IMPROVED TRIBOLOGICAL BEHAVIOUR OF MoS_2 THIN SOLID FILMS ALLOYED WITH WC.

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ABSTRACT

MoS_2 is a broadly accepted solid lubricant for space mechanisms. However, the tribological properties can be affected by the deposition parameters that can in turn influence structure and composition of the films. One important drawback of MoS_2 is its sensitivity to atmospheric water vapour which renders the film unsuitable for use under high humidity levels and forces the taking of precautions during ground qualification testing and storage of solid lubricated space mechanisms. Recently, and with developments made in magnetron sputtering PVD technology an interest has arisen in the production of more wear and moisture resistant MoS_2 films. This has been evaluated by alloying the film by co-depositing a range of metallic and non-metallic elements. This paper follows a previous report in which Ti metal was co-deposited with MoS_2 and a low friction under vacuum and atmospheric conditions was demonstrated. However, it was felt that extended durability was still needed for the benefit of space community. In this work, preliminary results on the deposition of WC-MoS_x films by magnetron sputtering are presented. Vacuum tribology of these films, at 0.75 and 0.95 GPa contact stresses, shows that the friction coefficients are similar to those obtained in conventional MoS_2 films, but there is a significant improvement in durability. When evaluating the performance of these films under atmospheric conditions and at various humidity levels (from 40 to 60 % RH), the tribological response has also been very good, with average friction coefficients as low as 0.07 and a durability as high as 450.000 wear cycles.

XPS analyses have shown that the films consist mainly of a MoS_x lubricating matrix in which a carbidic wear resistant WC phase is embedded. This combination ensures a low friction behaviour while providing a higher resistance to wear.

INTRODUCTION

Recently a significant attention has been given to the development of MoS_2 films alloyed with metals and ceramic phases [1-3]. This is explained by a tendency observed in mechanical engineering applications towards the use of solid lubricant coatings to reduce the need of liquid lubrication and hence alleviate some environmental problems.

The requirement for these solid lubricant coatings is that they should maintain friction coefficients very low, therefore transmitting lower stress levels to the tooling, at the atmospheric conditions encountered in most mechanical workshops. The challenge has thus been to develop MoS_2 films maintaining the known "tribological properties under vacuum", but with an extended wear life at higher humidity conditions. A degree of success has been achieved with Ti alloyed MoS_2 films [1,2], owing to the "oxygen gettering" effect of this element, allowing higher protection to the MoS_2 film against the deleterious oxidation effect on its tribology response.

The "space mechanisms community" can benefit from these developments since these modified MoS_2 films, can exhibit not only improved tribological properties under vacuum, but also under air, at higher humidity conditions without undue degradation. This means that pre-flight qualification testing of solid lubricated mechanisms could be done without present limitations with conventional MoS_2 films.

The motivation of this work is therefore the development of a new range of solid lubricant films based on MoS_2 with extended endurance life and reduced degradation under atmospheric conditions. Representative films fulfilling the ground qualification testing will be finally tested on bearings in the TriboLAB instrument at the International Space Station (ISS) [4].

EXPERIMENTAL WORK

Alloyed MoS_2 films were deposited on hardened and tempered AISI 440C bearing steel discs of 45 mm diameter and 5 mm thick with a surface finish of 0.01 µm Ra. A CemeCon CC800/8 magnetron sputtering PVD unit was used for the deposition work. Alloyed WC-MoS_x films were produced by magnetron sputtering from four targets (1 to 2 targets of MoS_2 and 1 to 2 targets of WC) in an Ar discharge at a pressure of 0.5 to 0.7 Pa. The thickness of deposited films were about 1.5 µm.

Hardness of the films was measured with a Fischerscope H100 dynamic microprobe apparatus using a conventional Vickers indenter at loads up to a maximum of 10 mN [5], to minimise the influence of the underlying steel base material.

Small Area X-ray Photoelectron Spectroscopy (SAXPS) combined with 4 keV Ar^+ was conducted to obtain composition and chemical analyses from the films. SAXPS analyses were performed in a Microlab MKII VG spectrometer with Al Ka radiation at 34 mA and 13 kV under a pressure of less than 2 x 10^{-9} mbar (without Ar). For each sample, detailed spectra (Mo 3d, S 2p, W 4f, C 1s, O 1s, Fe 2p and Cr 2p) were recorded at a pass energy of 20 eV and a step energy of 0.1 eV. Furthermore, deeper information on the chemical bonding states of the C 1s peak were obtained subtracting the background by Shirley's method [6] and deconvoluting the C 1s spectra to C-O, C-C and C-Metal bonds by a curve-fitting method, assuming a Gaussian distribution.

