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EFFECT OF POLYTETRAFLUOROETHYLENE DOPING ON TRIBOLOGICAL PROPERTY IMPROVEMENT OF MoS_2 NANO-THIN FILMS ON Ti-SUBSTRATE

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Abstract. In the present work, attempts have been made to dope MoS_2 films with moisture-repellent polytetrafluoroethylene (PTFE) by the co-sputtering technique, with the purpose to reduce the moisture sensitivity and to improve the tribological performance of the films. Several films have been produced by the combined direct current (DC) and radio frequency (RF) magnetron sputtering technique. These include pure MoS_2, graded MoS_2-PTFE and mixed MoS_2-PTFE films. The resultant films were characterised by a variety of experimental and analytical techniques, scanning electron microscopy for film morphology examination, nanoindentation for hardness and elastic modulus evaluation, and ball-on-disc sliding tests for tribology measurement, for instance, friction coefficient and film wear-life. The experimental results showed that doping MoS_2 with PTFE has several advantages over the pure MoS_2 film. These include increased film hardness and modulus, and more importantly reduced friction coefficient and increased film wear-life, particularly after prolonged storage of the specimens in open-air environments. The performance of the films relies on the content of PTFE in the film, which is controlled by sputtering power and co-deposition time. By appropriate doping with PTFE, the tribological performance of the film under ambient conditions could be significantly improved.

1. INTRODUCTION

Molybdenum disulfide (MoS_2) films have been developed for vacuum and space applications due to their super lubricity under vacuum conditions [1]. However, under normal ambient conditions, pure MoS_2 films show much poorer lubricating performance due to the interaction of the film with the moisture in the ambient atmosphere. Recently, there have been increasing interests in using MoS_2 films in the field of precision engineering, for example in bearing components and in manufacturing operations [2]. Efforts have been made to improve the moisture resistance of MoS_2 films (mainly by surface), interface and bulk modification of the film-substrate system, including doping MoS_2 films with various kinds of metals [3,4].

Polytetrafluoroethylene (PTFE or Teflon) or is known for its high thermal stability, chemical inertness, low surface tension and excellent tribological performance, properties that are advantageous for many applications [5,6]. Lui *et al*. [7] sputtered PTFE to improve the tribological performance of the substrate and endowing the surface with hydrophobicity.

In this present paper, attempts have been made to dope MoS_2 films with moisture-repellent polytetrafluoroethylene (PTFE) by the co-sputtering technique, with the purpose to reduce the moisture sensitivity and to improve the tribological performance of the films. The resultant films were characterised by a variety of experimental and analytical techniques, including scanning electron mi-

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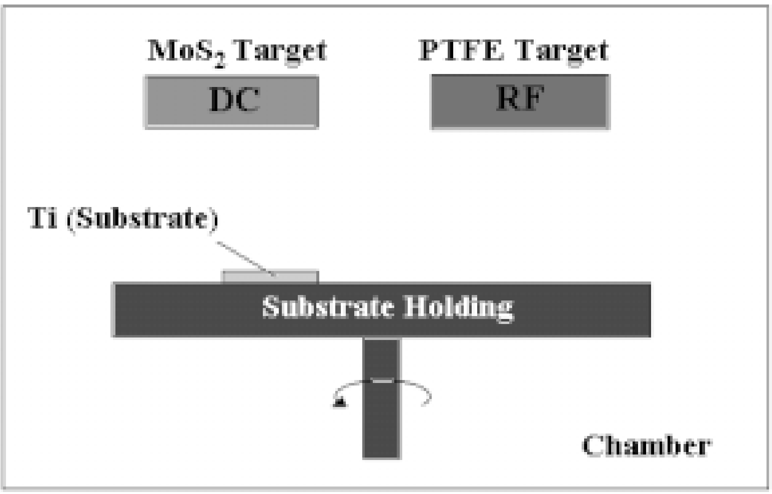


Fig. 1. Schematic of sputtering system.

Table 1. Deposition conditions.

