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Effect of carbon concentration and argon flow rate on the microstructure and triboperformance of magnetron sputtered WS₂/a-C coatings

Huatang Cao^a, Jeff Th.M. De Hosson^b, Yutao Pei^{a,*}

^a Department of Advanced Production Engineering, Engineering and Technology Institute Groningen, Faculty of Science and Engineering, University of Groningen, Nijenborgh 4, 9747AG, The Netherlands

^b Department of Applied Physics, Zernike Institute of Advanced Materials, Faculty of Science and Engineering, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

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ABSTRACT

WS₂/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 WS₂ or low-carbon WS₂/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} mm³ 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 (MeX₂, 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, WS₂ is a material well-known for their solid lubrication properties. WS₂ 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 WS₂ 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 MoS₂, WS₂ 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 WS₂ from oxidation [8,9].

Although previous research has reported breakthroughs in fabricating WS₂-C composite coatings with a low friction coefficient (< 0.05) in dry environment, the tribological properties of WS₂-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 MeX₂

* Corresponding author.

E-mail address: y.pei@rug.nl (Y. Pei).

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_2/C 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 scantily 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 $3\text{--}5 \times 10^{-4}$ Pa. The substrates were fixed at 290 mm distance to the targets and the rotational speed of the sample carousel was 3 rpm during the deposition of coating.

The substrates used were $35 \times 35 \text{ mm}^2$ silicon wafers of (100) orientation and $525 \pm 25 \mu\text{m}$ 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 $\sim 530 \text{ V}$ 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 centimeter per minute (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 $200\text{--}2000 \text{ cm}^{-1}$ to investigate the phases in the wear tracks. Raman probing area and depth were around $10 \mu\text{m}^2$ and 150 nm, respectively.

The tribological properties of these coatings were investigated using a CSM tribometer with a ball-on-disk configuration, against $\Phi 6 \text{ mm}$ 100Cr6 steel balls at a fixed sliding speed of 10 cm/s for 1000 m at room temperature ($20\text{--}23^\circ\text{C}$). The hardness value of the steel balls is 7.5 GPa, giving an initial mean Hertz contact pressure of $\sim 0.7 \text{ GPa}$ 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 ($\text{mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) 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: $c \parallel$), 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: $c \perp$) [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 -2 θ 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 $\sim 34^\circ$ and (110) at angle of $\sim 58^\circ$ respectively (JCPDS no. 008-0237).

Fig. 1. As-received WS_2 target: (a) TEM image showing lamellar structure; (b) XRD spectrum.

3.2. Chemical and structural character of WS_2 /a-C coatings

3.2.1. Elemental composition and morphology

Table 1 shows that the chemical composition of sputtered WS_2 /a-C coatings changes upon the sputtering current of graphite target and argon flow rate from 10 sccm to 25 sccm. A fixed current of 0.5 A (Coating No.1-12) and 0.3 A (Coating No. 13-14) was applied to each WS_2 target. For the coatings No. 11-14, the use of only one WS_2 target aimed at tailoring the carbon content to a maximum of around 65 at.%. As can be seen, around 1–3 at.% oxygen is contained in all the sputtered coatings due to residual oxygen in the PVD chamber. The carbon concentration increases with increasing current applied to one graphite target from 0.5 A to 1.5 A and the reduction of two WS_2 targets to one. For instance, carbon in these coatings increases from ~21 at.% (0.5 A applied on graphite target) to ~40 at.% (1.5 A applied on the graphite target). While the graphite target was sputtered at 1.5 A, the use of one WS_2 target with reduced current from 0.5 to 0.3 A could further increase the carbon content to ~65 at.%. In contrast, the content of both sulfur and tungsten shows a decreasing trend with increasing carbon. The content of sulfur maximizes at ~62 at.% when no carbon is added under 25 sccm Ar and reaches a minimum of ~20 at.% when a lowest current (0.3 A) is applied to the WS_2 target under 10 sccm Ar.

Ar flow rate, which directly correlates with the working pressure, strongly influences the coating chemical compositions. As shown in Table 1, the comparison between coating group No. 3-6 and group No. 7-10 manifests that a gradual increase in sulfur coincides with a decrease in tungsten as Ar flow rate rises from 10 sccm to 25 sccm. A slight variation in carbon concentration is also observed. More interesting is to note in Table 1 that the stoichiometric ratio of sulfur to tungsten (S/W), being more or less independent of carbon content fluctuations, increases from ~1.33 to 1.79 as a function of growing Ar flow rate. Särhammar et al. [26] combined Monte Carlo simulations and experiments to investigate the compositional variations of sputtered WS_2 and also concluded that S/W ratio was only slightly influenced by the target voltage (equal to the target current here), while the most significant variations were attributed to the processing pressure and the position of substrates relative to the targets. At lower pressure, substantial sulfur resputtering takes place due to both rising plasma potential and decreasing thermalization, triggering irradiation of the growing coating by energetic particles from the plasma (Ar^+) and also from the target, e.g. W, S or probably backscattered neutral Ar [26,27]. Therefore, the lowest sulfur content ($\text{WS}_{1.33}$) is found in the coating deposited at 10 sccm Ar. In the case of a higher argon pressure (25 sccm) and hence a short mean free path (λ_{mfp} positively correlates with P^{-1}) causing higher frequency of species scattering and collisions,

Table 1
Composition of WS_2 /a-C under different deposition conditions.

