THE PUBLISHING HOUSE
OF THE ROMANIAN ACADEMY

PROCEEDINGS OF THE ROMANIAN ACADEMY, Series
Volume 8, Number 3/2007, pp. 000-000

TRIBOLOGICAL PROPERTIES OF SOLID LUBRICANT NANOCOMPOSITE COATINGS OBTAINED BY MAGNETRON SPUTTERED OF MOS_2/METAL (TI, MO) NANOPARTICLES

Filip I. ILIE [*], Constantin M. TITA [**]

* Department of Machine Elements and Tribology, Polytechnica University of Bucharest, Spl. Independentei 313, 060042 Bucharest, Romania
** School Group «G-ral Magheru» Way of Traian 43, 240011 Rm.Valcea, Romania
E-mail:

In this paper we have investigated the tribological properties of solid lubricant coatings from Mo_2S nanoparticles. The MoS_2 were deposited on alloy substrate by magnetron sputtering. The methods were used to create two component coatings in which MoS_2 were embedded in a Ti matrix. The morphology and microstructure of the coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). The tribological properties of MoS_2/metal (Ti, Mo) nanocomposite coatings were investigated using a pin-on-disk (POD) tribometer in ambient air and in humidity conditions. A POD test was used to examine the friction behavior and mechanical stability of the coatings, and was carried out in both low and high humidity conditions. XRD and SEM were used to examine morphology of the wear track after the POD test. The MoS_2 nanoparticles can decrease the friction coefficient of lubricants obviously. However the results showed that their friction reductions have not obvious difference by the POD tribometer. The MoS_2/Ti nanocomposite coating showed lower frictions coefficient and higher wear resistance as compared to the pure MoS_2 coating, which were caused by the microstructure of the composite coating that serve as perfect intermediate lubricants between the contact surfaces. The analyses of surfaces composition coating characterized by XRD and SEM images showed that deposition nanoparticles, form a protective film allowing an increase in the load capacity of friction (rubbed) pairs. The main advantage of the nanoparticles is ascribed to the release and furnishing of the nanoparticles from the valley onto the rubbing metal surface and their confinement at the interface. Coatings of MoS_2 alone were found to perform well under low-humidity conditions, but poorly under high-humidity. Alloying of MoS_2 with Ti was found to provide some improvement under high humidity. The patterned film by MoS_2/Ti nanocomposite was found with friction and wear properties superior to either Ti or MoS_2 alone. The effects of metal inclusion in the non-composite were further discussed and compared with the former reports. The coatings investigated here have potential applications for cutting tools and metal forming dies that will enhance tool life and reduce the energy expended due to friction forces, as well as for use in various tribological fields such as seals, bearings or electrical motor brushes and, also, for applications needing excellent lubrication and wear-reducing properties.

Key words: lubricant, tribology, nano-composite, coating, MoS_2 – nanoparticles

1. INTRODUCTION

Solid lubricants have the advantages including long life, no contamination and usage in harsh environments that liquid lubricant cannot be used. It has been very well known that MoS_2, especially nanosized MoS_2, presents considerable applications in many fields such as solid lubrification and for lubricating oils and potential self-lubricating polymer materials [1].

It is reported that MoS_2 nanoparticles mixed in oil, grease or impregnated into matrix porous of powdered materials appear to enhance the tribological properties in definite loading range in comparison to typical metal dichalcogenides particles [2].

Magnetron sputtering and ion plating technology have been developed to deposit MoS_2 coatings. There are many different kinds of methods to prepare ultrafine MoS_2 (molybdenum disulfide) particles. However, using different preparation methods will result in the variations of morphology and performance of MoS_2 nanoparticles.

When pure MoS_2 coating is exposed to oxygen-rich atmosphere, however, tribological performance deterioration would occur due to the oxidation MoS_2. It has been found that co-sputtering MoS_2 with metal resulted in better tribological properties than that without sputtering metal. In particular, coatings with Ti inclusion exhibit a stable friction coefficient and better endurance than pure MoS_2 coatings in ambient condition.

During sputtering and rubbing process Ti could prohibit the act of entering of O_2 from destroy the constituent and the structure of the coatings at the same time TiO_2 generated could be used as lubricating material, too.

