Tribological properties of Ti-doped diamond-like carbon coatings under dry friction and PAO oil lubrication

Youzhi Guo1 2 | Peng Guo1 | Lili Sun1 | Xiaowei Li1 3 | Peiling Ke1 | Qiang Li2 | Aijing Wang1

1 Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China
2 School of Materials Science and Engineering, Shanghai University, Shanghai, China
3 Computational Science Center, Korea Institute of Science and Technology, Seoul, Republic of Korea

Correspondence
Aijing Wang, Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China.
Email: ayingwang@nimte.ac.cn

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1 INTRODUCTION

With the development of industrial technology, some engine components have to serve in harsh conditions, such as high speeds and rigorous loads.1 2 To improve the stability and safety of components, liquid lubricants are usually adopted to solve the wear replenishment problem and remove the wear debris during the friction process. However, in practical engineering application, starved-oil lubrication is a universal and unavoidable issue, leading to the lubrication failure of protective surface.3 Combining solid lubrication coating with liquid lubricating oil is an effective strategy to achieve the long-term reliability of various engines.

Taking advantages of the excellent self-lubricating properties and superior mechanical performance, diamond-like carbon (DLC) has become one of the promising candidates to be used as solid lubrication coating.4 5 Especially, metal-doped DLC (Me-DLC) coating has been given much attention because metal doping could not only reduce the intrinsic high residual stress of DLC coating, but also improve the tribological properties and adhesion strength to metallic substrate.6 9 Among of various Me-DLC coatings, Ti-DLC coatings showed the most promising benefits with the enhancement of abovementioned properties.1 0 1 2 In addition, previous study also proved that the microstructure of Ti-DLC coating was closely related to the doping content. With proper titanium content, a small number of TiC nanocrystallites would be distributed in the DLC matrix, which can endow Ti-DLC coatings with higher hardness and elastic modulus,9 1 3 that is one key issue for the application of solid lubrication coating.

Recently, many researches have focused on the interaction between the DLC coatings and lubricating oil (mainly base oil poly-
alpha-olefin (PAO), extreme-pressure additives, and friction-modifier additives) to explore the solid-liquid composite lubrication behavior. For example, Kano et al. reported that ultralow friction coefficient (0.03) was obtained by sliding hydrogen-free tetrahedral amorphous carbon (ta-C) against ta-C when PAO containing glycerol mono-oleate additive was used as lubricant, and revealed that the formation of OH$^-$ terminated DLC surface was the key factor to this friction phenomena. However, Gorbatchev et al. observed that dithiocarbamates reduced friction and wear for DLC/DLC mating contact, but its lubrication effect faded due to the severe chemical wear for DLC/steel contact surface. As to Ti-DLC coating, some studies also showed low friction and wear under oil lubrication condition. de Barros'Bouchet reported that Ti-DLC/Ti-DLC contact lubricated with PAO base oil resulted in slightly lower friction and wear than the nondoped DLC/DLC. Considering the higher reactivity with oils of Ti-DLC coating, Kalin reported that Ti-DLC boundary lubrication was promoted via binding sites at O vacancies present in the Ti-DLC coating due to oxidation of Ti. Furthermore, Ti-DLC coating showed higher friction with base oil only, and addition of additives always further reduced the friction. However, the tribological property of Ti-DLC/lubricating oil depends on the structure of Ti-DLC coating, kinds of lubricants, and friction-induced interfacial reaction, which involves multiple factors and is quite complicated; how the microstructure affects the friction and wear process is unclear. So, comprehensive studies on its tribological behaviors under both dry friction and boundary lubrication are of great importance to optimize the DLC/lubricating oil systems for practical engineering application, especially for the engine components working in both starved-oil and rich-oil lubrication conditions.

In the present study, Ti-DLC coatings with different microstructures were designed and prepared by a hybrid ion beam deposition system, namely one sample with Ti atoms dissolved in the DLC matrix at low (4 at.%) concentration and the other one with titanium carbide nanocrystallites at high Ti (27 at.%) concentration. The widely used base oil PAO was chosen as lubricant. The tribological properties of Ti-DLC coatings under both dry friction and boundary lubrication conditions were studied, and related lubrication mechanism was discussed in terms of the microstructural evolution and transfer film formed during the friction sliding.

