Results in Physics 8 (2018) 41–47

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Study on the property of low friction complex graphite-like coating containing tantalum

Zuoping Wang [a,b,c], Lajun Feng [a,b,*], Wenning Shen [a,b]

[a] School of Materials Science and Engineering, Xi'an University of Technology, No. 5 South Jinhua Road, Xi'an 710048, China
[b] Key Lab. of Corrosion and Protection of Shaanxi Province, No. 5 South Jinhua Road, Xi'an 710048, China
[c] SCIC NO. 12 Research Institute, Xingping 713102, China

ARTICLE INFO

Article history:
Received 27 May 2017
Received in revised form 27 October 2017
Accepted 21 November 2017
Available online 2 December 2017

Keywords:
Tantalum
Sputtering
Super-lubrication
Complex GLC coating
Tribological property

ABSTRACT

In order to enhance equipment lifetime under low oil or even dry conditions, tantalum was introduced into the graphite-like coating (GLC) by sputtering mosaic targets. The results showed that the introduction of Ta obviously reduced the friction coefficient and hardness of the GLC, while improved the wearability. When the atomic percentage of Ta was larger than 3%, the steady friction coefficient was lower than 0.01, suggesting the coating exhibited super lubricity. When the content of Ta was about 5.0%, the average friction coefficient was 0.02 by a sliding friction test under load of 20 N in unlubricated condition. Its average friction coefficient reduced by 75%, compared with that of control GLC (0.0825).

Introduction

Lubricity refers to the ability to reduce frictional forces in a boundary lubrication state [1]. The Lubricity of ceramic coatings is poor in dry environment in particular [2,3]. For instance, traditional ceramics, like nitrides, carbides and nitrides exhibit high hardness, while their lubricity is poor, leading to the poor friction reduction effect. Liu et al reported that TiN film possessed high hardness, but showed poor lubricating property, and its frictional coefficient was far greater than that of diamond-like film [4]. However, graphite coatings such as graphite-like coating (GLC) and diamond-like coating (DLC) exhibit good lubricity, thus their wear resistance is good. Fujisawa et al in their research showed that graphite-like coatings had more effective lubricity property in wet environment, resulting in good wear resistance [5]. Wang et al reported that the deposition of graphite-like carbon film on Si_3N_4, SiC and WC films significantly reduced their wear rate and improved the wear resistance [6]. However, the wear resistance of the GLC and DLC under high pressure condition cannot meet the requirements [7,8]. In the previous research, doped GLC coatings were prepared using magnetron sputtering by separately embedded Ce, Y and Ta into the carbon target and chrome target. It was found that the doping of Ta improved the wear resistance of the GLC coating and reduced its frictional coefficient [9,10]. However, the effect of Ta doping content on the wear resistance is still unclear, limiting the application of Ta in GLC coatings.

In this paper, Ta was incorporated with the carbon target and chromium target by insert process during magnetron sputtering to prepare GLC coatings doping with Ta. The effects of Ta doping amount on the friction coefficient, hardness and wear loss were studied, and the cause for the better friction property was analyzed. The results can provide a foundation for preparing new wearability and low friction coefficient coatings.

Experimental

Preparation of the coatings

The doping element was introduced into GLC by magnetron sputtering. The sputtering targets were composed of two Cr targets (Chengdu Ultra Pure Applied Materials CO., LTD) and two carbon targets (Beijing Zhongjinyan New Materials Science and Technology Ltd.), in which there has 6 through holes with the diameter of 10 mm in the Cr target's etching area, and 8 through holes with the diameter of 6 mm in the C target's etching area, as shown in Fig. 1. Then, A certain number of tantalum inserts (Chengdu Ultra Pure Applied Materials CO., LTD) were prepared and plugged into the holes of C targets. C inserts or Cr inserts were placed into the

* Corresponding author at: School of Materials Science and Engineering, Xi'an University of Technology, No. 5 South Jinhua Road, Xi'an 710048, China.
E-mail address: fenglajun@xaut.edu.cn (L. Feng).