Sample no.	Deposition condition			Deposition rate (nm/min)	Composition (at.%)				S/W ratio
	WS_2^a (A)	Graphite (A)	Ar flow (sccm)		C	O	S	W	
1	0.5	–	10	13.1	–	2.3 ± 0.2	59.5 ± 0.3	38.2 ± 0.3	1.56
2	0.5	–	25	30.3	–	2.9 ± 0.2	61.9 ± 0.3	35.2 ± 0.1	1.76
3	0.5	0.5	10	12.3	21.8 ± 0.5	2.0 ± 0.1	43.9 ± 0.4	32.3 ± 0.1	1.36
4	0.5	0.5	15	14.1	17.2 ± 1.6	2.0 ± 0.2	49.0 ± 1.0	31.8 ± 0.7	1.54
5	0.5	0.5	20	15.3	19.1 ± 0.7	2.1 ± 0.4	49.2 ± 0.5	29.6 ± 0.2	1.66
6	0.5	0.5	25	16.3	16.9 ± 0.2	2.1 ± 0.1	51.6 ± 0.2	29.4 ± 0.2	1.76
7	0.5	1.5	10	14.8	39.6 ± 0.5	1.3 ± 0.1	33.7 ± 0.4	25.4 ± 0.2	1.33
8	0.5	1.5	15	16.8	35.3 ± 1.1	2.0 ± 0.3	36.9 ± 0.6	25.8 ± 0.6	1.43
9	0.5	1.5	20	17.6	34.5 ± 1.4	2.3 ± 0.2	38.8 ± 0.9	24.4 ± 0.6	1.59
10	0.5	1.5	25	19.3	33.2 ± 1.1	2.1 ± 0.3	41.2 ± 0.8	23.6 ± 0.5	1.75
11	$0.5(\times 1)$	1.5	10	10.2	51.3 ± 0.1	1.2 ± 0.1	27.3 ± 0.3	20.2 ± 0.1	1.35
12	$0.5(\times 1)$	1.5	25	12.3	46.6 ± 0.4	2.1 ± 0.1	32.3 ± 0.3	19.0 ± 0.2	1.70
13	$0.3(\times 1)$	1.5	10	7.3	64.2 ± 1.0	1.3 ± 0.1	19.9 ± 0.6	14.6 ± 0.5	1.36
14	$0.3(\times 1)$	1.5	25	9.0	61.3 ± 0.4	1.9 ± 0.4	23.6 ± 0.5	13.2 ± 0.1	1.79

^a Two WS_2 targets were used for deposition, unless otherwise stated one WS_2 target by ($\times 1$).

Fig. 2. SEM micrograph (left) and AFM micrograph ($2 \times 2 \mu\text{m}^2$) showing the effect of Ar flow rate on the microstructure and surface morphology of pure WS_2 films deposited at (a) 10 sccm Ar and (b) 25 sccm Ar (note: R refers to root mean square roughness).

the energetic particles, i.e. particularly the large and heavy Ar atoms greatly lose their energy before reaching the substrate surface and thus sulfur resputtering is reduced because of the alleviated impingements [11,28].

In addition, Ar pressure also affects the surface topography to a large extent. Under 10 sccm Ar flow, Fig. 2a shows the pure WS_2 coating resembles a typical cauliflower-like PVD sputtered DLC coating with a rough surface ($\text{RMS} = 8.9 \text{ nm}$). On the other hand, the pure WS_2 coatings sputtered at 25 sccm Ar (see Fig. 2b) exhibits obviously a lenticular and porous microstructure with an exceedingly high $\text{RMS} = 37.8 \text{ nm}$, structurally similar to the sputtered porous pure MoS_2 coatings reported in [29,30]. The inset cross-section images of Fig. 2 show that the pure WS_2 thin coatings present columnar plate zone 2 morphology (Thornton model ref. [31]) with typical inherent porosities [31], corresponding to extremely low hardness and high wear rate that are discussed later. Large voids clearly appear in the WS_2 coating deposited under 25 sccm Ar shown in Fig. 2b.