2 EXPERIMENTAL DETAILS

Ti-DLC coatings were deposited by a hybrid ion beam deposition system consisting of a rectangular DC magnetron sputtering source with a Ti target (99.99%) and a linear anode-layer ion sources (LIS). Figure 1 shows the schematic diagram of used deposition system. Prior to deposition, single crystal P(100) silicon substrates were ultrasonically cleaned in acetone for 15 minutes and then etched in Ar plasma for 10 minutes to remove the surface contaminations. Then, precursor gases C$_2$H$_2$ (from ion source) at 10 sccm and Ar (from sputtering source) at 70 sccm were introduced into the chamber to deposit Ti-DLC coatings. Typical values of LIS voltage and current were 1500 V and 0.2 A, respectively. Ti content in the coatings was controlled by adjusting DC sputtering current. The DC pulsed negative bias of −100 V with a frequency of 350 kHz was applied to the substrate during etching and deposition process. The thickness of Ti-DLC coatings was kept at 520 ± 20 nm by changing deposition time. The target-substrate distance was strictly controlled at 20 cm, and all samples were deposited at room temperature. Deposition parameters and properties of Ti-DLC coatings in this study are listed in Table 1, where samples deposited at 2.0 and 3.5 A were named Ti$_{4at.\%}$-DLC and Ti$_{27at.\%}$-DLC, respectively.

The friction tests were carried out using a reciprocating ball-on-disk tribometer (Figure 2) under 5 N load, at velocity of 0.05 m sec$^{-1}$ for a total distance of 90 m, with GCr15 steel ball (Φ 6 mm, Ra = 0.05 μm) as sliding friction pair. Test temperature and humidity were 25°C and 70% RH, respectively. In order to keep verification and reproducibility of results, the tests were repeated at least three times for each condition.

The theoretical minimum film thickness ($h_{min}$) and dimensionless lambda ratio ($\lambda$) were calculated using Equations 1 and 2, respectively, to ensure a boundary lubricated regime.

$$h_{min} = 3.63RU^{0.68}G^{0.49}W^{-0.071}(1-e^{-0.46k}) \quad (1)$$

![Schematic diagram of the hybrid ion beam deposition system](image)

**TABLE 1** Deposition parameters and characteristics of Ti-DLC coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target Substrate Distance, cm</th>
<th>Deposition Temperature</th>
<th>DC Sputtering Current, A</th>
<th>Substrate Bias, V</th>
<th>Deposition Time, min</th>
<th>Ti Content, at%</th>
<th>Thickness, nm</th>
<th>Hardness, GPa</th>
<th>Elasticity Modulus, GPa</th>
<th>H/E</th>
<th>H$^2$/E$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_{4at.%}$-DLC</td>
<td>20</td>
<td>RT</td>
<td>2.0</td>
<td>−100</td>
<td>25</td>
<td>4</td>
<td>509</td>
<td>16.80</td>
<td>158.28</td>
<td>0.11</td>
<td>0.19</td>
</tr>
<tr>
<td>Ti$_{27at.%}$-DLC</td>
<td>20</td>
<td>RT</td>
<td>3.5</td>
<td>−100</td>
<td>33</td>
<td>27</td>
<td>516</td>
<td>23.55</td>
<td>221.52</td>
<td>0.11</td>
<td>0.27</td>
</tr>
</tbody>
</table>
\[ \lambda = \frac{h_{\text{min}}}{\sqrt{R_q^2 + R_q^2}} \]  

(2)

where \( R \) is the radius of the ball, \( U \) is a dimensionless speed parameter, \( G \) is a dimensionless coating parameter, \( W \) is a dimensionless load parameter, \( R_{q,a} \) is the surface roughness of the coating, and \( R_{q,b} \) is the surface roughness of the ball. The calculated lambda parameters were 0.33 and 0.12, respectively, which stated that lubrication regime was boundary lubrication.

