TRIBOLOGICAL PROPERTIES OF SOLID LUBRICANT NANOCOMPOSITE COATINGS ON BASE OF TUNGSTEN DISULPHIDE NANOPARTICLES

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ABSTRACT

Tungsten disulphide (WS_2) and molybdenum disulphide (MoS_2), which belong to the family of transition metal dichalcogenides, are well known for their solid lubricating behavior. Thin films of WS_2 and MoS_2 exhibit extremely low coefficient of friction in dry enviroments, and are typically applied by sputter deposition, pulsed laser ablation, evaporation or chemical vapor deposition, which are essentially either line-of-sight or high temperature processes. In this paper we have investigated the tribological properties of embedded solid lubricant coatings from WS_2 nanoparticles and compared them to monolithic and alloy films of the same constituents.

The WS_2/metal (Ti, W) nanocomposite were deposited on alloy substrate by magnetron sputtering. The patterning methods were used to create two component coatings in which WS_2 were embedded in a Ti matrix. Coatings were deposited using sputter deposition, and co-deposition of WS_2 and Ti was used to deposit the alloy coatings. A pin-on-disk (POD) test was used to examine the frictional behavior and mechanical stability of the coatings, and was carried out in both low and high humidity conditions.

The morphology and microstructure of the coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). The tribological properties of WS_2/metal (Ti, W) nanocomposite coatings were investigated using a POD tribometer in ambient air and in humidity conditions.

XRD and SEM was used to examine morphology of the wear track after the POD test. The nanoparticles WS_2 can decrease the friction coefficient of lubricant obviously. However the results showed that their friction reductions have not obvious difference by the POD tribometer.

The WS_2/Ti nanocomposite coating showed lower frictions coefficient and higher wear resistance as compared to the pure WS_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 conducted by XRD and SEM images showed that nanoparticles form a protective film (WO_3) allowing an increase 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 WS_2 alone were found to perform well under low-humidity conditions, but poorly under high-humidity. Alloying of WS_2 with Ti was found to provide some improvement under high humidity. The patterned film, which consisted of columns of WS_2 embedded in a Ti film was found to exhibit friction and

wear properties superior to either Ti or WS_2 alone. The coating 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 is used in various tribological fields such as seals, bearings or electrical motor brushes and, also for applications needing excellent lubrication and wear-reducing properties.

Keywords: Solid lubricant coatings, nanoparticles, nanocomposite, XRD, SEM.

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 and WS_2, especially nanosized MoS_2 or WS_2, presents considerable applications in many fields such as solid lubrification and additives for lubricating oils and potential self-lubrificating polymer materials [1,2,3].

It is reported that MoS2 or WS2 nanoparticles mixed in oil, grease or impregnated into porous matrix of powdered materials appear to enhance the tribological properties in definite loading range in comparison to typical metal dichalcogenides particles [1,2,3].

Magnetron sputtering and ion plating technology have been developed to deposite WS_2 coatings. There are many different kinds of methods to prepare ultrafine WS_2 (molybdenum disulphide) particles. However, using different preparation methods will result in the variations of morphology and performance of WS_2 nanoparticles[4].

When pure WS_2 coating is exposed to oxygen-rich atmosphere, however, tribological performance deterioration would occur due to the oxidation WS_2.

It has been found that co-sputtering WS_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 WS_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.

Solid lubricant coatings are attractive because they can reduce friction-generated heat [5]. WS_2 is a common solid lubricant. However, the use of WS_2 can limited by excessive wear, as well as a friction coefficient that is sensitive to humidity [1,6]. 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 [7,8].

Further studies [9,10] 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 results of the composite coatings and the effects of Ti and W inclusion in the composite coatings on their tribological performance in ambient air and in humidity conditions, respectively results on patterened coatings and compare them to alloyed and monolithic single phase coatings.

