



Properties of W/DLC/W–S–C composite films fabricated by magnetron sputtering

Ming-jiang DAI^{1,2,3}, Chun-bei WEI^{2,3}, Ke-song ZHOU^{1,2,3},
Min ZHU¹, Hui-jun HOU^{2,3}, Song-sheng LIN^{2,3}, Xin TONG^{2,3}

1. School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China;

2. New Materials Department, Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510650, China;

3. National Engineering Laboratory for Modern Materials Surface Engineering Technology,
Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510650, China

Received 27 October 2014; accepted 24 July 2015

Abstract: A kind of W/DLC/W–S–C composite film was fabricated by magnetron sputtering method. Effects of WS_x content on the structure and the adhesion of the composite films were investigated. In addition, tribological behavior of the composite films was studied in the conditions of the ambient air and N_2 gas atmosphere by ball-on-disk tester. The results indicate that the composite films show dense and amorphous microstructure. The WC_x and WS_x compounds are found in amorphous diamond like carbon matrix in the top layers of W–S–C. A proper WS_x content is beneficial for improving the adhesion of the composite films. In air atmosphere, the composite films with high C content have better wear resistance and the friction coefficients range from 0.15 to 0.25. In N_2 condition, high WS_x content is benefit for the wear resistance and the friction coefficients of the composite films range from 0.03 to 0.1.

Key words: W/DLC/W–S–C composite film; magnetron sputtering; adhesion strength; friction coefficient

1 Introduction

Transition metal dichalcogenides (MS_2) such as MoS_2 and WS_2 , are most widely used in the aerospace parts due to their low friction coefficient and high wear resistance in vacuum and dry gas conditions. Their low friction coefficient is based on the lamellar structure, where a sheet of M atom is sandwiched between two hexagonally packed sulfur layers. The bonding within the S–M–S sandwich is covalent, while weak van der Waals forces hold the sandwich together resulting in interlamellar mechanical weakness. Thus, under a shearing force, the basal planes slide back and forth over one another by intracrystalline slip and transfer to the rubbing counterface easily [1,2]. Compared with MoS_2 , WS_2 exhibits better thermal and oxidative stability and provides a ~ 100 °C increase in maximum operating temperature [3]. However, similar to MoS_2 , sputtered pure WS_2 films suffer severe deterioration in friction and wear properties in humid air environments and even have poor wear resistance in vacuum, due to the easy reaction of dangling and unsaturated bonds of the crystal WS_2

with the moisture [4,5]. In order to improve the comprehensive tribological properties of WS_2 both in humid ambient air and UHV environments, many works have been done such as incorporation of metal (Ni, Ti, Ag, etc) into dichalcogenide films [6–8] or fabrication of multilayers such as $TiAlSiN/WS_2$ [9]. The doped element occupies the boundaries of crystalline MS_2 and can cover the partial unsaturated bond sites at the edge planes, leading to the improvement of anti-oxidation capability. Moreover, the M dopant can hinder the grain growth and densify the structure significantly, which inhibit the transport of O or H_2O from the surface to inner in humid air [6,10,11].

Diamond like carbon (DLC) films have good mechanical properties, such as high hardness, good adhesion, low friction and high wear resistance in ambient air conditions, and they have been used as protective coatings in a great variety of industrial applications [12]. A graphitic transfer layer on the counter surface acts as a lubricant, leading to the low friction coefficient. The high hardness of the DLC coating contributes to its extremely low wear rate [13]. In order to achieve good tribological properties both in

humid air and high vacuum or dry air conditions, co-deposition of DLC and WS₂ coatings was studied in previous researches [14–16]. They proposed that carbon doped in W–S formed a “chameleon” nanocomposite structure WC/DLC/WS₂, which included dichalcogenide phases and nanocrystalline carbide phases encapsulated in an amorphous DLC matrix. In these films, WC nanocrystals provided overall hardness and wear resistance, amorphous DLC provided low friction and wear in ambient conditions and WS₂ provided lubrication in vacuum or dry gas conditions. As a result of these mechanisms, a thin lubricating layer is always presented on top of a hard support coating in both humid and dry environments. The structure-chemistry self-adaptation of the friction surface results in low friction coefficients and long endurance in dry and humid environments.

Co-deposition of DLC and WS₂ to form W–S–C could also lead to the improvement of the adhesion. It is reported that the adhesive critical loads of WS₂ films were within the range of 5–6 N, which would lead to poor wear resistance in most cases [15]. When the incorporation of C or N content was increased, the inwards diffusion of these elements for the Ti interlayer might have led to a mixed interface between both layers, improving adhesion of the films [16]. As they suggested, the critical load of the W–S–C films was only 7 N with low C content and it increased significantly to more than 50 N when the C content was up to 64.04% (mole fraction).

In this work, a kind of W/DLC/W–S–C composite film was designed and then fabricated by magnetron sputtering method. The W interlayer was applied between the substrate and DLC sublayer, and the DLC sublayer was used for supporting the W–S–C top layer. The W–S–C top layer was acted as a “chameleon” layer, which contributes friction lubrication. Therefore, this composite film was expected to have good endurance and friction lubrication under both humid air atmosphere and dry gas atmosphere.

2 Experimental

Ti6Al4V alloy (TC4, $d_{25} \text{ mm} \times 7 \text{ mm}$), K20 cemented carbide alloy and silicon wafer were used as the substrates. The TC4 substrate was polished with diamond paste to a roughness of 0.1 μm . K20 cemented carbide alloy was commercial bit tool with a roughness of 0.02 μm . All substrates were first ultrasonically cleaned by acetone and alcohol, and then fixed to a holder with a rotation speed of 2 r/min. W/DLC/WS₂ composite films were produced in a multifunctional ion plating system. Prior to deposition, the chamber was evacuated down to $5 \times 10^{-3} \text{ Pa}$, and pure Ar (99.99%) was let into the chamber to a pressure of 0.4 Pa. The

substrates were subjected to Ar⁺ ion bombardment at a negative bias of 500 V for about 20 min to remove impurities. After argon ion cleaning, tungsten target was switched on for 5 min to allow a W interlayer. Then, the DC power for W target decreased and concurrently the DC power for graphite target increased gradually to form a gradual interlayer. After that DLC sublayer with about 0.4 μm in thickness was deposited. Subsequently, graphite target and WS₂ targets were activated synchronously to deposit the W–S–C top layer for 120 min. During deposition process, the sputtered powers of WS₂ targets were set as 30, 70, 180 and 280 W respectively to get different WS₂ contents. The power of graphite target was kept at 1800 W all the time. During the entire deposition process, the pressure was fixed to 0.4 Pa and the substrate was negatively biased to 50 V. The pure DLC film with the thickness of 0.9 μm was deposited for 4 h with the sputtered power of 1800 W, while the pure WS_x film with the thickness of 3.7 μm was fabricated for 2 h with the sputtered power of 500 W.

