Tribological behaviours of PVD TiN and TiCN coatings in artificial seawater

Lei Shan, Yongxin Wang, Jinlong Li, He Li, Xuedong Wu, Jianmin Chen

ABSTRACT

To improve the tribological performance of sea frictional components, TiN and TiCN coatings, were used for surface protection of the components. The coatings were deposited on stainless steel and WC cemented carbides by arc ion plating. The coating topography was observed using scanning electron microscopy (SEM), and the composition and structure were analyzed by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Hardness and adhesion force were tested by nanoindentation and scratch tester, respectively. The friction and wear properties of the TiN and TiCN coatings were investigated by ball-on-disk tribometer in air, distilled water and artificial seawater. The results showed that both the TiCN and TiN coatings had a strong (111) preferred orientation. The friction coefficients of the coatings in distilled water and artificial seawater were lower than those in air. This indicates the influence of aqueous solutions on the friction coefficient due to the lubricative film formed on the coatings. However, the wear loss of the coatings in artificial seawater was larger than those in air and distilled water, this demonstrates a positive synergism between corrosion and wear in artificial seawater. The TiCN coating shows the best wear resistance in the artificial seawater.

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1. Introduction

The conjoint action of wear and corrosion leads to premature failure of engineering components in seawater environments. However, some crucial frictional components of marine equipment, such as pump, hydraulic system, valve, gear, shaft and propeller, have to be directly lubricated by seawater [1,2]. Their safety, reliability and service life greatly depend on their tribological and corrosive performances in harsh marine environments. Thus, it is imperative to improve the tribological performance of marine frictional components. One of the most effective approaches is to take advantage of advanced coatings with good lubrication and protection effects in seawater.

The TiN coatings are widely used to enhance the surface properties under wear and corrosion conditions because of their high hardness, high adhesion strength, low friction coefficient and good chemical stability [3–8]. For instance, the TiN coating can improve the corrosion response of a material if microstructural defects like porosity and pinholes controlled [9], and Mao reported that thick TiN coatings can remarkably improve the anti-corrosion property of bare carbon steel in 3.5 wt.% NaCl electrolytic solution [10].

The TiCN coatings have high hardness with superior chemical and thermal stability. The morphology, structure and composition of TiCN were investigated in several studies [11–13]. It has been shown that TiCN is a solid solution of TiN and TiC and would incorporate the advantages and characteristics of both. Especially in tribological applications, where abrasion is the dominant wear mechanism, TiCN is superior to TiN. Because TiCN has higher hardness and the presence of carbon lowers friction and wear as lubricant [14]. TiCN also shows good corrosion resistance, researchers reported a decrease of up to three orders of magnitude for the corrosion current density of TiCN-coated AISI 304 stainless steel [15,16].

However, there is little investigation carried out on the tribological behavior in water lubrication, especially in seawater. The aim of this work is to study tribological behaviors of the TiN and TiCN coatings in artificial seawater. Comparative experiments of the wear behaviors of PVD TiN and TiCN coatings were carried out air, distilled water and artificial seawater. The influences of medium on tribological property of the TiN and TiCN coatings were discussed.

2. Experimental

2.1. Coating deposition

The 304 stainless steel (24 mm × 12 mm × 2 mm) and WC cemented carbide disks (Φ30 mm × 4 mm) were used as the substrates. Their working faces were polished to a surface roughness of 30 nm and ultrasonically cleaned in acetone and ethanol, respectively. The coatings were prepared using a multi-arc ion plating system to sputter a titanium target (purity > 99.5 wt.%) in Ar (99.99%), N₂ (99.99%) and C₂H₂ (99.99%) mixed atmosphere, N₂ in the case of developing the TiN coating, and the mixture of N₂ and C₂H₂ in the case of developing the TiCN.
coating, respectively. Prior to deposition, the chamber was pumped down to a base pressure below 2 × 10⁻² Pa. Thereafter, the substrates were cleaned by Ar⁺ bombardments for 10 min with a pulsed substrate bias voltage of −200 V, to remove thin oxide layer and other adherent impurities on the substrates. Then deposition was conducted at a bias voltage of −200 V, a target current of 80 A and a distance from the substrate to the target of 100 mm. During deposition the substrate temperature increased to 250 °C, and the total pressure of sputtering gas was controlled at 0.45 Pa. The ratio of Ar/N₂/C₂H₂ was 25/250/80 in case of developing the TiCN coating, and Ar/N₂/C₂H₂ was 25/250/80 in case of developing the TiCN coating.

