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Effect of carbon concentration and argon flow rate on the microstructure and triboperformance of magnetron sputtered WS_2/a-C coatings

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ABSTRACT

WS_2/a-C coatings with various carbon contents (0–65 at.%) were deposited on silicon wafers by magnetron co-sputtering under different Ar flow rates. Increasing the argon flow rate increases the chemical stoichiometric S/W ratio, but the coating gradually becomes porous and columnar-like. The S/W stoichiometry is less influenced by the variation in carbon concentration. TEM and XRD confirm well crystallized basal (002) planes in the sputter deposited pure WS_2 or low-carbon WS_2/a-C coatings. The hardness of the composite coatings increases with increasing carbon content or decreasing Ar flow rate. The coating at 40 at.% C exhibits the highest hardness (10.6 GPa). Tribotests show that, together with a ultralow wear rate of 10^{-7} mm^3 m^{-1} N^{-1}, the coefficient of friction can be as low as 0.02 in dry air (5% R_H) and around 0.15 in moisture (55% R_H) and remains stable within a sliding distance of 1000 m. The wear resistance is strongly affected by the carbon concentration, deposition pressure and the testing atmospheres.

1. Introduction

Layered transition metal dichalcogenides (TMD) have a structure of *X–Me–X* type (MeX_2, Me = W, Mo; X = S, Se) with a strong anisotropy in their mechanical and electrical properties, making it the focal point of intensive studies. In this class of materials, WS_2 is a material well-known for their solid lubrication properties. WS_2 crystallizes in the hexagonal anisotropic structure, in which a layer of tungsten atoms is sandwiched between two hexagonally packed sulfur layers. The bonding within the layers is covalent, whereas the bonding between the adjacent layers consists of weak Van der Waals interactions, resulting in easy planar glide and low friction [1,2]. In addition, such crystals can be readily sheared to generate clean and almost atomically smooth surfaces under sliding [3]. Sputtered WS_2 coating has been widely used in aerospace applications due to its ultra-low friction coefficient (CoF) in high vacuum environment [4,5]. However, similar to MoS_2, WS_2 lubricants are soft, not abrasion resistant, and easily degrade in air and humid environment. To comply with endurance requirements of aerospace applications, other advanced approaches are being explored. One of them is self-lubricating composites, where solid lubricant is embedded into an amorphous diamond-like carbon (DLC) supporting matrix. DLC films are reported to have many features that contribute to excellent tribological characteristics, such as high hardness, anti-wear property with both low friction coefficient and low wear rate (W_R) against many different counterface materials [6,7]. The compliant amorphous carbon matrix may generate a high density of interphase interfaces that assist in crack deflection, termination of columnar growth and protection WS_2 from oxidation [8,9].

Although previous research has reported breakthroughs in fabricating WS_2-C composite coatings with a low friction coefficient (< 0.05) in dry environment, the tribological properties of WS_2-C based coatings are strongly influenced by the chemical composition and deposition parameters [9]. It is known that sputtered TMD coatings are usually not stoichiometric, i.e., MeX_{2-y}, where Me is Mo or W, and X is S or Se with $y > 0$ [5,9–14]. Since lubrication properties of these coatings rely strongly on the stoichiometry, a very precise control of the sputtering parameters is indispensable if TMD layers are to be prepared in a reproducible way with high quality. As reported by Cavaleiro et al. [13,15], the S/W ratio increased with carbon addition, but the Se/W ratio of co-sputtered WSeC coatings was recorded between 0.9 and 1.0, showing no significant influence of the carbon content on their variations [16]. The substoichiometry was generally attributed to the preferential resputtering of sulfur due to the bombardment of energetic ions reflected on the targets [17–19] and the reactions between MeX_2

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and residual atmosphere [9].

The sulfur stoichiometry also influences the crystallography and tribological behaviors of MeSC coating. As the sulfur content increases, the (002) lamellar crystallites become more pronounced and the size of grains increases in the form of dendritic-like branches [5,22–24]. Voevodin [5] found in WS_yC coatings when y = 0 WC nanoclusters surrounded by amorphous DLC. Beyond a sulfur concentration of y = 29 at.% the coating demonstrated the presence of hexagonal WS_2. Even more interesting is that the composite with sulfur content below 15 at.% had a surprisingly high friction coefficient of 0.5–0.7 in vacuum and 0.2–0.3 in dry nitrogen, in agreement with the single-phase unhydrogenated DLC in vacuum. The amorphous carbon with partial graphitization as confirmed by Raman tests on the wear tracks suggests that DLC played the predominant role in dry sliding when sulfur was depleted.

One should keep in mind that literature indicates (see [14,22,25]) that the coating deposition parameters such as argon pressure can strongly influence the microstructure and mechanical properties of the TMD tribocoatings. The present work concentrates on the synergetic effects of carbon content and argon flow rate on the microstructure, composition, morphology, mechanical behavior and tribological performance, which were scantly reported in detail before. In particular the following points will be addressed:

- What is the influence of carbon content and argon flow rate on the microstructure and composition of the nanocomposite coatings?
- Can the relatively soft sputtered pure WS_2 coatings also have a long wear life?
- What is the role played by S/W stoichiometry on tribological properties and will a WS_2 coating with a higher crystallinity necessarily lead to a superior wear performance?