https://doi.org/10.1016/j.rinp.2017.11.028
2211-3797/

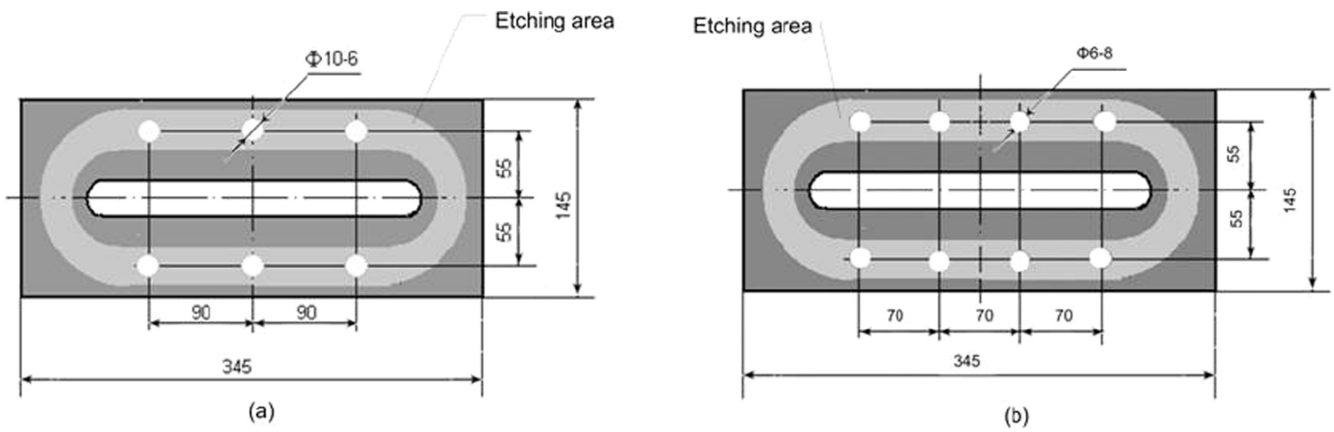


Fig. 1. Holes distribution allow etching area for (a) chromium target and (b) carbon target.

rest holes to form an integrated target. The effects of Ta on the properties of the complex GLC were studied by adjusting the inserted materials and numbers.

The number (n) of the inserts was calculated according to Eq. (1) [10]:

$$n = ks/\alpha\beta\omega S_1 \quad (1)$$

where k is atomic content of Ta element in the GLC coating (wt%); S is total target area of sputtering (mm^2); α means inserts to target sputtering coefficient ratio; β means inserts to target density ratio; ω is weight fraction of inserts (wt%); S_1 is cross-section area of one insert (mm^2).

Carburized AISI 3310 steel with a quenching hardness of HRC60 ± 2 was used as substrate. The ground surface was further polished to a roughness of Ra = 0.02 μm. Subsequently, the substrates were ultrasonic washed with acetone for 15 min and dried in hot air to remove the residual solvent. The substrates were then put on a sample holder in sputtering equipment for coating. The complex GLC were prepared using an industrial CFUBMSIP system (UDP 650/4) with two mosaic carbon targets and two mosaic chromium targets. The dimensions of vacuum chamber are Φ650 mm × 650 mm, and the length and width of the sputter targets were 380 mm and 175 mm, respectively. The purity of carbon targets and chromium targets were 99.5% and 99.95%, respectively. Pulsed bias power is controlled by an Advance Energy Pinnacle Pulse 10 KW and DC magnetron powers are controlled by two Advance Energy Pinnacle 6 × 6 power units which both provided by Advance Energy, Ltd. The rotation speed of the one rotation axis substrate holder was 4rpm. As the vacuum degree of the chamber was 3.0×10^{-5} Torr, the substrates were first precleaned through Ar plasma by using pulsed DC bias (−400 V). Then, 0.5 μm Cr interlayer was deposited on the substrates by DC magnetron sputtering with a high power of 6.0 A and a pulse DC bias voltage of −100 V. Subsequently, the Cr targets power was decreased from 6.0 A to 0.3 A and the carbon targets power was increased from zero to 7.0 A, followed by the deposition of a C/Cr/Ta multilayer of graded composition (approx 0.2 μm). After that, with the Cr target power of 0.3 A and the C target power of 7.0 A, the main carbon layer contented an amount of Cr and Ta (2 ∼ 3 μm) was deposited. The samples keep on rotating to ensure the uniformity of each step of deposition. The substrate temperature was kept at 300 °C during the deposition [11].

Characterizations

Adhesion was measured using a Teer Coatings ST3001 scratch tester. The radius of Rockwell diamond indenter was 0.2 mm. Additional testing parameters were: loading rate of 100 $N \cdot min^{-1}$ and sliding speed of 10 $mm \cdot min^{-1}$ [12].

Optical microscopy was used to examine the coatings. The thickness of coatings was assessed using the ball crater taper-section technique.

Plastic microhardness was measured using a Fischerscope H100 ultra microhardness tester with a load of 50 mN. Under an indentation depth being more than 10% of the coating thickness, a composite hardness value was obtained.

The microstructure of the complex GLC was analyzed using JSM-6700F scanning electron microscope (SEM). The composition and elements combining state of the complex GLC coating were analyzed by energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS).

Pin-on-disc sliding wear tests were performed on the coated samples using a Φ5 mm chrome steel (AISI52100) ball as the counterface. The test was carried out in air at room temperature and without lubrication. The counterface ball was fixed and coated samples slid beneath with a sliding distance of 360 m and a friction time of 0.5 h. A sliding speed of 0.2 $m \cdot s^{-1}$ was set for all the tests. Specific wear rates were determined from the abrasion loss [12]. Each type of samples was tested at normal applied forces of 20 N, 40 N and 80 N, giving an actual contact pressure of about 0.8 ∼ 3.2 GPa. The schematic diagram for the test setup is shown in Fig. 2.