2.2. Characterization

The microstructure of the as-deposited coatings was investigated by X-ray diffraction (Bruker D8 X-ray facility) using Cu Kα radiation (λ = 0.154 nm), which was operated at 40 kV and 40 mA with grazing incidence angle of 2°. The scanning angle was ranged from 20 to 80° at a scanning speed of 4°/min with 0.02° step size. The surface morphologies and cross-sectional images of the films were investigated by using a field emission scanning electron microscope (FESEM) (FEI Quanta FEG 250) equipped with EDS (OXFORD X-Max).

The adhesion force of the total film was determined by scratch tester (CSM Revetest) with a conical diamond tip of 0.2 mm radius and 120° taper angle. The parameters of the measurements were as follows: table speed 6 mm/min, loading rate 118 N/min, loading scale 0–100 N and scratch length 5 mm. The acoustic emission was detected when the film was broken and the load at the point of breaking was called the adhesive critical load (LC). Stanishevsky and Lappalainen [17] considered at least two stages in the film deformation and failure with the corresponding critical loads LC1 and LC2. LC1 was defined as the load at the first surface crack, and LC2 was named as the load at the whole film delaminated off the substrate.

Nanoindentation testing was carried out using a MTS Nano Indenter® G200 system fitted with a Berkovich indenter using the continuous stiffness measurement (CSM) option. The hardness and elastic modulus were obtained from the curves using the Oliver–Pharr method [18]. All the load–displacement curves were inspected prior to analysis. The maximum indentation depth was of 500 nm. 4 indentations in each sample configured on different areas were performed to have reliable statistics.

2.3. Tribological test

Wear tests were performed with a ball-on-disk reciprocating in sliding contact with a steel ball at room temperature of about 20 ± 5 °C and relative humidity of 60 ± 5%. The SUS440C steel balls were used as the counterparts with a diameter of 3 mm, a surface roughness of 53 nm and a hardness value of 7.2 GPa. The composition of the SUS440C steel balls was listed in Table 1. The artificial seawater is prepared according to Standard ASTM D 1141-98. The chemical composition of artificial seawater was listed in Table 2.

UMT-3MT tribometer (CETR, USA) was used in order to evaluate the friction and wear characteristics of the sliding couples. A sliding speed of 300 rpm, a constant normal load of 5 N and a sliding stroke of 5 mm were used in the experiments and the friction coefficient was continuously recorded during testing. Based on the wear track depth profiles detected by Alpha-Step IQ profiometer, the wear losses of the coatings V can be obtained after the sliding tests were completed. Then according to classical wear equation, the wear rate W can be calculated by the following equation:

\[ W = \frac{V}{(S \times L)} \]  \hspace{1cm} (1)

where S is the sliding distance and L is the normal load applied.

The wear rates for balls were calculated using the following equation:

\[ W_b = \frac{md^4}{(64RLS)} \]  \hspace{1cm} (2)

where R is the radius of the ball, d is the diameter of the ball wear scar, L is the normal load and S is the total sliding distance.

3. Results and discussion

3.1. Microstructure of the coatings

The X-ray diffraction patterns are shown in Fig. 1. According to Fig. 1, both the TiN and TiCN coatings show an f.c.c. structure with a strong (111) preferred orientation. All peaks corresponding to the (111), (200), (311) and (222) planes of the cubic TiCN and TiN phases are observed in the coatings. It is difficult to distinguish the two different compounds since the atom radii of C and N are too close.

We also notice that the diffraction peaks of the TiN coating shift toward higher diffraction angles compared with the TiCN coating, indicating a decrease in the lattice parameter. This shift is probably due to the substitution of C atoms with the smaller sized N atoms in the solid solution. Moreover, besides the (111) peak, the other peaks are difficult to be observed due to their weak signals. It implies that the coating structure is dense since the plane (111) is the densely packed plane [19]. Other researchers [20] reported that the (111) preferred orientation of the coatings could lead to the high hardness of the coatings.

