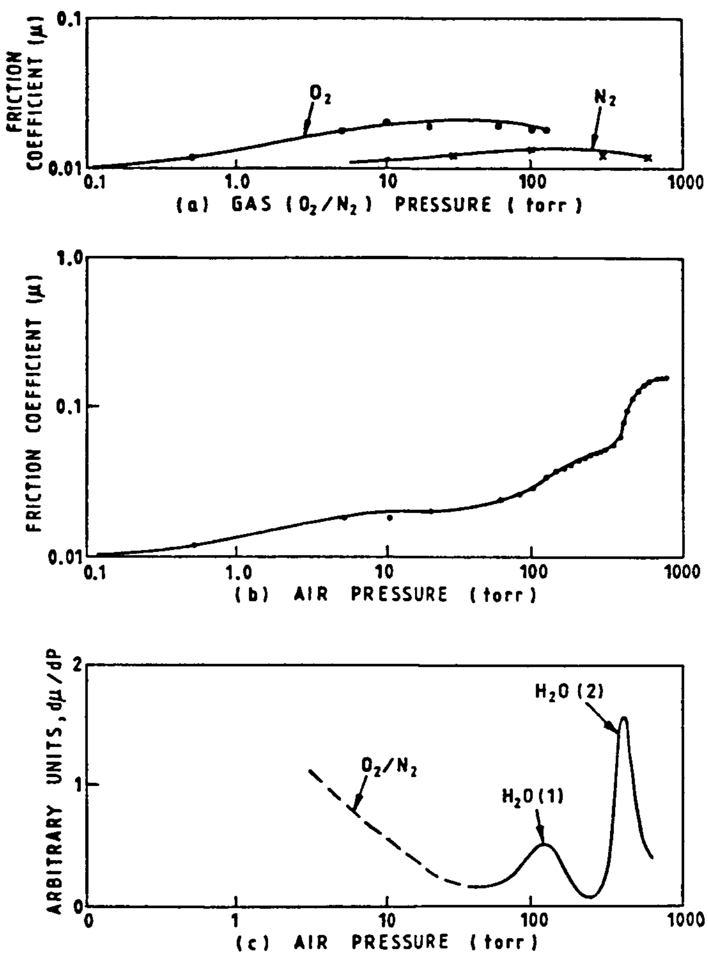

Figure 5. - Effect of gas pressure on friction coefficient of sputtered MoS_2.

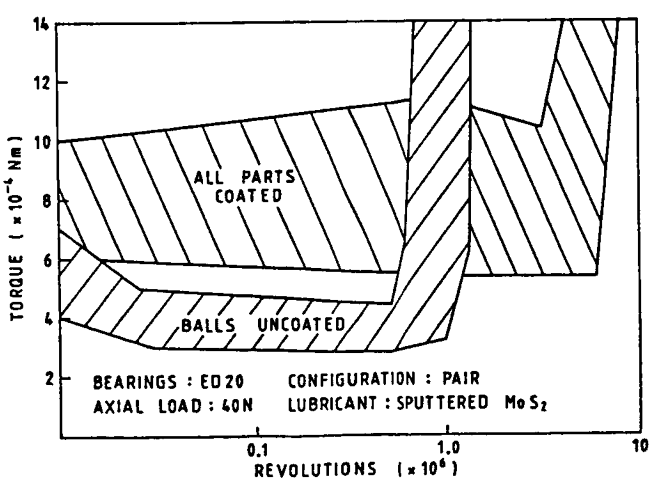

Figure 6. - Bearing torque vs. revolutions (in vacuum).

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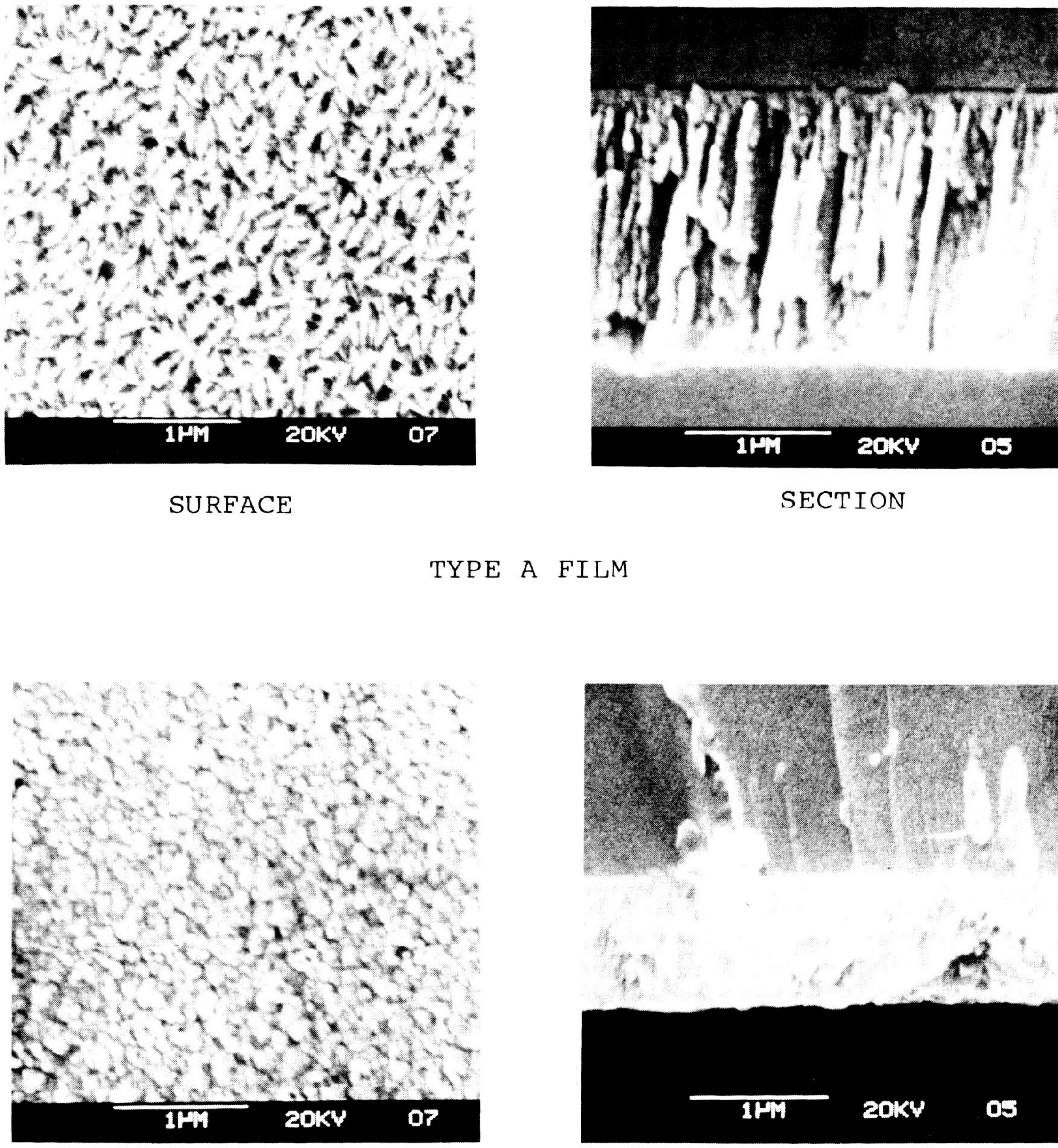