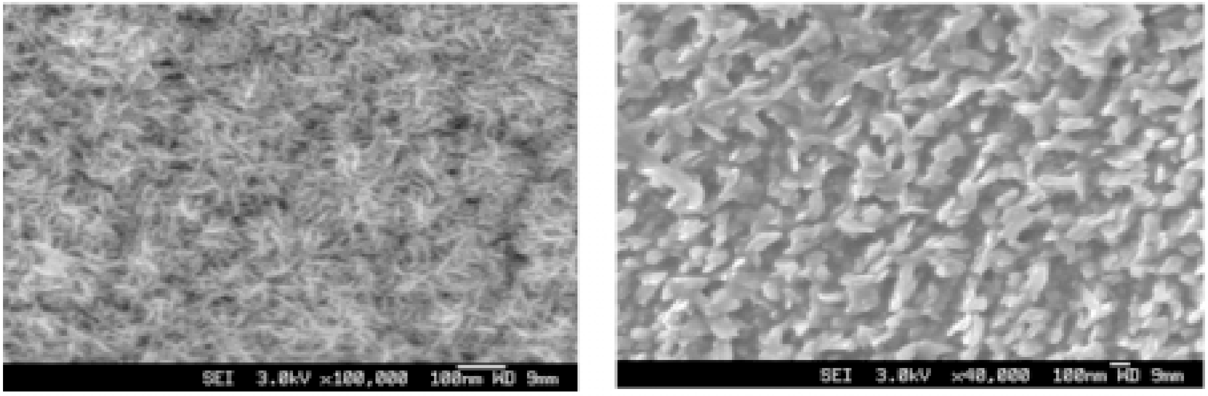
Specimen	Mode	Parameters Base Layer	Parameters Top Layer	Thickness of Film (μm)
1	Pure MoS_2	200 W MoS_2 for 2 Hrs	-	3.6
2	Graded MoS_2-PTFE	200 W MoS_2 for 1 Hr	200 W MoS_2 + 100 W PTFE for 1 Hrs	3.2
3	Graded MoS_2-PTFE	200 W MoS_2 for 1 Hr	200 W MoS_2 + 50 W PTFE for 1 Hrs	3.0
4	Mixed MoS_2-PTFE	200 W MoS_2 + 50 W PTFE for 2 Hrs	-	4.0

croscopy for film morphology examination, nanoindentation for hardness and elastic modulus evaluation, and ball-on-disc sliding tests for friction coefficient and film wear-life measurements.

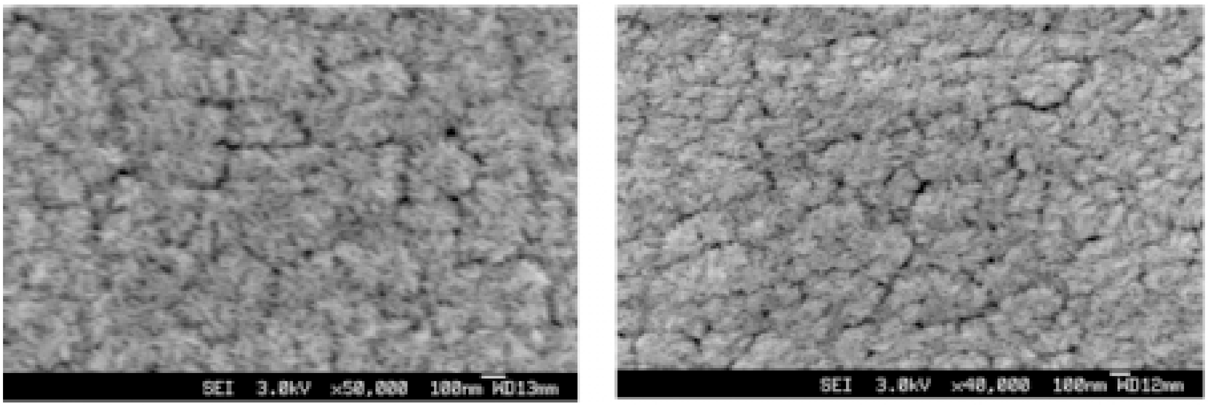
2. EXPERIMENTAL PROCEDURE

The films were prepared on titanium in a magnetron sputtering system (MSS3 by the Coaxial company, UK) equipped with DC system for the MoS_2 target and RF system for the PTFE targets and a substrate heater, as shown in Fig. 1. The base pressure of the system was $5{\cdot}10^{-6}$ torr. Pure (99.95%) iron disc of 75 mm in diameter and 5 mm thick, which was located 14 cm above the substrate, was used as the sputter source for iron.

