Enhanced Tribocorrosion Resistance of Superhard Ti-C-N Ceramics Coatings

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Abstract

Cubic transition-metal nitride coatings have been regarded as promising candidates for of marine engineering components in seawater environments. However, the excellent seawater lubrication is hard to achieve due to contradictory relations of hardness and toughness, as well as unstable behaviors at sliding contact surface. As discussed in our previous work about the enhanced tribological behaviors of hard yet tough CrN/Si₃N₄ multilayer coatings[14], superhard yet tough coatings are highly desired to improve wear resistance and durability in aggressive solutions. Here we report Ti-C-N coatings with Ti(C,N) and small sp²-C phases deposited by high power impulse magnetron sputtering exhibit simultaneously superhardness of 40.2 GPa and favourable toughness (without radial cracks in HRC indentations). Superhard yet tough Ti-C-N coatings show excellent seawater-lubricating behaviors with extremely low friction coefficient of 0.03 and smooth wear morphologies in 3.5wt.% NaCl aqueous solution. The enhanced tribocorrosion performance are attributed to superhard yet tough properties resulting in the increased resistance of crack initiation and propagation, which restrains synergistic actions of wear and pitting corrosion. In addition, stable self-lubricating amorphous carbon phase at sliding contact surface reduce friction and wear in seawater.

1. Introduction

With the rapid development of marine industries in recent decades, severe wear and corrosion failure of marine engineering components spawn a great number of economic loss and energy consumption. Anti-wear and -corrosion materials and their preparation techniques are highly desired for environment-friendly and energy-saving roles. However, stainless steels widely used as structural components are well known for good corrosion resistance, but their friction and wear properties are poor [1]. Moreover, tribocorrosion in seawater environment coupled with negative interactions of wear and corrosion would substantially result in the degradation and failure [2, 3]. Surface modification and advanced coatings are expected to improve seawater lubrication and durability of components to ultimately obtain high working performance and long service lifetime [4, 5]. One of achievable strategies for the enhancement of tribocorrosion performance is nanostructured coatings deposited on surface components for combined improvements of seawater lubrication and anti-corrosion [6–11]. In addition, what but is not allow to neglect, synergistic effects of hardness and toughness of surface coatings on crack initiation and propagation would make a positive contribution for the enhancement of seawater lubrication and corrosion resistance [12–14].

Lubrication behaviors are closely correlated with surface integrity and interface structure of the coated components, in which contact mechanisms is often varied [15]. There have been lots of studies that have shown how the tribo-films formed on contact surface originate from tribochemical reactions acts to reduce friction and wear as lubrication layers [16, 17]. In seawater environment, however, lubrication behaviors mainly depend on the combined effects of self-lubricating phases on contact surface, surface integrity and interface structure, due to few of the formed tribochemical phases [8, 18]. In addition, continuous passive films and surface wettability would act on lubrication on contact surface [19, 20].

Moreover, it has to be mentioned that hard yet tough properties of surface coatings/substrate system make a key contribution to cooperative deformation for the suppression for crack initiation and propagation [4, 12, 14].

Cubic transition-metal nitride coatings that are robust to harsh environments are needed in a broad range of applications due to their unique properties in terms of hardness, toughness, thermal stability, chemical inertness, and wear and corrosion resistance [2, 4]. Nevertheless, tribocorrosion resistance of the coatings are highly desired for seawater lubrication and durability by the control of surface integrity and interface structure. It is found that cubic CrN coatings deposited on stainless steels using plasma immersion ion implantation showed the enhanced wear and corrosion resistance [5]. However, micro-cracks induced by friction resulted in multi-degradation of the coatings with a typical columnar growth structure, such as intersecting cracks and layer delamination. That is due to micro-cracks acted as the diffusion channels for Cl^{-1} ions. Hence, the refinement or elimination of columnar structure are expected to enhance corrosion and tribocorrosion resistance by the formation of nanocomposite or multilayer structure [10, 11]. A lot of work has been done for the refined CrSiN [21] or TiSiN [9, 22] based nanocomposite and multilayer structure (CrN/TiN [23], CrN/NbN [24], etc.) by the addition of Si and the formation of coherent interfaces. Although tribocorrosion resistance is significantly improved in 3.5 wt% NaCl aqueous solution in terms of low friction coefficient of 0.1–0.2 and smooth wear tracks [4, 6], it is still far from the requirements of seawater lubrication with friction coefficient below 0.125[25]. Thus, seawater lubrication would be the only way to achieve durable performance in harsh environments.

