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Influence of C dopant on the structure, mechanical and tribological properties of r.f.-sputtered MoS_2/a-C composite films

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ABSTRACT

In present work, MoS_2/a-C composite films were synthesized by r.f. sputtering of MoS_2 and graphite targets, and the influence of C dopant on the structure, morphology, mechanical and the tribological properties of composite films in vacuum, ambient air and mutually alternated atmospheres were discussed in detail. Increasing the sputtering power applied on graphite target from 0 to 400 W, the film hardness increases significantly by one order of magnitude, and the optimized lubricant performance were obtained at 300 W. After sliding tests the morphology and structure of tribofilm and debris were investigated by using optical spectroscopy and Raman spectroscopy. The results reveal that the adaptive release of non-lubricant phase from tribofilm is a critical issue for determining the tribological performance of MoS_2/a-C composite films in different sliding atmospheres. The more exhaustive release of non-lubricant phase, the lower friction of rubbed counterparts can be obtained. More interestingly, the lubricant mechanism of tribofilms formed in alternated atmospheres is partially affected by their initial composition established at the beginning of sliding.

1. Introduction

Transition metal disulfides (TMD) typically as MoS_2 and WS_2 are well recognized as intrinsic self-lubricating materials used in the form of solid lubricant films. Due to the lamellar structure and inert basal planes existing in individual crystallites, these films may form low-shear strength tribofilms in vacuum or dry air atmospheres and lead to extremely low friction coefficients [1]. However, a critical problem of sputtered TMD films is the porous film structure, which results in a low hardness and limited load-bearing capacity in application. Besides, the porous structure may indulge the moisture-driven oxidation of TMD phases in humid terrestrial atmosphere and deteriorate film lubricant behaviors [2,3]. A commonly accepted concept to solve this problem is doping TMD films with other metallic elements or their compounds [4–6], or some non-metallic elements like C [7–9] to improve the film density by reducing the film crystallinity. As reported by Polcar et al. [7], the hardness of r.f. sputtered MoS_2/a-C composite films (carbon content 0–55 at.%) increased linearly with the doped carbon contents. Meanwhile, compared to the reference MoS_2 film, the composite films exhibited decreasing friction coefficients with the increase of carbon content in humid air and dry N_2 atmospheres. By comparison, Chen et al. [10] deposited a series of carbon-based (carbon content 85–93 at.%) composite films, using mixed Ar/CH_4 gases in various volume ratio as the working gas to sputter MoS_2 target. They found that the film deposited with the highest Ar/CH_4 ratio of 105/5 (lowest carbon content 85 at.%) exhibited the highest hardness and excellent anti-wear ability both in humid air and vacuum environments, probably due to the nanostructure with MoS_2 nanoparticles embedded in cross-linked a-C network. Similarly, a study of WS_2/a-C composite films by Cavaleiro et al. [11] suggested that the carbon content exceeding 51 at.% is not necessarily beneficial to the tribological improvement of these films, since in that case obvious third-body abrasions were observed on the wear tracks. It was argued that as additional carbon doped into the films, the possible formation of non-lubricant metal carbides may act as hard phases, which is positive for film hardness increasing but adverse for the formation and maintaining of wear resistant tribofilms. Proceeding from this angle, the release of non-lubricant phases from tribofilms to adapt to the sliding atmospheres is a critical process for determining the tribological performance of TMD/a-C composite films. Meanwhile, not only the carbon contents but also their bonding structures should be taken account for further understanding on the lubricant mechanism of C-doped TMD films. For example, a set of studies on sputtered W-S-C films by Nossa and Cavaleiro et al. [12–15] revealed that whatever the carbon content was, the adverse effect of humidity could not be overcome, i.e. the friction coefficient

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in humid air was relatively higher than that in dry air. Their AES and TEM analysis on wear counterface suggested that the carbon dopant played a secondary role in sliding process and was immediately released from the contact surface, while the property of TMD tribolayers is the key problem on friction [8,16]. By comparison, the Raman spectra of wear tracks collected by Rigney et al. [17] on WC/DLC/WS_2 nanocomposite films showed graphitic layer in humid air sliding but re-orientated WS_2 layer in dry N_2 atmosphere. However, as intensive attention have been paid on the structural transformation of lubricant phases under shear strength in previous reports [7–17], the tribological response and releasing behavior of non-lubricant phases from contact surfaces are widely ignored and have not been discussed clearly yet.

In this work, a series of MoS_2/a-C composite films with various carbon contents are deposited by r.f. sputtering of MoS_2 and graphite targets, and the films are investigated concerning the influence of carbon dopant on the film structure, morphology, mechanical and the tribological properties in different sliding atmospheres. Particularly, the release of non-lubricant phase from tribofilms into debris at the beginning of sliding and its role in determining the distinct lubricant mechanisms of MoS_2/a-C composite films in vacuum, ambient air and mutually alternated atmospheres are investigated.