During testing, the friction coefficient was monitored continuously. After testing, the profile of wear track was measured by a surface profilometer (Alpha-Step IQ, USA); the volume of the removed coatings \( V_{\text{coating}} \) and steel ball \( V_{\text{ball}} \) was calculated using Equations 3 and 4, respectively.

\[ V_{\text{coating}} = SL \]  

(3)

\[ V_{\text{ball}} = \frac{r^4}{3} \left[ 2R^3 - \left( 2R^2 + r^2 \right) \sqrt{R^2 - r^2} \right] \]  

(4)

where \( S \) and \( L \) are sectional area and length of wear track, respectively, and \( r \) is the radius of wear scar.

The wear rates were calculated using Archard wear equation:\( ^{22,23} \)

\[ k = \frac{V}{Fs} \]  

(5)

where \( k \) is the wear rate \((m^3 N^{-1} m^{-1})\), \( V \) is the wear volume \((m^3)\), \( F \) is the normal load \((N)\), and \( s \) is the total sliding distance. The morphology, chemical composition, and chemical bonds of wear tracks and wear scars were systematically analyzed and compared with as-deposited coatings. Specially, after oil lubrication tests, both Ti-DLC coatings and steel balls were immersed in n-hexane to remove adsorbed oil before characterization.

Mechanical properties were measured by the nanoindentation technique (MTS-G200) in a continuous stiffness measurement mode with a maximal indentation depth of 250 nm. A three pyramid diamond indenter with a tip ratio of 20 nm was used. The characteristic hardness of deposited coatings was chosen in the depth where the hardness with indentation depth was just stable and not affected by the substrate. And six replicate indentations were done for each sample.

Scanning electron microscopy (SEM, S-4800, Hitachi, Japan) was applied to investigate morphology of wear tracks and wear scars. Raman spectroscopy (Renishaw inVia-reflex, UK) with a laser wavelength of 532 nm was used to measure the atomic bonds of sample before and after tribological test, with the laser power 1.2 mW and detecting range from 800 to 2000 cm\(^{-1}\). The experimental spectrum was fitted using two Gaussian peaks after background correction. X-ray photoelectron spectroscopy (XPS, Axis ultradld, Japan) with Al (monochromatic) Ka irradiation at a pass energy of 160 eV was used to characterize the chemical bonds of the transfer films on the wear scars. Charge neutralization was used, and the binding energies were referenced to C 1s at 284.6 eV. Peak fits were performed with the CasaXPS software package, after the subtraction of a Shirley background and with mixed Gaussian-Lorentzian curves. High-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20, USA) was applied to characterize the microstructure of as-deposited coatings, which was operated at 200 kV with a pointed-to-point resolution of 0.24 nm.

### RESULT AND DISCUSSION

#### 3.1 Microstructural evolution of as-deposited coatings

Previous studies of Ti-DLC coatings have proved that the doped Ti content affected the microstructure significantly, which can change the tribological behaviors.\(^6,24\) Figure 3 showed the microstructural evolution of deposited Ti-DLC coatings by HRTEM and selected area electron diffraction (SAED). In case of Ti\(_{4at.\%}\)-DLC coating, no crystalline phase could be found in the HRTEM image, as shown in

![HRTEM images of (A) Ti\(_{4at.\%}\) DLC and (B) Ti\(_{27at.\%}\)-DLC coatings](image-url)
Figure 3A. The corresponding SAED just showed a diffused ring, indicating that doped titanium was uniformly dissolved in amorphous carbon matrix. However, for Ti_{27at.%}‐DLC coating, many nanocrystallites with size around 4–6 nm (labeled by red circle in Figure 3B) appeared in the amorphous carbon matrix. Moreover, the nanocrystalline diffraction patterns of the insert SAED were identified to (111), (200), (220), and (311) reflections of TiC (PDF#32-1383), respectively, demonstrating that the TiC nanoparticles were formed and embedded into DLC matrix.

