Structure and tribocorrosion behavior of CrMoSiCN nanocomposite coating with low C content in artificial seawater

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Abstract: CrMoSiCN nanocomposite coatings with a low C content were prepared on Ti-6Al-4V using an unbalanced magnetron sputtering system, and their corresponding microstructures, mechanical properties, and tribocorrosion performance were evaluated in detail. The results revealed that the CrMoSiCN coating had a compact nanocomposite microstructure consisting of CrN and Mo₂N nanocrystallites, (Cr, Mo)N solid solution, and Si-C-N amorphous phases. Moreover, the coating exhibited superior mechanical properties with a hardness of 28.6 GPa and an elastic modulus of 273 GPa, owing to the solid solution strengthening effect. The tribocorrosion test results showed that the dominant failure of the Ti-6Al-4V alloy was caused by the corrosion contribution to wear behaviors (synergistic effect). The CrMoSiCN nanocomposite coating could effectively alleviate the material loss caused by the synergistic effect of corrosion and wear behaviors, leading to pure wear behaviors during the entire tribocorrosion process. The corresponding tribocorrosion mechanisms under the open circuit potential and dynamic polarization conditions were discussed in terms of their tribocorrosion behaviors.

Keywords: CrMoSiCN coating; microstructure; mechanical properties; tribocorrosion; seawater

1 Introduction

With the rapid pace of marine resource exploration, the requirements for the quality of marine equipment are becoming more stringent. Currently, the most challenging limitation of marine equipment is that its metal components experience friction, wear, and erosion simultaneously in a strongly corrosive marine environment, which leads to the premature failure of these components. The service life and reliability of marine equipment primarily depend on the wear and corrosion performance of the components in seawater [1, 2]. Thus, the ideal solution is to protect the component surface using hard coatings with favorable

wear-resistant and anti-corrosion properties [3].

Among hard coatings, CrN-based coatings have attracted the most attention over the past decades [4–10]. However, there are two points that limit the development of CrN-based coatings: the first is that a single-component coating can no longer meet practical requirements, and the second point is that the traditional test methods cannot simulate real working conditions. For the first point, our previous research showed that the tribological performance of a CrN coating could be enhanced by doping it with C content [11]. However, Kong et al. [12] reported that excessive C content forms an amorphous phase in CrN coating, which results in a loose and porous

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Nomenclature

T	Total material loss volume	ΔT	Volume loss caused by synergistic effect
W	Volume loss caused by pure wear behaviors	i	Average current
C_o	Volume loss caused by pure corrosion behaviors	t	Total test time in tribocorrosion test
W_c	Volume loss caused by corrosion contribution to wear	M	Relative molecular mass
C_w	Volume loss caused by wear contribution to corrosion	n	Charge transfer number
ΔW	Volume loss caused by total wear behaviors	ρ	Material density
ΔC	Volume loss caused by total corrosion behaviors	i_{corr}	Current density
		E_{corr}	Corrosion potential
		F	Faraday constant (96,485.3 C/mol)

microstructure. In addition, Lu et al. [13] reported that Si doped into a CrN coating could refine the grain and change the grain structure from triangle to circle, thereby improving its mechanical properties and tribological performance. These studies indicate that CrN-based coatings have been developed from single-compound to multi-compound. Based on this development trend, we further studied the influence of C and Si co-doping on the mechanical and tribological properties of CrN coatings, and determined that nc-Cr(C,N)/(a-Si₃N₄, a-C(a-CN_x)) nanocomposite structures were formed in CrSiCN coatings, which exhibited comprehensive properties compared with those of ternary (CrCN) coatings [14]. Similarly, the Cr–Al–Si–N coatings with nanocomposite microstructure exhibited better anti-wear and anti-corrosion properties than Cr–Al–N and Cr–Si–N coatings [15–17]. Recently, many studies have focused on the effect of Mo doping on the mechanical properties and tribological performance of multi-component coatings [18–22]. These studies show that doping with Mo significantly enhances the hardness, toughness, and wear resistance of Ti–Si–C coatings [18]. This indicates that Mo is a favorable alternative doping element for multicomponent nanocomposite coatings.

