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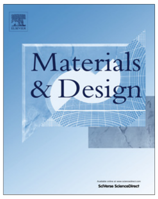

Influence of W content on tribological performance of W-doped diamond-like carbon coatings under dry friction and polyalpha olefin lubrication conditions

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ABSTRACT

The influence on tungsten content on the structure, mechanical properties and tribological performance of W-doped diamond-like carbon (DLC) coatings was studied by X-ray photoelectron spectroscopy, nano-indentation, scratch test, and ball-on-disk friction test. It was found that with increasing W content, the content of WC and free W in the coatings is increased while the content of sp^3-C in the coatings is decreased. The effect of W content on the hardness and elastic modulus of the coatings is indistinctive, but there exists the highest critical load of scratch test of above 100 N when W content is 3.08 at.%. With the increase of W content, the friction coefficients of W-doped DLC coatings under dry friction conditions are increased while the friction coefficients of W-doped DLC coatings under polyalpha olefin (PAO) lubrication are decreased. With the increase of W content, the wear rates of the DLC-coated samples under dry friction conditions show a minimum value; under pure PAO lubrication, the influence of W content on the wear rates of the DLC-coated samples is indistinctive when the W content is below 10.73 at.% while the wear rates are increased with increasing W content from 10.73 at.% to 24.09 at.%; when lubricated by PAO + thiophosphoric acid amine (T307) salt, the samples coated with the undoped DLC or the W-doped DLC with high W content exhibit low wear rates.

1. Introduction

With the trend of machine to service at high load, high velocity, severe wear is often the key bottleneck for mechanical design [1], so the improvement of the wear resistance of mechanical parts is very important for the development of modern machine. Diamond-like carbon (DLC) coatings, which are the ideal wear-resistant friction-reducing coatings for the mechanical parts due to their unique properties such as high hardness, wonderful wear-resistance, low friction coefficient, excellent chemical stability [2]. However, there exist some disadvantages restricting the application reliability of the DLC coatings, including the high stress and the poor coating-substrate adhesion [3]. Many methods, including depositing a graded transition layer [4], doping DLC coatings with transition metal elements [5–7], adopting multi-layered DLC structure [8], etc., have been studied to reduce the internal stress and enhance the adhesion of the DLC coatings.

Amongst the studied doping elements, tungsten is one of the fascinating doping elements for it can greatly reduce the structural differences at the coating/substrate interface and the internal stress in the DLC coatings, improve the thermal stability, hardness, coating-substrate adhesion, and wear resistance of the DLC coatings [9]. So the improvement of the DLC coatings by W doping has attracted much attention [6–7,9–11], but the most research emphasis is attached to the tribological performance of W-doped DLC coatings under dry friction [9–11]. However, the improvement of mechanical parts only by the DLC coatings is not enough under the severe service conditions. The DLC-coated parts are usually required to service under oil lubrication in order to obtain a satisfactory wear resistance and service life [12], but the influence of W content on the tribological behavior of the DLC coatings under oil lubrication has not been completely understood. The tribological performance of a part is related to both the surface materials of the counterparts and the service conditions [13,14]. Under different friction conditions, the variation of the wear rates of the DLC coatings with W content can exhibit different behavior. So, the study of the tribological performance of the DLC coatings under the possible service conditions is necessary for the application of the DLC coatings.

Polyalpha olefin (PAO), which has high thermal stability, high viscosity index, low pour point, and excellent hydrolytic stability,

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is a kind of the widely used base oil in engine oils [15]. Unveiling the effect of the composition of the DLC coatings under PAO lubrication conditions is important for the application of the DLC-coated parts. In order to understand the synergistic effect of lubrication additives with the concentration of the DLC coatings, a kind of widely used extreme pressure anti-wear lubricant additives, thiophosphoric acid amine salt (T307) was added into the lubricant oil of PAO.

In this paper, the DLC coatings with various W contents were fabricated by ion beam deposition/magnetron sputtering hybrid deposition method, and the influence of W content on the structure, mechanical properties, and tribological performance under both dry friction and PAO lubrication was studied.