Titanium was grinded by standard metallurgical silicon-carbide waterproof papers, which have grid size 180, 320, 800 and 1,000, and no polishing. The titanium was cleaned in an ultrasonic bath of acetone for 5 min before charging in the deposition chamber. High-purity Argon gas was introduced into the chamber after the chamber was evacuated to below $5{\cdot}10^{-6}$ torr. Then the pure MoS_2 and PTFE targets were pre-sputtered for 15 min with the target shutter closed. The working table was rotating at 2 rpm during the process. All the experiments were conducted at a constant working pressure at 5 mtorr, total gas flow rate at 20 sccm, and substrate temperature at 100 °C. The detailed deposition parameters were concluded and listed in Table 1. Scanning electron microscope (SEM) and high-resolution field emission scanning electron microscope (FESEM) were used to examine the morphology of the surfaces and fractured cross-sections of the films.



(a) Pure MoS_2 film (Sample 1) (b) PTFE doped MoS_2 film (Sample 2)



(c) PTFE doped MoS_2 film (Sample 3) (d) Mixed PTFE + MoS_2 film (Sample 4)

Fig. 2. FESEM images showing the surface morphology of the as-deposited films on titanium.

Nanoindentation test involves indenting a specimen by a very low load using a high precision instrument, which records the load and displacement continuously. The mechanical properties, hardness and elastic modulus, can be derived from the measure load-displacement loading/unloading curve through appropriate data analysis [8-10]. The thin film was indented by diamond Berkovich indenter in nano-scales and performed to a depth of 100 nm to avoid the substrate effect to the coating properties. The experiment is performed using the NanoTest$^{\text{TM}}$ (Micro Materials Limited, UK). The NanoTest$^{\text{TM}}$ device measures the movement of a calibrated diamond indenter penetrating into a specimen surface at a controlled loading rate. This device uses a pendulum pivoted on bearings, which are essentially frictionless. These tests are based on new technologies that allow precise measurement and control of the indenting forces and precise measurement of the indentation depths.

A ball-on-disc tribometer (CSEM 15-208 Instruments, Neuchatel, Switzerland) was used to perform dry sliding friction experiments on the film. The ball-on-disk test was performed on the film coated on sample by alumina ball (Al_2O_3), diameter 6 mm, was used as the counter face material against the films, The loading was 2 N for all test. The sliding velocity was 20 cm/s, and the test duration was 200 meters for all tests. The ball-on-disk tests were conducted in ambient air conditions, with temperature of 23 °C and relative humidity of 50% during the test.

3. RESULTS AND DISCUSSION

3.1. Film morphology

The morphology of the as deposited film surfaces was examined under FESEM, Fig. 2. The pure MoS_2 film (sample 1) exhibits a needle-like structure, typical of a porous columnar structure with

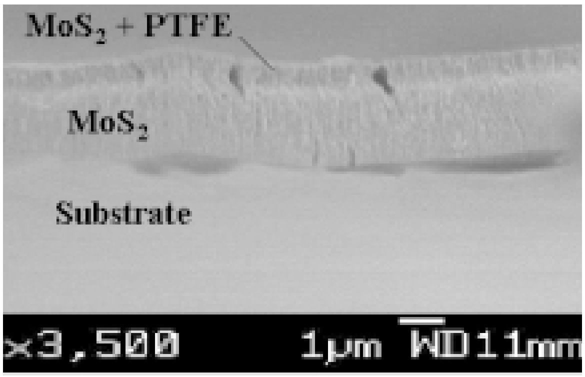


Fig. 3. FESEM image of fractured cross section of sample 2.