Surface and cross-sectional morphologies were examined by a S-3700N scanning electron microscope (SEM) (Hitachi, Japan). The composition of the films on silicon substrate was determined by energy dispersive X-ray spectroscopy (EDS) (Thermo NORAN, USA) at accelerating voltage of 20 kV using spectral display software package. The chemical composition is an arithmetic average of three values measured in different parts of the film. X-ray diffraction (XRD) was used to investigate the phase structure of the films by Philips X'Pert Pro using Cu K α radiation with the scanning rate of 0.05 (°)/s and the incidence angle of 1°. The X-ray photoelectron spectroscopy (XPS) analysis was conducted with an ESCALAB 250 (Thermo Fisher Scientific) using Al K α excitation source (1486.6 eV) operated at a voltage of 15 kV and a current of 10 mA. The analyzed area on the sample is set to be about 500 μm in diameter and the base pressure of the vacuum chamber was $2 \times 10^{-7} \text{ Pa}$. The hardness was measured by an indentation tester (Vickers). The maximum indentation load was 25 g and loading time was kept for 15 s. The adhesion of films was investigated by a scratch tester. The applied load was increased from 0 to 100 N with an increasing load of 100 N/min. The critical load was obtained by the inspection of the scratches by SEM. Friction and wear tests were conducted on a ball-on-disk wear tester using E52100 steel balls with 4 mm in diameter as counterbody. The tribological behavior was evaluated in a laboratory air (50%–60% RH) and dry N₂ gas conditions at room temperature (about 23 °C), with a normal load of 5 N, a radius of the wear track of 8 mm, and a sliding speed of 418.9 mm/s (total 60000 cycles) for a 3000 m sliding distance.

3 Results and analysis

3.1 Cross-section morphology and component

The SEM cross-section images of the composite films with varying WS_x contents are shown in Fig. 1. The pure DLC film is 0.9 μm in thickness, while that of the pure WS_x film is 3.7 μm . The composite films are composed of W interlayer, DLC sublayer and W–S–C top layer. The thickness of DLC sublayer is about 0.4 μm . The thickness of W–S–C top layers increases obviously with increasing WS_2 sputtered power, and it ranges from 0.55 to 0.96 μm . The pure DLC film and the DLC sublayer have obviously dense columnar structure, where the pure WS_x film exhibits a loose columnar morphology. However, the microstructure of the W–S–C top layers transforms from columnar to featureless morphology with the increase of WS_x content. YANG et al [17] suggested that in DLC films, additional atoms could prevent the formation of large carbon clusters, resulting in the easy formation of small amorphous carbon cluster. That is the columnar structure of DLC disturbed by the addition of W and S atoms, and the columnar structure transformed to a denser featureless morphology with increasing W–S content. Similarly, the structure of WS_2 films was also significantly influenced by C atoms. The crystalline of WS_2 was distorted by addition of C atoms and the columnar structure was restrained.

The relative components of W/DLC/W–S–C composite films on silicon substrate are shown in Table 1. The C content detected by EDS should come from both of the W–S–C top layers and the DLC sublayers due to

the thickness of the W–S–C top layers less than 1 μm . It is obvious that the films are deficient in sulfur element according to the S/W mole ratio, which is lower than the stoichiometry of WS_2 . As is reported in previous work [15], the films deposited in an argon atmosphere were deficient in sulfur in relation to the WS_2 target due to the bombardment by energetic particles. The difference in mass between the metals (W, Mo) and S leads to preferentially re-sputtering of the lighter sulfur atoms from the film by energetic particles during deposition, and sulfur is pumped out of the chamber. It is noticed that the W content is extremely high in the sample with low WS_x content (lower WS_2 sputtered power of 30 W), and the S/W mole ratio increases with the enhancement of the WS_2 sputtered power. This indicates that the lower sputtered power can lead to the higher loss of S element, which can be explained that the deposition rates as well as the re-sputtering increase with the increase of sputtered power. This is a dynamic process. When the deposition rate is higher than the re-sputtering rate, the loss of S atoms decreases relatively.

3.2 Analysis of XRD patterns

XRD patterns of the films are shown in Fig. 2. For the pure DLC film, it is hard to detect vestiges of any other crystalline phase except those of W and WC_x , indicating amorphous structure of the DLC film. W phase appears at 2θ of $\sim 40^\circ$, 58° and 72.9° corresponding to the W interlayer, and WC_x phase can be related to the gradual interface between the W interlayer and DLC sublayer. The pure WS_x films show WS_2 hexagonal phase preferentially oriented. The

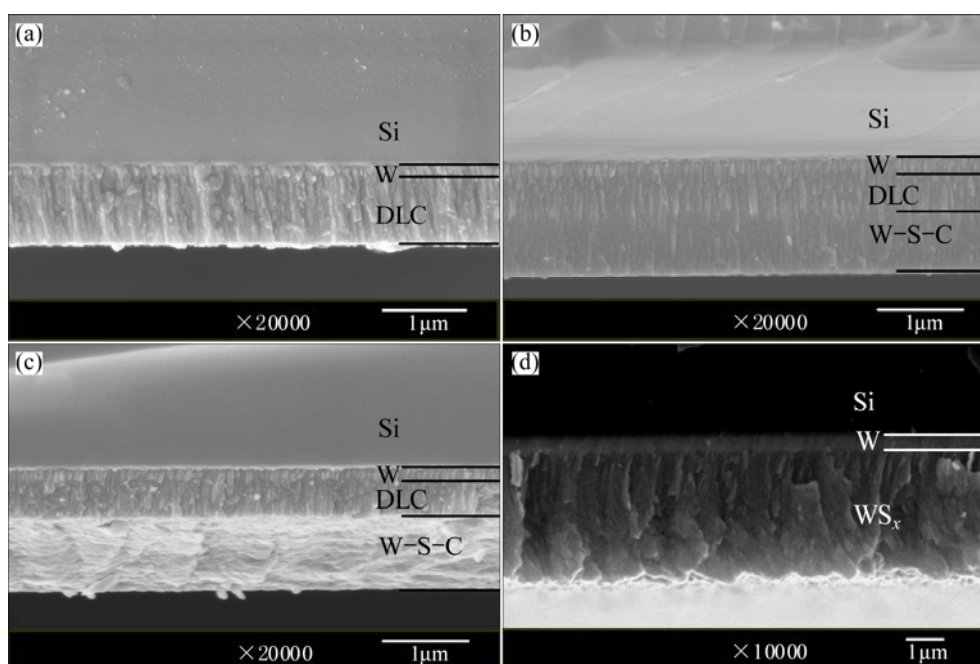
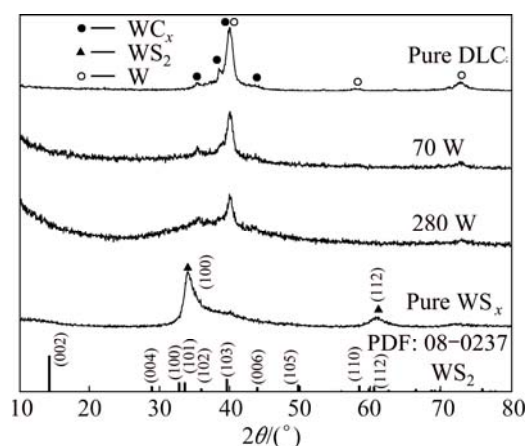