Another strategy for the enhanced tribocorrosion and seawater lubrication is the addition of C into cubic transition-metal nitride coatings, in which self-lubricating phases and superhard yet tough properties are strongly expected [8–10]. The challenge is how to balance phase control and surface/interface structure with high performance, and then one or two phases containing C coatings are preferred. (111)-textured TiCN coatings with high hardness of about 31.6 GPa and Young's modulus of 409.7 GPa synthesised by arc ion plating exhibit limited improvement in tribocorrosion resistance in artificial seawater due to their rough columnar structure and many small size microparticles on surface [26]. Moreover, it is reviewed that TiN and TiCN based composites are a remarkable class of cermets in terms of the significant combination of hardness, toughness, elevated temperature strength and surface stability in tribology, corrosive or oxidative environments[27]. Hence, superhard yet tough coatings with C content are expected to reduce the concern of cracking through thickness for ion diffusion channels of solute. Moreover, high surface integrity and dense interface structure free of voids, pores and micro-cracks, etc., are highly beneficial for tribocorrosion resistance and seawater lubrication [4, 9, 13]. In addition, surface wettability of the coatings has a close correlation with the formation of passive films and tribolayer. It is reported that favorable wettability of surface would result in the water-lubricated sliding contact surface to reduce friction and wear by hydrodynamic films [2]. Meanwhile, it is clearly observed that the sharp decrease of friction coefficient and wear rate are obtained when CrN/TiN superlattice coatings against Si_3N_4 counterpart balls and TiCN coatings against SUS440C steel counterpart balls sustain tribocorrosion in artificial seawater due to promising water lubrication on sliding contact surface [6, 14]. Complex

interactions between contact slider and coating surface in tribocorrosion process lead to complex tribocorrosion mechanism due to the transient evolution of passive films, tribolayer and hydrodynamic films [28, 29]. Therefore, it is very necessary to investigate tribocorrosion behaviors of superhard yet tough coatings to explore the related mechanisms.

Hence, in this work, Ti-C-N coatings were deposited using high power impulse magnetron sputtering by sputtering pure Ti target at various target power and substrate bias in the mixture gases of acetylene, argon and nitrogen. Tribocorrosion behaviors of the coatings were investigated in details to explore the related mechanisms of seawater lubrication of superhard yet tough Ti-C-N coatings.

2. Experimental Details

2.1 Depositions of Ti-C-N coatings

Ti-C-N coatings were deposited using high power impulse magnetron sputtering (HiPIMS) by sputtering pure Ti target with the purity of 99.95% at various target power from 4 to 8 kW and negative substrate bias from -60 to -200 V in the mixture gases of acetylene, argon and nitrogen. Rectangular Ti target (449 mm×75 mm×6 mm) are installed in cylindrical chamber (Φ760 mm×700 mm) structured with closed field unbalanced magnetron sputtering system. The schematic diagram of deposition system can be found elsewhere 9. HiPIMS pulse shapes of target current and voltage for the coatings are shown in Fig.1 a. Bright-finished AISI 316L stainless steel and Si(100) coupons (20 mm×20 mm ×3 mm) were used as substrates for coating depositions. All the substrates were ultrasonically cleaned in acetone and anhydrous alcohol solutions in turn to carefully remove dirty on their surface, and then they were dried in nitrogen gas flow. In final, they were fixed on substrate holder to keep the distance at 120 mm away from target surface. Base pressure in the chamber was pumped to the pressure of below 1×10^{-3} Pa. At first, the substrates are precleaned for 20 min using Ar gas ion source at 2 kW, 150 kHz and pulse-on time 26 μ s (Pinnacle Plus, Advance Energy). The gas flow rate and negative substrate bias were set at 120 sccm and -200 V, respectively. About 8 mm thick Ti-C-N coatings with a 200 nm TiN adhesion layer were deposited by various HiPIMS power (Huettinger, Highpulse 4001 G2) from 4 to 8 kW and various negative substrate bias (Huettinger, Truplasma bias DC 4020 G2) from -60 to -200V.