2. Experimental details

W-doped DLC coatings were deposited on 316L stainless steel plates with a multifunctional coater (AS600DMTG) equipped with rectangular unbalanced magnetron sputtering targets, vacuum cathodic arc sources and linear anodic layer ion sources (which can operate with all inert and reactive gases at a background pressure of several milliTorr or less and produce the ion beam with a high current density). After the substrates were ultrasonically cleaned in the bath solution of water and metal cleaning agent, the substrates were rinsed in deionized water and ethanol successively, and then dried in hot air. The substrate surface was further etched by argon ions produced by a linear anodic layer ion source and chromium ions produced using a vacuum cathodic arc source before the deposition in order to remove the undesirable oxide and contamination on the substrate surface. A gradual transition layer was deposited by ion beam assisted DC magnetron sputtering before depositing the W-doped DLC coatings in order to enhance the adhesion between the coatings and their substrates. During the deposition of the transition layer, a W target was sputtered with a target current of 7 A and the gas composition through the ion source was gradually changed from a mixture of argon and nitrogen, then a mixture of argon, nitrogen and methane, and finally a the mixture of argon and methane. After the deposition of the transition layer, the W-doped DLC coatings were synthesized through the decomposition of acetylene by the ion source and the W doping by sputtering the W target with a sputtering target current of 1–7 A. The W content in the DLC coatings was adjusted by changing the W target current. The W target with a purity of 99.5%, argon with a purity of 99.99%, and acetylene with a purity of 99.9% were used in the paper. The thickness of all the coatings was about 2.3 μm.

The chemical bonding status of the coatings was analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantera). The hardness and elastic modulus of the coatings was measured by a nano-indentation (MTS XP) equipped with a Berkovich diamond indenter and the indentation depth is 1000 nm; the hardness and elastic modulus were determined according to the platform values from 100 nm to 300 nm, and the average value was obtained from five times measurement results. The adhesion between the coatings and their substrates was evaluated by scratch test (MFT-4000) according to ASTM: C1624-05 (2010). According to the ASTM: G 99-05 (2010), the friction coefficients and wear rates of DLC-coated stainless steel samples were evaluated by a ball-on-disc friction test (MS-T3000) under dry friction with a load of 1.96 N or PAO lubrication with a load of 9.80 N; a friction counter-pair of Si_3N_4 ball with a diameter of 3 mm was used; the DLC-coated stainless steel plate was fixed on a rotary sample stage with a rotation rate of 400 rpm and the diameter of the wear trace was 6 mm; the average value was obtained from three times experiment results. Under PAO lubrication, the lubricants were pure PAO or PAO/T307 solution with a 1 wt.% T307.

3. Results and discussion

The deconvolution of typical high-resolution XPS of the DLC coatings is shown in Fig. 1. The typical C1s spectrum of the DLC coatings (Fig. 1a) can be deconvoluted into three components corresponding to C–W bonded carbon (WC), sp^2 bonded carbon (sp^2-C), and sp^3 bonded carbon (sp^3-C) respectively; the typical W4f7/2 spectrum of the DLC coatings (Fig. 1b) can be deconvoluted into three components corresponding to W–C bonded W (WC), free W (W), and W–O bonded W (W–O), which implies that there exist free W, W carbide, and W oxide in the coatings. The percentage of carbon atoms with different bonding status can be calculated with the ratio of the area of the deconvoluted C1s peak corresponding to a specific bonding status to the total areas of all C1s peaks, and the variation of the content of carbon atoms with different bonding status as a function of W content is shown in Fig. 2a. With the increase of W content, the content of sp^3-C in the coatings is decreased obviously while the content of sp^3-C is increased first, and then the influence of W content on the content of sp^3-C and sp^2-C becomes indistinctive when W content is beyond 10 at.%; the content of WC in the coatings are increased with the increase of W content and a considerable amount of WC exists in the coatings when W content is beyond 10 at.%. In metal incorporated DLC nanocomposite coatings, the presence of metal domains promotes the formation of sp^2-C [16], so the content of sp^2-C is increased with increasing W content in the low W content region. With further increasing W content, W atoms are preferentially reacted and bonded to sp^2-C to form W carbide due to the relatively lower bond energy [16]. The variation of the content of the W with different bonding status in the coatings, which is established from the