Fig. 1 SEM cross-section images of composite films with varying WS_2 sputtered power: (a) Pure DLC film; (b) 70 W; (c) 280 W; (d) Pure WS_x film

Table 1 Elemental contents of composite films

WS ₂ target power/W	<i>x</i> (C)/%	<i>x</i> (S)/%	<i>x</i> (W)/%
0 (Pure DLC)	96.1		3.9
30	76.7	7.9	15.4
70	65.7	17.9	16.4
180	62.6	21.4	16.0
280	57.9	24.3	17.8

**Fig. 2** XRD patterns of DLC and composite films

diffraction pattern presents an asymmetrical peak at 33°–44° indexed as (100), with a long shoulder on its right side due to planes of (101), (102) and (103). This feature has been explained as a turbostratic stacking of S–W–S single layer corresponding to a series of planes (10 L) ($L=0,1,2,3$) [15]. The density of the WS₂ (100) reflection decreases when C element is added in WS₂, which indicates a gradual loss of WS₂ crystallinity. A broad peak characteristic reveals amorphous or nanosized crystallites in the composite films. However, it is difficult to identify the formation of WC_x phase in the W–S–C top layers from the XRD reflection. VOEVODIN et al [14,18] revealed that in W–S–C coatings WS₂ nano-grains with size less than 10 nm and WC nano-clusters with size of 1–2 nm are randomly oriented in amorphous carbon matrix. POLCAR et al [19] reported that WS₂ platelets exhibit size of 5–10 nm with the lowest carbon content (up to ~35%) and it decreases with further increase of the carbon content. Tungsten carbide grains are not observed in any case. In this work, WS₂ may be in amorphous phase or nano crystallites in composite films. The WC_x phase may present in nano-clusters in the composite films that X-ray diffraction grazing angle did not reveal well defined peaks.

3.3 Chemical composition and bonding

XPS was firstly carried out on the as-deposited surfaces, and then again after removing approximately about 30 nm (with the sputtered rate of 0.22 nm/s) of the

film material. The elemental content of the film by XPS is shown in Table 2. Serious oxidation is observed on the surface with high oxygen content and it decreases noticeably after ion sputtering of the contamination layer. The S content in the films is lower compared with the result of EDS in Table 1 and the S/W mole ratio decreases to 0.53–0.64. It may be related to the preferential sputtering of S by Ar⁺ ion etching by XPS. Other researchers have also found that the S content decreases steadily as the etching time increases [20,21]. The XPS spectra of the W–S–C top layers after ion sputtering are presented in Fig. 3. The characteristic peak of W 4f can be deconvoluted into three doublets, i.e. W–S, W–C and W–O bonds. The W–S bonds are found at around binding energy (E_b) of 31.7 eV, W–C bonds at around binding energy of 32.4 eV and W–O bonds at around binding energy of 35.0 eV. The position of W 4f was kept approximately constant in spite of different C contents. Previous researches showed that there was a close relationship between the E_b values and the S/W mole ratio in WS₂ materials [20,21]. In this case, the mole ratios of S/W are very close on different surfaces after ion etching due to the preferential sputtering of S. Thus, the peaks of W 4f vary faintly on different surfaces.

Table 2 Elemental contents of composite films tested by XPS

WS ₂ target power/W	<i>x</i> (C)/%	<i>x</i> (S)/%	<i>x</i> (W)/%	<i>x</i> (O)/%
70 (as-deposition)	61.5	4.7	5.1	28.7
70 (after ion etching)	74.4	8.2	12.8	4.6
280 (as-deposition)	41.3	4.3	6.7	47.7
280 (after ion etching)	41.0	17.4	32.8	8.8

The S 2p peaks in Fig. 3 (b) present a broad peak. Deconvolution of the S 2p spectrum reveals two doublets. The S 2p_{3/2} peaks at about 161.9 eV correspond to S–W bonds. The S 2p_{3/2} peaks in the range of 163.1 to 163.3 eV may attribute to the sulfur element [22], which may have condensed on the film after discharge power was switched off during the deposition from the WS₂ target [23]. However, the sputtering before the XPS measurement should have eliminated the elemental sulfur from the surface, although vestiges could persist. A second possibility is the formation of S–C bond, indicating that a portion of sulfur in the films is in a carbon environment [22,24,25]. The literature value for S–C bond is 163.6 eV [25], which is close to that found experimentally from the peak fitting.