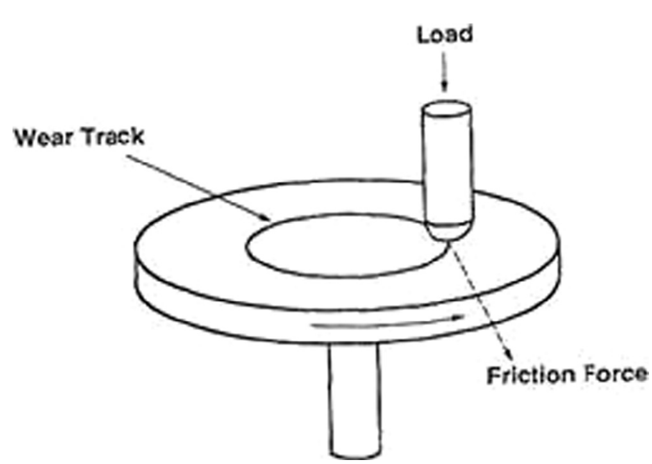


Fig. 2. The schematic diagram for pin-on-disk sliding wear test setup.

Results and discussion

Effect of tantalum on tribological properties of GLC

In order to study the effect of Ta on the property of GLC, GLC containing different amounts of Ta were prepared. The mosaic number of Ta in carbon target was 0, 3, 6, 9 and 12, and as-prepared coatings were marked with GLC, Complex-1, Complex-2, Complex-3, Complex-4 and Complex-5, respectively. Fig. 3 shows the EDS result of Complex-4. As shown in Fig. 3, the prepared composite coating was mainly consisted of Element C, Cr, Ta, O and Ar. Element Ar came from the pre-cleaning of the substrate by Ar plasma and element O might be caused by the oxidation of the coating under air [13]. The atomic percentage of Ta for the five coatings from EDS results were 0 atm%, 1.23 atm%, 2.03 atm%, 3.16 atm%, 3.95 atm% and 4.74 atm%, respectively.

The tribological properties of those coatings were tested in air under an applied load of 20 N with a sliding distance of 360 m. The change for friction force of the GLC containing different amount Ta are presented in Fig. 4. Friction forces of the complex GLC were obviously lower than that of blank GLC. Especially, friction force of Complex 3 ~ 4 tended to zero.

Variations in initial friction coefficient, steady friction coefficient and mean fiction coefficient of complex GLC are shown in Fig. 5. As shown in Fig. 5, the initial friction coefficient, steady friction coefficient and mean friction coefficient all decreased with the increase content of Ta during the whole test. The maximum value of the friction coefficient was observed at the start of the test (initial friction coefficient), and steady value occurred at the end of the test (steady friction coefficient). When the content of tantalum was larger than 3 atm%, the steady friction coefficient was less than 0.01, suggesting the complex GLC exhibiting super-lubrication properties. After sliding test, all the coatings remained the integrity without penetration or exfoliation.

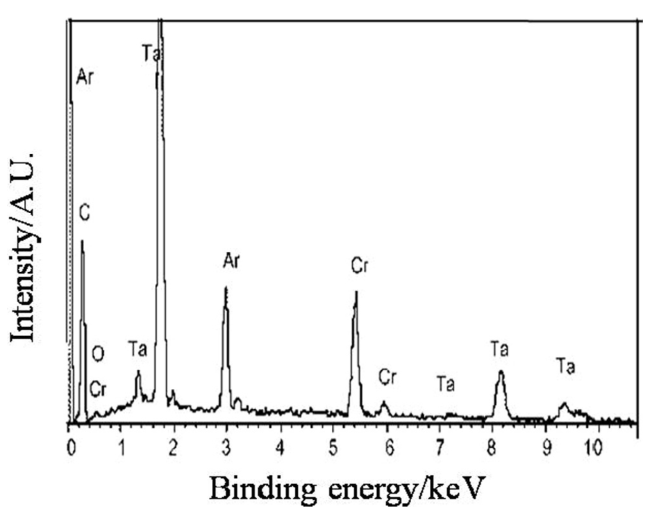


Fig. 3. The EDS result of Complex-4.

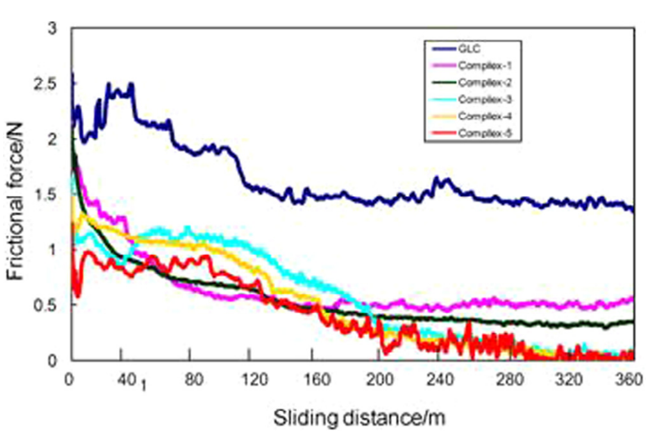


Fig. 4. Variations of friction force of the complex GLC with different tantalum inserts sliding against a chrome ball in air under a load of 20 N for a sliding distance of 360 m.