Fig. 2a, d shows the surface morphology of the TiCN and TiN coatings. It is clear that there are many white particles and dimples on the surface of the TiCN and TiN coatings. And those small size microparticles which distributed dispersedly in the coatings, have a conical shape and protrude out of the coating surface. Moreover, the micro-cavities are observed and distributed dispersedly in the coatings. As shown in Fig. 2c, the EDS analysis of the TiCN coating shows that there are Ti, C and N elements on the surface and the white particles which embeded out of the coating surface. Moreover, besides the (111) peak, the other peaks are difficult to be observed due to their weak signals. It implies that the coating structure is dense since the plane (111) is the densely packed plane [19]. Other researchers [20] reported that the (111) preferred orientation of the coatings could lead to the high hardness of the coatings.

Fig. 2f shows the similar results of TiN. It can be observed from Fig. 2b that the TiN coating displays a columnar structure, and the first surface crack, and LC2 was named as the load at the whole film delaminated off the substrate.

3.2. Mechanical properties

As shown in Fig. 3, the first cracking of the TiCN coating occurs at 11 N (Fig. 3a), and the first crack of the TiN coating appears at 15 N (Fig. 3b). The whole delamination of the TiCN and TiN coatings occurs

<table>
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<th>Table 1</th>
<th>The composition of the SUS440C steel balls.</th>
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<td>at.%</td>
<td>C</td>
</tr>
<tr>
<td>SUS440C</td>
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<th>Table 2</th>
<th>Chemical composition of artificial seawater.</th>
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<td>Constituent</td>
<td>NaCl</td>
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<td>Concentration (g·L⁻¹)</td>
<td>24.53</td>
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at 42 N (Fig. 3a) and 50 N (Fig. 3b), respectively. The values for LC of the TiN and TiCN coatings may vary in different studies because of the differences in the interlayer and coating processes. Both LC1 and LC2 of the TiN coating are higher than the TiCN coating, indicating that the adhesion of the TiN coating is better than that of the TiCN coating. This may be because of the lower residual stress due to the columnar structure of the TiN coating.

Fig. 4a shows the load–unload curves of the TiN and TiCN coatings with maximum indentation depth of 500 nm. The average hardness and elastic modulus of the TiCN coating are about 31.6 GPa and 409.7 GPa, respectively. For the TiN coating, the average hardness and elastic modulus decreased to 27.7 GPa and 394.4 GPa. Significant substrate contribution to the microhardness is observed as the indentation depth increased (Fig. 4b). The results are consistent with the literature [21]. The higher hardness of the TiCN coating compared to TiN may be partly attributed to the solid solution effect of carbon in the TiN lattice. In addition to the solid solution effect, the high compressive residual stress contributes to the hardness in the TiCN coating.

For the tribological coatings, the $H^3/E^2$ ratio as a key parameter always predicts the tribological behavior and the ability of a coating to resist mechanical failure. The values of $H^3/E^2$ for the TiCN and TiN coatings are 0.19 GPa and 0.14 GPa, respectively. Therefore, both the TiN and TiCN coatings have good resistance to plastic deformation due to $H^3/E^2 > 0.1$ [22].

3.3. Friction properties

Fig. 5 shows the friction behaviors of the TiCN and TiN coating sliding against SUS440C steel balls in different environments. The friction coefficients of the TiCN coating in different sliding conditions possess similar features: the first part represents run-in with rapid increase of the value, and the second part is obvious decrease of the value after about 150 s. Whereas for the TiN coating, the friction coefficients first increase to the maximum, and reach the relative steady-state wear stage after about 150 s. The decrease after run-in period is caused by the steel counterpart itself rather than the coatings. With rapid increase of the wear rate of the ball, the interface between tribo-pair becomes smoother. Moreover, wear debris generates oxide particles after adsorbed moisture (according to the EDS analysis in Figs. 7 and 8), which leads to the formation of a hydrated surface layer of low shear strength as a solid lubricant, and the decrease of the friction coefficients.

