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Tribocorrosion behaviors of PVD CrN coated stainless steel in seawater

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ABSTRACT

The tribocorrosion behavior of type 316L stainless steel and CrN coated 316L by PVD was investigated in seawater environment. Tests were carried out in a triboelectrochemical cell using a ball-on-plate tribometer integrated with a potentiostat for electrochemical control. Sliding contact against silicon nitride balls had a significant effect on the open circuit potential (OCP) and corrosion potential (E_{corr}) for 316L. However, the OCP for the CrN coating remained relatively stable during the sliding. Tribocorrosion tests performed under various applied potentials demonstrated that the friction coefficient decreased and wear-loss increased as the applied potential increased from −1 V to 0 V. Under cathodic potential of −1 V, abrasive wear form of mechanical wear dominated the wear of 316L stainless steel. As the potential increases, the general corrosion was observed and tribo-corrosive contributions to the wear increased. Plastic deformation dominated the wear process of CrN coating under a cathodic potential. With an increase in potential, the mechanical wear contribution decreased and corrosion-accelerated wear contribution increased. At high anodic potential (0.5 V), pitting corrosion occurred in the wear track and on the outer part of wear track on 316L and CrN coated 316L.

1. Introduction

With the ever-increasing exploitation of ocean resources, marine equipment should be improved to meet the growing demands, with respect to faster operation, higher environmental friendliness and longer continuous service life without maintenance. Some key frictional components of marine equipment, such as pump, hydraulic system, cylinder piston, bearing, shaft and propeller, directly operate in seawater [1]. However, tribocorrosion, the joint action of wear and corrosion, will subject these components to premature failure in seawater, leading to increased annual maintenance costs, high safety risk and even environmental pollution. Thus, it is imperative to improve the tribocorrosion performances of these components in seawater. A potential resolution is to apply PVD coatings, which have good lubrication and protection in seawater [2,3].

Our previous works prove the good tribological performance of high-hardness PVD coatings in seawater [4–7]. PVD CrN coatings are widely applied as protective layers for various tools in the industry due to high hardness, wear resistance, corrosive resistance and adhesive resistance [8–10]. CrN coating can improve the wear resistance of both 316 stainless steel and AISI H13 when sliding in air [11]. PVD CrN coating outperforms hard chrome plating under reciprocating sliding in oil lubricating environment [12]. CrN coatings can enhance the tribological performance of 2024Al alloy in water [13]. The PVD CrN coatings with various thickness can enhance the corrosion resistance at both anodic and cathodic conditions, compared with uncoated Al-5083 alloys in acid media [14]. CrN coating can also improve the corrosion resistance of AISI 304 in 3.5 wt% NaCl electrolytic solution [15] and erosion-corrosion resistance in slurries [16]. The synergetic effects of corrosion and wear grew with increase in potential for types 440B and 304 stainless steel and become the key damage mechanism under oxidizing conditions in 0.01 M NaCl solution [17]. PVD multilayer CrN/NbN coating on WC–12Co are superior with very low corrosion rates and the lowest tribocorrosion rate in 3.5% NaCl solution, compared with WC–12Co and Cr_3C_2–37WC–18Me coatings [18].

However, the fundamental understanding about the tribocorrosion of various materials in seawater is still limited [19,20]. Generally, the material loss due to tribocorrosion is often larger than the sum of material losses from wear and corrosion separately. This difference can be attributed to the synergic effect of wear and corrosion. In this work, the tribocorrosion behaviors of two typical materials, the 316L (as passive metal) and CrN coating (as ceramic coating), were investigated in seawater. The tribocorrosion behaviors under varying applied potentials were experimentally

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compared. The effects of the applied potentials on tribocorrosion performance in seawater were discussed in details.

2. Experimental

2.1. Coating deposition

After treatment in an ultrasonic bath in acetone and ethanol, the 316L stainless steel samples ($30 \times 20 \times 2\ mm^3$) were mounted on the turntable in the vacuum chamber of a multi-arc ion plating system (Hauzer Flexicoat 850). Yield strength of the 316L sample is about 245 MPa, tensile strength is about 485 MPa and hardness is about 2.5 GPa. Prior to coating deposition, the chamber was pumped down to a base pressure below 4×10^{-5} mbar and then heated to 400 °C. To remove contamination from the substrate, we cleaned the samples by Ar^+ ion bombardment sequentially with substrate negative bias voltage of 900, 1100 and 1200 V for 2 min. The CrN coating was deposited in 99.95% N_2 atmosphere. The deposition proceeded at a table rotation speed of 3 rpm and with three chromium targets (purity > 99.5 wt%, ⌀$63 \times 32\ mm^2$). The CrN coating was fabricated under negative bias voltage of 50 V, target current of 65 A, and gas pressure of 4 Pa. The deposition proceeded at 400 °C constantly for 4 h. Hardness of the CrN coating is about 23 GPa according to our previous study [21].