EXPERIMENTS

Films of WS_2 , Ti and WS_2-Ti alloys were all deposited by magnetron sputtering. WS_2/metal (Ti, W) coatings were deposited on aluminium alloy and silicon substrates at room temperature by magnetron sputering. The WS_2/metal ratio in the coatings was controlled by sputtering the composite targets. Pure Ti target (99,99%) and WS_2/metal composite targets (pure WS_2 mixed with Ti) with a diameter 20 mm were used.

The composite targets were fabricated by ball milling the mixture of pure WS_2 and metal powder, followed by pressing the mixture under a pressure of 60 MPa. Films of WS_2, Ti and WS_2-Ti alloys were all deposited by sputter deposition on Si an OLC45 steel substrates, at room temperature. Pre-sputtering was performed to clean the surface of the targets prior to the depositing process. For the WS_2 and WS_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 inclusion in the main bulk of the coatings was varied with using different composite targets.

Tribological properties of the composite coatings were performed on a pin-on-disk (POD) tribometer. The wear tracks of the coatings were examined by means of SEM. Table 1 shows the film deposition types and compositions.

Table 1. Film deposition types and compositions.

Sample	Type	% W	% S	% Ti	W/S ratio
1	WS_2	30.5	69.5	0	0.44
2	WS_2-Ti alloy	31.6	54.7	13.6	0.58
3	WS_2-Ti alloy	23.6	53.2	23.2	0.44
4	WS_2-Ti patterned	N/A	N/A	N/A	

The compositions given in this table 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 analysed used 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 speed of 135 rpm (~ 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 optical and scanning electron microscopy (SEM).

RESULTS AND DISSCUSION

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

The patterned film (4 from 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.

The rounded mounds are WS_2 and the adjacent film is a bilayer of Ti (lower) and WS_2 (upper section). The scale marker is equal 1μm.

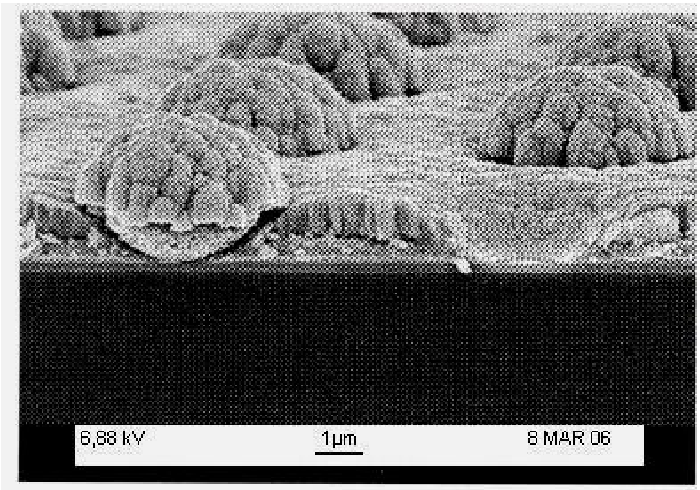

Figure 1. Cross-section SEM image of sample WS_2-Ti patterned.

Figure 2 shows the XRD patterns of the deposited coatings on silicon (Si) substrate. From the XRD analysis, it can be concluded that the deposition coatings has a disorderly structure. No peaks of crystalline phase are found from the pure WS_2 and WS_2/(Ti, W) coating. In contrast to the pure WS_2 and WS_2/(Ti, W) coatings, an apparent peak of W_3S_4 appears in pattern 3 for the WS_2/Ti coating, which is in agreement with the result of addition of Ti to the coatings inhibiting the formation of crystalline WS_2.

In this paper, the sufficient addition of Ti prohibited the crystalline of WS_2 and promoted the formation of W_3S_4. Relative sputtering without the addition of metal was difficult to produce the crystalline WS_2.