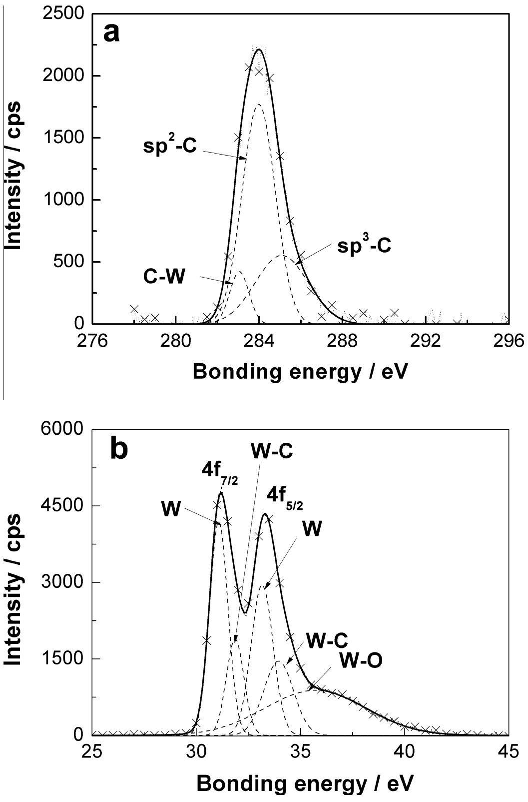

Fig. 1. Deconvolution of (a) C1s and (b) W4f spectrum of the DLC coatings with 24.09 at.% W.

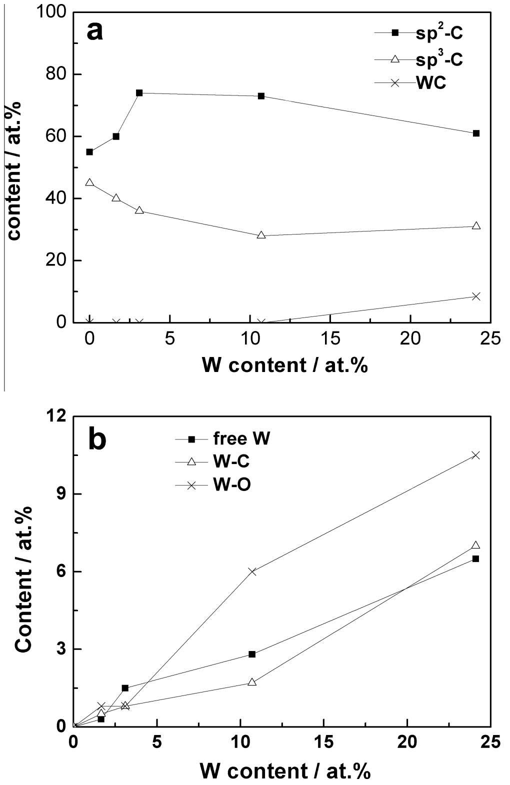

Fig. 2. Variation of the content of (a) carbon atoms with different bonding status and (b) tungsten atoms with different bonding status in the DLC coatings as a function of W content.

W4f spectrum of the coatings, is shown in Fig. 2b. It can be found that the content of the free W, W carbide and W oxide in the DLC coatings is increased with the increase of W content. When W content is no more than 3.08 at.%, the content of W carbide is slowly increased to 0.8 at.% with increasing W content; the content of W carbide is increased from 1.7 at.% to 7.0 at.% when the W content is further increased. The presence of W carbide in DLC coatings causes the formation of the nanocomposite structure composed of nanocrystalline W carbide phase dispersed in amorphous carbon matrix [17], which is beneficial to the improvement of the toughness of the coatings. However, the size of W carbide phase is abruptly increased when W content is beyond a critical value [18], which decreases the comprehensive performance of the coatings.