2.2 Structure and residual stress

Phase composition and crystal structure of Ti-C-N coatings deposited by HiPIMS at various target power and negative substrate bias were detected using X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical). Microstructure of the coatings were investigated using field emission scanning electron microscopy (FESEM, S-4800, HITACHI) and transmission electron microscopy (TEM, Philips/FEI CM200). Surface morphology and feature of the coatings were studied using atomic force microscope (AFM, Tosca 400, Anton Paar). Residual stress in Ti-C-N coatings on Si substrates were measured by Stoney equation as follow [30,31]:

$$\sigma = \frac{1}{6} \frac{E_s t_s}{(1 - \nu_s) t} \left(\frac{1}{R_n} - \frac{1}{R_0} \right) \quad (1)$$

where E_s , ν_s , t , t_s , R_0 and R_n are Young's modulus, Poisson ratio, Si substrate thickness, coating thickness, curvature radii of Si substrate and coatings, respectively.

2.3 Mechanical properties, adhesion and wettability

Hardness (H) and effective Young's modulus (E^*) of Ti-C-N coatings deposited by HiPIMS at various target power and negative substrate bias were determined using a nanoindenter (Nanotest system, NanoTest, Micro Materials) equipped with a Berkovich diamond indenter. The indentation depth below 10% of the coating thickness was set to reduce the substrate effect. In addition, in our case, 16 points were detected to calculate mean hardness and effective Young's modulus. Young's modulus was calculated using the formula of $E^* = E/(1 - \nu^2)$. The H/E^* and H^3/E^{*2} ratios were calculated. The adhesion of TiCN coating between substrates was studied by Rockwell C indentation test (HRC) equipped with a 200 μm radius HRC indenter under a standard load of 150 kg. HRC adhesion level of coatings/substrates was determined according to FESEM images of Rockwell C indentations according to VDI guidelines 3198, (1991) [4,32].

Fracture toughness K_{IC} of Ti-C-N coatings were determined using the length of radial cracks of Vickers indentations made by microhardness tester (MMT-X, Matsuzawa) under the applied load of 0.1 N [33]. Based on our previous work about the characterization of K_{IC} [14], the enhanced fracture toughness of the coatings were obtained without radial cracks of Vickers indentations. As reported in previous literatures, HRC indentation is a far more effective approach to characterize the adhesion of hard coatings deposited on soft substrate due to the clear observation of the severe deformation of the coatings along with that of substrate. The gas-liquid-solid interfaces will form when the droplets of distilled water are deposited on the coating surface. The wettability of coating surface was detected by contact angles, which is measured using the static drop micro-observation on a contact angle analyzer (Data Physics OCA20) with a water droplet of volume 4 μL at ambient temperature. The mean value of contact angle was calculated at least three different positions on coating surface. Fig.3g shows the schematic diagram of the calculated contact angles based on the classical Young's equation as follows [34]:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (2)$$

Where solid-gas, solid-liquid and liquid-gas interfacial tensions are represented by γ_{sv} , γ_{sl} and γ_{lv} respectively. Liquid-gas interfacial tension is always considered as surface tension.

