



Amorphous self-lubricant MoS₂-C sputtered coating with high hardness



Lei Gu^{a,b}, Peiling Ke^{b,*}, Yousheng Zou^{a,*}, Xiaowei Li^b, Aiying Wang^b

^a School of Materials Science and Engineering, Institute of Optoelectronics & Nanomaterials, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

^b Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

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ABSTRACT

MoS₂-C coatings with various carbon contents were deposited by direct current magnetron sputtering. Carbon concentration (from 40.9 at.% to 73.1 at.%) within the coatings was controlled by varying the number of MoS₂ plates bonded to the carbon targets. Ti interlayer fabricated by a hybrid high power impulse magnetron sputtering was used to obtain excellent adhesion. By sputtering the composite target, the deposited coatings exhibited a typical amorphous structure feature which contributed to the high hardness of the coatings. Meanwhile, the friction coefficient of the composite coating was lower than 0.1 in the ambient air and exhibited high wear resistance. Furthermore, the composite coatings exhibited an increasing hardness (from 7.0 to 10.8 GPa) with increasing carbon content.

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1. Introduction

Transition metal dichalcogenides (sulfides, selenides or tellurides of molybdenum, tungsten and niobium) as solid lubricant coatings exhibit excellent self-lubricant properties in vacuum and dry air environment [1,2]. Among these transition metal dichalcogenides, sputtered MoS₂ coating has been widely used in the space field due to its ultra-low friction coefficient and high wear resistance in high vacuum environment [3,4]. In spite of its mature application in aerospace industry, pure MoS₂ coatings performs poorly in humid air environment, which is attributed to its loose structure, low hardness and high chemical activity to oxygen [5,6]. To improve tribological performance of MoS₂ coatings in ambient air, compositing MoS₂ with metal components (including Ti, Ag, W) has been a most popular method. Among these metals, Ti doped MoS₂ coatings have acquired successful commercial application. However, doping Ti does not contribute to low friction in humid environment [7–9].

Therefore, MoS₂ compositing with nonmetallic elements (C, N included) is gaining increasing attention, due to its low friction

under humid air environment [10,11]. The concept is that MoS₂ as lubricant is distributed within hard carbon films and thus carbon matrix can protect MoS₂ from oxidation and improved mechanical properties of the coatings. Voevodin et al. used laser to process MoS₂ reservoirs into amorphous carbon matrix and found that the composite coating exhibited low friction coefficient of 0.15 in humid air [12]. However, the process is complicated. A simpler technique by co-sputtering MoS₂ and carbon targets was used to fabricate MoS₂-C composite lubricant coatings. Using a r.f. magnetron sputtering method, Pimentel et al. deposited Mo-S-C coatings and tested the tribological properties in humid air. It was concluded that the composite coatings with the C content of 55% showed the lowest friction [13]. Although previous works have made breakthroughs in fabricating MoS₂-C composite lubricant coatings and gained a low friction coefficient in humid environment, the hardness of the Mo-S-C coatings was too low (approx. 0.7–4 GPa) to maintain better wear resistance, which limited applications of these coatings on rougher substrates [14]. Meanwhile, considering different deposition conditions, the effects of C content on the structures and mechanical properties need further discussion. In addition, the low adhesion between steel substrate and the composite will limit the application of MoS₂-C coatings.

To improve the adhesion of the coatings, fabricating interlayer such as Ti or Si layer by magnetron sputtering is a feasible method. High power impulse magnetron sputtering (HIPIMS) is a magnetron

* Corresponding authors.

E-mail addresses: kepl@nimte.ac.cn (P. Ke), yshzou75@gmail.com (Y. Zou).

sputtering method developed in recent years [15], which exerts a pulsed and high power on targets [16]. HIPIMS could provide denser Ti interlayer than traditional magnetron deposition, due to the high sputtering particle ionization rate which is 2–3 orders of magnitude higher than that of conventional magnetron sputtering [17–19].

In this study, MoS₂-C coatings with various C contents were deposited by direct current magnetron sputtering using MoS₂ and C composite target and Ti interlayers were prepared by HIP-IMS. Microstructure, mechanical and tribological properties of the coatings were investigated and analyzed. Results show that the friction coefficient is lower than 0.1 and the hardness of the composite coatings is up to 10.8 ± 0.3 GPa.

2. Experimental details

2.1. Preparation of the MoS₂-C coatings

MoS₂-C coatings were fabricated by direct current magnetron sputtering (DCMS) technique. The sputtering material was a composite target, where small MoS₂ plates were stuck to a graphite target (380 mm × 140 mm × 7 mm). The Ti interlayer was deposited by HIPIMS using a Ti target. Details of the deposition system were described elsewhere [15]. All substrate including Si p (100) and mirror-finished high speed steel (HSS) were cleaned ultrasonically in acetone for 15 min and then dried in air. Before deposition, the base pressure in the vacuum chamber was pumped down to less than 3 × 10⁻⁵ Torr, and the substrates were pre-cleaned by argon plasma for 20 min. During deposition, the working pressure was kept at about 2.0 × 10⁻³ Torr, and the Ar gas flow was kept at 20 sccm. The bias voltage on substrates was -200 V. The Ti interlayer (approx. 200 nm) was first deposited. The impulse frequency was 100 Hz and the impulse width was 200 μs. The pulse voltage was 750 V and direct current of Ti target was 1.0 A. Direct current of DCMS was set as 1.0 A for MoS₂-C deposition. The carbon concentration in the coatings was controlled by changing MoS₂ plates stuck to the target.