Wear and friction tests were performed in two types of ball-on-disk tribometers. A CSEM equipment was used to carry out tests under vacuum (< 10^{-5} mbar), applying a load of 5 and 10 N to an AISI 440C steel ball of 6 mm dia. at a constant sliding speed of 0.5 m/s. A calculated estimate of Hertzian contact stress under these conditions is 0.75 and 0.95 GPa respectively. In addition, a Falex ISC 320 tribometer was used to obtain comparative data under atmospheric conditions. Identical loading conditions and sliding speeds were used in this case with the only difference of performing the tests at controlled humidity ranging from 40 to 80 % RH. All tests run until a friction coefficient of 0.2 was reached and the tests were in most cases triplicated.

Wear volume and surface morphology were evaluated on discs and balls after testing by using non-contact laser surface profilometry and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

A) XPS Surface analyses

XPS analysis showed a preferential sputtering of S and C making difficult an accurate stoichiometric determination of the elements. Despite the former consideration, the XPS element intensity depth profile demonstrated that a steady ratio between elements is obtained (see Fig. 1, obtained from sample 25956). Furthermore, oxygen contribution is only observed at the outer layers and can be attributed to the atmospheric exposure of the films.

Figures 2 and 3 show the Mo 3d and W 4f XPS spectra from sample 25956 at different sputtering times respectively. In these figures spectra from MoS_2 and WC are also included respectively as a reference. XPS spectra obtained from Mo 3d, S 2p, W 4f and C 1s regions at selected sputtering times demonstrated that high Mo-S and W-C bonding contributions are created together with low C-C contributions. Peak positions of S $2p_{3/2}$ spectra stays around 162.3 eV through all the film, which mainly correspond to Mo-S bonds (S $2p_{3/2}$: MoS_2 ~ 162.35 eV; WS_2 ~ 162.8). Furthermore, the Mo 3d spectrum for the outer layer (see Fig. 2, at 0 min sputtering time) shows three main contributions: Mo-S bonds ($3d_{5/2}$ ~ 228,8 eV; and $3d_{3/2}$ ~ 232,1 eV), M-O bonds (very low MoO_2: $3d_{5/2}$ ~ 229.6 eV and MoO_3: $3d_{5/2}$ ~ 232.8 eV contribution that could not be disregarded) and S 2s. Due to the coating stoichiometry (S/Mo < 2) the Mo-S peak contribution has a lower binding energy (BE) than in MoS_2 (Mo $3d_{5/2}$ ~229.25 eV). After sputtering a shift to lower BE is produced and a steady value is quickly achieved without a noticeable oxide contribution. The shift in the Mo 3d peak position to lower BE reflects the changing electrostatic environment around Mo atoms caused by the loss of neighbouring S atoms to which is bonded. The sputtering behavior of the Mo 3d and S 2p peaks is similar to that observed on MoS_2 films alloyed with Ti and reported previously [2]. Despite the almost identical peak position for metallic or carbidic Mo-C bonds (Mo° ~ 227.85 eV and Mo_2C ~ 227.8 eV), the contribution that is present can be attributed mainly to the metallic bond, as W shows a clear carbide contribution (Fig. 3).

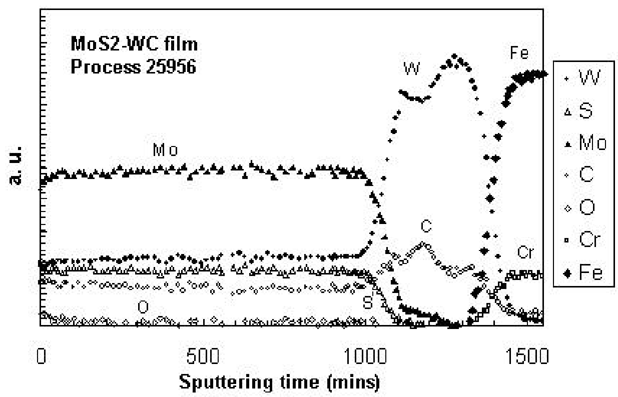

Figure 1: XPS element intensity depth profile of MoS_2 / WC film as a function of the sputtering time.