2.4 Tribocorrosion performance

Tribocorrosion performance of Ti-C-N coatings deposited using HiPIMS at various target power and negative substrate bias in 3.5wt.% NaCl aqueous solution was evaluated by a liner reciprocating tribometer integrated with a three-electrode cell configuration (MFT-EC4000, HUAHUI) against Si_3N_4 counterpart balls (Φ 6 mm) at a sliding time of 60 min. More detailed information about tribocorrosion equipment and schematic diagram can be found in Ref. [4]. The reciprocating length, frequency and normal load were 5 mm, 1 Hz and of 5 N, respectively. In the process of tribocorrosion tests, in-situ electrochemical response was investigated in terms of the change of open circuit potential (OCP) and coefficient of friction as a function of sliding time to explore the evolution of passive films. Surface morphology of wear tracks was observed by optical microscope to study tribocorrosion mechanisms. And then, Taylor Hobson surface profilometer was used to measure wear track profile to calculate specific tribocorrosion rate of worn samples.

3. Results And Discussion

3.1 Depositions, chemical composition and structure

Ti-C-N coatings with the thickness of about 8 nm were deposited by HiPIMS at various target power from 4 to 8 kW and negative substrate bias from -60 to -200 V in closed field unbalanced magnetron sputtering system in the mixture gas of acetylene, argon and nitrogen. The typical HiPIMS pulses are shown in Fig.1a. At constant width of micro-pulse, the increased HiPIMS power indicates the increased number of micro-pulse, i.e., the frequency was increased. Thus, the increased unit of power density produce much more ionized target species to form high density of plasma. With an increase of negative substrate bias, the ion bombardment into substrate surface was enhanced by the increased impact energy of energetic ions in plasma. In addition, the ion bombardment has a sensitive correlation with films growth in terms of the migration of adatoms and growth of metastable phases in a nonequilibrium condition. A strong impact into surface always results in rough surface morphology along with the increased sputtering yield and residual stress [35-37]. Hence, the optimized reactive HiPIMS depositions with the appropriate target sputtering power and negative substrate bias are beneficial for high-performance coatings.

Fig.1b shows XRD patterns of Ti-C-N coatings deposited by HiPIMS at various power and substrate bias. As shown in Fig.1b, (111) and (222) peaks with broadening width overlapped by TiN and Ti-C-N phases are detected in XRD patterns of Ti-C-N coatings except the diffraction peaks labeled as "SS" from 316L stainless steel substrates and Ti adhesion layers. The diffraction peaks from TiN and Ti-C-N are hard to be completely distinguished to the same face-centered structure and similar atomic radius. In addition, the broadening width and shifting towards low angle of (111) and (222) peaks indicate significant refinement of grains. At 4 kW and -60 V, the coatings are dominated by cubic Ti-C-N phase even at a lower density of Ti plasma due to a wide range of chemical composition of $\text{TiC}_x\text{N}_{1-x}$ ($0 < x < 1$) phase [38,39]. When the negative substrate bias is fixed at -60 V, the (111)-textured coatings are gradually obtained with increasing target power from 4 to 8 kW. It is noted that the coatings deposited at 4 kW and -60 V show random orientations of (111) and (220). According to our previous researches, the disappearance of the preferred orientation is attributed to the formation of ultrafine grains [40,41].

Fig.1c-e presents TEM images of cross-sectional morphologies of Ti-C-N coatings deposited by HiPIMS at 5 kW and -60 V. As shown in Fig.1c, Ti-C-N coatings are composed of Ti adhesion layer, TiN transition layer and Ti-C-N coatings. Both Ti and TiN layer possess dense columnar structure, but Ti-C-N coatings have a highly dense and discontinuous nano-columnar. Moreover, there are also highly dense interfaces, so that no obvious interfaces between layers are observed. Hence, according to structure zone diagram (SZD) modified by Anders [42], the fine-nanograins with preferred orientation of coatings belongs to Zone T. The inserted selected area electron diffraction (SAED) patterns reveal distinct diffraction rings assigned to (111), (200) and (220) reflections from *f.c.c* crystal structure of Ti-C-N coatings including Ti(C,N) and TiN, due to their little difference in lattice constant. These agree well with XRD results of Fig.1b.