The correlation between the hardness of the DLC coatings and W content is shown in Fig. 3. It can be found that the hardness and elastic modulus of the coatings is appreciably decreased with the increase of W content up to 3.08 at.%, and then the hardness and elastic modulus become slightly increased. The decrease of the hardness and the elastic modulus with increasing W content up to 3.08 at.% is mainly attributed to the decrease of sp^3-C content in the DLC coatings, and the increase of the hardness and elastic modulus with increasing W content from 3.08 at.% to 24.09 at.% is mainly attributed to the increase of the content of WC in the coatings. Since the increase of the hardness and elastic modulus due to the increase of the content of WC is counteracted by the decrease of the content of sp^3-C, the change of the hardness and elastic modulus of the coatings is indistinctive.

A good adhesion between the coatings and their substrate is very important for the application reliability of the coated parts, and the critical load of scratch test of 60 N is usually considered as an acceptable value for the application of the coatings under moderate service conditions [19]. The critical load for scratch test of the coatings with various W contents is shown in Fig. 4. It can be found that the adhesion of the coatings can be greatly improved by increasing W content up to 3.08 at.% first, but then the critical load is slightly decreased with the increase of W content from 3.08 at.% to 24.09 at.%; the best adhesion is beyond 100 N for the coatings with the W content of 3.08 at.%. The residual stress in the undoped DLC coatings is very high, and the residual stress is greatly decreased when the DLC coatings are doped by W at a moderate content; but the DLC coatings with a high content have a high residual stress [20]. The reduction of the residual stress is beneficial to the improvement of the adhesion of the coatings [21], so the DLC coatings with the optimum W content of 3.08 at.% exhibit the best adhesion.

The friction coefficients and wear rates of the DLC coatings under dry friction conditions as a function of W content is shown in Fig. 5. It can be found that the friction coefficients of the coatings are increased with the increase of W content first, but when W content is above 3.08 at.%, W content has little influence on the friction coefficients of the coatings. The variation of the friction coefficients of the coatings with W content may be attributed to the increase of the content of WC and free W in the coatings. With increasing the content of WC and free W in the coatings, the DLC coatings are apt to be adhered to the counterpart surface, which increases the friction coefficients of the DLC coatings. The wear rates of the DLC-coated stainless steel samples is decreased with increasing W content up to 3.08 at.% for doping the DLC coatings by W can greatly improve the adhesion and toughness of the coatings; but when W content is beyond 3.08 at.%, the appearance of more free W phase and WC phase in the coatings causes severe adhesive wear and the adhesion decreases with W content from 3.08 at.%, so the wear rates of the DLC-coated samples are increased with increasing the W content from 3.08 at.% to 24.09 at.%.

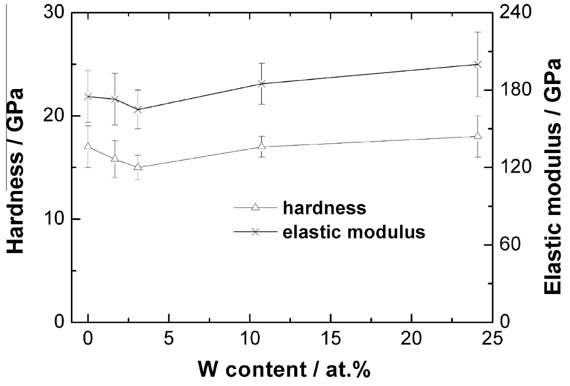

Fig. 3. Hardness and elastic modulus of the DLC coatings as a function of W content.