Fig. 3 depicts the W 4f spectra obtained from the same film. In this figure, the W $4f_{7/2}$ lines for W-S (WS_2 ~ 33.2 eV), W-C (WC-Co ~ 31.6 eV; WC ~ 31.5), W° (~ 31.32 eV) and the Mo 4p / WO_3 contribution (Mo ~ 38 eV, WO_3 ~ 35.7 eV) are drawn as a reference. The figure shows that, even with the Mo 4p contribution to the high BE side of the W 4f spectra and the external oxide contribution (WO_3 and WO_2 ~ 32.7 eV), the carbide W-C and the metallic W° should be considered as the two main contributions inside the film. The shifts in BEs between both chemical states are very low. The W 4f spectra show that the BEs for W $4f_{7/2}$ stay around 31.7 eV in the film range where the lowest WC has been deposited (Fig. 1, up to 990 mins sputtering time) and shift to a lower energy, staying around 31.5 eV when the rich WC interlayers are reached during analysis. Regardless of the preferential sputtering of carbon, which contribute to this shift due to loss of neighbouring C atoms to which W is bonded, the W $4f_{7/2}$ peaks show a carbidic bonding through all the film. Nevertheless, the metallic contribution should not be disregarded and other surface analysis technique should be applied to determine if there is a W^o contribution. Observation of the C 1s spectra corroborated the previous results. A contaminated outer layer (i.e. C-C ~284.9 eV and C-O ~ 286.3 bonds) and a high carbidic contribution (283.4 eV) was found through all the film. In addition, curve fitting to the C 1s spectra shows that some C-C bonds are also formed.

From XPS analysis two main contributions are found in the outer coating: Mo-S and W-C rich phases together with a low C-C bond contribution. There is no evidence of W-S bonds and since the low percentage of C atoms are mainly bonded to W and C, the presence of Mo-C bonds can be disregarded. Nevertheless, an additional surface analysis technique should be applied to determine if there are some contributions from Mo-C and/or W^o.

It seems that the Mo-S and W-C rich phases remain independent and despite the preferential sputtering of S, the S/Mo ratio in the film can be calculated as reported previously [2] applying the relationship determined by M.A. Baker et al. [7]. A ratio of 1.55 is found in this film, therefore anticipating good lubricating behaviour.

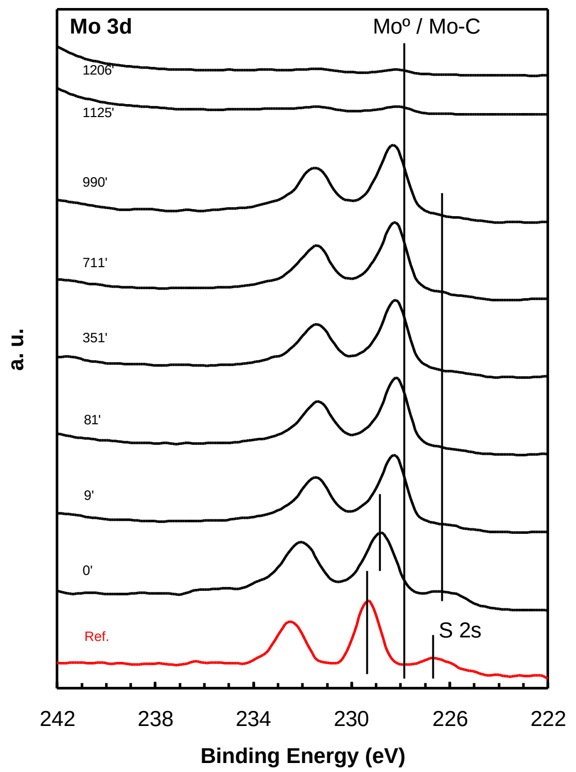

Fig 2: Mo 3d XPS spectra from sample 25956 at different sputtering times. A reference spectrum from MoS_2 is included.