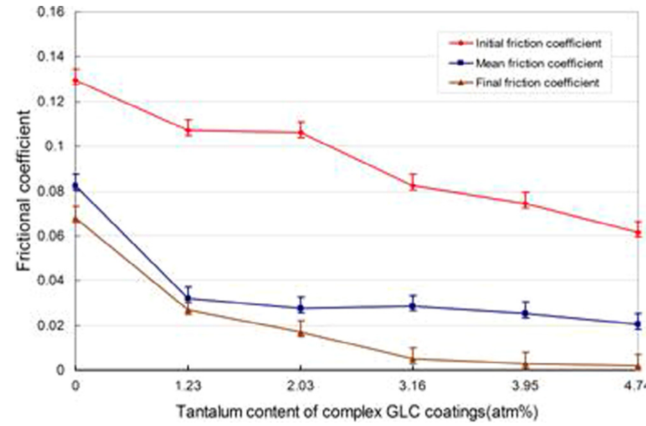


Fig. 5. Variations in initial friction coefficient, steady friction coefficient and mean fiction coefficient of complex GLC coatings.

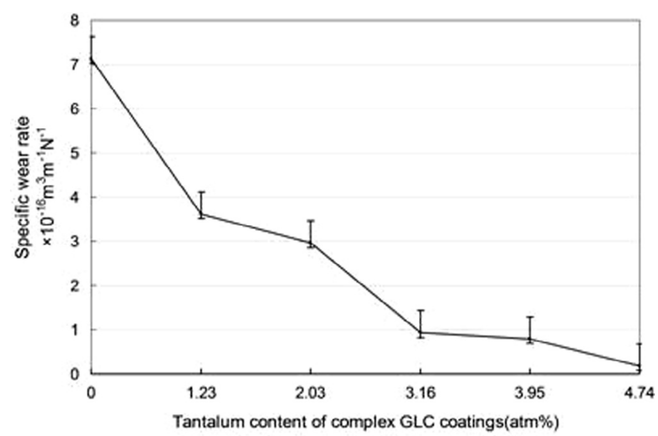


Fig. 6. Variations of specific wear rate of the complex GLC with different tantalum contents after sliding against a chrome ball in air under a load of 20 N for a sliding distance of 360 m.

Fig. 6 shows the wear rates of these coatings. With the increase content of Ta, the specific wear rates of the complex GLC reduced and the wear resistance improved.

Analysis of tribological properties

Based on the above analysis, it can be concluded the complex GLC with a Ta content of 4.74 atm% exhibited best friction and wear behavior. Therefore, the sliding wear behavior of this complex GLC was studied and compared with blank GLC in air under a load of 20 N, 40 N and 80 N for a sliding distance of 360 m, respectively.

The friction force under sliding distance and the tribological properties for blank GLC and the complex GLC under a load of 20 N were shown in Fig. 7(a) and (b), respectively. As for blank

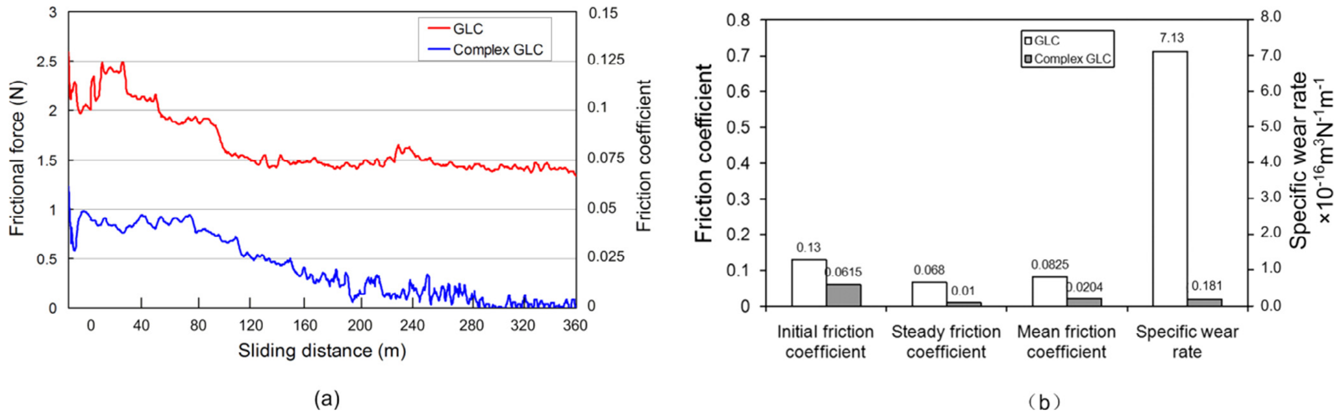


Fig. 7. Wear behavior of blank GLC and complex GLC in air under a load of 20 N for a sliding distance of 360 m. (a) Variations of friction coefficient with sliding distance and (b) Tribological properties.