The C 1s peaks change significantly with the WS₂ sputtered power in the W–S–C films. On the surface with WS₂ sputtered power of 70 W, the C content reaches 74% and the C 1s peaks locate at 284.4 eV corresponding to the C-based phases [22]. When the C

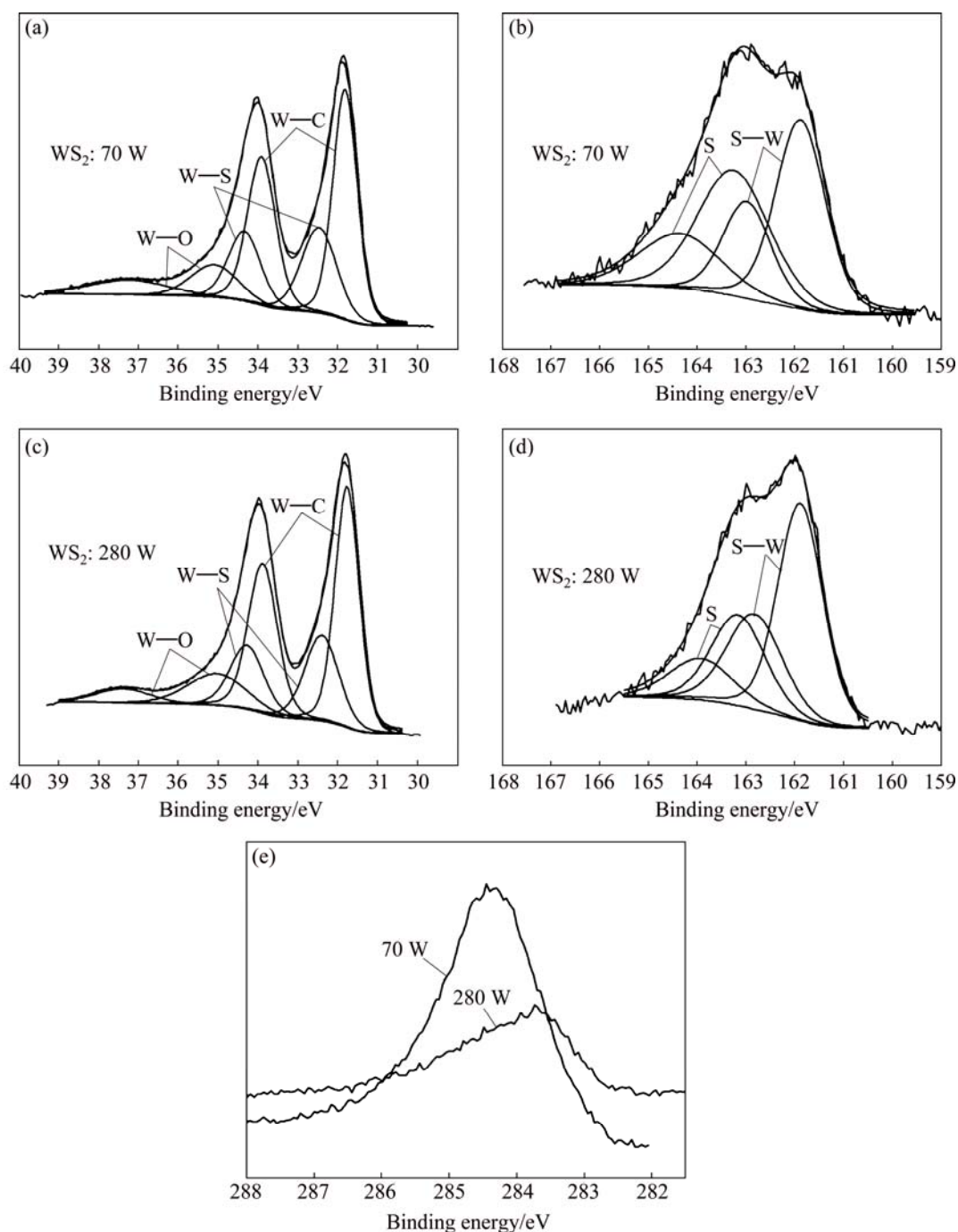


Fig. 3 XPS spectra of composite films: (a, c) W 4f; (b, d) S 2p; (e) C 1s

content decreases to 41% (WS₂ sputtered power of 280 W), the position of C 1s peaks shifts to lower E_b value (~283.7 eV), which can be attributed to the formation of C—W bond, i.e., a carbide phase. ABAD et al [26] found similar trends in the W—C films, i.e., for lower C content, the C 1s peaks present the main component at 283.5 eV corresponding to C—W bonds. For C contents higher than 50%, the position of C 1s peaks shifts to higher values because the relative contribution of the C—C peak increases corresponding to the formation of an amorphous carbon bonded-matrix.

3.4 Analysis of microhardness

The microhardness of the films is shown in Fig. 4. The pure DLC films have the highest hardness (HV 1573 on K20 substrate and HV 698 on TC4 substrate) while the pure WS₂ films exhibit the lowest hardness (about HV 250–HV 270). For the composite films, the hardness reduces gradually with an increase of the WS_x content. However, the hardness of the composite films has been improved effectively compared with that of the pure WS_x films. This is because that the introduction of C can disturb the loose columnar grain of WS₂, leading to a

denser structure. The formation of nanosized crystallites of WS_x and WC_x in amorphous DLC can contribute to the improvement of hardness. The enhanced hardness may provide lower wear rates and longer endurance for the composite films. In addition, the hardness is influenced by the substrate due to the thin thickness. Thus, lower surface hardness has been detected on the TC4 alloy compared with that on the K20 carbide alloy.

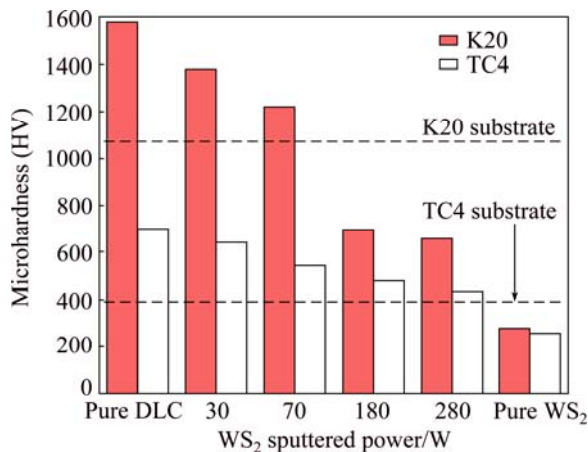


Fig. 4 Microhardness of films on TC4 substrate and K20 substrate

3.5 Adhesion properties of films

The critical loads of the composite films on K20 carbide alloy substrate presented in Table 3 are obtained by the inspection of the scratches by SEM. The morphologies of scratch tracks are presented in Fig. 5. In the pure WS_x samples, the film failure is almost immediate and abrupt. The poor adhesion of the pure WS_x films can be attributed to the easy plastic fracture of the films originated from the coarse columnar platelets with significant pores [6]. The critical load of the pure DLC film is 55 N, indicating that DLC film can provide good adhesion to the substrate. The composite films with low WS_x content show good adhesion properties and the critical load reaches up to 62–63 N, which is even higher than that of the pure DLC film. However, it gets worse with further increasing the WS_x content. The films with the highest WS_x content (sputtered power of 280 W) show very low adhesion strength and delamination occurs at the interface between the DLC sublayers and W–S–C top layers at the initial sliding test as shown in Fig. 5(c). When the applied load reaches about 24 N, spalling takes place between the interface of the films and the substrate (Fig. 5(d)). This demonstrates that the DLC sublayers can provide good adhesion to the substrate. However, increasing the WS_x content could deteriorate the adhesion of the W–S–C layers to the DLC sublayers. These could be related to the reduction of film hardness. As is known that the soft films cannot support