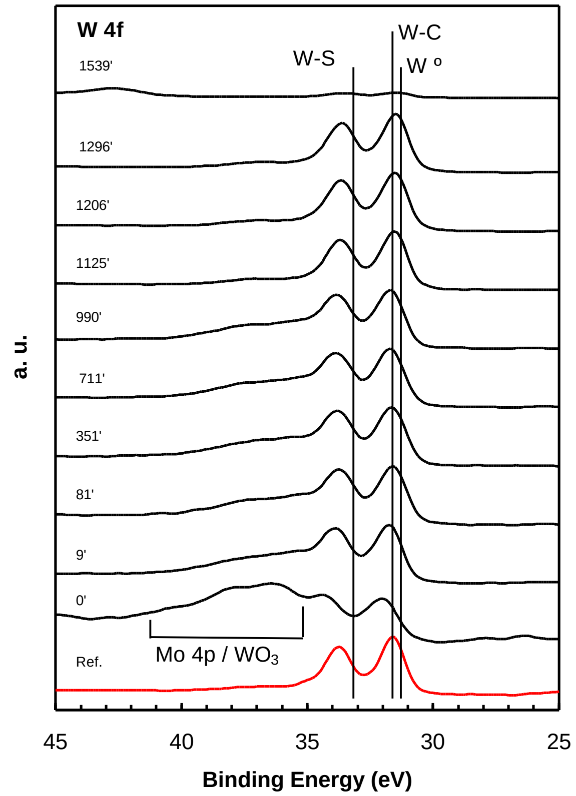

Fig. 3: W 4f XPS spectra from sample 25956 at different sputtering times. A reference spectrum from WC-Co is included.

B) Tribology and mechanical properties.

The microhardness test performed on the MoS_2-WC film showed a hardness under a maximum load of 10 mN of 5179 N/mm^2 and an elastic work of 34.29 %. The loading and unloading curve for this coating is shown in Figure 4.

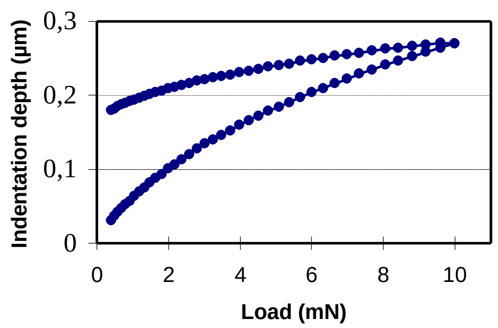

Fig. 4: Load-indentation depth curve for MoS_2-WC.

The wear and friction testing results obtained from the MoS_2-WC films are presented in Table I and Figure 5 (tribology under vacuum) and Table II and Figure 6 (tribology under atmospheric conditions). The tables present summarised tribology data of a representative type of film, that include the mean and peak coefficient of friction, wear rate of the coated disc as well as the endurance life in wear cycles of films before the onset of failure. The failure was determined when the test reached a friction coefficient higher than 0.2 for a prolonged time, due to delamination or depletion of the film and its lubricating protection.

The alloyed MoS_2-WC solid lubricant film exhibits a very low friction coefficient ranging from 0.02 to 0.04, when tested under vacuum, that is characteristic of conventional sputtered MoS_2 films (Table I). The maximum endurance of the film under the conditions tested (0.75 GPa mean contact stress) was nearly as much as 1.2 million wear cycles, which compares very favourably with conventional solid lubricating films according to the results presented in the Space Tribology Handbook [8]. When the same film was tested at a higher contact stress (10 N load, 0.95 GPa), as expected the durability decreased to a mean value in excess of 150.000 wear cycles, still a noticeable result.

Table I: Representative wear test results under vacuum (Ref. MoS_2-WC 25956). Test conditions: 5 N, 0.5 m/s, 6 mm diameter ball of AISI 440C steel.

Test	Endurance (revolutions)	Disc wear rate (mm^3/Nm)	Peak friction μ_{peak}	Mean friction μ_{mean}
AM 1014	657.260	2.4×10^{-7}	0.26	0.04
AM 1015	1.196.049	1.3×10^{-7}	0.20	0.03
AM 1024	609.563	9.5×10^{-8}	0.41	0.02

The evolution of the friction coefficient in most cases was very similar, with a marginal higher friction at start up that soon diminished to a steady state low friction after a short running in process. After about 250.000 cycles a slightly higher torque noise was observed, probably linked with the wearing in the WC rich area of the thin film, but always maintaining very low friction values. Once that the solid lubricating properties depleted in the contact area, the friction started to raise until the cut off value of 0.2 was reached and the test stopped. The transition from a low to higher friction was never abrupt, a characteristic friction curve of the MoS_2-WC thin film evaluated can be seen as an example in Fig. 5.