3.2 | Friction and wear behavior

Figure 4A shows the friction coefficient of Ti_{4at.%}‐DLC and Ti_{27at.%}‐DLC coatings under dry friction and oil lubrication, respectively. Figure 4B is the close view of the first 300 seconds of the friction coefficient curve. When tested under dry friction, Ti_{4at.%}‐DLC coating exhibited a run‐in period (about 300 seconds), then reached the lowest and stable friction with average friction coefficient 0.07. For theTi_{27at.%}‐DLC coating, the friction coefficient curve showed obvious fluctuation phenomenon during a much longer run‐in period (about 600 seconds), and it was almost entirely worn out after 10 minutes. However, when the PAO oil was used during the friction sliding, both Ti_{4at.%}‐DLC and Ti_{27at.%}‐DLC coatings illustrated low and stable friction curve, in which the average friction coefficient was around 0.09−0.13 and no distinct run‐in period was visible. Figure 4C shows the wear rates of Ti_{4at.%}‐DLC and Ti_{27at.%}‐DLC coatings for comparison. The Ti_{4at.%}‐DLC coating exhibited high wear resistance under both dry friction and oil lubrication, with corresponding wear rate about 2.15 × 10⁻¹⁶ m³ N⁻¹ m⁻¹ and 1.60 × 10⁻¹⁶ m³ N⁻¹ m⁻¹, respectively. However, the Ti_{27at.%}‐DLC coating displayed obviously different behaviors. Under dry friction, the coating failed rapidly and the wear rate could not be achieved. But the wear rate of Ti_{27at.%}‐DLC coating was significantly reduced to the lowest value of 1.12 × 10⁻¹⁶ m³ N⁻¹ m⁻¹ under oil lubrication condition. Figure 4D shows the wear rates of corresponding GCr15 steel balls; under both conditions, the balls against Ti_{4at.%}‐DLC coating exhibited lower wear rate, and the lowest wear rate of 1.26 × 10⁻¹⁷ m³ N⁻¹ m⁻¹ was obtained under oil lubrication. While the balls against Ti_{27at.%}‐DLC coating showed serious wear, especially under dry friction, which had the highest wear rate of 3.52 × 10⁻¹⁶ m³ N⁻¹ m⁻¹.

3.3 | Wear track and wear scar analysis

In order to clarify related lubrication mechanism, the morphology, component, and structure of wear tracks on coating surface and wear scars on steel ball were systematically analyzed. Figure 5 shows the SEM micrographs of wear tracks, and the illustrations were cross‐sectional profiles of the wear tracks. For Ti_{4at.%}‐DLC coatings, the wear tracks obtained under both dry friction (Figure 5A) and oil lubrication (Figure 5D) conditions were very narrow. Moreover, almost no debris could be observed both inside and outside of wear tracks. Nevertheless, for Ti_{27at.%}‐DLC coating, complete delamination on the wear track surface occurred when tested under dry friction, as shown in Figure 5B. Figure 5C shows the corresponding EDS mapping image, which confirmed that no C and Ti but distinct Si element emerged in the wear track area. When tested under oil lubrication, as shown in Figure 5E and 5F, the wear track was still covered with DLC coatings, suggesting that after adding PAO oil, the wear resistance of Ti_{27at.%}‐DLC coating was improved obviously.

Raman spectroscopy was used to characterize evolution of carbon atomic bonds on the surface of the coatings and steel balls before and
after friction tests. Generally, Raman spectra of DLC can be normally deconvolved into D peak (breathing vibration mode of sp² carbon in aromatic rings) and G peak (stretching vibration mode of all pairs of sp² carbon in both aromatic rings and chains)\textsuperscript{25}; an increase in the intensity ratio of D peak to G peak ($I_D/I_G$) indicates the surface graphitization of DLC coatings. Figure 6A shows Raman spectra of the as-deposited Ti$_{4\text{at.\%}}$-DLC coating and wear tracks after friction tests under both dry friction and oil lubrication, with a similar $I_D/I_G$ ratio (0.831, 0.827, and 0.828). Figure 6B and 6C exhibits Raman results of the corresponding wear scar after friction tests under both dry friction and oil lubrication, respectively, and the inserted images are optical images of wear scars. In order to deep reveal its difference in

![Image](https://example.com/image1)

**FIGURE 5**  SEM micrographs of wear tracks of (A) Ti$_{4\text{at.\%}}$-DLC coating tested under dry friction, (B) Ti$_{27\text{at.\%}}$-DLC coating tested under dry friction and (C) corresponding EDS mapping, (D) Ti$_{4\text{at.\%}}$-DLC coating tested under oil lubrication, and (E) Ti$_{27\text{at.\%}}$-DLC coating tested under oil lubrication and (F) corresponding EDS mapping

![Image](https://example.com/image2)