As shown in Fig. 6, the average friction coefficient for the coatings in air is higher than that in distilled water and artificial seawater, which is attributed to adsorbed water molecules that may provide boundary lubrication to a certain degree. The continuous removal of reaction layers by sliding creates extremely smooth surfaces and the upon water condensation from the ambient provided hydrodynamic lubrication [23]. For the same coating, the friction coefficient in artificial seawater is slightly lower than in distilled water. This is because when the tribo-pair is sliding in artificial seawater, active element Cl will react with the iron on the surface of steel ball, and thus form an easy-shear-triob-layer containing ferric oxide, ferric sulfide and ferric chloride which are good lubricants [24]. Furthermore, while the tribo-pair is sliding in the artificial seawater, the debris wrapped by the lubricative media may act as rolling balls, and thus made the wear process smoother [25]. Therefore, the friction coefficients decrease in the seawater compared with distilled water. It is clear from Fig. 6 that the friction coefficients for the coatings are much lower than those of uncoated substrates in the same environment.

3.4. Wear properties

Fig. 7 shows the morphologies of wear scar on the balls and wear track on the TiCN coating and the corresponding EDS analysis of the wear track. When the TiCN coating slides against steel ball in air, besides original cavities, there are many shallow scratch grooves on the surface of the ball and the wear scar surface on SUS440C ball is smooth and flat (Fig. 7a). The wear track of the TiCN coating is rough and there are many wear debris on the surface of the wear track (Fig. 7b). The EDS analysis shows, that not only Ti, C and N, but also Fe, Cr and O elements are on the wear track (Fig. 7c). It indicates that the transfer of elements from ball to coating and oxidation of steel ball occurred during friction sliding. Increased transfer of Fe-rich oxidized steel ball to the TiCN coating can contribute to negative wear rates. This leads to the passivation layer in the wear track. But in distilled water, the wear scar surface on the steel balls displays many grooves (Fig. 7d). Delamination and lot wear debris are observed on the wear track (Fig. 7e). In artificial seawater, the deeper grooves and cavities are observed on the scar surface of steel balls (Fig. 7g). The wear track surface on the TiCN coating is also covered with many deep grooves (Fig. 7h). This is because the high concentration of Cl− ions in artificial seawater which is destructive to passivation layer, corrodes the balls and coatings during sliding. According to the EDS analysis on the wear track in distilled water and artificial seawater, Ti, Fe, C, N, Cr, S and O elements were found on the wear track (Fig. 7i), which indicates that transfer of elements from ball to coating occurs during friction sliding. The aqueous environment induces a corrosion process in the wear track, more because the coatings in the wear track are activated by the wear process and therefore more prone to anodic dissolution in an electrolyte. The depth of grooves increases because passivation of the TiCN coating in the wear track is not easy in aqueous environments, so the track is not protected from corrosion. In other words, the tribochemical reaction between tribo-pairs and distilled water is occurred during sliding. The comparison of wear topographies indicates that the mix wear (abrasive wear + tribochemical wear) occurs as the TiCN coating slides against steel balls in distilled water and artificial seawater.
As for the TiN coating, the similar plowing grooves and debris are observed on the ball wear scars and the wear track on the coating. But the plowing grooves are shallower on the steel ball scars compared with those against the TiCN coating in all three conditions (Fig. 8a, d, g), which could be attributed to the higher hardness and $H^3/E^2$ value of the TiCN coating. The plowing grooves on the wear tracks of the coating...
become deeper in distilled water and artificial seawater (Fig. 8e, h), which indicates that the aqueous solution has a destructive effect on passivation layer and coating. The wear debris is accumulated at the edge of the wear tracks on the TiN coating (Fig. 8b, e, h) and the EDS analysis on the wear track also indicates that Ti, Fe, C, N, Cr, S and O elements are found on the wear track (Fig. 8f). It also indicates that the tribochemical reaction between tribo-pairs and distilled water is occurred, and transfer of elements from ball to coating occurs during friction sliding.

Fig. 9 shows the cross-sectional profiles of the wear track on the coatings in air, distilled water and artificial seawater. From Fig. 9a we observe that the depth of the wear track on the coatings in air which arises from the formation of passivation layer, and is much smoother than the uncoated substrate. It is clear from Fig. 9b that the depth of the wear track on the TiCN coating is smoother than the TiN coating in distilled water. The similar results are observed in artificial seawater in Fig. 9c. The maximum depth of the TiCN coating is lower than that of the TiN coating in distilled water and artificial seawater. We also observed that the depth of the wear track is higher than the original depth in some place; this is because wear debris adheres to the coating surface. From Fig. 9a, b, c, it is obvious to observe that the maximum depth of the wear tracks on the uncoated substrates is much higher than those of the TiCN and TiN coatings in each case.