2.2. Characterization

The phase structures were investigated by an X-ray diffractometer (Bruker D8) using Cu Kα radiation ($\lambda = 0.1541$ nm), operated at 40 kV and 40 mA. The scanning angle ranged from 20° to 90° at a speed of 4°/min with step size 0.02°. The cross-section images and wear track morphologies of the coatings were observed by a field emission scanning electron microscope (Hitachi S4800).

2.3. Tribocorrosion tests

Before the tests, the samples were polished with abrasive paper (#7000) down to roughness (*Ra*) of 0.05 μm, and then ultrasonically cleaned in distilled water for 10 min. Artificial seawater (chemical composition listed in Table 1), used as the electrolyte, was prepared according to Standard ASTM D 1141-98. Tribocorrosion tests were carried out in a ball-on plate tribometer (RETC MFT5000) with a three-electrode system. Saturated calomel electrode (SCE) was used as the reference electrode, Pt electrode was used as the counter electrode, and Samples (316L or CrN coated 316L) was used as the working electrode in the tests. The CrN coating is semi-conductive. Before each test, the samples were immersed in seawater for 1 h to stabilize the open circuit potential. Then the samples were mounted with an exposed area of 3 cm^2 in a cell containing the electrolyte (Fig. 1). The cell was installed in the tribometer. The samples in a ball-on-disk reciprocating mode were sliding against Si_3N_4 balls at room temperature of 20 ± 5 °C. The 6-mm-diameter Si_3N_4 balls were used as the counterparts due to high hardness, high corrosion resistance and low electroconductibility in seawater. The test conditions were: stroke frequency of 2 Hz, constant normal load of 10 N, sliding stroke 5 mm and total sliding time of 3600 s. Hertzian contact pressure of 316L and CrN coating coupled with Si_3N_4 ball are about 1484 MPa and 1769 MPa, respectively. The coefficient of friction (COF) was recorded in situ.

To illustrate the tribocorrosion behaviors of 316L and the CrN coating, we conducted the following tests: (1) The OCP of each sample with and without sliding contact was measured continuously; (2) potentiodynamic tests during sliding with and without contact at a sweep rate of 1 mV/s were measured; (3) in wear tests under constant potentials, the current destiny was continuously recorded. The area of the wear track depth profile can be detected by an Alpha-Step IQ profilometer. The wear-loss (V) in the wear track is calculated as area × sliding distance.

3. Results and discussion

3.1. Coating microstructure

The fractured cross-section image shows the CrN coating is dense, compacted and about 5.5 μm thick, without obvious columnar crystal feature (Fig. 2a). Its surface morphology shows that many irregularly-shaped microparticles are distributed dispersedly on and protruding out of the coating surfaces, resulting in rough surfaces (Fig. 2b). Microparticles, which result from the droplets emitted from the arc spots of the targets, are typical of multi-arc plating coatings [22].

Fig. 3 shows the X-ray diffraction patterns of the CrN coating deposited on 316L. Strong peaks appear at 37.6°, 43.7° and 75.6°, which correspond to CrN(111), CrN(200) and CrN (311), respectively. Since no obvious peak related to Cr or Cr_2N orientation appears, it can be concluded that the coating mainly contains the CrN phase [23].

3.2. Effects of sliding contact on corrosion response

Fig. 4 shows the continuous evolutions of OCP before and during the sliding, as well as COFs of 316L and CrN coated 316L. The OCP of 316L is relatively steady before sliding, but during sliding, it gradually decreases with time, which can be attributed to the destruction of the passive layer and the increase of contact area exposed to the electrolyte [24,25]. It is known that OCP is related to the electrochemical state of a material in the solution: OCP is normally high in a passivated material, but would decrease if the passive layer is destroyed. When the sliding process has done, the potential increases sharply due to the repassivation on the wear track. As for the CrN coating, its OCP slightly decreases during sliding. The increase of OCP after sliding, which is due to the repassivation of the wear track, is also not distinct. That is, CrN has high corrosion resistance as the passive layer (mainly Cr_2O_3) [26]. As shown in Fig. 4, the COF of the CrN coating also decreases compared with 316L.

Potentiodynamic polarization curves of 316L and CrN coated 316L specimen under sliding condition with and without contact are shown in Fig. 5. The polarization curves of 316L show obvious difference between samples with and without sliding contact. Under sliding contact, 316L has lower corrosion potential and much higher anodic current density. As for the CrN coating, there are no large differences in either corrosion potential or anodic current density between samples with and without sliding

Table 1
Chemical composition of artificial seawater.

Constituent	NaCl	Na_2SO_4	$MgCl_2$	$CaCl_2$	$SrCl_2$	KCl	$NaHCO_3$	KBr	H_3BO_3	NaF
Concentration (g/L)	24.53	4.09	5.20	1.16	0.025	0.695	0.201	0.101	0.027	0.003