2. Experimental details

2.1. Deposition of MoS_2/a-C composite films

The MoS_2/a-C composite films were synthesized by applying a multi-target r.f. magnetron sputtering system, schematically as shown in Fig. 1. The MoS_2 and graphite targets in diameter of 75 mm and 99.99% purity were sputtered onto p-type Si(100) wafer substrates. The substrates were cleaned super-sonically in alcohol for 20 min, and then placed on a sample stage vertically under the sputtered targets with a distance about 80 mm. During the vacuum pumping and deposition processes, the stage rotated at a speed of 1.5 rev./min and was continuously infrared heated to 150 °C. Prior to deposition, a base pressure lower than 1.3×10^{-3} Pa was achieved, and then the substrate were etched by Ar^+ ions for 20 min with a pulse bias voltage of 500 V (frequency of 10 kHz, duty ratio of 30%). The working pressure was controlled as 0.75 Pa. To prepare composite films with various contents of carbon, the MoS_2 target power was fixed at 275 W, and the graphite target power was varied within 50–400 W with a floating bias voltage on substrates. All the films were deposited for 60 min.

2.2. Characterization of film structure and mechanical properties

The morphology and cross-sectional microstructures of deposited films were investigated by using field-emission scanning electron microscopy (FESEM, JSM-6701F, JEOL, Japan). The composition and crystallographic phases of deposited films were investigated by using Energy dispersive spectroscopy (EDS, JSM-5601LV, JEOL, Japan), Raman spectroscopy (Horiba LabRam HR800) and grazing incidence X-ray diffraction (GIXRD, Rigaku RINT2400), respectively. The Raman spectra were measured by a 532 nm wavelength excitation, using a low laser power of D2 filter and one acquisition cycle for 120 s to avoid film damage. The GIXRD measurements were carried out using Cu Kα radiation $\lambda = 1.54056$ Å and the diffractograms were acquired from 10° to 70°. The nanoindented hardness and Young's modulus of deposited films were determined by applying an Nano Indenter DCM nano-mechanical system (MTS, America), by which the maximum indentation depth were controlled to be 100 nm (<10% of film thickness) to eliminate the effects of Si(100) substrate deformation [18]. Five repeated indentations were made at different regions of each sample for average evaluation.

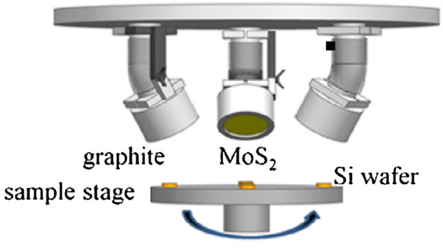

Fig. 1. The schematic diagram of multi-target r.f. magnetron sputtering system.

2.3. Pin-on-disk friction and wear tests

The tribotests were conducted by using a standard pin-on-disk tribometer with GCr15 steel balls in diameter of 3 mm as the counterpart material in rotating mode. The tests were performed under a normal load of 3 N, which created a Hertz contact pressure about 1.5 GPa. The ultrasonically cleaned balls were stationary and the disk fixed with tested samples rotated in the speed of 1000 rev./min, producing wear tracks in radius of 3 mm on tested films. For low vacuum tests, a pressure of 0.08 Pa was achieved at room temperature and the relative humidity in testing chamber was about 20 ± 5%. For ambient air tests, the relative humidity was about 35 ± 5%. After friction tests, a Micro XAM 3D non-contact surface profilometer (AD Corporation, Massachusetts, America) was applied to observe the morphology of wear tracks, and the wear rate of tested films were evaluated using the relationship of $K = V/(LN)$ where V is the wear volume loss in cubic meter, N the normal load applied on ball counterpart in Newton and L the sliding distance in meter.

3. Results and discussion

3.1. Composition and bonding structure

The deposition parameters and composition of selected MoS_2/a-C films measured by EDS are listed in Table 1, in comparison with the pure sputtered MoS_2 film, and the listed film thickness were measured by SEM cross-sectional observation. The symbols, namely C5–C40 in the first column, refer to the graphite sputtering power during deposition. It is noted that the content of carbon measured by EDS can be only considered as a comparative study due to the usage of beryllium window in EDS testing system [19] plus the carbon tapes on sample holder, so that an offset carbon content about 25 at.% is observed as a background in the pure sputtered MoS_2 film, and is not manually subtracted from the carbon contents of other composite films. However, a clear tendency can be seen that by increasing the graphite sputtering power, the carbon contents in composite films gradually increase and show weak correlations with the S/Mo ratio. The S/Mo ratios obtained by EDS agree well with that measured by Rutherford backscattering spectroscopy (not shown). As reported before [7], the sub-stoichiometry of S and Mo in sputtered films is attributed to the reactions of sulfur with residual atmosphere (particularly with H_2 and O_2), plus the preferential re-sputtering effects of sulfur due to the bombardment of neutral argon atoms reflected on the target during sputtering process. Besides, the film thickness reduces linearly with the increase of graphite sputtering power from 0 to 200 W and then fluctuates slightly around 1 μm. Agreed with previous reports on Mo(W)-S-C films [7–17], the incorporation of a-C phase may inhibit the growth of columnar structure of pure sputtered TMD phase, so