As shown in Fig.1d, high resolution TEM image of selected red frame in Fig.1c presents dense microstructure without distinct grain boundaries. (111) and (220) reflections for TiN and Ti(C,N) are detected in selected area electron diffraction (SAED) patterns inserted in Fig.1c. Fig.1e shows uniform element distributions of Ti, C and N in the selected red frame of Fig.1c detected by EDS lateral scanning. It is clearly observed that much more Ti than N and C elements, indicating Ti is enough to react with N and C to form TiN and Ti(C,N) in TiCN coatings. Based on XRD and XPS results, it is also noted that there are no halos and less content of C than Ti and N, revealing few amorphous CN_x phase in the coatings. The increased HiPIMS target sputtering power and appropriate substrate bias are efficient to generate high ionization rate of target species and the increased metal ion bombardment [40,43]. Thus, a mass of momentum transfer between the growing film and the incoming metal ions results in the refinement of microstructure with a less coarse columnar. Hence, high surface integrity including high density, free of defects and uniformity is obtained for Ti-C-N coatings deposited by HiPIMS at appropriate conditions (5 kW and -60 V).

XPS core level spectra of Ti 2p, C 1s and N 1s were determined to analyze chemical bonding state of the elements in Ti-C-N coatings deposited by HiPIMS at 4-8 kW and -60 V, as shown in Fig.2. At 4 kW, the asymmetric Ti 2p spectrum is composed of two main peaks originated from Ti 2p_{3/2} and Ti 2p_{1/2} peaks at Binding energies (BE) of 457.1/463.1 eV, 455.9/461.8 eV and 458.4/464.4 eV (Fig.2a), indicating 3 possible species for Ti-(C,N), Ti-N and Ti=O bonds, respectively [38,40,44]. There are no Ti-C bonds detected in the coatings. Fig.2b shows a broaden peak overlapped by four peaks in C 1s spectra at 282.9 eV for C-(Ti,N), 284.5 eV for sp²C-C/C-N, 285.4 eV for sp³C-C/C-N and C-O bonds for 286.7 eV. As for N 1s spectra (Fig.2c), a main asymmetric peak with two shoulder peaks is obtained indicating N-(C, Ti) at 396.5 eV, TiN at 397.3 eV, sp²C-N at 398.4 eV and sp³C-N at 399.9 eV. Hence, it is inferred that TiCN and TiN phase in the coatings, while TiC phase is hard to form at plasma temperature conditions (lower sputtering power) due to it's a higher formation energy as compared with that for Ti(C,N) and TiN [38].

Small C-O signal results from the surface contamination. With an increase of target sputtering power, Ti-C bond appears and its intensity increases, which reveals the formation of TiC phase (Fig.2d-i). Thus, Ti-C-N coatings are mainly composed of Ti(C,N) and TiN phases, agreed with XRD results in Fig.1b. Based on XPS results above, Ti ions are easy to react with N to form TiN, while C atoms exit in the TiN crystal

structure as interstitial atoms to form Ti(C,N). The small amount of sp^2 C would react with N to form CN_x phase. The increased sputtering power produce more Ti ions to promote the formation of TiN, which would reduce the amount of sp^2 C amorphous and CN_x phases in the coatings. Therefore, Ti-C-N coatings mainly contain Ti(C,N) and TiN, as well as a small amount of CN_x phases. As is reported that Ti-C-N coatings are easy to be reactively deposited to form Ti(C,N) and TiN [44], while the amorphous CN_x phases would be generated at a higher C content conditions [38].

