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Electrochemical and tribological properties of CrBCN coatings with various B concentrations in artificial seawater

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ABSTRACT

CrBCN coatings with various B concentrations were deposited by using a closed field unbalanced magnetron sputtering system. Their electrochemical and tribological properties in artificial seawater were performed using a conventional three electrode cell and the ball-on-disk tribometer, respectively. The results showed that the CrBCN coatings' corrosion resistance increased continually when the CrB_2 target current increased. Furthermore, the CrBCN coatings exhibited better tribological properties than the CrCN coatings. The lowest friction coefficient (0.15) and the lowest wear rate (1.8×10^{-7} mm^3/Nm) were obtained simultaneously.

1. Introduction

Marine equipments are widely used for the exploration of sea resources, and oil lubrication systems were extensively adopted in the mechanical transmission equipments due to the great lubrication performances under various working environments [1]. However, during the operation of the marine equipments, the leakage of lubricative oil would seriously pollute natural environment and be harmful to the marine organisms. One promising method to deal with this problem effectively was to deposit hard coatings with great good friction and wear properties in seawater [2–4]. As is known, the transmission and seal components of marine equipments (such as valves, bearings, shafts and hydraulic system) would face a complex working condition including wear and Cl^- ion corrosion [5]. Thus, the electrochemical and tribological properties of hard coatings in seawater were crucial to guarantee the service life and working reliability of these marine equipments.

TiN-based coatings have already been widely employed in industrial applications to enhance the performance of cutting tools and dies due to the inherent excellent performance of anti-wear and anti-corrosion properties [6–8]. As compared with TiN-based coatings, CrN-based coatings have displayed better mechanical and physicochemical performances such as high hardness, great chemical inertness, oxidation resistance and tribological properties [9–11]. It was reported that CrN coatings exhibited better electrochemical properties in simulated body fluid than TiN, TiCN and a-C:N coatings due to the positive effect of Cr_2O_3 particles in the CrN coatings [12]. However, with the rapid growth of advanced industry, hard coatings with further improved performances are required. Now, there are mainly two methods to further enhance the performance of coating, the first method is to deposit coatings with interlayer design or multilayer structure design [13–15]. Wang et al. [16] investigated a series of graphite-like carbon (GLC) coatings with Cr interlayer, Ti interlayer and Cr/C gradient layer respectively and pointed out that the interlayer design could effectively improve the adhesion strength and load-bearing capacity by the nano-interlocked structure. Shan et al. [17] compared the tribological and electrochemical properties of CrN coatings and Cr/CrN multilayer coatings in seawater and indicated that multilayer coating design could enhance the wear and corrosion resistance of coatings in seawater due to less cracks and other defects as well as the limitation for the propagation of cracks. The second method is to dope metallic (Ti, Al and Mo) or nonmetallic (B, C and Si) elements into transition metal nitride coatings [18–21]. It was reported that the addition of C elements into CrN coatings could increase the volume fraction of graphite phases in coatings, which was thought to play a role in improving the tribological properties of coatings [22–24]. Hu. et al. [25] reported that the formed sp^2C—C bonds could reduce the friction coefficient and the wear rate of coatings when the CrCN coatings slid against GCr15 balls in air. The friction tests of CrCN coatings were also conducted in water environment and the results also showed that CrCN coatings had better tribological properties than CrN coatings [26]. Wang et al. [27] investigated the anti-corrosion properties of CrCN coatings in simulated body fluid and indicated that the CrCN coatings with 15.4 at.% C presented the best corrosion resistance due to the large amount of a-

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CN_x phases. Furthermore, according to Refs. [28–30], the introduction of B elements into CrN-based coatings has been also widely investigated. The CrBN coatings presented nanocomposite structure. Due to the finer grain size and the increased resistance to the grain boundary sliding, the mechanical properties of CrBN coatings increased effectively. It was also reported that the tribological properties of CrN and TiN coatings in water environment were improved by doping B elements, which was attributed to the lubrication effect of boric acid (H_3BO_3) film with layered structure similar to graphite [31,32]. The increasing demand for coatings with further improved mechanical, tribological and electrochemical properties has led to the research for quaternary or even more complex coatings. The works related to TiBCN coatings have already been widely carried out, while few works have been done for the CrBCN coatings. Our group [33] has first investigated the effect of B element on the microstructure and tribological properties of CrBCN coatings in tap water environment, and pointed out that introduced B element could improve the mechanical and tribological properties of CrCN coatings. However, up to now, no report about the electrochemical and tribological properties of Cr-B-C-N coatings in seawater has been published.

In here, the CrBCN coatings with different B concentrations were deposited using closed field unbalanced magnetron sputtering system, and their electrochemical and the tribological properties of CrBCN coatings in artificial seawater were investigated, respectively.