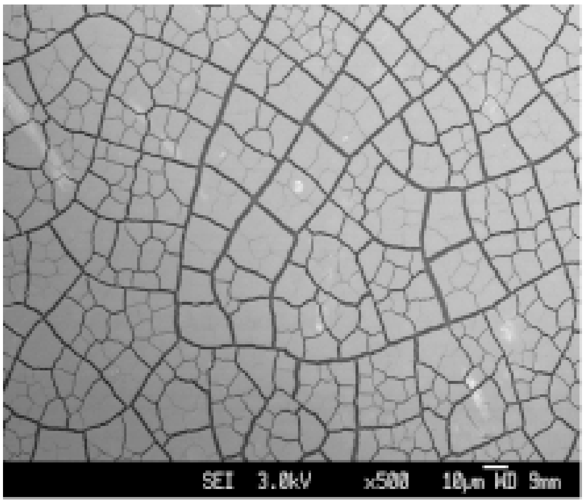


Fig. 4. Pure MoS_2 film surface after storage in ambient environment for 4 months.

Table 2. The measured results of mechanical properties by nanoindentation method.

Coating Film Specimen	Thickness (μm)	Maximum Depth (nm)	Hardness (GPa)	Elastic Modulus (GPa)
1	3.6	100	0.60	7.20
2	3.2	100	0.80	12.80
3	3.0	100	0.68	9.42
4	4.0	100	0.70	11.20

random orientation in the film deposited at relatively high pressures (Fig. 2a). Doping the top part of the film or the whole MoS_2 film with a small amount of PTFE (50 W RF power on the PTFE target), the film morphology changes to cauliflower-like (Figs. 2c and 2d), which is less porous and thus indicates improvement in film quality and basal plane orientation. This reflects the benefits of doping with PTFE. Increasing the PTFE target power such that more PTFE is incorporated in the top part of the film results in a significant change in film morphology (Fig. 2b). The incorporation of a significant amount of PTFE also leads to the roughening of the film surface, as can be seen from Fig. 2b. The formation of relatively large PTFE particles is probably due to the increased amount of sputtered polymer macromolecules which have a low mobility on the growing film surface.

Fig. 3 shows the FESEM image of the fractured cross section of sample 2, revealing the graded nature of the resultant film, which is characterised by the MoS_2 base layer and the PTFE doped MoS_2 top layer. The columnar growth and nano-structure of the film are also noted. The morphology and quality of the resultant films were examined again after several months storage in laboratory environment. It was found that the quality of all the films was deteriorated after prolonged exposure to the ambient atmosphere, in terms of water condensation on to the film surface, partial flaking and cracking of the film. Such a deterioration is the most serious for the pure MoS_2 film, and is obviously associated with the moisture sensitivity of MoS_2, particularly when basal plane orientation is not achieved as in the present MoS_2 film. It is anticipated that the condensation of water on to the film surface and then the penetration of water molecules along the exposed basal planes to the film-substrate interface would weaken the cohesive strength of MoS_2 and weaken the film-substrate adhesion strength [11], and thus would result in film cracking and debonding. The crack pattern formed