2.2. Characterization of the MoS₂-C coatings

A surface profilometer (Alpha-Step IQ) employing a step formed by a shadow mask was used to measure the thickness of as-deposited coatings. X-ray photoelectron spectroscopy (XPS, Axis ultraDLD) using Al K α radiation with photo energy of 160 eV and radio frequency glow discharge optical emission spectrometry (RF-GD-OES, GDA 750HP) was applied to measure the film composition. Before the measurement, the surface of samples was etched by an Ar⁺ ion beam of 2 kV for 30 s. Raman spectroscopy (RENISHAW) with a 532 nm Ar⁺ laser was used to evaluate the information of bonding structure. High-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20) was used to analyze the microstructure of the deposited coatings in cross-section. X-ray diffraction (XRD, Bruker AXS D8) measurements were also used to characterize the phase structure of the coatings.

The nano-indentation system (MTS NANO G200) was used to measure the hardness and elastic modulus of the coatings. A CSM scratch tester with a diamond indenter (200 μm tip radius) was applied to study the adhesion of the coatings. During scratching, the normal load increased from 1 N to 70 N and the scratch length was 3 mm at a sliding speed of 3 mm/min. The tribological behavior was tested on a ball-on-plate tribometer (Center for Tribology UMT-3) at room temperature with the humidity of 50% under dry sliding condition. GCr15 steel balls (hardness-HCR60) with a diameter of 6 mm were used as sliding counterparts. All the friction tests were performed under a load of 5 N with a sliding speed at 50 mm/s, the length of wear tracks was 5 mm and the reciprocating frequency

was 5 Hz. The total sliding time was 3600 s. After tests, the wear track profiles were measured by the surface profilometer. And the wear rates were evaluated as volume per sliding distance per load [13].

3. Results and discussion

3.1. Structure and chemical composition

Table 1 shows the composition and thickness of the coatings. Before the measurement, Ar⁺ erosion is applied to remove the contamination of the surface. Carbon concentration rises with the increasing number of MoS₂ plates. The S/Mo ratios fluctuate in the range 1.0–1.1. Due to the fact that S being sputtered out of the surface more easily than Mo, Ar⁺ erosion would cause content deviation from the stoichiometry in the target [20]. In addition, the reaction between MoS₂ and residual atmosphere (particularly H₂ and O₂) would also reduce S content. Thus, actual S/Mo ratios are higher than those calculated values and close to the level where MoS₂ coating could maintain its lubricating character. The result of GD-OES analysis shows that the S/Mo ratio of the MoS₂-C coating (73.1 at.% C) is approximately 1.5 which is also higher than the XPS result. The sputtering yield of MoS₂ is much stronger than carbon under the same deposition condition, therefore the thickness of coatings varied linearly [21], as shown in Table 1.

The chemical bonds of the MoS₂-C coatings with different carbon contents are characterized by XPS spectra as shown in Fig. 1. In order to further analyze the chemical forms, the C 1s, S 2p and Mo 3d spectrum of the coating with C content of 40.9% is fitted by Gaussian-Lorentzian function. In the S 2p and Mo 3d spectrum, the intensity decreases obviously with carbon content. Fig. 1(a) shows the C 1s XPS spectra of the composite coatings with different C contents. The C 1s spectrum is fitted into three components. Two of them represent the C–C bond (285.4 eV) and C=C bond (284.6 eV) and a shoulder at approximately 283.6 eV corresponds to molybdenum carbide [22–24]. Fig. 1(b) shows the S 2p XPS spectra of the coatings with different carbon contents, which were fitted into four components, representing the MoS₂ structure (162.3 eV and 163.4 eV) and MoS (162.8 eV and 161.6 eV), respectively [15,26]. In Fig. 1(c), Peaks representing Mo⁴⁺ in MoS₂ (229.3 eV and 232.4 eV) and MoS (228.5 eV and 231.6 eV) structure are also found. The Mo 3d spectrum of all samples show a small shoulder at approximately 226.1 eV represented as the S 2s peak [27]. The Mo–C bond is also confirmed in the Mo 3d spectra at 228.2 eV and 231.3 eV, which tallies with the analysis on the C 1s spectrum [13,23]. The high ionization rate during deposition contributes to the existence of molybdenum carbide. Besides, with increasing carbon content, the peak intensity of C–C bond decreases, which indicates the addition of MoS₂ induces the formation of sp³ bonds.

The Raman spectra provide a further insight into the structure of the as-deposited coatings. The spectra shown in Fig. 2(a) can be divided into three pieces, which denote MoS₂ (250–500 cm⁻¹), MoO₃ (750–1000 cm⁻¹) and C (1000–1700 cm⁻¹), respectively [13,20]. There are two major peaks (approx. at 370 and 410 cm⁻¹) corresponding to MoS₂. The comparatively sharp peaks of MoS₂ in the as-deposited films can be attributed to the thermal crystallization by its high laser energy during Raman tests [25], since the sharp peaks will disappear when using a lower laser energy. Peaks corresponding to MoO₃ at 820 and 960 cm⁻¹ are observed. Raman spectra of the carbon can be deconvoluted into two peaks, the G peak centered at around 1560 cm⁻¹ and the D peak centered at around 1390 cm⁻¹. The G peak is due to the bond stretching of sp² atoms in both rings and chains, and the D peaks due to the breathing modes of sp² atoms only in rings. Changes of I_D/I_G and the G peak position can indirectly reflect the content change of sp² and sp³ carbon

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