3.2 Surface morphologies and wettability

As is reported, surface integrity including smooth surface, highly dense microstructure, free of defects, low residual stress and high uniformity is vital for high-performance coatings [4,45]. Surface morphologies of Ti-C-N coatings deposited by HiPIMS at various target power and negative substrate bias were investigated using AFM. As shown in Fig.3a, rough surface morphologies with large package of grains and distinct gap between grain boundaries are observed for the coatings deposited at 4 kW and -60 V. Smooth surface morphology with smaller grains is formed at 5 kW and -60 V due to the increased number of energetic ions and ion bombardment leading to the migration of adatoms to promote films growth (Fig.3b). At 8 kW and -60 V, the increased ion bombardment results in the decrease of grain size, but also rough surface with craters is obtained on coating surface (Fig.3c). Meanwhile, residual stress in the coatings sharply increases from -1.3 to -4.1 GPa. When HiPIMS sputtering power was fixed at 5 kW, the evolution of surface morphology changes from dune shape to foothills feature with increasing negative substrate bias from -60 to -200 V, as shown in (Fig.3d-f). Thus, strong ion bombardment results in a rougher surface with craters and foothills. It is inferred that the appropriate energetic ions flux and ion bombardment closely related with target power and substrate bias promoted the high surface integrity and low residual stress by controlling the migration of surface adatoms. The combined improvement is attributed to the precise control of micro pulse of HiPIMS and reactive deposition conditions of the coatings [42,46].

Tribological hard coatings have been widely used in the field of marine engineering as protective coatings [47,48]. Hence, the surface and interface features have a key influence on the performance due to surface hydrophily and hydrophobicity [49]. The surface wettability reveals unique properties of gas-liquid-solid interfaces, which strongly depends on surface nanostructures and roughness attributed to the varied surface free energy [50,51]. Surface wettability is thus of interest in the field of tribocorrosion behaviors working on water solution environment. The wettability can be characterized by surface free energy using the measurement of contact angles. Thus, Fig.3g-m illustrates contact angles of droplets of distilled water on the surface of Ti-C-N coatings deposited using HiPIMS at various target power and negative substrate bias. Fig.3g presents the schematic diagram of contact angles. As shown in Fig.3h-j, the increase of target power results in the decrease of contact angle from 64.6° to 42.4° , followed by increase to 55.2° . The increased negative substrate bias results in the increased contact angle from 56.7° to 81.5° (Fig.3k-m). The evolution of surface morphology of Ti-C-N coatings is responsible for changes of contact angle. It is clearly seen from surface morphology that the variation of contact angle is induced by surface

roughness. The Ti-C-N coatings deposited at 5 kW and -60 V with smooth surface morphology exhibits good wettability with low contact angle of 42.4°.

3.3 Mechanical properties and adhesion

Fig.4 exhibits hardness (H), effective Young's modulus (E^*), H/E^* and H^3/E^{*2} ratios of Ti-C-N coatings deposited using HiPIMS at various target power and negative substrate bias. As shown in Fig.4a-d, at 4 kW and -60 V, the values of H, E^* , H/E^* and H^3/E^{*2} are 30.5 GPa, 332.4 GPa, 0.092 and 0.257, respectively. Whereafter, H and E^* gradually increase to 42.8 GPa and 437.4 GPa, respectively, with increasing target power to 8 kW. However, H/E^* and H^3/E^{*2} reach the highest value of 0.104 and 0.433 at 5 kW, respectively. Hence, when target power was fixed at 5 kW, substrate bias was increased from -60 to -200 V, H and E^* gradually increase to 44.2 GPa and 476.3 GPa, respectively. However, H/E^* and H^3/E^{*2} show a decrease to 0.093, and 0.381, respectively. In addition, the micro-indentation inserted in Fig.4b,d under the load of 0.1 N is well declared that the coatings possess excellent fracture toughness. It is clearly seen that no radial cracks of Vickers indentations were observed with increasing HiPIMS power and negative substrate bias. At 5 kW and -60 V, the coatings have smooth and smaller indentations, indicating a higher fracture toughness[12-14].

Although hardness and toughness are always considered as the contradiction because they are hard to achieve simultaneously, heterogeneous interfaces are gradually introduced into nanomaterials to enhance them both as interfacial engineering rapidly develops. Hence, hard yet tough and flexible hard multilayer or nanocomposite coatings formed by nanocrystalline, amorphous materials and their interfaces exhibit excellent friction and wear properties [5,13,40]. Moreover, superhard yet tough coatings are always expected by the precise control of chemical composition and microstructure to achieve the combined improvement of hardness and toughness¹². Thus, it is demonstrated that Ti-C-N coatings deposited at 5 kW and -60 V exhibit superhard yet tough feature. Moreover, the related mechanism of superhard yet tough is attributed to the block of dislocation motion across interfaces at boundaries between dense and refined grains, as well as the contribution of the solution strengthening of Ti(C,N) with C interstitial atoms in TiN. In addition, the fully dense composite structure with refined Ti(C,N) and TiN grains promotes the enhanced cohesion strength.