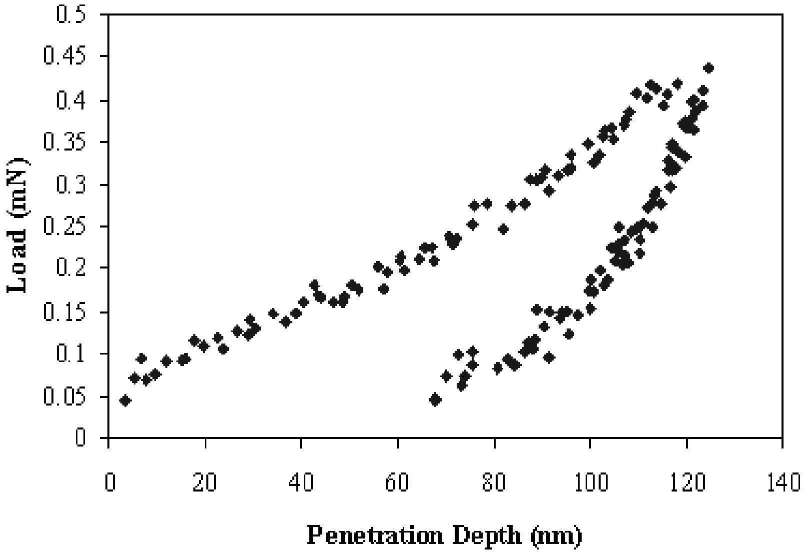


Fig. 5. Nanoindentation load–displacement curves for MoS_2 film obtained with a Berkovich indenter during loading and unloading.

on the pure MoS_2 film after 4 months exposure is illustrated in Fig. 4.

The deterioration in film quality after prolonged storage is not so severe in the PTFE doped films. Less amount of water condensation, less film cracking and flaking were observed in these films. In particular, film sample 2, which contains a relatively large amount of PTFE in the top part, is almost intact after several months exposure. This important improvement in film quality by PTFE doping is obviously derived from the moisture-repellent ability of PTFE.

3.2. Nanoindentation test

There have been very limited reports on the mechanical properties such as hardness and elastic modulus of MoS_2 films, probably due to the difficulties in assessing the properties of thin solid lubricant films and the many factors that can influence MoS_2 film properties. Indeed, a wide range of hardness and modulus values have been reported for MoS_2 film with different orientation and produced under different conditions. Fig. 5 shows load-displacement curve of sample 1 tested at 100 nm penetration depth. It can be seen that loading curve with the unloading one. This is to extract the intrinsic mechanical properties of the tested samples by calculating the coating properties from the unloading curve. A general anticipation is that MoS_2 with basal plane orientation parallel to the surface should exhibit higher hardness and modulus. This is indeed true in the present case, as can be seen from the summarised nanoindentation results for the films tested (Table 2). All the PTFE doped films show higher hardness and elastic modulus values, in accordance with the observation that PTFE doping promotes basal plane orientation, which gives rise to hardness and modulus of the film.

3.4. The results of tribology test

Fig. 6a shows SEM image analysis results of the friction-wear track in specimen 1. It was observed that plastic deformation of titanium substrate occurred during the ball-on-disc test. The plastic deformation and ball impact contributed to local debonding of MoS_2 film coating from titanium substrate and obviously the MoS_2 film was flaked out from titanium substrate around the peripheral rounded track.

Wear debris particles are expected to detach from the transfer film layers that accumulate in a contact. Wear debris from the ball-on-disk tests was also by scanning electron microscopy imaging shown in Fig. 6b. It was observed that the wear debris were trapped in the contact area as the third body and caused micro-cutting on the film. Fig. 7