**FIGURE 6**  Raman spectra of (A) as-deposited Ti$_{4\text{at.\%}}$-DLC coating and wear tracks, (B) wear scar on steel ball tested under dry friction, (C) wear scar on steel ball tested under oil lubrication, and (D) $I_D/I_G$ ratio, G peak position under all conditions
component, Figure 6D compares the fitted I_D/I_G ratio value and G peak position of amorphous carbon under all conditions. Compared with as-deposited coating, no distinct difference could be observed in the spectra of wear track, implying a similar carbon atomic bond between wear tracks and as-deposited coating. Besides, Raman spectra with typical amorphous carbon characteristics were observed on wear scar, and compared with as-deposited coating, noted that higher I_D/I_G ratio (from 0.831 to 0.995 and 1.086, respectively) and G peak position (from 1553 to 1581 and 1562 cm⁻¹, respectively) were observed from the wear scar surface under both conditions. The results demonstrated that a friction-induced graphitized carbon layer was formed and transferred from wear track to steel ball due to the easily shear characteristics of the graphite-like lamellar structure, which will not be affected by PAO oil.²⁶,²⁷

Figure 7 shows the Raman spectra of the as-deposited Ti₂₇at.%-DLC coating, wear track as well as wear scar after friction tests under oil lubrication. Compared with as-deposited coating, the I_D/I_G ratio of wear track increased from 0.996 to 1.146, and the G peak position shifted to higher wave number, indicating that a graphitized carbon layer was formed on wear track. However, no amorphous carbon signal was observed from wear scar, suggesting that no graphitized carbon layer was transferred to steel ball in this case.

In general, graphitization may occur in the tribological contact because of friction-induced heating under contact and high contact stress.²⁶ And the formation of graphitized carbon layer can cause an easy slip between the tribo pairs, thereby minimizing friction. However, a higher degree of graphitization and the transfer of graphitized carbon layer will increase the consumption of coating and lead to high wear rate.²⁸ Therefore, for Ti₄₄at.%-DLC coating, more material will lose from the surface due to transfer of graphitized carbon layer, leading to a slighter higher wear rate (Figure 4) compared with Ti₂₇at.%-DLC coating under oil lubrication.

The above results showed that under oil lubrication condition, the two coatings showed similar tribological behaviors, which may be mainly caused by the oil film formed in the contact area, with theoretical thickness 16 and 6 nm for Ti₄₄at.%-DLC coating and Ti₂₇at.%-DLC coating, respectively, and under dry friction, Ti₂₇at.%-DLC coating was quickly worn out. So, more investigations were performed on the friction results of Ti₄₄at.%-DLC coating in the following section.

Since the tribological properties were closely related to transfer film, we first investigated the component changes in different locations on the wear tracks by SEM and EDS analysis. As shown in Figure 8, three typical positions were selected and characterized, corresponding to the wear debris region (spectrum 1 and 4), wear track region (spectrum 2 and 5), and as-deposited coating (spectrum 3 and 6), respectively, and the atomic percentages of C, O, Ti, and Fe are also present in Table 2. It could be noted that the composition was almost the same between as-deposited coating and wear track, regardless of the test environment. However, the wear debris exhibited distinct compositional variation. As shown in Figure 8A, small pieces of wear debris aggregated around the wear track under dry friction, where a significant increase of O and Fe was observed in spectrum 1, indicating that the steel ball was worn (Figure 4D) and the accumulated debris were mainly composed of ferric oxides. However,
for the case under oil lubrication shown in Figure 8B, Fe concentration of the accumulated debris (spectrum 4) greatly decreased from 17.66 to 1.38 at.%, and Ti concentration exhibited a significant increase from 4.67 to 26.87 at.%, indicating that there was only slighter abrasion of the steel ball (Figure 4D) and the debris were mainly composed of titanium compound.