The combined improvements in hardness, toughness and cohesion/adhesion are essential for hard coatings in wear and corrosion applications. Thus, Rockwell C indentations under a standard load of 150 kg were used to determine the cohesion/adhesion between the coatings and substrates by the large deformation of the coatings along with substrates. In addition, as for superhard yet tough coatings deposited on soft substrates (316L stainless steels), the enhanced hardness and toughness also account for the improved adhesion due to their close correlations with H, H/E^* and H^3/E^{*2} . [14,43].

Fig.4e-j reveal Rockwell C indentations for the coatings Ti-C-N coatings deposited using HiPIMS at various target power and negative substrate bias. With an increase of target power from 4 to 8 kW, the adhesion shows an initial increase from HF4 to HF1, followed by a decrease to HF3. While the adhesion

level presents a gradually decrease from HF1 to HF3 with increasing substrate bias from -60 to -200 V. Besides, residual compressive stress shows an increase from -1.3 to -4.1 GPa with increasing target power and from -2.4 to -3.8 GPa with increasing substrate bias, respectively. It is noted that the coatings with high H , H/E^* and H^3/E^{*2} exhibits the reduction of cracking at the edge and inside of indentations corresponding to HF adhesion level and cohesion, respectively, due to the enhanced cracking resistance. The similar results are also reported that CrN/TiN superlattice coatings and TiAlSiN nanocomposite coatings deposited by deep oscillation magnetron sputtering, known as an alternative HiPIMS technique. The improvement in cohesion/adhesion of coatings is ascribed to the enhanced H , H/E^* and H^3/E^{*2} due to smooth surface morphology, highly dense microstructure and low residual stress.

3.4 Tribocorrosion resistance

Fig.5 presents tribocorrosion behaviors in 3.5 wt.% NaCl aqueous solution of Ti-C-N coatings deposited using HiPIMS at various target power and negative substrate bias, compared with those for hard coatings. Tribocorrosion resistance of the coatings are evaluated by instantaneous coefficient of friction (COF), in-situ response of open circuit potential (OCP) and worn surface morphologies. As shown in Fig.5a, fluctuant COF and OCP at 4 kW and -60 V are observed during tribocorrosion tests, and the average values are 0.21 and -0.036 V, respectively. That is because the coatings suffer from severe abrasive wear leading to distinct long grooves parallel to the friction direction resulted from hard wear debris polishing the sliding contact surface. Besides, low surface wettability is not useful for the decrease of wear and friction. Severe plastic deformation on worn surface is attributed to low hardness of the coatings. Noted that no macro cracks are observed on worn surface during sliding wear. Hence, the diffusion distance of Cl^{-1} in tribocorrosion is limited between sliding contact surface and sublayer. Thus, the severe polishing and plastic deformation result in micro cracks in sublayer of the coatings owing to dense microstructure and high cohesion/adhesion. The calculated specific wear rate is $3.52 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$.

When the target power is increased to 5 kW, a sharp decrease to 0.04 of COF and a slight decrease to -0.055 V of OCP are obtained, as shown in Fig.5b. At the beginning of 10 min, OCP is higher -0.05 V due to the formation of passive films. And then, the OCP gradually decrease and achieve the stable value of about -0.055 V during sliding wear, revealing durable passive films formed on contact surface. The worn surface presents smooth and clean morphologies along with shallow grooves, indicating a mild abrasive wear. The calculated specific wear rate is $1.3 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$.