For the second point, tribocorrosion damage occurred constantly for marine equipment [23]. The separate wear and corrosion tests that are typically conducted could not reflect the real working condition; thus, the material consumption caused by the joint action of wear and corrosion should be considered [24]. Currently, tribocorrosion tests that simultaneously consider the effects of friction and corrosion are being studied [25–27]. Shan et al. [27] studied the

tribocorrosion performance of CrN coatings and indicated that a high applied potential accelerated material loss caused by corrosion behavior and further sped up the material loss caused by wear behavior. In addition, the tribocorrosion performance of nanocomposite coatings has also been studied [22, 28–30]. When Mo was added to the CrSiN coating, it reduced the material loss caused by the synergistic effect of corrosion and wear, thereby greatly improving the tribocorrosion performance of the Cr–Si–N coating [22]. Wang et al. [29] identified that the tribocorrosion performance of a Ti–Si–N coating could be improved by doping with C; however, excessive doping with C content degraded the tribocorrosion performance of the Ti–SiN coating. Recently, we studied the mechanical, tribological, electrochemical, and tribocorrosion properties of CrMoSiCN nanocomposite coatings with 15.3–22 at% C content [31, 32], and indicated that the CrMoSiCN nanocomposite coating with optimum C content presented good mechanical properties and tribocorrosion performance. However, the hard coating with excessive C content (15.3–22 at%) exhibited deterioration in coating performance [11, 12].

Given this information, a series of CrMoSiCN nanocomposite coatings with low C content were deposited on a Ti–6Al–4V alloy using an unbalanced magnetron sputtering system. Subsequently, the microstructure and mechanical properties of the CrMoSiCN coating were investigated in detail as a function of the Mo content. The tribocorrosion performance of the resultant coatings was primarily studied in artificial seawater, and the corresponding tribocorrosion mechanisms are discussed in detail in terms of their tribocorrosion behaviors.

2 Experimental details

2.1 Depositions of CrMoSiCN coatings with low C content

CrMoSiCN coatings with different Mo contents were fabricated on Si (100) wafers and Ti-6Al-4V substrates (Φ 30×4 mm) using an unbalanced magnetron sputtering system (UDP-650, Teer Coatings Limited, UK). Before the coating deposition, the Ti-6Al-4V substrates were polished using an automatic polishing machine (UNIPOL-820, Sykejing, China), until the surface roughness was less than 30 nm, and then ultrasonically cleaned for 30 min in alcohol and deionized water. Subsequently, the substrates were mounted on a substrate holder, which was rotated at a constant speed of 10 rpm. Before the deposition started, the pressure of the chamber was evacuated to 4×10^{-4} Pa. The surfaces of the substrates were sputter-cleaned by Ar^+ bombardment for 30 min to eliminate the adherent contaminants. The deposition of the CrMoSiCN coating consisted of two steps: first, two Cr targets with a purity of 99.9 at% were used as the sputtering resource to deposit the Cr interlayer. The current for each Cr target was set to 4 A, and the interlayer deposition process occurred for 10 min. Second, two Cr targets and one Mo target were used as the sputtering resources, and trimethylsilane (TMS) and nitrogen (N_2) were the reactive gases. The flow rate of the TMS was adjusted to 10 sccm using an MKS (Beijing sevenstar flow co., LTD., China) mass flow meter, and the flow rate of the N_2 was controlled at 50% by an optical emission monitor (OEM, Teer Coatings Ltd., England). In particular, the C in the CrMoSiCN nanocomposite coating was only derived from the decomposition of TMS. The detailed deposition conditions of the CrMoSiCN coatings are listed in Table 1. According to the current sets of Mo targets (1, 2, and 3 A), the corresponding CrMoSiCN coatings were named S-1, S-2, and S-3, respectively.

2.2 Microstructure characterizations of CrMoSiCN coatings

The thickness, surface, and cross-sectional morphologies of the coatings were observed using a scanning electron microscope (SEM, Regulus 8100, Japan).