Manufacturing processes used to cut and shape metals can involve severe high-speed and high-temperature surface interactions between the work piece and cutting tool or die. Coatings for tools and dies can provide reduced friction and improved tool life.

Solid lubricant coatings are attractive because they can reduce friction-generated heat. MoS_2 is a common solid lubricant. However, the use of MoS_2 can limited by excessive wear, as well as a friction coefficient that is sensitive to humidity [3]. Nonetheless, several studies on solid lubricant coatings demonstrated success in lubricating dry sliding contacts over very long periods in pin-on-disk (POD) or reciprocating sliding experiments [4]. Further studies [3, 4] showed that reservoirs developed where lubricant storage can take place, such as on the ball, around the perimeter of the wear scar, or at the terminal points of a reciprocating wear track.

In this paper, we present tribological properties of the composite coatings and the effects of Ti and Mo inclusion in the composite coatings on their tribological performance in ambient air and in humidity conditions, respectively results on patterned coatings and compared them to alloyed and nanolithic single phase coatings.

2. EXPERIMENTS

Films of MoS_2 , Ti and MoS_2-Ti alloys were deposited by magnetron sputtering. MoS_2/metal (Ti, Mo) coatings were deposited silicon substrates at room temperature by magnetron sputering. The MoS_2/metal ratio in the coatings was controlled by sputtering the composite targets.

Pure Ti target (99,99%) and MoS_2/metal composite targets (pure MoS_2 mixed with Ti) with a diameter of 10 mm were used.

The composite targets were fabricated by press milling the mixture of pure MoS_2 and metal powder, followed by pressing the mixture under a pressure of 60 MPa. Films were deposited on Si and OLC45 steel substrates.

Pre-sputtering was performed to clean the surface of the targets prior to the depositing process.

For the MoS_2 and MoS_2-Ti alloy films, a bond layer of aproximately 50 nm of Ti was first deposited on the substrate, because could improve the coating adhesion.

Afterwards, the composite coatings with a thickness 1 μm were obtained by sputtering the composite targets. The content of metal inclusions in the main bulk of the coatings was varied by using different composite targets.

Tribological properties of the composite coatings were performed on a pin-on-disk (POD) tribometer. Table 1 shows the film deposition parameters and compositions.

Table 1. Film deposition parameters and compositions.

Sample	Type	% Mo	% S	% Ti	Mo/S ratio
1	MoS_2	30.5	69.5	0.0	0.44
2	MoS_2-Ti alloy	33.1	56.9	10.0	0.58
3	MoS_2-Ti alloy	24.4	55.4	20.2	0.44
4	MoS_2-Ti patterned	N/A	N/A	N/A	

The compositions given in Table 1 were established by energy dispersive spectroscopy (EDS) in the SEM. The wear tracks of the coatings were examined by means of SEM.

The tribological properties of deposited films were analyzed using a pin-on-disk (POD) test tribometer.

All tests were carried out using a 10 mm diameter steel pin as the contraface. The tests were run using a load of 1 N and sliding speed of 0.2 m/s , with track diameters between 25 and 35 mm.

The environment was air, but the humidity was set at either a low humidity (LH) range 25-35% r/h or a high humidity (HH) range of 65-75% r/h. During the test the sliding load was monitored and recorded every 5 seconds in order to determine the friction coefficient vs number of cycles. After the test, the sample was examined using both X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

The film compositions analyzed by EDS analysis are shown in Tabe 1, along with the Mo/S ratio for all films. With exception of a sample 2 the films appear substoichiometric with respect to S content.

The patterned film (4 in Table 1) was examined in the SEM, and a cross-section of the as-deposited film on Si is shown in Figure 1. X-ray difraction (XRD) was also carried out for these films, and the results showed the films were mostly amorphous.