Superhard yet tough Ti-C-N coatings exhibit high resistance of elastic and plastic deformation to reduce the formation of micro cracks and polishing. In addition, superhard yet tough coatings with the high cohesion/adhesion possess high cooperative deformability to reduce cracking and adhesion failure, which build a strong barrier for Cl ions diffusion to accelerate tribocorrosion failure, due to high surface integrity. Moreover, the high surface wettability promotes the uniform water films and passive films formed at sliding contact surface to reduce the friction and wear. As we reported in our previous works, the enhanced surface integrity and interface structure contribute for the combined improvement of

hardness and toughness, leading to high wear, corrosion and tribocorrosion resistance [4,14,26]. At 8 kW, although COF is still about 0.05, it appears a quite unstable tendency. In addition, oscillating changes in corrosion potential is detected, and the average value is about -0.23 V (Fig.5c). The calculated specific wear rate is $3.34 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. With an increase in substrate bias from -60 to -200 V (Fig.5d-f), the COF and OCP exhibits a sharp fluctuation and increases to 0.34 and -0.05 V due to severe abrasive wear resulting in cracking and adhesive failure during tribocorrosion tests. The calculated specific wear rate increases from 0.29 to $6.87 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. Meanwhile, the deterioration of Ti-C-N coatings would be accelerated owing to high residual stress and surface defects caused by ion bombardment with increasing substrate bias. Fig.5i summarized that hardness against coefficient of friction in seawater for typical metal and ceramic coatings. It is clearly seen that COF of ceramic coatings presents an increase with increasing hardness. For traditional lubricating materials, DLC based coatings exhibit good tribocorrosion resistance with low coefficient of friction of 0.036 due to the combination of hardness and toughness [52,53]. However, in this work, superhard yet tough Ti-C-N coatings possess excellent seawater lubrication with ultra-low COF of 0.03.

4. Conclusion

In conclusion, we have demonstrated that superhard yet tough Ti-C-N coatings with Ti(C,N), $\text{sp}^2\text{-C}$, CN_x and TiN were deposited by high power impulse magnetron sputtering by the precise control of target power and reactive gas flow rate. Superhard yet tough Ti-C-N coatings exhibits the enhanced water-lubricating performance in 3.5wt.% NaCl aqueous solution with extremely low coefficient of friction of 0.03 and stable open circuit potential of -0.05 V. The enhanced surface wettability and the resistance of crack initiation and propagation and adhesion failure contribute for the increased tribocorrosion properties.

Declarations

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Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Deposition and structure of Ti-C-N coatings deposited by high power impulse magnetron sputtering. a HiPIMS pulse shape. b XRD patterns. c, bright field TEM images with selected area electron diffraction inserted. d, HRTEM image. e, EDS analysis of red frame in c.

Figure 2

Deposition and structure of Ti-C-N coatings deposited by high power impulse magnetron sputtering. a HiPIMS pulse shape. b XRD patterns. c, bright field TEM images with selected area electron diffraction inserted. d, HRTEM image. e, EDS analysis of red frame in c.

Figure 3

Surface morphologies and surface wettability of Ti-C-N coatings deposited by HiPIMS at various target power and substrate bias. a-c AFM image at 4-8 kW and -60 V. d-f AFM image at 5 kW and -60 V. g Contact angle measurement formula. h-j Contact angles at 4-8 kW and -60 V. k-m Contact angles at 5 kW and -60 V.

Figure 4

Mechanical properties and adhesion of Ti-C-N coatings deposited by HiPIMS at various target power and substrate bias. a Hardness (H) and effective Young's modulus (E^*) at 4-8 kW and -60 V. b H and E^* at 5 kW and -60- 200 V. c H/E^* and H^3/E^{*2} at 4-8 kW and -60 V. d H/E^* and H^3/E^{*2} at 5 kW and -60- -200 V. e loading-unloading curve at 5 kW and -60 V. f HRC adhesion.

Figure 5

Tribocorrosion behaviors in 3.5 wt.% NaCl aqueous solution of Ti-C-N coatings deposited using HiPIMS at various target power and substrate bias. a-f, Coefficient of friction and open circuit potential with the inserted worn surface; g, Hardness against coefficient of friction in seawater for typical coating materials.