Table 1 Deposition conditions for CrMoSiCN coatings by magnetron sputtering system.

Process parameters	Values
Cr targets (2) current	4.0 A (for each target)
Purity of Cr target	99.99%
Mo target (1) current	1, 2, and 3 A
Purity of Mo target	99.99%
Base pressure	4×10^{-4} Pa
Working pressure	0.22 Pa
Bias voltage	−80 V
OEM setting for N_2	50%
Flow rate of TMS	10 sccm
Substrate temperature	150 °C
Rotating speed of holder	10 rpm
Flow rate of Ar	50 sccm
Deposition time	80, 70, and 60 min for S-1, S-2, and S-3

The crystal phase structure of the coating was determined using X-ray diffraction (XRD, Ultima IV, Japan) with $\text{Cu K}\alpha$ radiation with a wavelength of 0.154 nm. The XRD characterization was conducted in the scanning range of 20° – 80° at a speed of $5^\circ/\text{min}$. The configuration of the resultant coating was observed using a transmission electron microscope (TEM, TECNAI G2 S-TWIN F20, USA) operated at 200 kV; the detailed structural phase and lattice parameter of the CrMoSiCN coating were determined using high-resolution TEM (HRTEM) and selected area electron diffraction (SAED). The chemical composition and bonding structure of the CrMoSiCN coating were characterized using X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific, USA) with an $\text{Al K}\alpha$ X-ray source at a power of 164 W. The C1s peak located at 284.8 eV was used for calibration. The pass energies were set as 150 eV and 20 eV for the measurement scan and the detailed scan, respectively. Before the XPS test, the coating surface was etched by Ar^+ bombardment for 4 min to eliminate the contaminants. In addition, the XPS spectra were deconvoluted using a 20% Lorentzian and 80% Gaussian-based function on a nonlinear Shirley-type background.

2.3 Mechanical properties of CrMoSiCN coatings

The elastic modulus and hardness of the resultant

coatings were measured using a dynamic ultra-micro hardness tester (DUS-211, Japan) in load–unload mode. The indentation depth was 0.25 μm and the load speed was 2.22 mN/s. The indenter type was a triangular pyramid indenter with a tip angle of 115° and Poisson's ratio of 0.07. The indentations of each sample were tested 12 times at different areas to guarantee reliable statistics. The adherent strength of the resultant coatings was determined using a scratch tester (WS-2005, Scratch tester, China) with a cone diamond tip with a top radius of 0.2 mm. The applied load was increased from 0 to 30 N with a loading speed of 30 N/min. The total scratch distance was 3 mm, and each sample was tested 5 times to ensure accuracy.

2.4 Tribocorrosion test of CrMoSiCN coatings

The tribocorrosion test was performed using a linear reciprocating tribometer (MFT-EC4000, China) equipped with a traditional three-electrode system. The platinum wire was used as the counter electrode, the saturated Ag/AgCl electrode as the reference electrode, and the sample with a 5 cm^2 exposed area as the working electrode. The tribocorrosion performance was evaluated by grinding the resultant coatings with SiC balls in artificial seawater under open circuit potential (OCP) and dynamic polarization conditions. The electrolyte solution was artificial seawater, which was synthesized according to the ASTM 1141-98 standard; its chemical composition is shown in Table 2. The counter-body was a SiC ball with a diameter of 8 mm, hardness of 17.7 GPa, elastic modulus of 407 GPa, and a Poisson's ratio of 0.2. All tribocorrosion tests were conducted for 1 h at room temperature (24 $^\circ\text{C}$). The applied load was 3 N, the sliding speed was 0.05 m/s, and the sliding stroke was 6 mm. Before the tribocorrosion tests commenced, the samples were immersed in a solution of artificial seawater for 30 min to ensure that the sample surface reached a stable electrochemical state. For the tribocorrosion test performed under OCP conditions, the OCP value was continuously recorded for 10 min before and after the tribocorrosion test to investigate the electrochemical state of the sample surface and its passivation behaviors. The variation in the friction coefficient was recorded in real-time throughout the tribocorrosion experiment.