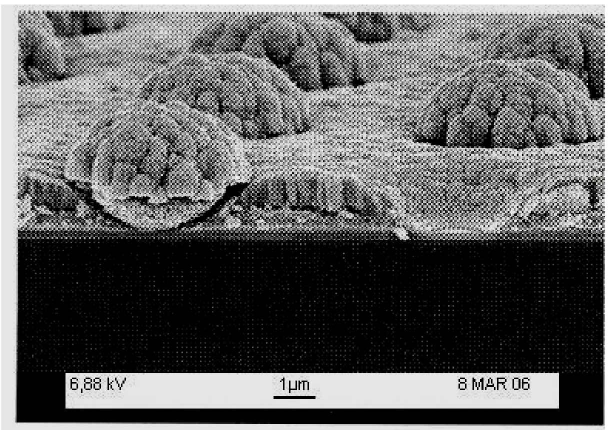

Figure 1. Cross-section SEM image of sample MoS_2-Ti patterned.

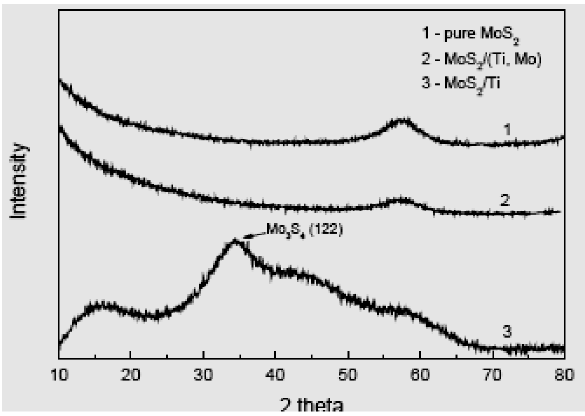

Figure 2. X-ray diffraction patterns of the composite coatings deposited with different targets.

The rounded mounds are MoS_2 and the adjacent film is a bilayer of Ti (lower) and MoS_2 (upper section). The scale marker is equal 1μm.

Figure 2 shows the XRD patterns of deposited coatings on silicon (Si) substrate. From the XRD analysis, it can observed that the deposition coatings has a disorderly structure. No peaks of crystalline phase are found from the pure MoS_2 and MoS_2/(Ti, Mo) coating.

In contrast to the pure MoS_2 and MoS_2/(Ti, Mo) coatings, an apparent peak of Mo_3S_4 appears in pattern 3 for the MoS_2/Ti coating, which is in agreement with the result of addition of Ti to the coatings inhibiting the formation of crystalline MoS_2.

In this present paper, the sufficient addition of Ti prohibited the crystalline of MoS_2 and promoted the formation of Mo_3S_4.

Relative sputering without the addition of metal was difficult to produce the crystalline MoS_2.

The variations of friction coefficient vs. number cycles functioning of the coatings in ambient air at a sliding speed of 0.2 m/s and an applied load of 1N are shown in Figure 3. After running-in, the coatings show the steady friction state and long wear endurance. The pure MoS_2 coating demonstrated a friction coefficient of 0.05 and did not fail until 36000 cycles.

The addition of Ti in MoS_2 coating decreased the friction coefficient, as presented in curve (3), consequently, the steady friction coefficient reached about 0.03. However, the addition of Mo in the composite coatings increased the friction coefficient to obout 0.08 when rubbing state was stabilized. Under lower applied load as our paper, Ti assisted the sliding of the MoS_2 coating more easily.