2. Experimental details

As read in Ref. [33], CrBCN coatings were prepared on 316L stainless steel disks (Φ30 mm × 4 mm) and Si(100) wafers using closed field unbalanced magnetron sputtering system (UDP-650, Teer Coatings Limited). According to the CrB_2 target current of 0–4 A, the CrBCN coatings were signed as CrCN, CrBCN1, CrBCN2, CrBCN3 and CrBCN4. The electrochemical properties of CrBCN coatings were analyzed using a conventional three electrode cell (CHI660E), which consisted of saturated Ag/AgCl reference electrode, working electrodes (test specimens) and platinum wire auxiliary electrode. At first, the specimen with bare area of $1 \times 1\ cm^2$ and a copper wire were connected and sealed with 704 silicon rubber. Then, the open circuit potential test was started when once the specimen was immersed in artificial seawater, and the test time was 1 h. Subsequently, the electrochemical impendence spectroscopy (EIS) tests were performed at the steady OCP value. During the EIS testing, the AC excitation was fixed at 10 mV, and the frequency was varied from 1 mHz to 100 kHz. Finally, the anodic polarization measurement was done as the voltage varied from −1 V to 1 V at the scanning rate of 20 mV/min. The all experiments were tested at room temperature. The EIS data were further fitted with ZsimpWin software. The corrosion current (j_{corr}) and potential (E_{corr}) could be deduced from the Tafel plot. The polarization resistance (R_p) of each coating could be calculated using Ster-Geary equation:

$$j_{corr} = \frac{\beta_a \beta_c}{2.303 R_p (\beta_a + \beta_c)} \tag{1}$$

where β_a was the Tafel anodic slope and β_c was the Tafel cathodic slope. The artificial seawater was prepared according to the American National Standard (D 1141–98), and the chemical composition of artificial seawater was illustrated in Table 1. The friction tests of CrBCN coatings sliding against SiC balls (Φ = 8 mm) in artificial seawater were performed using ball-on-disk tribometer, and their tribological parameters and measurement methods had been described in Ref. [33].

3. Results and discussion

3.1. Electrochemical properties of CrBCN coatings in artificial seawater

Fig. 1 illustrates the OCP curves of CrBCN coatings in artificial seawater. It was clear that the CrBCN coatings displayed higher OCP values than CrCN coatings. This meant that all CrBCN coatings had better corrosion resistance than CrCN coatings. Moreover, the CrBCN coatings deposited at higher CrB_2 target current possessed higher open circuit potential. This indicated that the corrosion resistance of CrBCN coatings was enhanced when the CrB_2 target current increased. Fig. 2 represents Nyquist plots, Bode plots and equivalent circuit model of CrBCN coatings in artificial seawater. As seen in Fig. 2a, all the Nyquist plots showed incomplete capacitive resistance arcs with two time constants, which consisted of a capacitive resistance arc with smaller diameter and a loop with higher diameter. Therefore, the EIS results indicated two interfacial reactions occurred in the coating/solution interface and substrate/coating interface. It was obvious that CrCN and CrBCN1 coatings showed similar diameter, but CrBCN2, CrBCN3 and CrBCN4 coatings showed a relatively bigger diameter. As seen in Fig. 2b, CrCN, CrBCN3 and CrBCN4 coatings showed similar frequency range at low frequency domain (10^{-3}–10^{-1} Hz) and high frequency domain (10^1–10^3 Hz) with the phase angle beyond 70°, while CrBCN1 coatings only showed a broad range at high frequency domain (10^1–10^4 Hz) with the phase angle higher than 70°. In contrast, CrBCN2 coatings showed the widest frequency range (10^{-3}-10^3 Hz) with the phase angle beyond 70°. This indicated that CrBCN2 coatings could provide more protection in comparison to other four coatings. Fig. 2c shows the equivalent circuit model for the CrBCN coatings in artificial seawater. As seen in Fig. 2c, the equivalent circuit contained electrolyte resistance (R_s), pore resistance (R_{po}), charge transfer resistance (R_{ct}) and double layer resistance (CPE_{dl}). Here, R_s was related to the ohmic contribution of electrolyte between the reference electrode and working electrode. R_{po} was related to the coatings' block effects and which could hinder the electrolyte reaction. R_{ct} was originated from the double charge layer formed at the substrate/electrolyte interface. And CPE_{do} and CRE_{dl} are corresponded to the coatings' capacitance and double-layer capacitance, respectively. Besides, the

Table 1
Chemical composition of artificial seawater based on D 1141-98.

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

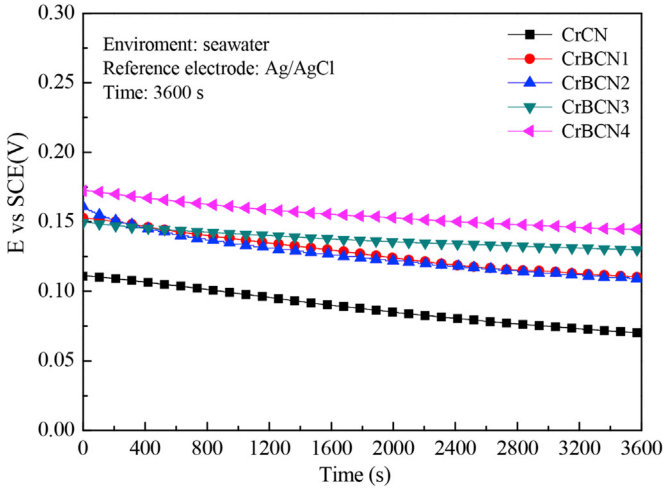

Fig. 1. OCP curves of CrBCN coatings in artificial seawater.