Co-deposition of carbon forms $\text{WS}_2/\text{a-C}$ coating that exhibits densified structure and fine surface morphology. Fig. 3a–d shows the surface morphology and fractured cross section of $\text{WS}_2/\text{a-C}$ coatings deposited at 0.5 A applied to the graphite target yielding $\sim 20 \text{ at.}\%$ C and different Ar flow rates. It can be seen that higher porosity and sharper columnar microstructure are developed with increasing Ar flow rate from 10 sccm (Fig. 3a) to 25 sccm (Fig. 3d). Particularly the one under 25 sccm Ar presents typical columnar structure even close to the pure WS_2 coating under 10 sccm Ar indicated in Fig. 2b. AFM images displayed in Fig. 3i–l confirm that the increasing pressure leads to coarsened surface morphology, as characterized by an increasing roughness. However, compared with pure WS_2 , it should be pointed out that the RMS drops from 8.9 nm to a minimum of 3.6 nm (both 10 sccm Ar), indicating the formation of a denser coating with ever flatter top morphologies due to the contribution of carbon additions. When the carbon content rises to the range of $\sim 40 \text{ at.}\%$, further compact coatings are formed as shown in Fig. 3e–h. The inset of Fig. 3e indicates that $\text{WS}_2/\text{a-C}$ coating deposited at low Ar pressure turns out column-free and featureless. This is because the intense ion impingement under low pressure condition and carbon addition significantly densify the microstructure.

It is worth mentioning that the deposition rate also increases with increasing Ar flow rate as listed in Table 1. Possible reasons are that higher gas pressure results in higher ion density and thus more amount of materials are sputtered away from the targets [32]. Also the sputtering yield is enhanced due to increased probability of an ion colliding with gas atoms during its traverse across the cathode dark space, which promotes the percentage of ions striking the target at oblique angles of incidence [32]. The pure WS_2 coating under 25 sccm Ar features with the highest deposition rate reaching a striking high value of $\sim 30 \text{ nm/min}$. This is, however, mainly because of the porous structure leading to the lowest density of such WS_2 coating [17].

3.2.2. Structure and crystallinity

Grazing incidence X-ray diffraction patterns of sputtered WS_2 and $\text{WS}_2/\text{a-C}$ coatings as a function of Ar flow rate and carbon content are shown in Fig. 4. Fig. 4a shows the typical hexagonal WS_2 peaks (002) at $2\theta = \sim 14^\circ$, fitting in well with that of WS_2 powders as indicated in Fig. 1b. Such strong-intensity (002) reflection indicates that numerous WS_2 crystals are oriented with basal planes parallel to the coating surface, which is typical type II structure for sputtered TMD coatings. TEM image of Fig. 5a further confirms that the lamellae extend $> 20 \text{ nm}$ in length (with $c \perp$) and are exclusively parallel with silicon substrate. However, consistent with Refs. [22,33], such wider ($\sim 0.6 \text{ nm}$) spaced (002) basal planes only grow for tens of nanometers along substrate and then (002) planes turn random or even perpendicular to the substrate (see Fig. 5a). Even narrower (0.3 nm) edge planes such as (101), (103) starts to form (see Fig. 5b). Moser et al. [33] suggested that the transition from the parallel layer to the perpendicular crystallites occurs via a branching process during growth as the crystallites seems to be preferentially oriented vertical to one another. Fig. 4b shows that the diffraction patterns become less distinct with increasing carbon. From 10 sccm to 25 sccm, a slight increase in crystallinity could be observed, and under 25 sccm and 20 sccm Ar the (110) peak is also visible. Fig. 4b also indicates that an asymmetrical (100) peak around $2\theta = 33^\circ$ with a long tail. This is commonly attributed to the effect of the turbostratic stacking of WS_2 basal planes. It is known that in the hexagonal lattice structure the (00l) reflections correspond to the ordering in the c-direction while the (hk0) reflections to the basal planes.

Fig. 3. Effect of carbon and Ar flow rate on the surface morphology and microstructure of $\text{WS}_2/\text{a-C}$ coatings: (a–d) 0.5A C with Ar flow rate indicated; (e–h) 1.5A C with Ar flow rate indicated; (i–l) AFM surface topography ($2 \times 2 \mu\text{m}^2$) of $\text{WS}_2/\text{a-C}$ coatings of (a–d) respectively.

Weise et al. [14] suggested that the referred XRD patterns of TMD points to a two-dimensional (2D) organization of the basal planes which could have several tenths of unit cells. The stacking of the a-b basal lattice planes in the c-direction, provided lateral dimensions within the range of a few nanometers, leads to a sharp peak at approximately the position for the (100) reflections. It tails towards larger angles suggesting other reflections of the (10L) family with $L = 1, 2, 3, \dots$ [14,27,34–36] and presenting a broad peak typical of an amorphous structure. Another slightly asymmetric peak is observed at the position for the (110) reflections at $2\theta = \sim 58^\circ$. As stated previously, $\text{WS}_2/\text{a-C}$ coatings bring out enhanced structural densification and the diffraction pattern starts to exhibit broader peaks, indicating smaller or shorter crystallites than that in pure WS_x coatings. It is worth mentioning that the most important diffraction pattern of (002) basal plane, which was in fact absent in the most reported XRD spectra of TMDs [9,34,35], remains visible in the coatings No. 3–6 over the entire range of argon flow rates from 10 to 25 sccm. This is further verified by Fig. 4c, where