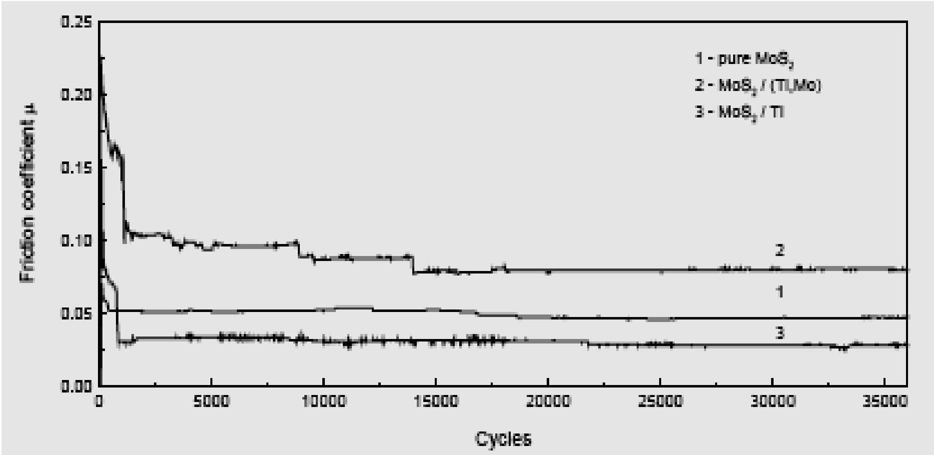

Figure 3. SEM micrographs of the surface morphology of the coatings: 1 - pure MoS_2; 2 - MoS_2/(Ti, Mo); 3 – MoS_2/Ti.

Figure 4 shows the wear tracks of the coatings after microfriction tests. No spalling of the coatings were observed, which was coincided with the steady friction coefficient until the sliding end of 36000 cycles.

In comparison with the wear tracks of the coatings shown in Figure 4 a, b, c, it can be found that morphology of rubbing surface of MoS_2 /Ti coating is smoother than the other two coatings. In the contrast to the MoS_2 /Ti coating, the obvious scratch tracks on the MoS_2 /(Ti, Mo) coating are observed, as shown in Figure 4b.

Lots of wear scar are presented on the rubbing surface. As indicated in XRD pattern (see Figure 1), the MoS_2 /(Ti, Mo) coating has poor crystalline MoS_2 structure. Otherwise, MoS_2/Ti coating has not the distinguished MoS_2 structure, the main structure is Mo_3S_4.

Therefore, simultaneous addition of Mo and Ti increase the formation of the MoS_2, which is adverse for the friction coefficient and wear resistence proved by our experiments. While sufficient addition of Ti alone would facilitate the formation of Mo_3S_4, Mo_3S_4 resulted from addition of Ti improved the tribological properties, also, the formation of TiO_2 in the coating as a result of oxygen gettering during the rubbing test could facilitate superior friction coefficient and wear resistance.

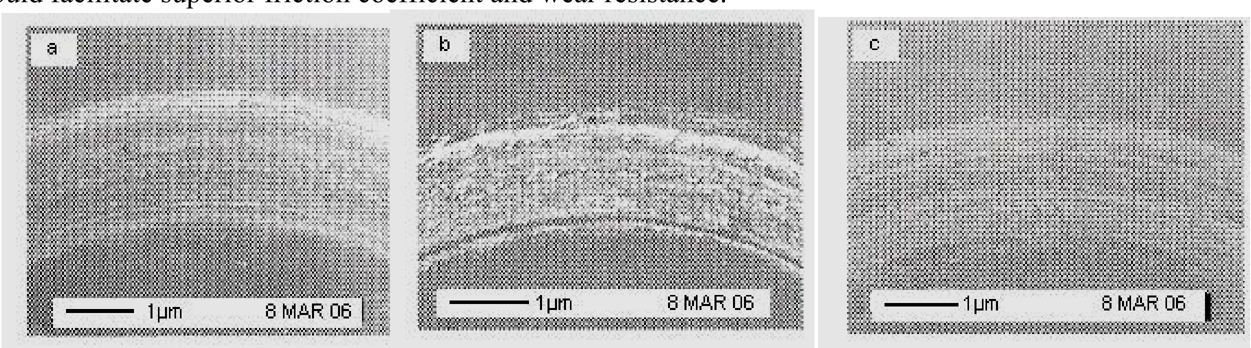

Figure 4. SEM micrographs of the wear tracks of the coatings: a - pure MoS_2; b - MoS_2/(Ti, Mo);c - MoS_2/Ti.

Tribological testing of the MoS_2 coatings was carried out under dry and humid conditions. For the dry condition, the friction coefficient remained at 0.08 for 8000 cycles, at which point the test was termined (see Fig. 5). Under humid conditions, the friction coefficient started at 0.2 and rose to 0.5 after 5000 cycles.

This test confirmed the well-known effect of humidity through the friction behavior of MoS_2 coatings [3].

The friction behavior of the MoS_2-Ti alloy coatings were also tested under both low and high humidity conditions.