As shown in Fig. 10, there are two wear models named as positive wear and negative wear. The positive wear means that the wear debris is removed from the friction surface of tribo-materials immediately,
Fig. 5. Friction behavior of the coatings and substrates sliding against steel balls in various medium: (a) in air (b) in distilled water and (c) in artificial seawater.
which leads to the low friction coefficient and the smooth wear track. The negative wear means that the balls' wear debris adheres to the wear track surface, which induces the high friction coefficient and the wear rate of balls becomes higher. When sliding in air, the TiCN and TiN coatings showed the negative wear, indicating that the transfer of wear debris from ball to coating occurs. However, the coatings show the positive wear in distilled water and artificial seawater, and the volume of wear track decreased. It is obvious from Fig. 10 that the wear rates of the TiCN coating are lower than those of the TiN coating both in distilled water and artificial seawater, indicating that the TiCN coating performs better than the TiN coating sliding in distilled water and artificial seawater, and that was consistent with as mentioned H^3/E^2.

Another reason might attribute to the columnar structure of the TiN coating, which is beneficial for ion and water molecules to reside in and thus have more opportunity to erode the coating. The corrosion strongly accelerates the wear under the cooperation of the mechanical and chemical functions. However, the TiCN coating presented a featureless structure and it was more difficult for ions to degrade the coatings. The wear rate of the TiCN coating, $1.07 \times 10^{-6}$ mm$^3$/N m, was much lower than that of the uncoated substrate, $9.56 \times 10^{-6}$ mm$^3$/N m in artificial seawater.

![Fig. 6. Average friction coefficient of the coatings and substrates sliding against steel balls in three mediums.](image)

![Fig. 7. Optical image of ball wear scar and SEM image with corresponding EDS analysis of the wear track on the TiCN coatings.](image)
We also observe from Fig. 10 that the wear rates of the coatings in aqueous solution are higher than those in air, which are attributed to the significant influence of water on wear due to tribochemical reactions. Water can have an ambiguous effect on wear rates by either contributing toward high wear by accelerating crack growth and microfracture, or reducing wear by the formation of extremely smooth lubricant tribo-layers formed by tribochemical reactions. Although the wear rates of the coatings by the mechanical wear mechanism should be lower in aqueous environments than in air, it might be higher in practice when oxidation wear dominates the wear mechanism. The wear rates of the coatings sliding in artificial seawater, including the anodic dissolution by corrosion in seawater, were higher than those in distilled water. Sliding in the artificial seawater is a typical tribocorrosion system, in which corrosion and wear degrade materials by both mechanical and chemical processes [26]. In artificial seawater, the high Cl\(^-\) ion concentration has a strong destructive effect on passive layers, which mainly contain Ti, Fe and O elements (according to the EDS analysis in Figs. 7 and 8). It can be easily disintegrated or removed by the action of the rapid tribo-ball during sliding, producing a track of clean surfaces exposed to corrosive environment. The corrosive medium activates the coating, causes anodic dissolution during sliding, and increases the wear-loss (corrosion accelerates wear). The increased wear-loss induces more defects and accelerates the corrosion speed. As a result, a positive synergism between corrosion and wear leads to the higher wear rates in artificial seawater.

4. Conclusions

The friction and wear behaviors of the TiCN and TiN coatings have already been investigated in air, distilled water and artificial seawater. The conclusions are summarized as follows:

1. The friction coefficients of the coatings in artificial seawater are lower than those in air and distilled water.
2. The wear rates of the coatings in artificial seawater are higher than those in distilled water. The high concentration of Cl\(^-\) in artificial seawater has a strong destructive effect on passive layers, leading to a positive synergism between corrosion and wear, finally increasing the wear rate in artificial seawater.

Fig. 8. Optical image of ball wear scar and SEM image with corresponding EDS analysis of the wear track on the TiN coatings.
Fig. 9. Sectional profile of the wear track on the coatings: (a) in air, (b) in distilled water, and (c) in artificial seawater.
Compared to uncoated steel, the friction coefficients and wear rates of the coated samples decreased significantly in artificial seawater, and the TiCN coating presented the best wear resistance among them.

Acknowledgments

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References


Fig. 10. Wear rates of the coatings and uncoated substrates.