Table 2 Chemical composition of the artificial seawater.

Compound	Concentration (g/L)
NaF	0.3
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	2.1
H_3BO_3	2.7
KBr	10.0
KCl	69.5
NaHCO_3	20.1
NaCl	24.5
Na_2SO_4	4.1
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	555.6
CaCl_2	57.1

For the tribocorrosion test performed under dynamic polarization conditions, the scanning potential range varied from -0.9 to 0.3 V in increments of 20 mV/min. To analyze the effect of wear and corrosion on material loss during the tribocorrosion test, the pure wear test was conducted in artificial seawater at the cathodic protection potential of -0.8 V for 1 h. The applied load was 3 N, the sliding speed was 0.05 m/s, and the sliding stroke was 6 mm. The pure electrochemical polarization test was also performed in the potential range of -0.6 to 0.6 V at a scanning rate of 20 mV/min without performing a wear testing.

3 Results

3.1 Microstructure characterizations of CrMoSiCN coatings

Figure 1 shows the surface and cross-sectional SEM images of the prepared coatings. The surface morphologies of the CrMoSiCN coatings presented a similar cauliflower morphology, suggesting its columnar features. As observed in Figs. 1(a1)–1(c1), the cross-sectional images of the S-1, S-2, and S-3 coatings presented a dense columnar structure. Their cauliflower surface morphologies and columnar cross-sectional morphologies could be explained by referring to the sputtering thin film growth model proposed by Thornton [33, 34]. During the deposition process of each coating, the other operating parameters were unchanged, except for the parameter of the Mo target. For all the prepared coatings, a high Mo target current provided high-energy Mo particle bombardment, which induced a coating deposition process

dominated by the diffusion process. Consequently, the cross-sectional SEM image of the prepared coatings presented a flat column grain boundary [33]. The thicknesses of the prepared coatings were measured according to the cross-sectional SEM images of the coatings, and the results are listed in Table 3. The chemical composition of the prepared coating was determined using XPS analysis results. As observed in Table 3, the doped Mo content gradually increased as the Mo target current increased. The S-3 coating exhibited the highest Mo doping content of 10.3 at%. Moreover, the Cr and N contents presented a decreasing trend. From the energy dispersive X-ray spectroscopy (EDS) elemental mapping result in Fig. 2, each element was well distributed in the fabricated coating, proving that Mo had been uniformly doped into the coating.

Figure 3 depicts the XRD patterns of the resultant coatings. Four strong diffraction peaks located at 37.42° , 43.66° , 63.44° , and 76.14° were detected for the S-1 coating. These four peaks were correlated

to the (111), (200), (220), and (311) crystal planes of the cubic CrN phase (cell parameters of $a = b = c = 4.14$), respectively. Moreover, the Mo_2N phase with cell parameters of $a = b = c = 4.16$ (PDF No. 25-1366) had a similar cubic lattice structure to the CrN phase, and their cell parameters were too close to distinguish them in the XRD pattern. Thus, these four peaks indicate the simultaneous existence of the CrN and Mo_2N phases in the coatings. For the S-2 and S-3 coatings, the four typical diffraction peaks corresponded to the CrN and Mo_2N phases in the XRD patterns; however, compared with the S-1 coating, the (200) crystal plane for the S-2 and S-3 coatings shifted by a small angle of 0.44° and 0.5° , respectively. This shift could be ascribed to the formation of a substitutional solid solution (Cr, Mo)N [35–37], which could produce internal stress in the coating and change the inter-planar spacing. In addition, no crystal phase related to C and Si was detected, suggesting an amorphous state in the coating.

Table 3 Chemical composition, thickness, H/E , and H^3/E^2 of CrMoSiCN coatings.

Coating	Chemical composition (at%)					Thickness (μm)	H/E	H^3/E^2 (GPa)
	Cr	Mo	Si	C	N			
S-1	37.3	3.6	3.8	10.7	44.6	2.42	0.103	0.274
S-2	34.4	7.6	4.2	11.4	42.4	2.11	0.101	0.272
S-3	32.7	10.3	3.7	12.7	40.6	2.10	0.105	0.316

Fig. 1 Surface and cross-sectional SEM images of CrMoSiCN coatings. (a, a1) S-1; (b, b1) S-2; (c, c1) S-3.