the (002) basal planes start to disappear when the carbon content surpasses 33 at.%. Furthermore, the (10L) turbostratic stacking planes also become even broader when the carbon concentration goes up to 46 at.%. It indicates that the $\text{WS}_2/\text{a-C}$ coatings with high carbon content lose crystallinity and gradually turning out x-ray amorphous. Some diffraction peaks from the Cr interlayer and Si substrate (refer to Fig. 4a) arise due to the decreased thickness (only 0.3 Å applied to one WS_2 target) of the high-carbon coatings illustrated in Table 1. Furthermore, comparison of Fig. 4b with pure WS_2 coating in Fig. 4a shows that a slight shift of (002) peak towards lower diffraction angle occurs after WS_2 doping with carbon, implying an increased lattice parameters of WS_2 after carbon addition [34]. HRTEM images of Fig. 5c show that the nanocrystalline WS_2 phases, with a platelet shape, are randomly oriented in an amorphous carbon matrix, see also [5,23,24,37,38]. TEM micrographs in Fig. 5d and f show short-range ordering of WS_{2-y} with Ar flow rate reduced from 25 to 10 sccm. From the high-carbon $\text{WS}_2/\text{a-C}$ coating (Fig. 5d, S/W = 1.33), the tiny WS_2 platelets are almost

Fig. 4. Grazing incidence X-ray diffraction spectra: (a) sputtered pure WS_2 and Si substrate; (b) as a function of Ar flow rate (~20 at.% C unless stated); (c) as a function of carbon content (Cr peak emerges from the Cr interlayer due to thinner coatings [30]).

completely surrounded by the C-matrix. The circled darkened areas in Fig. 5d indicate possible formation of some WC nanoclusters similar as reported in [5,23], although no distinct peaks of WC nanocrystalline carbide are visible in each XRD spectrum. TEM images also confirm gradual loss of WS_2 crystallinity with lowering Ar flow rate, which correlates with decreasing sulfur content because of strong resputtering of sulfur occurring in low pressure deposition [22].

3.3. Mechanical and tribological properties

3.3.1. Mechanical characterization

Fig. 6 shows the average hardness and elastic modulus of the coatings measured by depth-sensing nanoindentation using a Berkovich tip. The pure WS_2 coating deposited under 25 sccm Ar has an extremely low hardness (0.31 GPa) and elastic modulus (12.68 GPa), which is reasonable considering its high porosity and columnar structure (see

Fig. 5. HR-TEM images of sputtered pure WS_2 film: (a) first tens of nanometers growth of (002) basal orientation along the substrate; (b) further growth of edge orientations; and $\text{WS}_2/\text{a-C}$ films under different deposition conditions: (c) 0.5A C, 25 sccm Ar; (d) 0.5A C, 10 sccm Ar; (e) 1.5A C, 25 sccm Ar; (f) 1.5A C, 10 sccm Ar.

Fig. 6. (a) Hardness and (b) elastic modulus of WS₂ and WS₂/a-C coatings deposited at different argon flow rates and of different carbon contents measured by nanoindentation.

Fig. 2b). This is comparable to the early reported hardness values of TMD (< 0.5 GPa) [17,20]. However, an increase in hardness of more than one order of magnitude is achieved whenever WS₂ coating is alloyed with C or with decreasing Ar flow from 25 sccm to 10 sccm. Fig. 6a indicates that a lower Ar pressure promotes the hardness enhancement among the coatings of the same content of carbon. Deposition pressure of 10 sccm Ar yields a hardness of 8.66 GPa in comparison to reduced 5.43 GPa in 25 sccm Ar. Elastic modulus variations accompany closely the same trend of hardness variations (see Fig. 6b). Also it is important to note that WS₂/a-C coatings, apart from significantly harder than the pure WS₂ coatings, become harder with increasing carbon content until ~ 40 at.%, at which the coating reaches a maximum hardness value of 10.60 GPa, comparable to the previous results [15,21,34,37]. Higher carbon content promotes the formation of amorphous carbon matrix. However above ~ 40 at.% C, the hardness and elastic modulus slightly decrease as the coating at 65 at.% C retreats to 9.96 GPa and 96.58 GPa, respectively. Polcar et al. [20] attributed the hardness reduction to the fact that no more W is available to form W–C bonds because thereafter the dominance of carbon phases takes over considering the only 7 GPa hardness for pure carbon coatings. This behavior suggests changes in the microstructure, where existing pores in the columnar morphology are favorably eliminated and the compactness and density of the coatings are thus enhanced as reflected in Fig. 3e in comparison to Fig. 2b.

Fig. 7. Tribological performance of WS₂/a-C films as a function of Ar flow rate and carbon content after sliding 1000 m: (a) mean friction coefficient; (b) wear rate.