The clarification of chemical composition changes of wear scars was also undertaken by SEM and EDS elemental mapping analysis. Under dry friction shown in Figure 9A, the contact area on steel ball was covered with a transfer film, and the corresponding EDS mapping images showed the intensive Ti and O element signals, suggesting that the main ingredient of transfer film might be the oxides of coatings. This result coincided well with the former EDS analysis of the wear tracks, which indicated that the Ti from coating was formed to transfer film due to tribochemical reaction. However, when the test was under oil lubrication condition shown in Figure 9B, there was no obvious transfer film, but only oil stains adhered around the wear scar. In addition, no remarkable signal of Ti and O element emerged. Therefore, it is reasonable to state that titanium compounds will be easily thrown out from the contact area with PAO oil. On account of no Ti 2p peak was observed under this condition, the O 1s peak was analyzed to judge the existence of titanium oxide. The results showed that no Ti-O peak appeared in the O 1s spectra, and it could only be fitted into three peaks corresponding to sp² C–C bond (284.5 eV), sp³ C–C bond (285.3 eV), and C=O bond (288.6 eV), respectively. It should be also noted that there was a strong O 1s peak at about 529.9 eV shown in Figure 10D, which was assigned to ferric oxides instead of titanium oxide.

### 3.4 Related mechanism discussion

The H/E and H²/E² ratios are two factors to assess wear-resistant properties and plastic deformation resistance of hard coatings, respectively. Massive titanium carbide nanocrystallites lead to a significant increase in both the hardness and elastic modulus of the Ti₂₇₄₅₁₃₆-DLC coating as shown in Table 1. However, the similar H/E ratio shows that the two coatings show similar toughness. The higher hardness and H²/E² ratio of Ti₂₇₄₅₁₃₆-DLC imply that the coating has a higher carrying capacity. While it was quickly worn out under dry friction.

<table>
<thead>
<tr>
<th>Element</th>
<th>C, at.%</th>
<th>O, at.%</th>
<th>Ti, at.%</th>
<th>Fe, at.%</th>
<th>Total, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>54.40</td>
<td>23.27</td>
<td>4.67</td>
<td>17.66</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>96.05</td>
<td>0.92</td>
<td>3.03</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>94.56</td>
<td>1.29</td>
<td>4.14</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>44.63</td>
<td>27.12</td>
<td>26.87</td>
<td>1.38</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>94.96</td>
<td>1.68</td>
<td>3.36</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>94.40</td>
<td>1.87</td>
<td>3.73</td>
<td>0.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

TABLE 2 Atomic percentages of C, O, Ti, and Fe in the coating surface, wear tracks, and wear debris of Ti₄₅₋₆₋DLC coatings

Here, XPS analysis was done after 3-minute etching by Ar⁺ beam of 2 keV to remove the contamination on surface. Figure 10A and 10C shows the C 1s and Ti 2p XPS spectra of wear scar tested under dry friction. The C 1s spectrum, as shown in Figure 10A, was fitted into four components, that was correlated to sp² C–C bond (284.2 eV), sp³ C–C bond (285.6 eV), C=O bond (288.2 eV),²⁹,³⁰ and C–Ti bond (282.3 eV).³¹ In Ti 2p spectrum (Figure 10C), the peaks at 458.4 and 464.2 eV are usually assigned to the Ti 2p₃/₂ peak and Ti 2p₁/₂ peak of TiO, respectively, and the peaks at 456.6 and 462.4 eV are usually attributed to the Ti 2p₃/₂ peak and Ti 2p₁/₂ peak of TiC.³¹ Hence, the Ti 2p XPS spectra showed that TiC and TiO simultaneously existed in the transfer film, indicating that the Ti from Ti₄₅₋₆₋DLC reacted with C and O during the friction process. Figure 10B and 10D present the C 1s and O 1s XPS spectra of the wear scars tested under oil lubrication. However, when the test was under oil lubrication condition shown in Figure 9B, there was no obvious transfer film, but only oil stains adhered around the wear scar. In addition, no remarkable signal of Ti and O element emerged. Therefore, it is reasonable to state that titanium compounds will be easily thrown out from the contact area with PAO oil. On account of no Ti 2p peak was observed under this condition, the O 1s peak was analyzed to judge the existence of titanium oxide. The results showed that no Ti-C peak appeared in the C 1s spectra, and it could only be fitted into three peaks corresponding to sp² C–C bond (284.5 eV), sp³ C–C bond (285.3 eV), and C=O bond (288.6 eV), respectively. It should be also noted that there was a strong O 1s peak at about 529.9 eV shown in Figure 10D, which was assigned to ferric oxides instead of titanium oxide.
Actually, during friction process, the interaction between wear track and counterpart will decide its tribological behavior, besides the transfer film and PAO oil can also play an important role under different conditions.21,28 Under dry friction, Ti_{27}at.\%-DLC showed serious wear compared with Ti_{4}at.\%-DLC coating due to the different microstructures, which have a great influence on mechanical properties and sliding interface. As shown in Figure 11, for Ti_{4}at.\%-DLC coating tested under dry friction, there was a run-in period with high friction coefficient (Figure 4A and 4B) due to adhesive wear.32 The Ti atoms from coating would easily react with C and O to form TiC and TiO hard phase, whereafter aggregating to form transfer film, and then, the transfer film would adhere to steel ball (Figure 9A). It has been certified that the existence of transfer film in sliding interface can effectively decrease friction coefficient and simultaneously protect the underlying coating from further removal.33,34 In addition, friction-induced graphitization is considered as one of the main causes of low friction because of the graphite-like lamellar structure, which can easily shear between each plane.27 Therefore, the combined effects of transfer film and graphitization lead to the lowest friction coefficient in steady friction stage when tested under dry friction. With regard to the Ti_{27}at.\%-DLC coating, the doped Ti atoms bonded with the surrounding C atoms, and subsequently formed massive carbide nanoparticles that were embedded in the DLC matrix (Figure 3B). A large amount of hard phase compounds of titanium in the sliding interface could lead to large fluctuations of friction coefficient in the running-in period (Figure 4A) and serious abrasive wear, even the completely wear of the coating under dry friction. Besides, the microstructure of Ti_{27}at.\%-DLC coating would increase the coating compressive stress and promoted the graphitization, which will also accelerate the failure of the coating.35