Fig. 2 Elemental mapping of CrMoSiCN coating (sample No. S-3).

Fig. 3 XRD patterns of CrMoSiCN coatings.

Figure 4(a) shows the cross-sectional TEM image of the resultant coating. A Cr interlayer with a thickness of 250 nm was clearly observed between the coating and substrate, which was consistent with the SEM result. Moreover, the cross-sectional microstructure of the prepared coating was compact with no obvious defects, proving its homogeneity during the deposition. In Fig. 4(b), CrN (111), CrN (200), and Mo₂N (200) with lattice fringe spacings of 0.238, 0.206, and 0.208 nm were observed in the high-resolution TEM image. It can be observed that the CrN and Mo₂N phases were randomly distributed in the amorphous phase. Figure 4(c) shows the result of the SAED pattern with typical diffraction rings. The (111), (200), (220), and (311) crystal planes were determined in the pattern, which were in agreement with the previous XRD analysis results.

To confirm the bonding structure and amorphous phase in the coating, the Cr 2p, Mo 3d, Si 2p, C 1s, and N 1s core level XPS spectra of the S-1, S-2,

and S-3 coatings are shown in Fig. 5. As shown in Fig. 5(a), the major peaks in the Cr 2p XPS spectra were Cr–N bonds located at 574.9 and 584.1 eV [38]. The other peaks were assigned to Cr–O bonds, which could be ascribed to the presence of residual oxygen in the chamber during deposition. Interestingly, the intensity of the Mo 3d spectra increased gradually as the Mo content increased from 3.6 to 10.3 at% (Fig. 5(b)). Three valence states of Mo (Mo^{x+}, Mo⁴⁺, and Mo⁶⁺) were detected in the Mo 3d XPS spectra. The peaks of Mo^{x+} located at 228.7 and 232.2 eV corresponded to Mo–N bonds [39]. The binding energies of Mo⁴⁺ located at 229.9 and 233.2 eV, and the binding energies of Mo⁶⁺ located at 231.8 and 235.5 eV were attributed to MoO₂ and MoO₃, respectively. The Si 2p core level XPS spectra were deconvoluted into four peaks located at 395.2, 396.9, 397.3, and 398.9 eV, which were assigned to the Mo 3p, N–Cr, N–Mo, and N–C/N–Si bonds [22, 38], respectively. In particular, the intensity of the Mo 3p peak increased as the Mo content in the coating increased from 3.6 to 10.3 at%, which indicated an increase of Mo₂N phase content in the coating. Figure 5(d) shows the deconvolution results of the Si 2p core-level XPS spectra. The peaks at 99.3, 101.4, and 102.7 eV corresponded to the Si–C–N, Si–N, and S–O bonds [40], respectively. According to the XRD results, there was no information related to the Si-relevant crystal. Consequently, according to the XPS results, the Si element was

Fig. 4 (a) TEM, (b) HRTEM, and (c) SAED images of CrMoSiCN coating (sample No. S-3).

Fig. 5 XPS spectra of CrMoSiCN coatings. (a) Cr 2p; (b) Mo 3d; (c) N 1s; (d) Si 2p; and (e) C 1s.

considered to exist in the coating as the amorphous phases of SiN_x and SiCN . The C 1s core level XPS spectra of the S-1, S-2, and S-3 coatings were deconvoluted into four peaks at 282.8, 284.8, 285.2, and 288.5 eV, which corresponded to the C–Si, $\text{sp}^2\text{C–C/C–N}$, $\text{sp}^3\text{C–C/C–N}$, and C–O bonds, respectively. Similarly, the crystal information related to C was absent in the XRD results. It could be deduced that C existed in the form of a-C and a- CN_x amorphous phases in the coating. Based on the XRD analysis results, the cubic crystal phases of Mo_2N and CrN were confirmed in the S-1, S-2, and S-3 coatings. Furthermore, the Mo atom entered the CrN phase to replace the position of the Cr atom to form a substitutional solid solution (Cr, Mo)N. XPS results confirmed the formation of amorphous phases for SiN_x , SiCN , a-C, and a- CN_x in the coatings. After considering the TEM result, it was determined that the crystal phases were surrounded by amorphous phases to form the nanocomposite structure. Finally, the cubic nanocrystals (CrN, Mo_2N) were embedded in the amorphous matrix (SiN_x , SiCN , a-C, and a- CN_x) to compose the nanocomposite microstructure of the resultant coating.