SURFACE SECTION

TYPE A FILM

SURFACE SECTION

TYPE B FILM

Figure 7. - SEM micrographs of sputtered MoS_2 films.

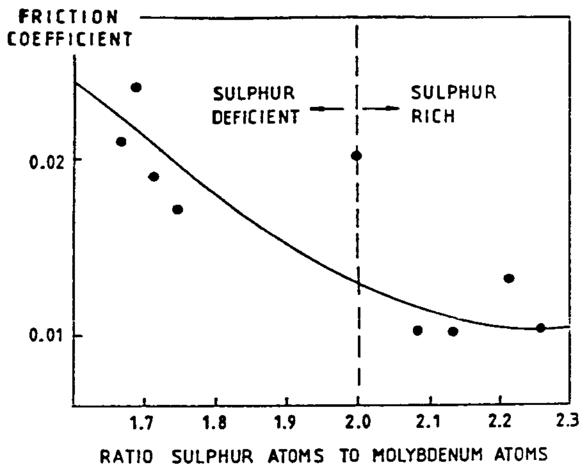

Figure 8. - Friction coefficient of MoS_2 films as function of sulphur content.

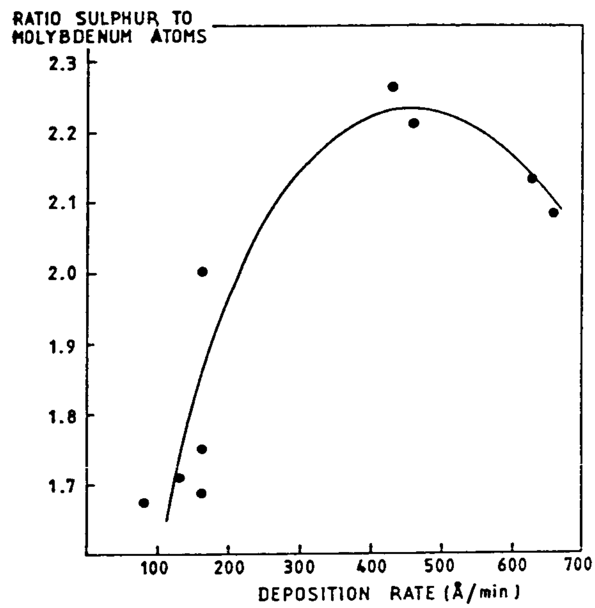

Figure 9. - Sulphur content as function of deposition rate.

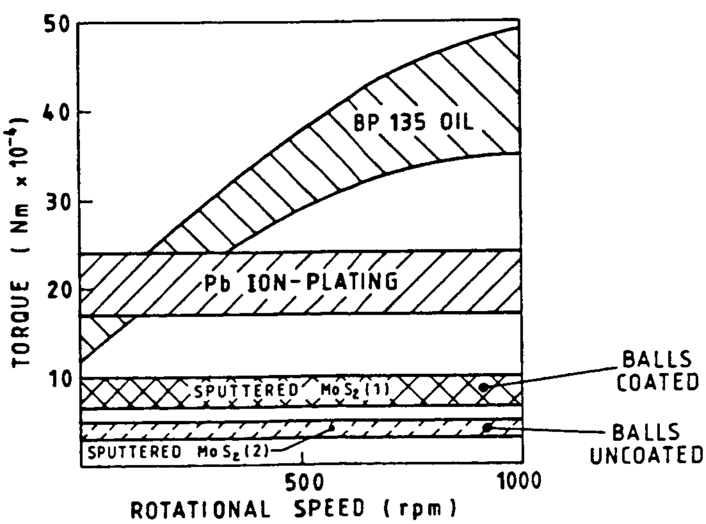

Figure 10. - Torque vs. rotational speed of ED20 bearing pairs employing different lubricants (under vacuum).