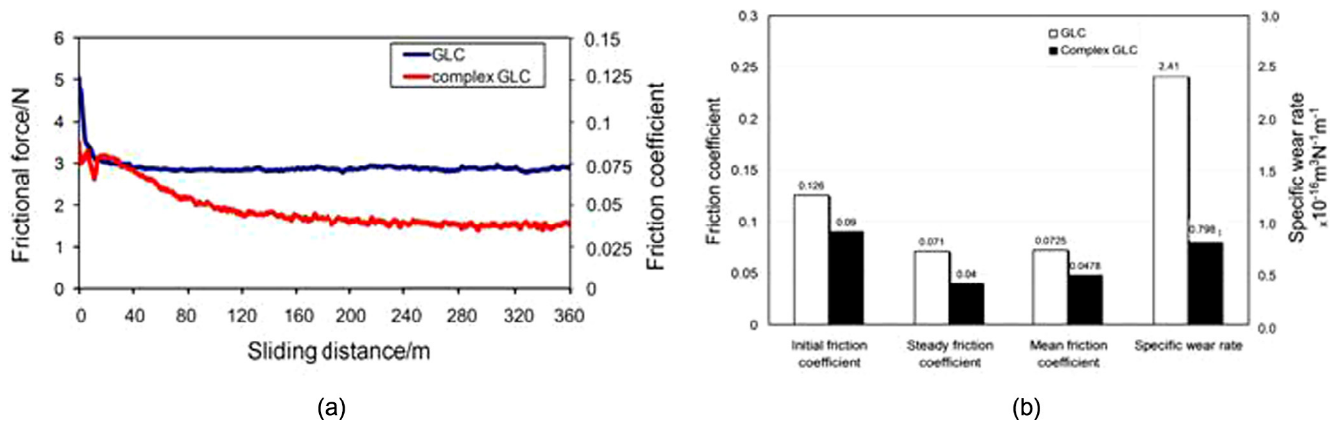


Fig. 8. Wear behavior of blank GLC and complex GLC in air under a load of 40 N for a sliding distance of 360 m. (a) Variations of friction coefficient with sliding distance and (b) Tribological properties.

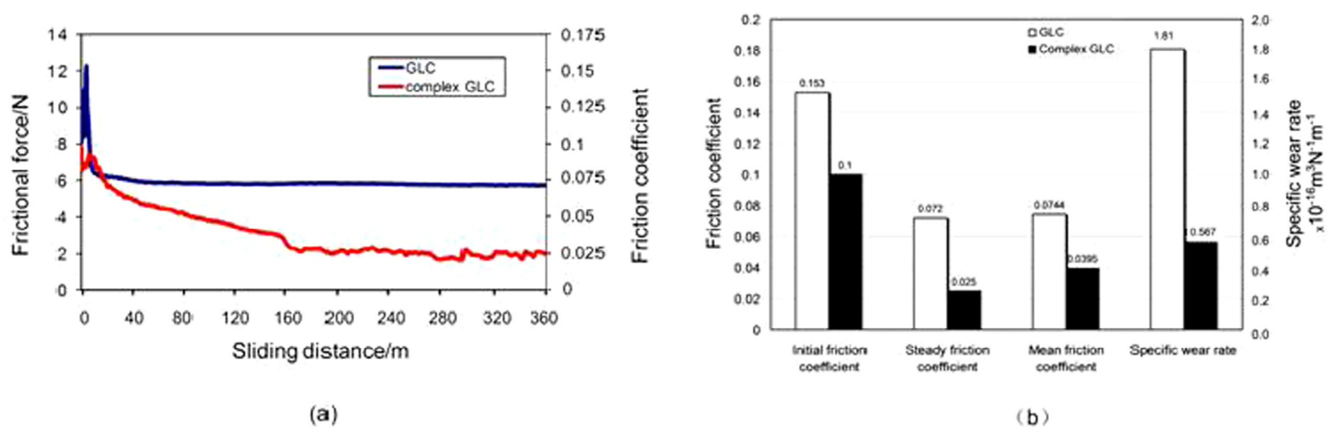


Fig. 9. Wear behavior of blank GLC and complex GLC in air under a load of 80 N for a sliding distance of 360 m. (a) Variations of friction coefficient with sliding distance and (b) Tribological properties.

GLC, the initial friction coefficient was about 0.13. After friction for a short distance, it arrived at steady friction and the friction coefficient reduced to 0.07. Its mean friction coefficient was about 0.0825. The initial friction coefficient of the complex GLC was less than 0.07. After friction for a longer distance than that of blank GLC, it reached a steady friction stage and the friction coefficient reduced to <0.01 and the mean friction coefficient was about 0.02. It can be found that the friction coefficient of the complex GLC reduced by about 75% and its specific wear rate was obvious lower, compared with those of blank GLC.

The sliding wear behavior under a 40 N or 80 N loads was found to be similar to that of 20 N. The friction coefficients and specific wear rates were also found much lower than those of blank GLC, as shown in Fig. 8 and Fig. 9.