3.2 Mechanical properties of CrMoSiCN coatings

Figure 6 illustrates the coating adhesion strength and the corresponding light images of the S-1, S-2, and S-3 coatings. The L_{c1} value was determined by the first acoustic emission signal value that appeared on the curve [22]. The L_{c2} value was defined as the value corresponding to the first peeling-off region that appeared on the optical image [22]. For the S-1 coating, L_{c1} and L_{c2} were 11.8 and 17.6 N, respectively. Clearly, L_{c1} and L_{c2} increased to 20.2 and 20.9 N for the S-2 coating, respectively, suggesting an enhancement of the coating adhesion strength. For the S-3 coating, no acoustic signal appeared on the curve. The light image of the scratch track was smooth with no obvious peeling-off phenomenon, indicating its superior coating adhesion strength among all the coatings. Undeniably, the high Mo content contributed to improving the adhesion strength of the CrMoSiCN nanocomposite coating.

The hardness and elastic modulus of the S-1, S-2,

Fig. 6 Light images, L_{c1} and L_{c2} values of CrMoSiCN coatings during the scratch test.

and S-3 coatings were evaluated using the indentation test. Figure 7(a) illustrates that the load curve on the sample varied with the displacement of the coating surface. It was clear that the load on the sample for the S-3 coatings exhibited the maximum value with the same indentation depth as that of the other coatings, suggesting the high hardness of the S-3 coating. Figure 7(b) shows the hardness and elastic modulus values for the S-1, S-2, and S-3 coatings. It is clear that the hardness and elastic modulus exhibited an increasing trend with an increase in the doped Mo content. The S-3 coating presented the highest hardness (28.6 GPa) and elastic modulus (273 GPa). In addition, the H/E value indicates the crack damage resistance [41], and the H^3/E^2 value may reflect the plastic deformation resistance [38]. The H/E and H^3/E^2 values are listed in Table 3. The S-3 coating presented the highest H/E (0.105) and H^3/E^2 (0.316) values, indicating that the CrMoSiCN nanocomposite coating with a high Mo content contributed to improving its mechanical performance. The enhancement of the mechanical properties may be attributed to the compact multi-phase nanocomposite structure, which limited the grain boundary sliding [38]. In addition, the formation of a substitutional solid solution (Cr, Mo)N contributed to limiting the crack growth [42], refining the grain [43], and inhibiting the generation of dislocations [44]. Therefore, the mechanical performance of the CrMoSiCN coating was enhanced, and the S-3 coating with 10.3 at% Mo exhibited the best mechanical performance.

Fig. 7 (a) Variation of load on sample with the displacement into surface, and (b) the hardness and elastic modulus of CrMoSiCN coatings.