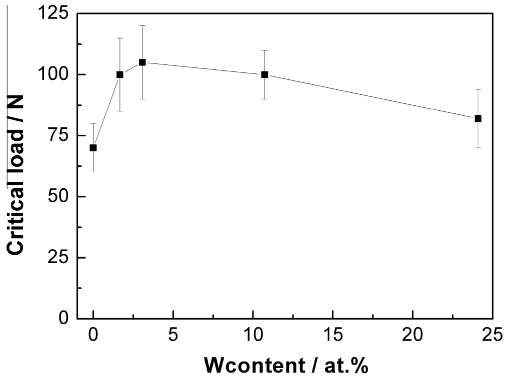

Fig. 4. Critical load for scratch test of the DLC coatings with various W contents.

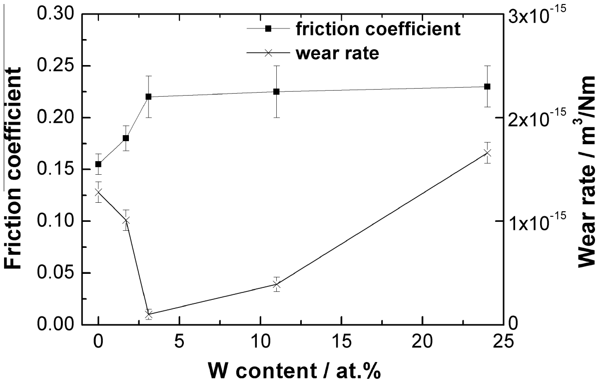

Fig. 5. Friction coefficients and wear rates of the DLC coatings under dry friction.

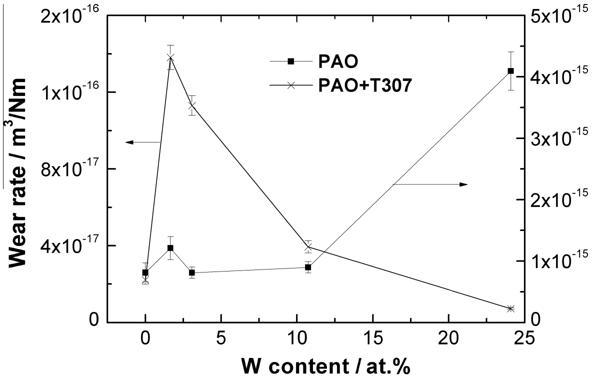

Fig. 7. Wear rates of the DLC coatings under PAO lubrication.

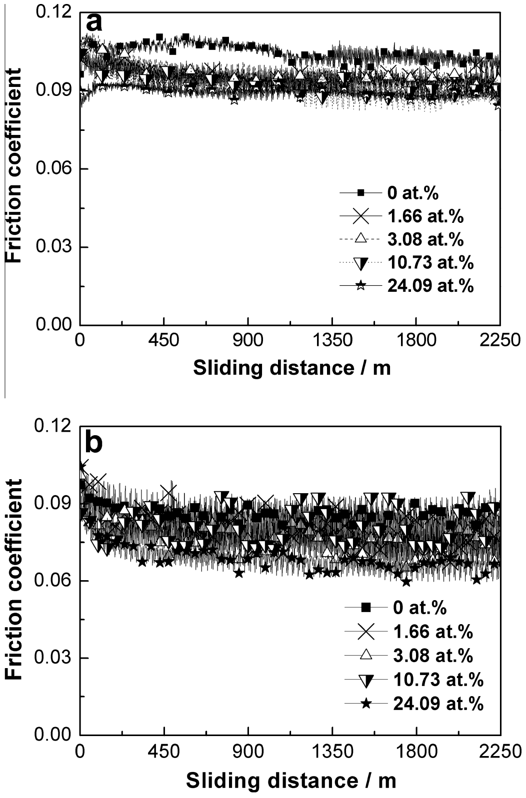

Fig. 6. Friction coefficients of the DLC coatings lubricated by PAO (a) without lubricant additives and (b) with 1 wt.% T307.