While, under oil lubrication condition, both coatings showed similar low and stable friction coefficient and the wear rate of coatings and steel balls decreased obviously. Especially for Ti_{27}at.\%-DLC coating, PAO oil can greatly improve its tribological properties. The results of oil film thickness indicated that both the two tests were under boundary lubrication. Consequently, both of oil film and transfer film will govern the friction property normally. Different from test in dry friction, the introduction of PAO oil resulted in the more stable friction coefficient curve without run-in period (Figure 4A and 4B). Besides, no transfer film was formed in the sliding interface, and some titanium compound particles were observed around the wear track, as shown in Figures 8B and 9B. This indicated that PAO oil can inhibit the formation of transfer film and throw the TiO and TiC hard particles out from sliding interface, which can account for the lower wear rate of coatings tested in oil lubrication. Besides, compared with Ti_{4}at.\%-DLC coating, the absence of the transfer of graphitized carbon layer for Ti_{27}at.\%-DLC could reduce the consumption of coating, resulting in the lowest wear rate of Ti_{27}at.\%-DLC coating under oil lubrication condition (Figure 4C).
Ti-DLC coatings with 4 at.% and 27 at.% Ti content were prepared by a hybrid linear ion beam deposition system. HRTEM results showed that the Ti atoms were dissolved in the DLC matrix for Ti$_{4\text{at.\%}}$-DLC coating, while massive titanium carbide nanocrystallites were formed in Ti$_{27\text{at.\%}}$-DLC coating. Tribological tests were carried out under dry friction and oil lubrication, respectively. Under dry friction, Ti$_{4\text{at.\%}}$-DLC coating showed low friction and wear due to the formation of transfer film and graphitized carbon layer, which all adhered to steel ball, and Ti$_{27\text{at.\%}}$-DLC showed serious wear since a large amount of hard phase compounds of titanium in the sliding interface could lead to serious abrasive wear and eventually the failure of the coating. While, under oil lubrication condition, both coatings showed similar low friction and wear due to the existence of oil film (16 nm for Ti$_{4\text{at.\%}}$-DLC coating and 6 nm for Ti$_{27\text{at.\%}}$-DLC coating) in sliding interface, which can inhibit the formation of transfer film and throw the TiO and TiC hard particles out from sliding interface. And Ti$_{27\text{at.\%}}$-DLC coating exhibited lowest wear rate under this condition.

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ORCID

Youzhi Guo https://orcid.org/0000-0003-0791-1360

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