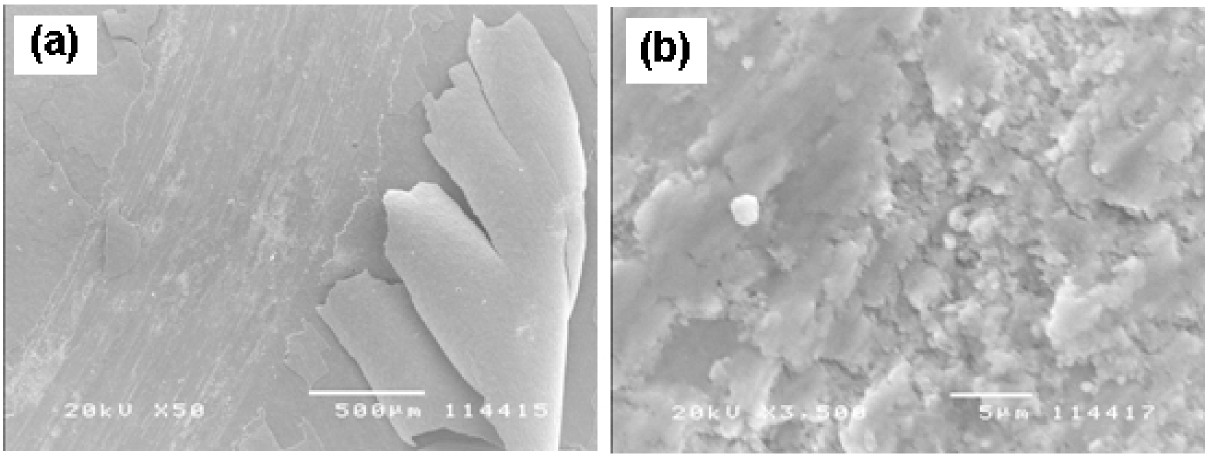
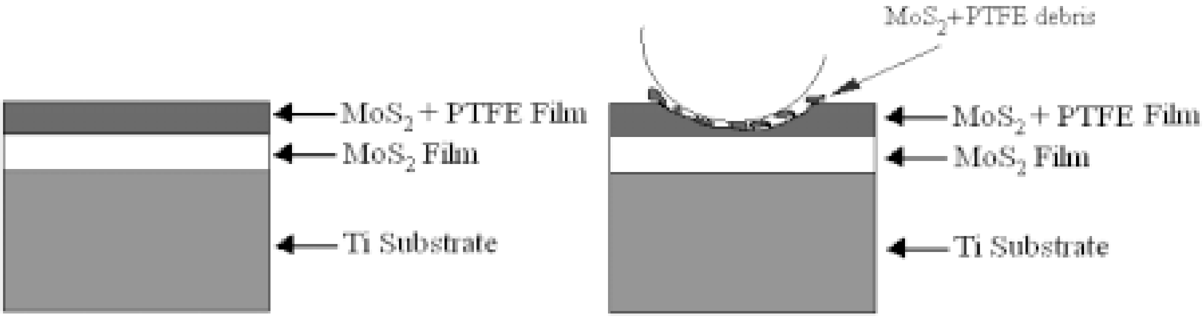
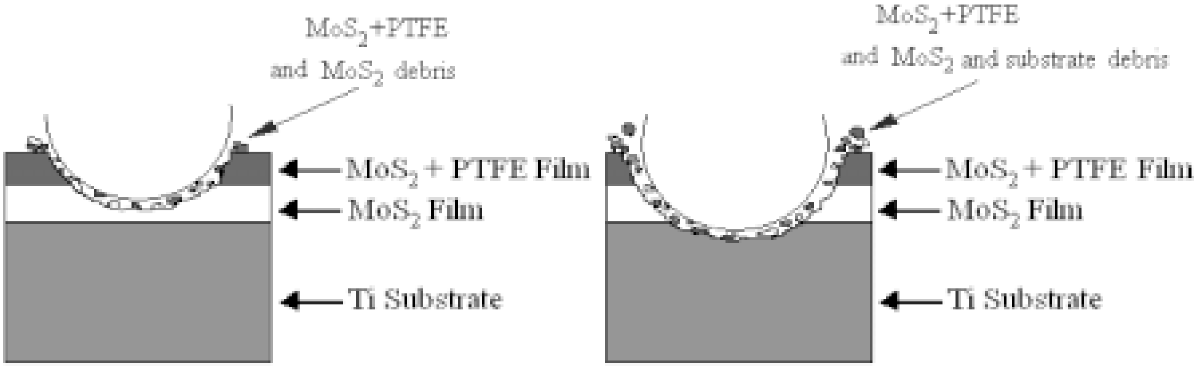


Fig. 6. Scanning electron micrographs showing tracks image and surface microstructure of MoS_2 film on titanium specimen.



(a) Before wear test (b) Wear of MoS_2 + PTFE layer



(c) Wear of MoS_2 Film (d) Wear through of all coating

Fig. 7. Schematic illustrations of wear process of the graded MoS_2–PTFE coating.

shows the wear process of the graded MoS_2–PTFE film that undergoes three stages i.e. the wear of MoS_2–PTFE surface layer; the wear of rich MoS_2 interlayer; and the wear of the substrate through the test process.