3.3.2. Frictional and wear behavior

The influence of Ar pressure and of the carbon content on the tribological properties of WS₂/a-C coatings under dry or ambient air was systematically investigated by using a pin-on-disk tribometer. As clearly shown in Fig. 7a, for all tribotests below $< 5\%$ R_H , the coefficients of friction can stabilize in the ultralow range of 0.017–0.028, almost independently of Ar flow rate and carbon changes. Such a low friction is rarely reported to achieve with un-hydrogenated DLC in dry atmosphere, which usually has a friction coefficient of above 0.1 before graphitization and failure occurs [5]. The observed ultralow friction is predominantly attributed to the lubrication effect of WS₂ phase. Low friction of WS₂ is due to the weaker Van der Waals bonds between hexagonal basal planes, offering an easy slip during frictional contact. These slip mechanisms require released WS₂ crystals with basal planes parallel to the sliding direction. As XRD (see Fig. 4b) confirms the presence of hexagonal basal (002) peaks in the low-carbon WS₂/a-C coatings, there are reasons to consider that agglomeration of WS₂ nanolaminae on the wear tracks are easily formed [39]. In terms of sliding in a humid environment, the CoF evidently increases due to the reactions of WS₂ with water molecules to form inferior lubricant WO₃. The coating at ~ 40 at.% deposited at 10 sccm Ar has the lowest CoF of 0.102 tested in humid air (55% relative humidity). 20 sccm Ar produces a maximum CoF of 0.174, which belongs to the typical CoFs of WS₂ in moist air that are commonly reported to be 0.15–0.20 in Refs. [10,40].

The wear rate (W_R) of WS₂/a-C coatings is strongly affected by the deposition pressure, carbon content and environmental conditions.

With the carbon content at the level of ~ 20 at.%, the wear rate in dry sliding is lower than that in humid environment. For instance, a lowest W_R of $1.84 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ is recorded in dry sliding for the $\text{WS}_2/\text{a-C}$ coating deposited under 10 sccm Ar. The wear rate goes up with increasing Ar flow rate in deposition to $4.11 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ of the coating deposited under 25 sccm Ar. Meanwhile, W_R are always higher in humid air (55% R_H), from 2.93×10^{-7} to $4.37 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ as Ar pressure increased from 10 sccm to 25 sccm, respectively. It could be concluded that higher Ar pressure triggers worse wear resistance, mainly due to a lower hardness and porous structure of the coating. Therefore the coating deposited under 10 sccm Ar is advisable from the anti-wear point of view since no marked CoF reduction is observed in $\text{WS}_2/\text{a-C}$ coatings with higher sulfur stoichiometry and crystallinity, as a result of higher Ar flow rate.

In fact, Aubert et al. [41] also found out that the sub-stoichiometric MoS_y ($y \approx 1.5$) yielded the lowest CoF even compared with the stoichiometric one. The rather low wear rate of low carbon $\text{WS}_2/\text{a-C}$ coatings in dry air is primarily attributed to the superior basal WS_2 induced lubrication, i.e. weaker contribution comes from amorphous DLC in the coatings. The addition of C to the level of ~ 40 at.% decreases the W_R for all the ranges of investigated Ar flow rates. Particularly when testing in humid air, W_R seems to be slightly lower than that tested in dry conditions. This is because carbon addition increases coating density and hardness. Also, DLC initiates to play a predominant role in reducing wear as unhydrogenated DLC generally performs better in moisture.

Further study of tribological behavior as a function of carbon content (10 sccm Ar) is depicted in Fig. 8. Fig. 8a indicates that under 5% R_H the addition of C up to 40 at.% C reduces the average CoF from 0.039 in pure WS_2 and 0.026 in the ~ 20 at.% C to 0.021 in the ~ 40 at.% C coating. However, with further carbon additions up to above 51 at.% C, CoFs start to increase to 0.069 for the ~ 65 at.% C coating. Also this changing trend of CoFs with carbon variations is verified at humid testing (see Fig. 8a).

Fig. 8b shows that W_R decreases with an increasing carbon content until ~ 40 at.% C. Unlike most reported wear life of pure TMD coatings, which usually exhibit rapid failures [36,42], Fig. 8b and c still prove that WS_2 coating of high enough hardness (~ 3 GPa) deposited in a low pressure could have a low W_R of $4.09 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ after

sliding 1000 m in dry air. However, the W_R in humid air comes to one order of magnitude higher, i.e. $5.91 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, indicating the poor wear resistance of WS_2 in moisture. Fig. 9 shows the confocal 3D topography of wear tracks of $\text{WS}_2/\text{a-C}$ coatings as a function of carbon content. A relatively narrow wear track ($173.80 \mu\text{m}$ width $\times$ $0.84 \mu\text{m}$ depth) of pure WS_2 coating tested under 5% R_H (Fig. 9a) was formed in contrast to an extraordinary large ($407.44 \mu\text{m}$ width $\times$ $1.41 \mu\text{m}$ depth) track tested under 55% R_H (Fig. 9b). Fig. 9c presents the wear track of much reduced depth ($0.35 \mu\text{m}$) and width ($140.15 \mu\text{m}$) for the ~ 40 at.% C coating, corresponding to a remarkably low wear rate of $1.76 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ in dry sliding. As pointed out in [2], a wear rate of $1 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ represents an average removal rate of < 1 atomic layer per cm pass of a counterpart at 5 N normal load. Therefore, such a low wear and friction coefficient (0.021) potentially fulfill the criteria of self-lubricated wear resistant coatings for aerospace applications, which is proposed to be $< 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for wear rates and < 0.1 for friction coefficients [4].