Table 3 Critical load of films on K20 substrate

WS ₂ sputtered power/W	Pure DLC film	30	70	180	280	Pure WS _x film
Critical load/N	55	62	63	32	2	–

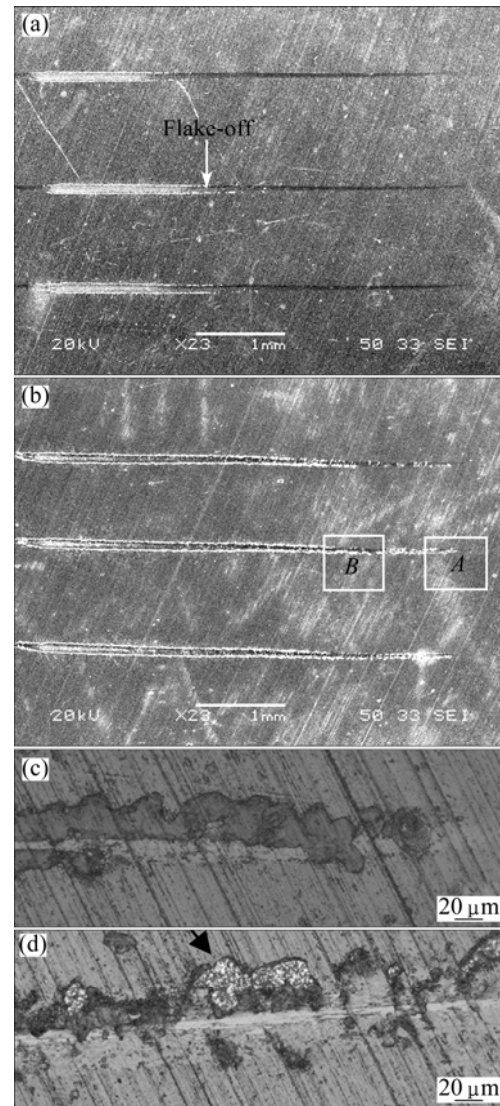


Fig. 5 SEM images of scratch tracks: (a) 30 W; (b) 280 W; (c, d) Magnified picture of areas A and B in (b)

the applied load effectively. With the increase of WS_x content, the hardness of the W–S–C layers decreases, resulting in the rapid failure of W–S–C layers from DLC layer under applied scratch load. Moreover, for the high carbon films, high C contents in the W–S–C films may lead to a mixed intergraded interface between the W–S–C layers and DLC layers, making it stronger and avoiding the spalling for low applied scratch loads. It is worth to note that the composite films (sputtered powers of 30 W and 70 W) even show higher adhesion strength than that of the pure DLC film. This may be attributed to the decrease of internal stress, which can increase the stability of the composite films.

3.6 Tribological properties

Figure 6 shows the friction coefficients of the films tested in ambient air. The pure DLC film shows a rather high friction coefficient (~ 0.27). Previous researches [27] proposed that compared with hydrogenated diamond-like carbon films, non-hydrogenated diamond-like carbon films usually present higher friction coefficient in humid conditions. This is because the presence of humidity in the testing atmosphere in conjunction with the dangling bonds existing in the C-matrix will promote the formation of strong bonds between the graphitic clusters, impeding the easy sliding between their basal planes. The pure WS_x film exhibits a lower friction coefficient (about 0.1) due to its good lubrication effect. However, the pure WS_x film suffers low endurance and it fails after about 30 min sliding test due to its low hardness and poor adhesion. For the composite films, the friction coefficient is between that of the pure WS_x film and that of the pure DLC film. With increasing the WS_x content, the friction coefficient decreases, and the sliding process becomes much smoother. This can be attributed to the very small particles of WS_x working as a third lubricating body.

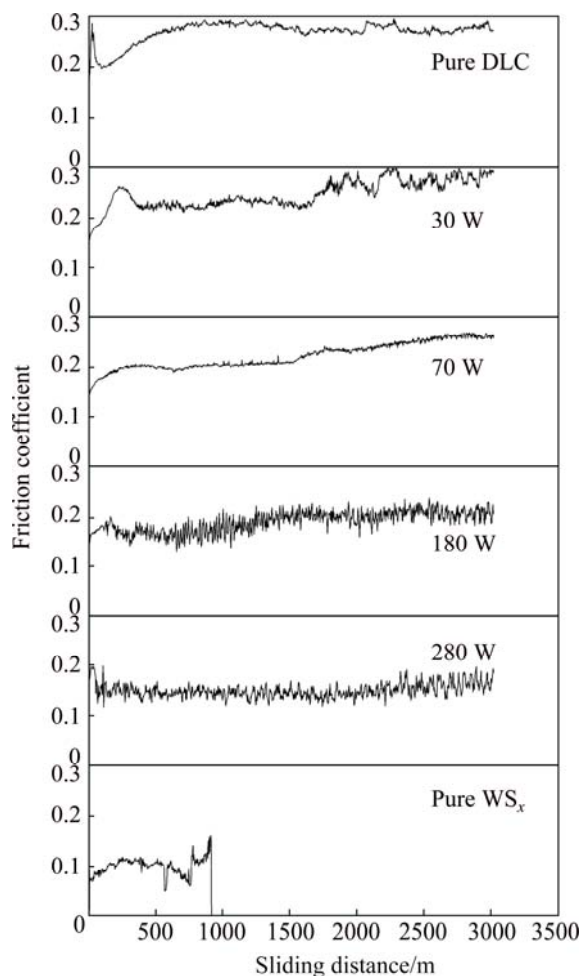


Fig. 6 Friction coefficients of composite films tested in ambient air

The wear tracks after sliding in ambient air are shown in Fig. 7. The wear tracks are smooth and no debris has been found due to the solid lubrication effect. It has been well established that contact and wear transforms DLC at the contact area into graphitic layers to form transfer layer. For WS_2 , it is easy to form transfer layer on counterbody due to its interlamellar mechanical weakness. They behave as a solid lubricant to decrease the friction coefficient and wear. In this experiment, transfer layer formed on the counterbody as shown in the insert images supplies a solid lubricant effect, protecting the counterpart steel and the composite films from serious damage. Some flakings appear in the pure WS_x films after about 30 min wear test, indicating its rapid failure in humid air. This is because the pure WS_x films have a loose columnar platelet structure and the porosity between the platelets is in favor of transporting O or H_2O from the film surface to inner layer. So, it gets easily oxidized, which leads to the rapid failure of the films in