Under low humidity conditions sample 2 (see Table 1) maintained a low friction coefficient (0.1) while sample 3 was slightly heigher in friction (0.18). Under high humidity conditions, the coating of sample 1 (MoS_2-Ti alloy) has a reasonable friction coefficient (average near 0.2), but exhibits a high scattering compared to the result for the same coating under low humidity conditions. Sample 3 (see Table 1) appeared worse and the test was terminated after 3500 cycles. Overall, the addition of a smaller amount of Ti (10 %) improves the friction behavior under high humidity conditions, but does not completely cancel the effects of humidity.

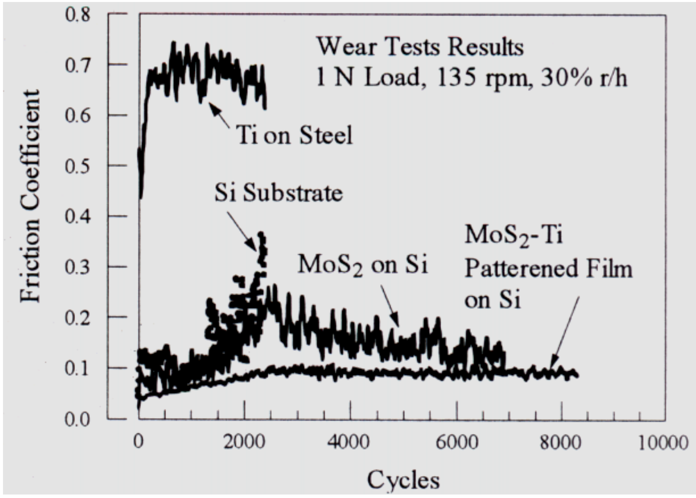

Fig. 5. Pin-on-disk test result for the patterned MoS_2-Ti coating and comparison to MoS_2, Si and Ti.

Fig. 5 shows the results for the patterned MoS_2-Ti coating (on Si substrat) and others under low humidity conditions.

The patterned coating mantained a low friction coefficient of 0.1 for the duration of the 8000 cycles test. The test result for the Si substrate is shown, and a similar result is obtained for MoS_2 on Si, which indicates the coating had worn through the Si substrate. A coating of Ti on steel is also shown, and this coating exhibited a very short life. Therefore, for coatings on Si, the patterned MoS_2-Ti coating gave a longer wear life and a lower friction coefficient than those of the constituent (Ti or MoS_2) coatings alone.

4. CONCLUSIONS

Addition of Ti helps the formation of Mo_3S_4, which is favourable to the decrease of the friction coefficient. The MoS_2/Ti composite coating showed the superior friction coefficient and wear resistance in ambient air.

Except Ti, the addition of Mo helped the formation of MoS_2 structure. The bigger flakes in the MoS_2 (Ti, Mo) composite coatings were not favourable to the improving tribological properties as compared to the coatings without metal inclusions.

Effect of humidity through the friction behavior of MoS_2 coatings is different as a function of humidity conditions (low or high humidity) and of the Ti percent.

The coatings on Si, the patterned MoS_2 –Ti coating gave friction and wear properties superior (a longer wear life and a lower friction coefficient) than those of the constituent (Ti or MoS_2) coatings alone.

REFERENCES

1. WO H., HU K., HU X, *Tribology* **24**, 33-37 (2004).
2. URCENBERG R., HALPERIN G., ETSION I., TENNE R., *Tribology Letters* **17**(2), 179-186, 2004.
3. E. ARSLAN, F. BÜLBÜL, I. ERFEOGLU, *Tribology Transactions*, No. 47, 218-226 (2004).
4. WAHL K. J., DUNN D., SINGER I. L., *Wear* No. **237**, 1-11, 2000.
5. KRZANOWSKI J. E., NUNNA D., Proceedings of WTC 2005, World Tribology Congress III, September 12-16, 2005, Washington, D.C. USA.
6. XIA Z. Z., TU J. P., LAI D. M., ZHANG L. L., WANG Q., CHEN L. M., HE D. N., *Proceedings of WTC 2005*, World Tribology Congress in September 12-16, 2005, Washington, D.C. USA.

Received September 12, 2007