2. Experimental details

2.1. Preparation of the WS_2/a-C coatings

WS_2/a-C nanocomposite coatings were deposited with non-reactive magnetron sputtering in a TEER UDP400/4 closed-field unbalanced magnetron sputtering system. The system was configured of one Cr target (99.5%), one graphite target (99.99%), and two WS_2 targets (99.9%) opposite to each other. The two magnetrons with a Cr and graphite target respectively were powered by a Pinnacle 6/6 kW double channel DC power supply (Advanced Energy) and the other two magnetrons with WS_2 targets were powered by a Pinnacle Plus 5/5 kW double channel pulsed DC (p-DC) power supply (Advanced Energy). All the power supplies for sputtering were operated in a current control mode. The substrates were biased by a Pinnacle Plus 5 kW single channel p-DC power supply (Advanced Energy) for plasma cleaning. The base pressure of the vacuum chamber before deposition was $3–5 \times 10^{-4}$ Pa. The substrates were fixed at 290 mm distance to the targets and the rotational speed of the sample carrousel was 3 rpm during the deposition of coating.

The substrates used were 35×35 mm^2 silicon wafers of (100) orientation and 525 ± 25 μm thickness. Prior to deposition, the ultrasonically acetone-washed Si substrates were further cleaned with Ar plasma etching for 20 min at -400 V bias voltage (p-DC at 250 kHz and 87.5% duty cycle). A Cr interlayer of 300 nm thickness was first deposited to enhance the interfacial adhesion between the top coating and Si substrate. Thereafter, the WS_2/a-C nanocomposite coating was deposited under the condition of 0.5A sputtering current applied to each of the two WS_2 targets corresponding to a voltage of ~530 V at 150 kHz pulse frequency and 62.5% duty cycle, while the current applied to one C graphite target and the number of WS_2 targets used were altered to change the carbon content in the nanocomposite coating. The substrates were self-biased using a floating potential. The coating deposition process time was 2 h for all samples. In order to study the microstructure, composition, morphology and deposition rate as a function of argon flow rate, the coatings were deposited at 10, 15, 20 and 25 standard cubic center meter per min (sccm). 10 sccm Ar flow rate corresponds to an Ar pressure of around 0.3 Pa. The deposition rate was estimated by dividing the cross-section thickness of the coating by the deposition time.

2.2. Characterization of the WS_2/a-C coatings

The microstructure was investigated using an environmental scanning electron microscope (ESEM, FEI FEG-XL30), and high resolution transmission electron microscope (HRTEM, 2010F-JEOL). Energy-dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 20 kV in FEI XL30 SEM was employed to determine the chemical composition of the coatings, averaged from three EDS analyses each sample. Atomic force microscope (AFM, Digital Instruments NanoScope 3100) was used to characterize the surface morphology of WS_2/a-C coatings, and the surface roughness of a coating was averaged from three AFM scans. Standard theta/two theta X-ray diffraction spectrum of the WS_2 powder was measured by Bruker D8 diffractometer while grazing incidence X-ray diffraction (GIXRD) spectra were measured by PANalytical-X'Pert MRD to probe the top surface phases using a 2.5° incident angle in parallel beam geometry. MTS Nano indenter XP® equipped with a Berkovich indenter was employed to measure the hardness (H) and elastic modulus (E) of the coatings, averaged from at least 25 tests for each coating. The maximum indentation depth for measuring H and E was approximately 200 nm, corresponding to < 10% of the coating thickness. Raman spectra with a He–Ne laser (532 nm) at approximately 1.5 mW were obtained in a wavelength range of 200–2000 cm^{-1} to investigate the phases in the wear tracks. Raman probing area and depth were around 10 μm^2 and 150 nm, respectively.

The tribological properties of these coatings were investigated using a CSM tribometer with a ball-on-disk configuration, against Φ6 mm 100Cr6 steel balls at a fixed sliding speed of 10 cm/s for 1000 m at room temperature (20–23 °C). The hardness value of the steel balls is 7.5 GPa, giving an initial mean Hertz contact pressure of ~0.7 GPa at 5 N normal load. All tribotests were conducted in both dry air (relatively humidity of 5%, wear track radius 7.5 mm) and under high humidity (relatively humidity of 55%, wear track radius 9 mm) respectively, controlled by a home-made humidity modulator. After wear tests, the wear scar of the counterpart balls and the wear track of the coatings was characterized by SEM. To obtain the specific wear rate (mm^3 N^{-1} m^{-1}) of the coatings under different deposition and tribological conditions, 3D confocal micrographs of the wear tracks on the coatings were captured to measure the wear volume using a Matlab code.

3. Results and discussions

3.1. Basic characteristics of WS_2

In general, sputtered MeS_2 has two types of orientations: type I films with structurally well-developed lamellae vertical to the coating substrate (edge orientation: c‖), complemented by dendritic branches that are sensitive to oxygen leading to poor wear; type II films with microcrystallized layers parallel to the substrate that are inert to environmental attacks and could afford superior lubrication (basal orientation: c ⊥) [22]. Crystal structure of hexagonal 2H-WS_2 with easy shear plane (002) is apparently evidenced in the WS_2 target material as indicated in Fig. 1a. Furthermore, the θ-2θ XRD spectrum (see Fig. 1b) indicates the strongest and well crystallized basal orientation peaks of (002) and some other typical peaks showing the edge orientations such as (101) at angle of ~34° and (110) at angle of ~58° respectively (JCPDS no. 008-0237).