3.3 Tribocorrosion test of CrMoSiCN coatings

3.3.1 Tribocorrosion test under OCP condition

Figure 8 depicts the evolution of the OCP values before, during, and after the tribocorrosion test and the friction coefficients of the Ti-6Al-4V and Ti-6Al-4V alloys coated with CrMoSiCN. Before the tribocorrosion started, all the samples were immersed in artificial seawater for 30 min to reach a stable electrochemical state. During the static soaking period before the tribocorrosion test, the OCP value of the Ti-6Al-4V alloy was approximately -0.17 V. This was lower than that of the prepared coatings, indicating its poor electrochemical response in artificial seawater. During the tribocorrosion period, the Ti-6Al-4V alloy and CrMoSiCN coating presented different behaviors. When the SiC ball came into contact with the sample surface, the OCP of the Ti-6Al-4V alloy sharply decreased to a negative value of -0.88 V with significant fluctuation; however, the OCP of the CrMoSiCN coatings presented a slight decreasing trend during the tribocorrosion period and tended to be stable faster. The sudden decrease in the OCP may be owing to the mechanical removal of the passive layer formed on the coating surface [45], leading to the re-exposure of the fresh surface of the wear track in seawater. Subsequently, the new passive film repeated the rebuilt–destroy–rebuilt process, resulting in a slightly fluctuating OCP value [29]. Particularly, the OCP values of the coatings increased regularly with respect to the Mo content for the S-1 coating (-0.58 V) < S-2 coating (-0.45 V) < S-3 coating (-0.38 V). When the sliding contact stopped, the OCP of the Ti-6Al-4V alloy and CrMoSiCN

coating rapidly increased in the positive direction, owing to the rebuilding of the passive film on the sample [22]. In particular, the variation of the friction coefficient presented an opposite trend compared with that of the OCP with regards to the Mo content. In addition, the friction coefficient of the Ti-6Al-4V alloy was significantly higher than that of the CrMoSiCN coating, suggesting its poor tribocorrosion performance under OCP conditions in artificial seawater. The friction coefficient of the prepared coating was stabilized rapidly when the SiC ball made contact with the sample surface. It decreased from 0.18 for the S-1 coating to 0.12 for the S-3 coating, which was owing to the occurrence of the tribo-oxidization reaction between the high Mo content contained in the S-3 coating and the diffused oxygen in seawater [22, 46]. According to the tribocorrosion test under OCP conditions, the CrMoSiCN nanocomposite coating showed favorable tribocorrosion performance compared with the Ti-6Al-4V alloy, suggesting its superior protective effect in artificial seawater.

Fig. 8 Variation of OCP and friction coefficient as a function of time during the tribocorrosion test in artificial seawater.

Figure 9 shows the SEM images of wear tracks for the Ti-6Al-4V, S-1, S-2, and S-3 coatings after the tribocorrosion test under OCP conditions. After magnifying the wear track (red square in Fig. 9(a)), it is clear that a severe plow groove along the sliding direction was detected on the wear track of Ti-6Al-4V (Fig. 9(a1)). As shown in Fig. 9(b), the wear track of the S-1 coating was clear and smooth; however, some wear debris adhered to the wear track. After magnifying the local area of the wear track, many plow grooves were observed on the wear track of the S-1 coating (Fig. 9(b1)). After the SiC ball came into contact with the coating surface, the material started to flake under the actions of compressive and shear stresses caused by the applied load and sliding behaviors. The spalling debris moved along the sliding direction and scratched the surface of the wear track, owing to inadequate lubrication [22]. Consequently, it could be deduced that the primary wear mechanism of the S-1 coating was abrasive wear. For the S-2 coating, the wear track became smoother compared with the S-1 coating (Fig. 9(c)); even so, many plow grooves were still observed on the wear track (Fig. 9(c1)). In contrast, the plow groove phenomenon on the wear track of the S-3 coating was significantly alleviated (Fig. 9(d)). This phenomenon was closely related to the higher Mo content in the S-3 coating. Moreover, tribo-oxidization occurred and provided sufficient lubrication during the tribocorrosion test for the S-3 coating in artificial seawater [47]. The inconspicuous furrow on the wear track (Fig. 9(d1)) indicated that the wear mechanism transformed from abrasive wear to tribochemical wear.

3.3.2 Tribocorrosion performance under dynamic polarization condition

Figures 10(a) and 10(b) show the dynamic polarization curves for the pure corrosion and tribocorrosion conditions for the Ti-6Al-4V alloy, S-1, S-2, and S-3 coatings. The corresponding current density (i_{corr}) and corrosion potential (E_{corr}) were obtained using the Tafel extrapolation method and are listed in Table 4. Under pure corrosion conditions, the i_{corr} value and corrosion rate of the Ti-6Al-4V alloy were almost twice those of the CrMoSiCN coatings. The S-3 coating exhibited the lowest i_{corr} value