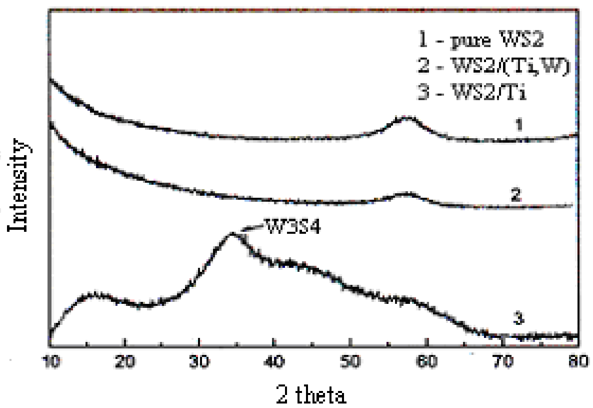

Figure 2. X-ray diffraction patterns of the composite coatings deposited with different targets.

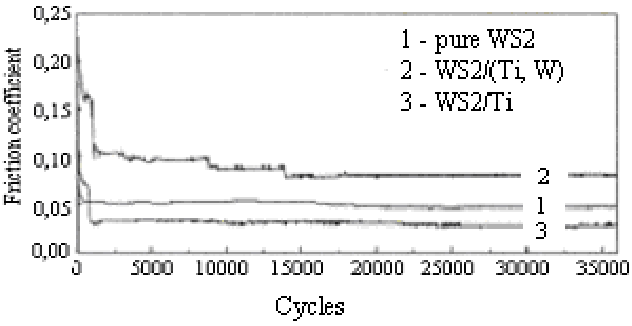

Figure 3. Friction coefficients vs. number cycles of the coatings: 1-pure WS_2; 2-WS_2/(Ti, W); 3–WS_2/ .

The variations of friction coefficient vs. number cycles functioning of the coatings in ambient air at a sliding speed of 0.2 m/s (135 rpm) and an applied load of 1N are shown in Figure 3. After running-in, the coatings show the steady friction state and therefore how they behave at wear (long wear endurance), because the friction coefficient is indicating wear. The pure WS_2 coating demonstrated a friction coefficient of 0.05 and does not destroy until 36,000 cycles (after this value, the results are unconclusives, because the coating starts to onself distroy).

The addition of Ti in WS_2 coating decreased the friction coefficient, as presented in curve (3), consequently, the steady friction coefficient reached about 0.03. However, the addition of W 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 WS_2 coating more easily.

Figure 4 showns 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 36,000 cycles.

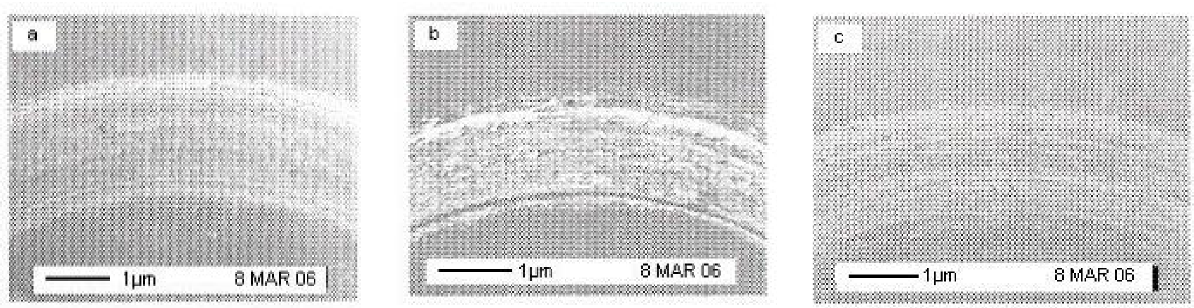

Figure 4. SEM micrographs of the wear tracks of the coatings: a - pure WS_2; b - WS_2/(Ti, W); c - WS_2/Ti.