Observation of the worn coated surface of the disc under the SEM revealed a smooth surface with very fine wear particles accumulated at the edges of the track. An X-ray mapping carried out on the worn area on the ball demonstrated that there was transference of material from the film, therefore performing as a conventional MoS_2 film where there is a constant transfer of platelets between contacting surfaces that accounts for the low friction. In this case, the presence of a wear resistant material such as WC does not appear to degrade the excellent lubricating properties of MoS_2, but on the contrary extends its durability. The XPS results presented earlier appear to show that the major chemical state in the film is that of a carbidic WC, very low C-C contribution, possibly some unresolved metallic contribution, but no trace of a W-S bond. The lubricating properties were therefore mainly due to the Mo-S bonds present in the film.

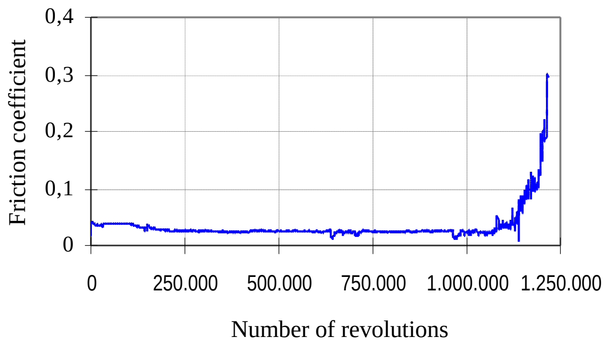

Fig. 5: Characteristic mean friction curve from MoS_2-WC thin film when tested under vacuum conditions at 0.75 GPa.

No electron probe microanalyses (EPMA) have been carried out as yet on these films; however, prior results from the authors with Ti doped MoS_2 films showed very low oxygen concentrations (less than 2%) [2] and S/Mo ratios higher than 1.2 that exhibit good lubricating properties according to Moser et al [9]. It is expected that, as it is showed by XPS analysis on sample 25956, the MoS_2-WC should present also similar low oxygen content and S/Mo ratio, as it is shown by XPS analysis on sample 25956 (S/Mo ratio = 1.55). Figure 2 also shows that there is not a presence of the detrimental MoO_3 phase on the films after deposition, which account for the good tribological behaviour. Unfortunately, there is not much vacuum tribology data of metal alloyed MoS_2 thin films other than the early work of Hinterman and co-workers [10], Spalvins [11], and the more recent of Hilton et al [12]. In most of these reports the emphasis was placed in achieving a solid lubricating film with a higher moisture resistance and therefore enhanced tribological properties under atmospheric conditions. In addition, these films were produced initially using rf sputtering and yielding in most cases a duplex structure consisting of a dense, coherent very thin film followed by a loose columnar structure, that was valid for vacuum and water vapour free environments.

Over the last few years there has been a growing industrial interest in the development of solid lubricant films that could eventually substitute partial or totally the use of liquid lubricants or cutting fluids in some industrial processes. This has been promoted by the increasing environmental pressure on manufacturing processes. One of the coating systems that has been investigated has also been MoS_2, but new advances in magnetron sputtering technology have allowed to produce coatings that alloyed with a variety of metals present a lower sensitivity to high moisture contents in the working environment. One of the groups that has been more actively working in the development of such films is that of D.G. Teer and co-workers [1]. This group has deposited non multiplayer MoS_2 films alloyed with different Ti contents and also with Cr, W and Zr, showing that harder and more wear resistant coatings can be obtained when tested under atmospheric conditions. Unfortunately the data obtained is not correlated with vacuum tribology data to evaluate how adequate are these coatings for application in solid lubricated space mechanisms.

The present authors in a recent publication [2] showed that Ti alloyed MoS_2 films presented a relatively low and stable friction coefficient of about 0.07 - 0.1 when tested under atmospheric conditions and relative humidity below 50-60 %. Higher relative humidity conditions led to degradation in the performance of these films, raising the friction coefficient up to values of 0.2 to 0.6.

In this work, the motivation has been to achieve a MoS_2 film that not only had excellent vacuum tribology response, with low friction and increased durability, but also good resistance to moisture conditions to ease ground qualification testing of solid lubricated space mechanisms.