Although extremely broad X-ray diffraction peaks shown in Fig. 4c and disordered phases in Fig. 5f reveal no strong (002) basal planes, extensive research have documented friction induced degree of crystallinity from otherwise pure amorphous film to realignment of TMD (002) basal planes. In other words, the $\text{WS}_2/\text{a-C}$ coating can adapt itself during sliding contact forcing nano-laminae to favor an orientation where their basal planes are parallel to the sliding interface, and thereby attaining ultralow friction values [2,39,43,44]. Fig. 10 shows the Raman spectra on the wear tracks formed under different tribo-test conditions. Fig. 10a indicates the sputtered a-C coating is Raman active in the $1300\text{--}1600 \text{ cm}^{-1}$ region, corresponding to the typical D (1380 cm^{-1}) and G (1550 cm^{-1}) peaks of amorphous carbon and also E_{2g} (355 cm^{-1}) and A_{1g} (421 cm^{-1}) peaks presenting hexagonal WS_2 [36]. As shown in Fig. 10b, reorientation and conglomeration of oriented hexagonal WS_2 nano-laminae together with D and G peaks are verified on all wear tracks formed in dry air sliding. Furthermore, it is clear that the WS_2 phase is rich in low-carbon coatings while in high-carbon $\text{WS}_2/\text{a-C}$ the DLC peaks are intensified. The formation of amorphous carbon in wear tracks is detected (see Fig. 10c) and is responsible for low friction in moist air, explaining CoF to be around 0.15 approaching the typical CoF value of DLC in humid conditions. In addition, WO_3 peaks around 710 cm^{-1} and 810 cm^{-1} are presumably

Fig. 8. Tribological performance as a function of carbon content: (a) average coefficient of friction; (b) wear rate; (c) coefficient of friction curves of $\text{WS}_2/\text{a-C}$ coatings; (d) coefficient of friction curves showing $\text{WS}_2/\text{a-C}$ with high carbon content deposited under 25 sccm Ar fails in dry sliding.

Fig. 9. Confocal micrographs ($705 \times 725 \mu\text{m}^2$) showing 3D views of the wear scars as a function of carbon content: (a) 0 at.% C, 5% R_{H} ; (b) 0 at.% C, 55% R_{H} ; (c) 40 at.% C, 5% R_{H} ; (d) 65 at.% C, 5% R_{H} ; (e) 61 at.% C, 25 sccm Ar, 5% R_{H} ; (f) SEM image confirming fully delaminated coating of (e). Note: besides (e) was tested for 750 m due to earlier failure, all others were sliding for 1000 m.

Fig. 10. Raman spectra of the a-C, WS₂ and WS₂/a-C coatings in the wear tracks after sliding 1000 m under different deposition conditions: (a) as-sputtered a-C and WS₂ films; (b) wear tested under 5% R_{H} ; (c) wear tested under 55% R_{H} ; (d) a typical wear morphology of WS₂/a-C coatings (0.5 A C, 10 sccm Ar) in dry sliding.

detected by Raman in low-carbon WS₂/a-C coatings (Fig. 10c). EDS mappings also verify varied concentrations of oxygen covering the ball scar (not shown), implying the formation of WO₃. Further increase in carbon to 65 at.% leads to poor wear resistance, particularly in dry air as indicated in Figs. 8b and 9d. In humid air, increased contribution of the C-based phases decreases wear rate significantly, corresponding to lubrication dominated by DLC. DLC predominantly Raman-active in the tracks of high-carbon coating further confirms this hypothesis (see Fig. 10c).

In particular the coatings with high carbon content but deposited at high argon pressure exhibit catastrophic failure. In fact, the third-body graphitic debris are quickly formed, leading to an instant high CoF of ~0.6 within a sliding distance of only 200 m (see Fig. 8d), a typical value of dry sliding of direct metal contact [45]. Fully delaminated topography is clearly visible in Fig. 9e and confirmed by SEM observations, see Fig. 9f. Similar wear behavior was found in Mo-Se-C system [46], i.e. the highest carbon content (58 and 68 at.%) coatings fail to survive in low R_H. These justify the conclusion that WS₂/a-C coatings with scarce sulfur perform worse in dry conditions, consistent with the findings by Voevodin et al. [5]. Thus, a relatively high absolute content of sulfur in the coatings rather than only high S/W ratio should be taken into consideration.