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 WS_2 /Ti coating is smoother than the other two coatings. In the contrast to the WS_2 /Ti coating, the obvious scratch tracks on the WS_2 /(Ti, W) coating are observed, as shown in Figure 4 b. Lots of wear scar are presented on the rubbing surface. As indicated in XRD pattern (see Figure 2), the WS_2/(Ti, W) coating has the poor crystalline WS_2 structure. Otherwise, WS_2/Ti coating has not the distinguished WS_2 structure, the main structure is W_3S_4. Therefore, simultaneous addition of W and Ti increase the formation of the WS_2, which is unfavourable for the friction coefficient and wear resistance proved by our experiments. While sufficient addition of Ti alone would facilitate the formation of W_3S_4. W_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.

Tribological testing of the WS_2 coatings was carried out under dry and humid conditions. For the dry condition, the friction coefficient remained at 0.08 for 8,000 cycles, at which point the test was termined (see Figure 5). Under humid conditions, the friction coefficient started at 0.1 and rose to 0.25 after 3,500 cycles. This test confirmed the well-known effect humidity on the friction behavior of WS_2 coatings [1,6].

The friction behavior of the WS_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 sightly higher in friction (0.13). Under high humidity conditions, the coating of sample 2 (WS_2-Ti alloy) had a reasonable friction coefficient (average near 0.15), but had a high scatter compared to the result for the same coating under low humidity conditions. Sample 3 (Table 1) appeared worse and the test was terminated after 3,500 cycles. Overall, the addition of a smaller amount of Ti (13.6%) improved friction behavior under high humidity conditions, but does not completely nullify the effects of humidity.

Figure 5 shows the results for the patterned WS_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 8,000 cycles test. The test result for the Si substrate is shown, and a similar result is obtained for WS_2 on Si, which indicates the coating had traces of wear to 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 WS_2-Ti coating gave a lower friction coefficient and a longer wear life than either of the constituent (Ti or WS_2) coatings alone.

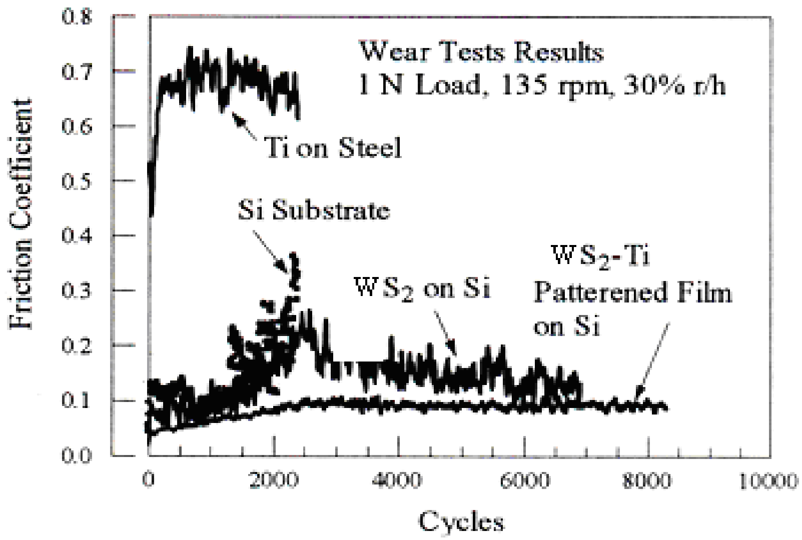

Figure 5. Pin-on-disk test result for the patterned WS_2-Ti coating and comparison to WS_2, Si and Ti.

CONCLUSIONS

- Addition of Ti helps the formation of W_3S_4, which is favourable to the decrease of the friction coefficient. The WS_2/Ti composite coating showed the superior friction coefficient and wear resistance in ambient air.
- Except Ti, the addition of W helped the formation of WS_2 structure. The bigger particles in the WS_2/(Ti, W) composite coatings were not favourable to improving tribological properties as compared to the coating without metal inclusion.
- Effect of humidity on the friction behavior of WS_2 coatings is different in function humidity conditions (low and high humidity) and of percent of Ti.
- The coatings on Si, the patterned WS_2 –Ti coating gave friction and wear properties superior (a lower friction coefficient and a longer wear life) than of the constituent (Ti or WS_2) coatings alone.

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