A ball-on-disc friction test of the coated samples was first conducted within 2 days after deposition. This is to minimise the effect of moisture condensation on friction behaviour. The recorded friction curves are shown in Fig. 8. The coating sample 1

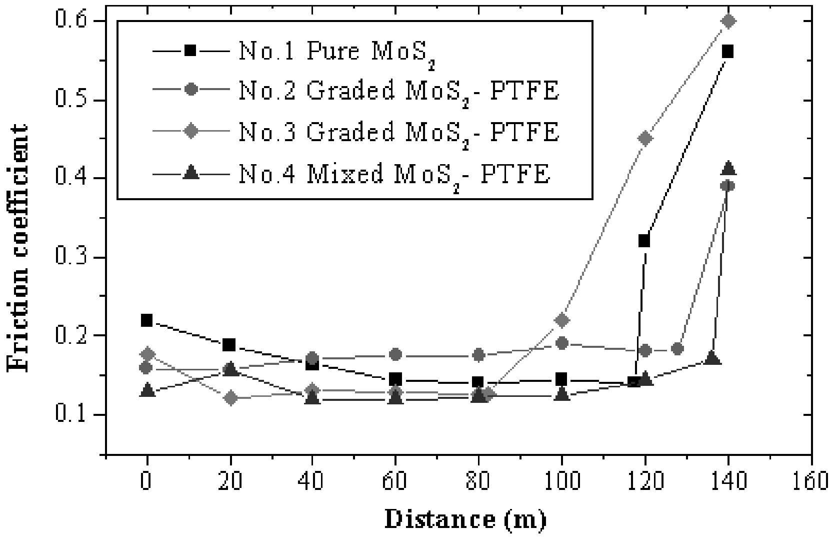


Fig. 8. Variation of friction coefficient of four specimens of coating with sliding distance.

Table 3. Results of sliding friction and wear test.

Coating Specimen	Wear area (x10^{-3} mm^2)	Wear Volume (mm^3)	Sliding Distance (mm)	Wear Rate (x10^{-6} mm^2)
1	15.40	0.484	200,000	2.42
2	9.35	0.293	200,000	1.47
3	11.40	0.358	200,000	1.79
4	7.70	0.242	200,000	1.21

showed the typical frictional behaviour of pure MoS_2: the friction coefficient is relatively high at the start of the test (due to the existence of adsorbed water), decreases to a steady state value around 0.15 (due to frictional heating which removes the adsorbed water), and after a certain distance of sliding, increases abruptly, which marks the total failure and the wear-life of the solid lubricant film. The PTFE-doped films behave slightly differently from the pure MoS_2 film. The benefit of PTFE doping in reducing the initial friction coefficient is obviously due to the moisture repellent effect of PTFE, such that less water is adsorbed on to the film surface.

The wear volume of each sliding tests can be estimated using a profliometer to trace the surface roughness on the specimen. A probe is slide horizontally across the wear track and the resultant surface profile is being printed on a piece of paper in the form of grid such that the cross-sectional are of each track can be estimated and hence, the wear volume can be determined.

The wear volume values are summarised in Table 3. It is clear to demonstrate the benefit of PTFE in order to improve the wear-life of the MoS_2 films. With doping PTFE such as sample 4, the wear volume of pure MoS_2 film was reduced from 0.484 to 0.242 mm^3 (50% by volume). This has shown the promising results of the benefit of doping PTFE due to the reduced moisture sensitivity effect of PTFE.

4. CONCLUSIONS

(1) Composite MoS_2-PTFE solid lubricant films can be fabricated by co-sputtering of MoS_2 and PTFE targets.

(2) Doping MoS_2 film with PTFE is beneficial for improving the mechanical and tribological properties, such that the PTFE doped films exhibit improved density, increased hardness and modulus.

(3) PTFE doping improves the quality of MoS_2 film after prolonged storage, due to the reduced moisture sensitivity effect of PTFE.

(4) Mixed MoS_2-PTFE film has shown the lowest value of friction coefficient (about 0.12). It also has shown the longest wear-life compared with without PTFE and graded MoS_2-PTFE mode.

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