The friction coefficients of the DLC coatings under PAO lubrication are shown in Fig. 6. The friction coefficients of the coatings under PAO lubrication are appreciably decreased with the increase of W content. Due to the inertness of the undoped DLC coatings, the adsorption of lubricant oil molecules on the coatings surface is difficult, so the optimum boundary lubrication films cannot be formed; with increasing W content, the content of active free W and WC in the coatings is increased, so the adsorption of lubricant oil molecules on the coatings surface becomes easier, which makes the lubrication between the counterparts more effective; therefore, so the friction coefficients of the DLC coatings under PAO lubrication can be reduced by introduction of W into the DLC coatings. The friction coefficients of the DLC coatings lubricated by PAO with 1 wt.% T307 is lower than those lubricated by pure PAO. T307 arrives at the surface of the DLC coatings by physical adsorption and forms sulphide and polyphosphate via the reaction between the surface of the coatings and S, P generated from T307 [22]. The formation of W sulphide with low hardness and low shear strength contributes to reducing the friction coefficients [23]. With increase of the W content, the amount of W sulphide is increased, so the friction coefficients are further decreased for the DLC-coated samples with a high W content.

The wear rates of the DLC-coated stainless steel samples under PAO lubrication are shown in Fig. 7. It can be found that when lubricated by pure PAO, the wear rates of the DLC-coated samples are almost invariant with the increase of W content in a low W content range, but the wear rates of the DLC-coated samples are abruptly increased with increasing W content from 10.73 at.% to 24.09 at.%, which is similar to the variation of the content of the free W phase and WC phase with the W content, so the increase of the wear rates of the DLC-coated samples is related to the free W phase and the WC phase in the coatings. When lubricated by PAO with 1 wt.% T307, the wear rates of the undoped DLC-coated samples are lower than those of the DLC coatings with a W content of from 1.66 at.% to 10.73 at.%; and the wear rates of the W-doped DLC-coated samples are decreased with increasing W content. Under PAO + T307 lubrication, the wear of the samples depends on the structure and properties of the tribofilm formed by the reaction between T307 and the surface of the coatings. For the undoped DLC coatings, less tribofilm is formed via the reaction between T307 and the coatings due to the inertness of undoped DLC, and the formed tribofilm is similar to that lubricated by pure PAO, so the wear rates of the samples under pure PAO and PAO + T307 lubrication exhibit little difference. For the lubricant additives containing S and P, the tribofilm of short chain polyphosphate is formed initially, but the tribofilm of a bilayered structure composed of long chain polyphosphate overlaying a mixed transition metal short chain phosphate is formed after more rubbing [24,25]. The hardness of the short chain polyphosphates is higher than that of the long chain polyphosphate [26]. The addition of metal sulphide into the lubricant contributes to the friction reaction [27]. The tribofilm produced on the DLC coatings with a low W content is mainly composed of short chain polyphosphate, and the formed short chain polyphosphates promotes the wear. With increase of the W content, more W sulphide is formed during friction, which promotes the conversion of the tribofilm from short chain polyphosphate to the bilayered structure and decreases the wear rates. Therefore, the wear resistance for the W-doped DLC coatings is improved by increasing W content.

4. Conclusions

The content of WC and W in the DLC coatings is increased with the increase of W content, and the influence of W content on the hardness and elastic modulus is not insignificant. The adhesion between the coatings and their substrates can be obviously improved by the introduction of W at an optimal content of 3.08 at.%. Under dry friction, the friction coefficients of W-doped DLC coatings are increased with the increase of W content from 0 at.% to 3.08 at.%, and the lowest wear rates of the DLC-coated stainless steel is obtained when W content is 3.08 at.%. Under pure PAO lubrication conditions, the friction coefficients can be reduced with the increase of W content in the coatings while the influence of W content on the wear rates of the DLC-coated sample is less pronounced when W content is less than 10.73 at.%. When lubricated by PAO + T307, the wear rates of the W-doped DLC-coated samples are decreased with increasing W content while the undoped DLC-coated samples exhibit low a wear rate.

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