In addition, from Fig. 8c an interesting observation is that WS₂/a-C coatings with a carbon content < 40 at.% have rather low initial CoFs in dry air (0.013, 0.127, 0.185 respectively for the pure WS₂, 20 at.% C and 40 at.% C WS₂/a-C coatings) and it only takes around 10 m to stabilize; thereafter it remains extremely stable (~0.02) during the entire rests. In the case of 65 at.% C, an initial transient CoF of 0.568 is observed and it further increases to ~0.8. After fluctuating within about 500 m sliding with a decreasing tendency, it falls to 0.02. This implies CoF reduces with the number of cycles for the high-carbon WS₂/a-C deposited under low pressure. The deficient sulfur (~20 at.%) in high-carbon WS₂/a-C entails a longer time to accumulate or align WS₂ crystallites along the sliding surface. This explains the extended running-in time before it ultimately approaches the stabilized ultralow CoF value as that of WS₂ rich coatings.

4. Conclusions

WS₂/a-C nanocomposite coatings were fabricated by magnetron co-sputtering. This work leads to an in-depth understanding of the synergistic effects of carbon content and argon deposition pressure on the S/W stoichiometry, surface morphology, microstructure and related structure-property relationship.

- 1) The coatings consist of approximately 10–40 at.% W, 20–65 at.% C, and 20–60 at.% S, neglecting 1–3 at.% oxygen contamination. The S/W stoichiometric ratio is larger in lamellar coatings and smaller in compact coatings. Crystallinity of WS₂ phase is found to be improved by increasing Ar pressure, which also elucidates larger lamellae size and roughened surface. Preferential re-sputtering of sulfur reinforced by impingement at low Ar pressure explains a low stoichiometric ratio in the coatings.
- 2) TEM reveals obvious feathery WS₂ laminae randomly distributed in amorphous carbon matrix, and the nanocomposite coating turns more amorphous-like when carbon content increases. XRD confirms favorable basal plane orientation (002) in WS₂/a-C coatings with increasing carbon concentration up to ~22 at.%. Nanoindentation tests show that the hardness and elastic modulus of the coatings are one order of magnitude higher compared with that of pure WS₂ coatings via carbon addition or alternatively decreasing argon flow rate from 25 sccm to 10 sccm.

- 3) CoF as low as 0.02 could be reached in dry air (< 5% R_H) in all investigated compositional variations of WS₂/a-C coatings below 51 at.% C. Moreover, CoF remains very stable within a long sliding distance of 1000 m and appears to be almost independent of S/W ratio (from 1.33 to 1.79). On the other hand, CoF goes up to 0.15 in humid air.
- 4) Pure WS₂ coating deposited under low pressure can survive over 1000 m dry sliding. WS₂/a-C coating with ~40 at.% C exhibits the best wear resistance while the high-carbon coating (~65 at.%) easily fails in dry air. Although high Ar flow rates could enhance the crystallinity of WS₂ and yield higher S/W ratio, the lower deposition pressure, promoting hardness and low wear rate, is recommended from a tribological point of view.