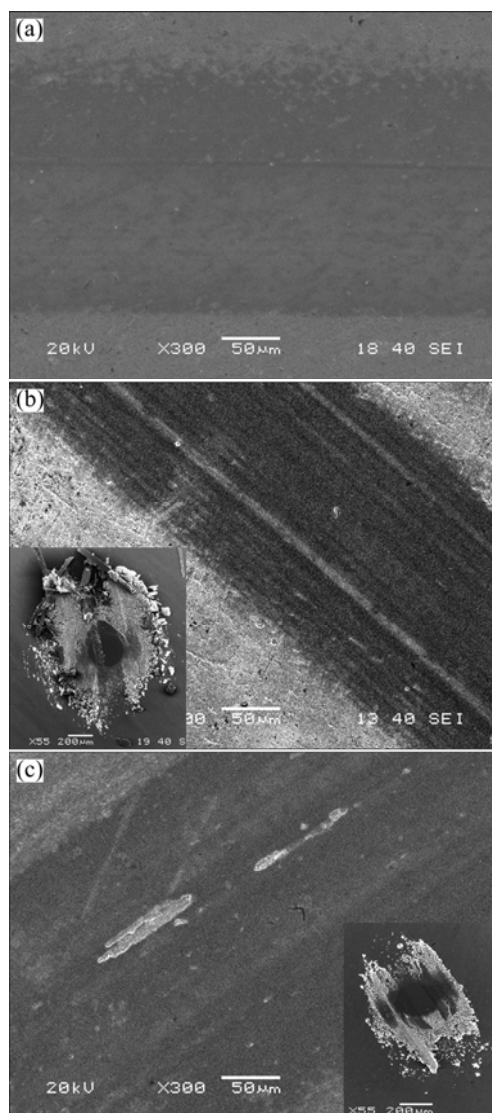


Fig. 7 Morphologies of wear tracks tested in ambient air: (a) 30 W; (b) 280 W; (c) Pure WS_x film

humid air [6]. It is generally accepted that the formation of a good, adherent MoS_2 or WS_2 transfer layer on the contact surface can contribute to the good wear properties. However, the WS_2 tribofilms formed in humid air are less beneficial. The adsorption of water molecules decreases the cohesion between the wear particles so that the re-coalescence of wear debris that builds up the tribofilm is disturbed and wear occurs quickly, or a tribofilm is still formed, but the structure contains much more defects and is not well aligned when tested in humid air [28]. The composite films exhibit higher wear resistance and moderate friction coefficient in humid air. The cooperation of DLC and WS_2 can densify the microstructure of the films significantly and the loose columnar platelet structure is restrained. This indicates that the transport of O or H_2O from the film surface to inner becomes difficult when the composite films are exposed to the humid air. So, the oxidation is confined to the film surface and the wear properties are improved. The formation of nanosized crystallites of WS_x phase in graphite transfer layer could be benefit to the reduction of the friction coefficient. The composite films with higher C content show shallower wear tracks, indicating the high-carbon films with a lower wear rate. As is known that DLC adjusts the ambient environment lubrication, the amorphous DLC and hard WC_x phase in the composite films provide wear resistance effectively in air conditions due to their high hardness and stable properties in moist air. Higher C content relates to higher hardness, thus corresponding to higher wear resistance in moist air. Moreover, the improvement of adhesion by a proper amount of WS_x phase in W–S–C layer (such as in samples with sputtered powers of 30 W and 70 W) may also lead to the higher wear resistance. It is noted that the sample with high WS_x content (sputtered power of 280 W) shows no failure after 120 min wear test in spite of its very low adhesion strength. Thus, it could be concluded that the composite films possess better wear resistance due to its better combinational properties than that of the pure WS_x films, though it presents low adhesion.

Generally, the wear properties are subject to the composition and structure of the films, such as component, microstructure and film thickness. However, in this experiment, the thickness shows little influence on the wear properties. No improvement of the wear life has been found with the increasing thickness in the composite films. For example, the sample with small thickness (sputtering power of 30 W) shows better wear resistance than the sample with large thickness (sputtering power of 280 W) in air conditions. This demonstrates that the component and microstructure play a major role in the wear properties of the W–S–C composite films.

Figure 8 shows the friction coefficients of the composite films tested in N_2 environment. The pure WS_x film shows the lowest friction coefficient (~ 0.02) and the friction curve is very smooth. The adherent material is accumulated at the edge of wear track making a positive relief as presented in Fig. 9(a). The excellent lubrication of WS_2 in dry atmosphere depends mainly on a good, adherent self-lubricant tribolayer formed on the worn surfaces. The transfer film prevents the direct contact between the metals and the occurrence of adhesion and scuffing. For the composite films, the friction coefficient in N_2 atmosphere is in the range of 0.03–0.10, which is much lower than that tested in ambient air. Moreover, the composite films with higher WS_x content exhibit lower friction coefficients and smoother friction curves. It is noted that a failure happens in the high-carbon sample (WS_2 sputtered power of 30 W) after about 100 min sliding test, suggesting that high-carbon films suffer higher wear in dry N_2 atmosphere. In humid air, high wear resistance could be attributed to amorphous DLC due to its stable properties in moist air. However, in vacuum or dry gas condition, low friction in W–S–C films could be attributed to the WS_2 phase due to the formation of excellent self-lubricant tribolayer in the friction contact. In high-carbon films, there is insufficient WS_2 phase available to form a stable self-lubricant tribolayer, leading to the fluctuant friction curves and rapid failure of the films. Figure 9(b) shows that the free