In order to analyze the cause that the friction coefficient of the coatings decreased after the introduction of Ta, XPS was carried out

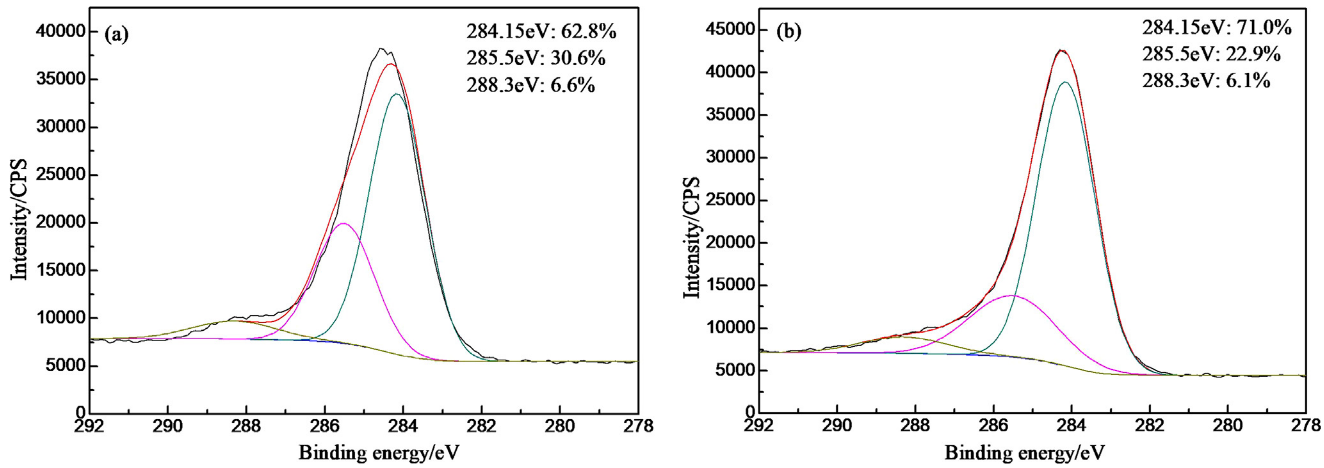


Fig. 10. The XPS C1s spectra for Complex-2 (a) and Complex-4 (b).

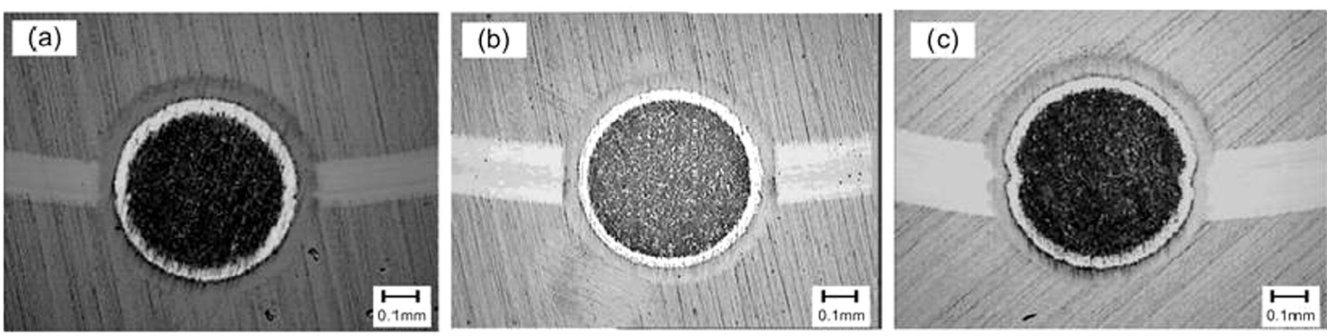


Fig. 11. Taper cross-section of coating wear track following Pin-on-disc testing of complex GLC coating in air after a sliding distance of 360 m under an applied load of (a) 20 N, (b) 40 N, (c) 80 N.