Vacuum tribology of MoS_2 – WC has been presented above, the tribological results from these films under atmospheric conditions are summarized in Table II and Fig. 6. Tests at higher moisture levels will also be conducted by the authors.

Table II: Representative wear test results under atmospheric conditions (Ref. MoS_2-WC 25956). Test conditions: 5 N, 0.5 m/s, 6 mm diameter ball of AISI 440C steel, 40 to 60 % RH

Test	Endurance (revolutions)	Disc wear rate (mm^3/Nm)	Peak friction μ_{peak}	Mean friction μ_{mean}
40% RH	322.169	3.1×10^{-7}	0.15	0.07
50% RH	238.541	4.7×10^{-7}	0.12	0.09
60% RH	447.622	1.3×10^{-7}	0.19	0.15

The results of the wear tests performed under atmospheric conditions can be considered as very promising. The results appear to be better than those obtained by Matsumoto et al [13] when testing pure MoS_2 under different humidity conditions. However, no direct comparison can be done with those results of Renevier et al [1], since the testing conditions were very different.

Comparing these results with the vacuum tribology data from Table I and Fig. 5, the endurance levels obtained up to 60% RH can be regarded as very good. The average friction coefficient increases from 0.07 to 0.15 with increasing humidity from 40 to 60%, but the high endurance and the low disc wear rate seem to indicate that ground testing could be done with these films without risk in subsequent vacuum performance of a mechanism.

Figure 5 shows a characteristic plot of the variation of the average friction coefficient of a MoS_2-WC film as a function of the number of revolutions, when testing at 50% RH. The results can be regarded as similar to those obtained by other workers when alloying with other elements [1], but with a better frictional behaviour when compared to films without alloying elements [14], although in the latter case the films evaluated had a remarkable low sulphur content.

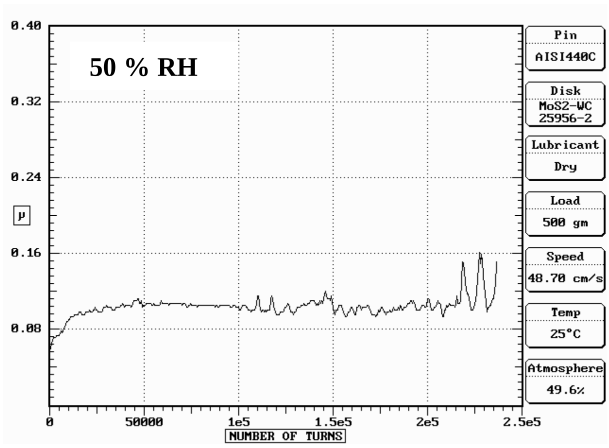

Fig. 6: Characteristic friction curve from MoS_2-WC thin film when tested under atmospheric conditions, 50% RH.

CONCLUSIONS

The following summarised conclusions can be drawn:

- MoS_2-WC thin films have been deposited by means of magnetron sputtering which have good tribological properties, both under vacuum and at different humidity levels.
- Vacuum tribology of these films shows that the endurance at 0.75 GPa can be as high as 1.2 million wear cycles, which is significantly higher than the values obtained from unalloyed, conventional MoS_2 thin solid films. The extended endurance life of the films is not achieved at the expense of a low friction, the films exhibit a steady state friction coefficient from 0.02 to 0.04.

- As it occurs with conventional MoS_2 thin solid films, there is transference from the coated material to the mating surface.
- These MoS_2-WC thin films have also good tribological behaviour under atmospheric conditions at different humidity levels (from 40 to 60% RH), showing an endurance of as high as 450.000 wear cycles and average friction coefficients as low as 0.07.
- The W content in the films is mainly in carbidic form (W-C), although some metallic (W^o) contribution might be present. There is no evidence of W-S bonds as revealed by the XPS analyses.
- The good tribological response of the films is thought to be mainly due to the Mo-S bonds and the low oxygen content of the film, therefore delaying the formation of the deleterious MoO_3 phase. The presence of the WC phase within the MoS_x matrix ($x > 1.2$) helps in the establishment of a low wear rate without impairing a low frictional behaviour characteristic of the solid lubricating film. Tests are still in progress to determine the resistance of the films at higher humidity and contact stress levels.

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