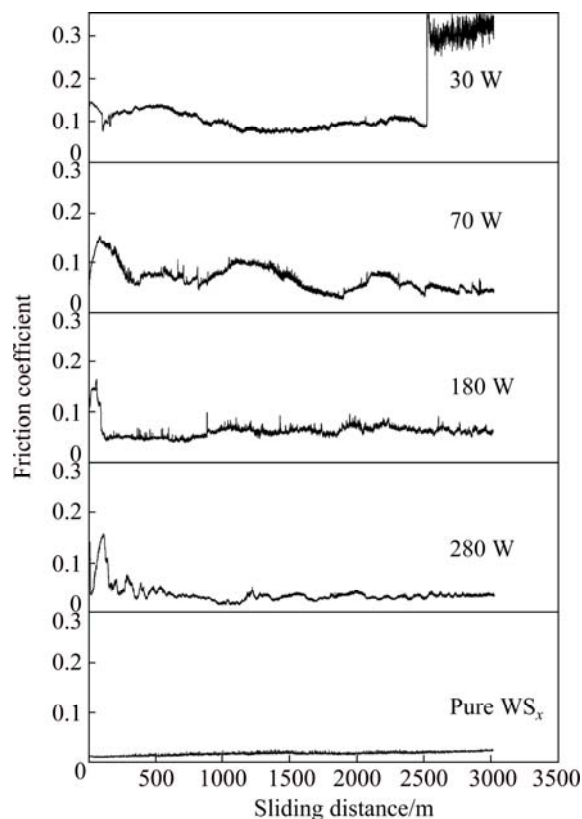


Fig. 8 Friction coefficients of films in N_2 gas atmosphere

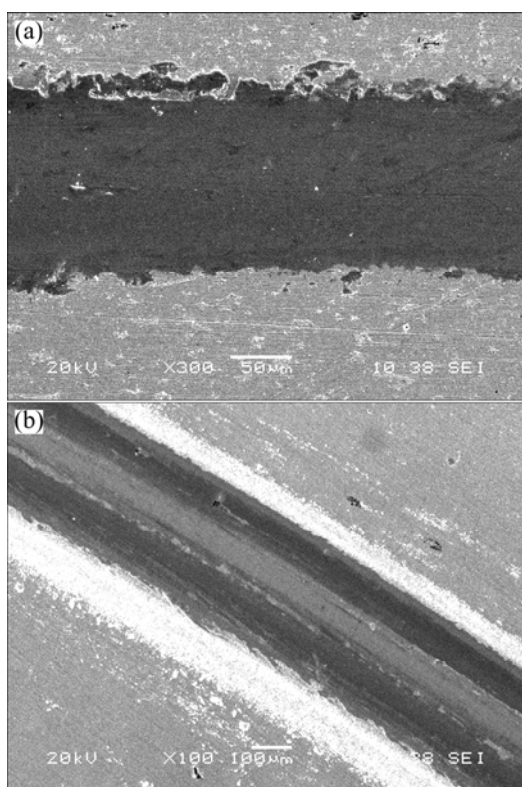


Fig. 9 SEM images of wear tracks tested in N_2 atmosphere: (a) Pure WS_x film; (b) 70 W

wear debris is pushed out of the wear track, indicating that it is difficult to form a stable self-lubricant tribolayer in the friction contact. As a result, the wear rate is high in the films with high C content.

According to the results, higher DLC contents imply higher hardness, adhesion and better wear resistance in humid air. In dry gas condition, higher WS_2 content indicates lower friction and good wear resistance. Thus, a proper cooperation of WS_2 and DLC can be benefit to the tribological properties either in humid air or in dry gas atmosphere. At WS_2 sputtered power of 180 W, the composite film possesses intermediate friction coefficient in humid air and low friction coefficient in N_2 atmosphere, as well as the good wear endurance.

4 Conclusions

1) W/DLC/W–S–C composite films were designed and fabricated by magnetron sputtering method. The effect of WS_x content on the properties of the composite films was investigated. Compared with the pure WS_x films, the composite films show a more compact structure, and the WS_x and WC_x compounds are found in amorphous DLC matrix in the W–S–C layers.

2) A proper WS_x content can be of good adhesion properties and the critical loads reach up to 62–63 N in

the films with WS_2 sputtered power of 30 and 70 W. However, higher WS_x content can deteriorate the adhesion strength.

3) In ambient air atmosphere, the composite films present longer endurance compared with the pure WS_x film. With increasing the WS_x content, the hardness as well as the friction coefficient (in the range of 0.15–0.25) of the composite films decreases.

4) In dry N_2 condition, the pure WS_x film exhibits an excellent lubrication effect and good endurance. Thus, higher WS_x content in the composite films creates better tribological properties. The friction coefficient of the composite films ranges from 0.03 to 0.10, and it reduces with increasing the WS_x content.

References

- [1] SCHARF T W, PRASAD S V, DUGGER M T, KOTULA P G, GOEKE R S, GRUBBS R K. Growth, structure, and tribological behavior of atomic layer-deposited tungsten disulphide solid lubricant coatings with applications to MEMS [J]. *Acta Materialia*, 2006, 54: 4731–4743.
- [2] WANG Ji-hui, CHEN Hua, WIEERS E, STALS L M, CELIS J P. Comparison of tribological properties of industrial low friction coatings [J]. *Transactions of Nonferrous Metals Society of China*, 2002, 12(1): 78–82.
- [3] WONG K C, LU X, COTTER J, EADIE D T, WONG P C, MITCHELL K A R. Surface and friction characterization of MoS_2 and WS_2 third body thin films under simulated wheel/rail rolling-sliding contact [J]. *Wear*, 2008, 264: 526–534.
- [4] PRASAD S V, ZABINSKI J S, MCDEVITT N T. Friction behavior of pulsed laser deposited tungsten disulfide films [J]. *Tribology Transactions*, 1995, 38(1): 57–62.
- [5] WEISE G, MATTERN N, HERMANN H, TERESIAK A, BÄCHER I, BAUER H D, VINZEL-BERG H, REISS G, KREISSIG U, MÄDER M, MARKSCHLÄGER P. Preparation, structure and properties of MoS_x films [J]. *Thin Solid Films*, 1997, 298: 98–106.
- [6] XU Shu-sheng, GAO Xiao-ming, HU Ming, SUN Jia-yi, JIANG Dong, ZHOU Feng, LIU Wei-min, WENG Li-jun. Nanostructured WS_2 –Ni composite films for improved oxidation, resistance and tribological performance [J]. *Applied Surface Science*, 2014, 288: 15–25.
- [7] SCHARF T W, RAJENDRAN A, BANERJEE R, SEQUEDA F. Growth, structure and friction behavior of titanium doped tungsten disulphide (Ti – WS_2) nanocomposite thin films [J]. *Thin Solid Films*, 2009, 517: 5666–5675.
- [8] WANG Q, TU J P, ZHANG S C, LAI D M, PENG S M, GU B. Effect of Ag content on microstructure and tribological performance of WS_2 –Ag composite films [J]. *Surface and Coatings Technology*, 2006, 201: 1666–1670.
- [9] XIE Zhi-wen, WANG Lang-ping, WANG Xiao-feng, HUANG Lei, LU Yang, YAN Jiu-chun. Mechanical performance and corrosion behavior of $TiAlSiN/WS_2$ multilayer deposited by multi-plasma immersion ion implantation and deposition and magnetron sputtering [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(S): s470–s475.
- [10] RENEVIER N M, FOX V C, TEER D G, HAMPSHIRE J. Coating characteristics and tribological properties of sputter-deposited MoS_2 metal composite coatings deposited by closed field unbalanced magnetron sputter ion plating [J]. *Surface and Coatings Technology*, 2000, 127: 24–37.