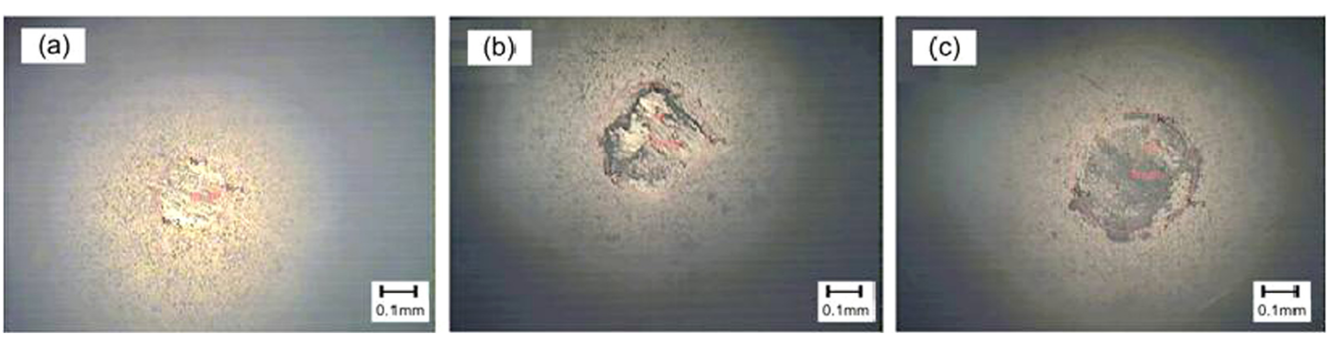
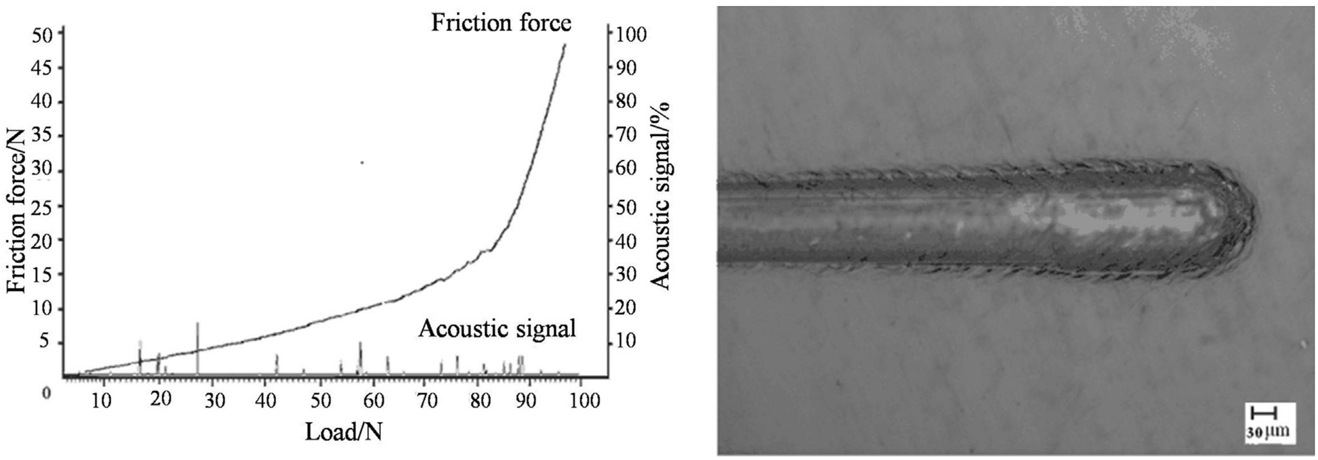


Fig. 12. Wear scar and coating debris on chrome steel ball following Pin-on-disc testing of complex GLC coating in air after a sliding distance of 360 m under an applied load of (a) 20 N, (b) 40 N, (c) 80 N.

for the complex GLC. Fig. 10 shows the XPS C1s spectra for Complex-2 and Complex-4. As shown in Fig. 10, the peaks at 284.15 eV and 285.5 eV could be assigned to sp^2 and sp^3 respectively, and the peak at 288.3 eV corresponded to C=O band. The formation of C=O band might be caused by the oxidation of sample or residual gas in the preparation equipment [14]. As the amount of Ta in the complex GLC increased, the content of sp^3 bond in high resolution C1s XPS spectra decreased, while that of sp^2 bond increased. Since the outer shell electron distribution of C is $2s^2p^2$, it can form regular tetrahedron sp^3 hybrid orbit. However, the formation energy for sp^3 hybrid orbit is higher than that of sp^2 hybrid orbit. Furthermore, the outer shell electron distribution of Ta is $5d^36s^2$, which is easier to be bonded than Cr ($3d^54s^1$). Thus, driving force for the formation of sp^3 hybrid orbit decreased, i.e. C easily bonds with Ta to form TaC structure with sp^2 hybridization. The sp^2 hybridization in coatings exhibits the properties of graphite and sp^3 hybridization has the properties of diamond [15]. As a

Table 1
Properties of the complex DLC coatings.

Coating	Total thickness (μm)	Composite hardness (Gpa)	Critical scratch load, Lc (N)
GLC	2.645	17.1	85
Complex GLC	2.568	14.7	87



(a) (b)

Fig. 13. Load scratch test (a) Graph of friction force and acoustic signal with load and (b) scratch track of complex GLC coating.

result, the increase sp^2 content led to the lower hardness and good wear resistance for the complex GLC.

The wear performances, following Pin-on-disc testing of complex GLC in air under an applied load of 20 N, 40 N and 80 N after a sliding distance of 360 m are shown in Fig. 11 and Fig. 12. Taper cross-section area of wear tracks for the coating increased with increase of load. The wear scar of chromium steel ball had the same trend. The ball surface was observed under an optical microscope. It can be found a transfer layer on the ball contributed to the lower friction behavior and the protection of the counterface ball.

Generally, the graphitization occurs at the surface of GLC under the effect of force and heat during friction process. Crystal graphite with lubricating effect is then formed, reducing the friction coefficient and wear loss. In the same external environment, the friction coefficient of the GLC coating was mainly controlled by the sp^2 content [16]. Since the introduction of Ta increased the sp^2 content, the graphitization was promoted. Moreover, the introduction of Ta with high ductility can make the graphite particles bind together effectively [17]. In addition, since Ta exhibited high temperature resistance, it can overcome the problem of strength decreases caused by the friction heat in dry environment for the coating. Therefore, the friction coefficient and wear loss of the complex GLC were very small under the action of 3.2 GPa frictional stress.