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References

- [1] S. Prasad, J. Zabinski, *Nature* 387 (1997) 761–763.
- [2] C. Muratore, A.A. Voevodin, *Annu. Rev. Mater. Res.* 39 (2009) 297–324.
- [3] T. Spalvins, National Aeronautics and Space Administration, Cleveland, OH (USA), Lewis Research Center, 1984.
- [4] A.A. Voevodin, J.S. Zabinski, *Compos. Sci. Technol.* 65 (2005) 741–748.
- [5] A.A. Voevodin, J.P. O'Neill, J.S. Zabinski, *Surf. Coat. Technol.* 116–119 (1999) 36–45.
- [6] Y.T. Pei, D. Galvan, J.T.M. De Hosson, A. Cavaleiro, *Surf. Coat. Technol.* 198 (2005) 44–50.
- [7] J. Fontaine, C. Donnet, A. Erdemir, *Fundamentals of the tribology of DLC coatings*, in: C. Donnet, A. Erdemir (Eds.), *Tribology of Diamond-like Carbon Films: Fundamentals and Applications*, Springer US, Boston, MA, 2008, pp. 139–154.
- [8] Y. Pei, D. Galvan, J. Dehosson, *Acta Mater.* 53 (2005) 4505–4521.
- [9] L. Gu, P. Ke, Y. Zou, X. Li, A. Wang, *Appl. Surf. Sci.* 331 (2015) 66–71.
- [10] A.A. Voevodin, J.S. Zabinski, *Thin Solid Films* 370 (2000) 223–231.
- [11] H. Dimigen, H. Hübsch, P. Willich, K. Reichelt, *Thin Solid Films* 129 (1985) 79–91.
- [12] A. Nossa, A. Cavaleiro, *Surf. Coat. Technol.* 142–144 (2001) 984–991.
- [13] M. Evaristo, T. Polcar, A. Cavaleiro, *Int. J. Mech. Mater. Des.* 4 (2008) 137–143.
- [14] G. Weise, N. Mattern, H. Hermann, A. Teresiak, I. Bäcker, W. Brückner, H.D. Bauer, H. Vinzelberg, G. Reiss, U. Kreissig, M. Mäder, P. Markschräger, *Thin Solid Films* 298 (1997) 98–106.
- [15] T. Polcar, M. Evaristo, A. Cavaleiro, *Vacuum* 81 (2007) 1439–1442.
- [16] M. Evaristo, T. Polcar, A. Cavaleiro, *Vacuum* 83 (2009) 1262–1265.
- [17] J. Xu, L. Chai, L. Qiao, T. He, P. Wang, *Appl. Surf. Sci.* 364 (2016) 249–256.
- [18] M.J. Dai, C.B. Wei, K.S. Zhou, M. Zhu, H.J. Hou, S.S. Lin, X. Tong, *Trans. Nonferrous Metals Soc. China* 25 (2015) 3002–3011.
- [19] J. Sundberg, L. Lindblad, M. Gorgoi, H. Rensmo, U. Jansson, A. Lindblad, *Appl. Surf. Sci.* 305 (2014) 203–213.
- [20] T. Polcar, A. Nossa, M. Evaristo, A. Cavaleiro, *Rev. Adv. Mater. Sci.* 15 (2007) 118–126.
- [21] M. Evaristo, A. Nossa, A. Cavaleiro, *Surf. Coat. Technol.* 200 (2005) 1076–1079.
- [22] F. Lévy, J. Moser, *Surf. Coat. Technol.* 68–69 (1994) 433–438.
- [23] A. Nossa, A. Cavaleiro, N.J.M. Carvalho, B.J. Kooi, J.T.M. De Hosson, *Thin Solid Films* 484 (2005) 389–395.
- [24] C.S. Sandu, T. Polcar, A. Cavaleiro, *Microsc. Microanal.* 14 (S3) (2008) 7–10.
- [25] H. Dimigen, H. Hübsch, P. Willich, K. Reichelt, *Thin Solid Films* 64 (1979) 221.
- [26] E. Särhammar, E. Strandberg, J. Sundberg, H. Nyberg, T. Kubart, S. Jacobson, U. Jansson, T. Nyberg, *Surf. Coat. Technol.* 252 (2014) 186–190.
- [27] M. Regula, C. Ballif, J.H. Moser, F. Lévy, *Thin Solid Films* 280 (1996) 67–75.
- [28] M. Ohring, Chapter 5 - plasma and ion beam processing of thin films, *Materials Science of Thin Films*, 2nd ed., Academic Press, San Diego, 2002, pp. 203–275.
- [29] X. Zhang, L. Qiao, L. Chai, J. Xu, L. Shi, P. Wang, *Surf. Coat. Technol.* 296 (2016) 185–191.
- [30] D.Y. Wang, C.L. Chang, W.Y. Ho, *Surf. Coat. Technol.* 111 (1999) 123–127.
- [31] J.A. Thornton, *J. Vac. Sci. Technol.* 11 (1974) 666–670.
- [32] C.R.D. Priestland, S.D. Hersee, *Vacuum* 22 (1972) 103–106.
- [33] J. Moser, F. Lévy, *J. Mater. Res.* 7 (1992) 734–740.
- [34] J. Sundberg, H. Nyberg, E. Särhammar, F. Gustavsson, T. Kubart, T. Nyberg, S. Jacobson, U. Jansson, *Surf. Coat. Technol.* 232 (2013) 340–348.
- [35] T. Polcar, M. Evaristo, A. Cavaleiro, *Wear* 266 (2009) 388–392.
- [36] T.W. Scharf, A. Rajendran, R. Banerjee, F. Sequeda, *Thin Solid Films* 517 (2009) 5666–5675.
- [37] T. Polcar, M. Evaristo, A. Cavaleiro, *Plasma Process. Polym.* 6 (2009) 417–424.

- [38] T. Polcar, M. Evaristo, R. Colaço, C. Silviu Sandu, A. Cavaleiro, *Acta Mater.* 56 (2008) 5101–5111.
- [39] T.W. Scharf, S.V. Prasad, *J. Mater. Res.* 48 (2013) 511–531.
- [40] S.V. Prasad, J.S. Zabinski, N.T. McDevitt, *Tribol. Trans.* 38 (1995) 57–62.
- [41] A. Aubert, J.P. Nabot, J. Ernoult, P. Renaux, *Surf. Coat. Technol.* 41 (1990) 127–134.
- [42] N.M. Renevier, J. Hampshire, V.C. Fox, J. Witts, T. Allen, D.G. Teer, *Surf. Coat. Technol.* 142–144 (2001) 67–77.
- [43] T. Polcar, A. Cavaleiro, *Surf. Coat. Technol.* 206 (2011) 686–695.
- [44] F. Gustavsson, S. Jacobson, A. Cavaleiro, T. Polcar, *Surf. Coat. Technol.* 232 (2013) 541–548.
- [45] Y. Pei, D. Galvan, J.T.M. De Hosson, *J. Vac. Sci. Technol.* 24 (2006) 1448–1453.
- [46] T. Polcar, M. Evaristo, M. Stueber, A. Cavaleiro, *Wear* 266 (2009) 393–397.