- [11] TEER D G. New solid lubricant coatings [J]. Wear, 2001, 251: 1068–1074.
- [12] ROBERTSON J. Diamond-like amorphous carbon [J]. Materials Science and Engineering R, 2002, 37: 129–281.
- [13] MARTINEZ E, ANDUJAR J L, POLO M C, ESTEVE J, ROBERTSON J, MILNE W I. Study of the mechanical properties of tetrahedral amorphous carbon films by nanoindentation and nanowear measurements [J]. Diamond and Related Materials, 2001, 10: 145–152.
- [14] VOEVODIN A A, O'NEILL J P, ZABINSKI J S. WC/DLC/WS₂ nanocomposite coatings for aerospace tribology [J]. Tribology Letters, 1999, 6: 75–78.
- [15] NOSSA A, CAVALEIRO A. The influence of the addition of C and N on the wear behaviour of W–S–C/N coatings [J]. Surface and Coatings Technology, 2001, 142–144: 984–991.
- [16] NOSSA A, CAVALEIRO A. Mechanical behaviour of W–S–N and W–S–C sputtered coatings deposited with a Ti interlayer [J]. Surface and Coatings Technology, 2003, 163–164: 552–560.
- [17] YANG B, HUANG Z H, LIU C S, ZENG Z Y, FAN X J, FU D J. Characterization and properties of Ti-containing amorphous carbon nanocomposite coatings prepared by middle frequency magnetron sputtering [J]. Surface and Coatings Technology, 2006, 200: 5812–5818.
- [18] VOEVODIN A A, O'NEILL J P, ZABINSKI J S. Nanocomposite tribological coatings for aerospace applications [J]. Surface and Coatings Technology, 1999, 116–119: 36–45.
- [19] POLCAR T, EVARISTO M, CAVALEIRO A. Self-Lubricating W–S–C nanocomposite coatings [J]. Plasma Processes and Polymers, 2009, 6: 417–424.
- [20] BERNÈDE J C. About the preferential sputtering of chalcogen from transition metal dichalcogenide compounds and the determination of compound stoichiometry from XPS peak positions [J]. Applied Surface Science, 2001, 171: 15–20.
- [21] BAKER M A, GILMORE R, LENARDI C, GISSLER W. XPS investigation of preferential sputtering of S from MoS₂ and determination of MoS_x stoichiometry from Mo and S peak positions [J]. Applied Surface Science, 1999, 150: 255–262.
- [22] WAGNER C D, RIGGS W H, DAVID C E, MOULDER J F, MUILENBERG G E. X-ray photoelectron spectroscopy [M]. Eden Prairie, MN, USA: Perkin-Elmer Corporation, Physical Electronics Division, 1979.
- [23] ZABINSKI J S, DONLEY M S, PRASAD S V, MCDEVITT N T. Synthesis and characterization of tungsten disulphide films grown by pulsed-laser deposition [J]. Journal of Materials Science, 1994, 29: 4834–4839.
- [24] NOSSA A, CAVALEIRO A. Chemical and physical characterization of C(N)-doped W–S sputtered films [J]. Journal of Materials Research, 2004, 19: 2356–2365.
- [25] PIMENTEL J V, POLCAR T, EVARISTO M, CAVALEIRO A. Examination of the tribolayer formation of a self-lubricant W–S–C sputtered coating [J]. Tribology International, 2012, 47: 188–193.
- [26] ABAD M D, MUÑOZ-MÁRQUEZ M A, MRABET S EI, JUSTO A, SÁNCHEZ-LÓPEZ J C. Tailored synthesis of nanostructured WC/a-C coatings by dual magnetron sputtering [J]. Surface and Coatings Technology, 2010, 204: 3490–3500.
- [27] MOURA E SILVA C W, BRANCO J R T, CAVALEIRO A. How can H content influence the tribological behaviour of W-containing DLC coatings [J]. Solid State Science, 2009, 11: 1778–1782.
- [28] GUSTAVSSON F, SVAHN F, BEXELL U, JACOBSON S. Nanoparticle based and sputtered WS₂ low-friction coatings—Differences and similarities with respect to friction mechanisms and tribofilm formation [J]. Surface and Coatings Technology, 2013, 232: 616–626.

磁控溅射 W/DLC/W–S–C 复合膜的制备及其性能

代明江^{1,2,3}, 韦春贝^{2,3}, 周克崧^{1,2,3}, 朱敏¹, 侯惠君^{2,3}, 林松盛^{2,3}, 佟鑫^{2,3}

1. 华南理工大学 材料科学与工程学院, 广州 510640;

2. 广州有色金属研究院 新材料研究所, 广州 510650;

3. 广州有色金属研究院 现代材料表面工程技术国家工程实验室, 广州 510650

摘要: 采用磁控溅射方法制备 W/DLC/W–S–C 复合膜, 研究不同 WS_x 含量对复合膜结构和结合强度的影响; 采用球–盘式摩擦试验机研究复合膜在大气环境以及氮气环境下的摩擦磨损性能。结果表明: 复合膜结构致密, 在非晶类金刚石基质中存在 WS_x 和 WC_x 化合物。合适的 WS_x 含量有利于提高复合膜的膜/基结合强度。在大气环境下, 随着 C 含量的增加复合膜的耐磨性能提高, 其摩擦因数在 0.15~0.25 之间; 在氮气环境下, 随着 WS_x 含量的增加复合膜的耐磨性能提高, 其摩擦因数在 0.03~0.10 之间。

关键词: W/DLC/W–S–C 复合膜; 磁控溅射; 结合强度; 摩擦因数

(Edited by Xiang-qun LI)