Other property of the complex GLC

The thickness, hardness and adhesion strength of the complex GLC are shown in Table 1. It can be seen from Table 1 that, the hardness of the complex GLC with a Ta content of 4.74% was lower, while the adhesion strength was close to that of blank GLC. The decrease of hardness for the complex coatings might be caused by two facts. On the one hand, the introduction of Cr and Ta caused the decrease of sp^3 content. As a result, the spatial hinge degree of carbon net constructed by sp^3 reduced and the hardness decreased [18]. On the other hand, the ductility of Ta also caused the decrease of hardness. The scratching curves and morphology of the complex GLC are shown in Fig. 13. Very few cracks were observed on the scratch trace and the coating did not flake off. It indicates that the adhesion strength between the complex GLC and the substrate was similar to that between blank GLC and substrate. The Cr transition layer and C/Cr multilayer provided better adhesion between the coating and the substrate.

Conclusions

The introduction of Ta into the GLC could reduce the friction coefficient, improve friction and wear behavior, but not affect the binding performance. With the increase of Ta content, the friction coefficient and specific wear rates of the complex GLC decreased. When the Ta content was larger than 3 atm%, the steady friction coefficient was lower than 0.01, suggesting the complex GLC exhibited super-lubricity. As the Ta content was about 5 atm%, the average friction coefficient was 0.02 sliding under a load of 20 N in air. It reduced by 75%, compared with that of graphite-like coating in the same conditions. The introduction of Ta can reduce the content of sp^3 hybridization, leading to the hardness decrease of the coatings.

Acknowledgement

The authors appreciate Mr. Shihua Yang and Guohua Yu's help to fabricate carbon coatings. Our thanks are also extended to Mr. Pengbo Chen and He Yuan for their kind help.

References

[1] Qian XL, Chen G. Lubricants and additives. Beijing: Higher Education Press; 1993 (in Chinese).
[2] Michael B, Richard G, Per H. Influence of recoated on the mechanical and tribological performance of TiN-coated HSS. J Surf Coat Technol 1995;76–77:481–6.
[3] Liu QX, Guo XM, Zhao J, Li DJ. A comparison on structural and tribological properties of diamond-like carbon and titanium nitride films. J Tianjin Norm Univ 2003;23:58–61 (in Chinese).
[4] Liu QX, Li DJ. Synthesis and mechanical properties of TiNC coating. J Tianjin Norm Univ (Nat Sci Ed) 2001;21:19–22 (in Chinese).
[5] Fujisawa N, Swain MV, James NL, Woodard JC, McKenzie DR. Carbon coating of Ti-6Al-4V for reduced wear in combined impact and sliding applications. Tribol Int 2003;36:873–82.
[6] Wang YX, Wang LP, Xue QJ. Improvement in the tribological performances of Si_3N_4 SiC and WC by graphite-like carbon films under dry and water-lubricated sliding conditions. Surf. Coat. Technol. 2011;205:2770–7.
[7] Yang S, Li X, Renevier NM, Teer DG. Tribological properties and wear mechanism of sputtered C/Cr coating. J. Surf. Coat. Technol. 2001;142–144:85–93.
[8] Ma ZW, Wang ZP, Yuan H, Zhang RX. Tribological properties of graphite-like carbon films in different lubrication ambient. J. Chin. Ceram. Soc. 2011;39:1368–72 (in Chinese).
[9] Wang ZP, Ma ZW, Chen PB, Wen JT. Effects of rare earth on electrochemical corrosion behavior of graphite-like carbon coatings. Adv. Mater. Des. 2011;199–200:1978–83.
[10] Wang ZP, Ma ZW, Chen PB, Xing JD, Sun HL. Effects of rare earth and tantalum on graphite-like carbon coatings. Appl. Surf. Sci. 2011;257:1876–80.

[11] Wang QJ, Chung YW. Encyclopedia of tribology. New York Inc., New York: Springer-Verlag; 2013.
[12] Yangs S, Camino D, Jones AHS, Teer DG. Deposition and tribological behaviour of sputtered carbon hard coatings. J. Surf. Coat. Technol. 2000;124:110–6.
[13] Wang JF, Wang YX, Chen KX, Li JL, Guo F. Effect of Cr doping on the microstructure and tribological performances of graphite-like carbon films. Tribology 2015;35:206–13.
[14] Zhang YH, Ma J, Jiang BL. Influence of Cr content on hardness and valence bond structure of graphite-like carbon coating. Trans. Mater. Heat Treat. 2007;28:106–10.
[15] Michio I, Kang FY. Carbon materials science and engineering—from fundamentals to applications. Beijing: Tsinghua University Press; 2006.
[16] Gassner G, Mayrhofer PH, Mitterer C. Structure-property relations in Cr-C/a-C:H deposited by reactive magnetron sputtering. Surf. Coat. Technol. 2005;200:1147–50.
[17] Liu H. Effects of silicon carbide addition on microstructure and mechanical properties of tantalum carbide ceramics. Harbin: Harbin Institute of Technology; 2013.
[18] Robertson J. Diamond-like amorphous carbon. Mater. Sci. Eng. R Rep. 2002;37:129–281.