Fig. 9 SEM images of wear tracks for Ti-6Al-4V alloy and CrMoSiCN coatings under OCP condition. (a, a1) Ti-6Al-4V; (b, b1) S-1; (c, c1) S-2; and (d, d1) S-3.

and corrosion rate of 1.98×10^{-8} A/cm² and 0.23×10^{-3} mm/yr, respectively, suggesting the lowest corrosion speed under pure corrosion conditions. In particular, the Ti-6Al-4V alloy exhibited poor tribocorrosion performance with a high i_{corr} of 1.86×10^{-5} A/cm² during the tribocorrosion test, which was almost 100 times higher than that of the resultant coatings. The corrosion rate of the Ti-6Al-4V alloy reached 218.12×10^{-3} mm/yr, indicating its rapid material consumption during the tribocorrosion test. In contrast, the CrMoSiCN coating still maintained its low corrosion rate during the tribocorrosion test in artificial seawater. The S-3 coating exhibited the lowest i_{corr} value and corrosion rate of 1.39×10^{-7} A/cm² and 1.63×10^{-3} mm/yr, respectively. In addition, the i_{corr} in the tribocorrosion test was significantly higher than that in the pure corrosion test, proving that the wear behavior could accelerate the corrosion of the coating. Figures 10(c) and 10(d) illustrate the two-dimensional (2D) cross-sectional profiles of the

wear tracks of the pure wear test and tribocorrosion test for the Ti-6Al-4V alloy, S-1, S-2, and S-3 coatings. The profiles of the wear tracks for the Ti-6Al-4V alloy in the pure wear test and tribocorrosion test were significantly deeper and wider than those of the resultant coatings in Figs. 10(c) and 10(d). In addition, the corresponding friction coefficients are also recorded in Fig. 10(e); the Ti-6Al-4V alloy exhibited a maximum friction coefficient of 0.23 during the tribocorrosion test. The mean friction coefficients of the S-1, S-2, and S-3 coatings were 0.13, 0.11, and 0.08, respectively. The friction coefficient exhibited a decreasing trend as the Mo content increased. The loss volumes during the pure wear test and tribocorrosion test were calculated according to the corresponding 2D profiles of the wear tracks, and the calculated

results are shown in Fig. 10(f). The loss volume during the pure wear test was 1.42×10^{-2} , 1.32×10^{-3} , 1.19×10^{-3} , and 0.93×10^{-3} mm³ for the Ti-6Al-4V, S-1, S-2, and S-3 coatings, respectively. In addition, the loss volume for the Ti-6Al-4V alloy was 3.41×10^{-2} mm³ during the tribocorrosion test, which was 30 times higher than that of the CrMoSiCN coatings in Fig. 10(f). The wear loss volume of the S-1 coating was 1.53×10^{-3} mm³, and it gradually decreased to the minimum value of 1.21×10^{-3} mm³ for the S-3 coating during the tribocorrosion test. This indicated that the CrMoSiCN coatings exhibited superior tribocorrosion performance in comparison to the Ti-6Al-4V alloy in seawater. The S-3 coating with 10.3 at% Mo content presented the lowest friction coefficient of 0.08 and wear loss volume of 1.21×10^{-3} mm³, suggesting its superior

Fig. 10 Dynamic polarization curves under the condition of (a) pure corrosion and (b) tribocorrosion; (c) 2D profiles of wear tracks of pure wear test and (d) tribocorrosion test; (e) the corresponding friction coefficient during tribocorrosion test and (f) wear loss volumes for Ti-6Al-4V alloy and CrMoSiCN coatings at pure wear test and tribocorrosion test.

Table 4 Dynamic polarization results of CrMoSiCN coatings under sliding contact condition in artificial seawater.

Type	Sample	i_{corr} (A/cm ²)	E_{corr} (V)	Corrosion rate (×10 ⁻³ mm/yr)
Pure corrosion	Ti-6Al-4V	4.98×10^{-8}	-0.30	0.60
	S-1	2.25×10^{-8}	-0.34	0.27
	S-2	2.26×10^{-8}	-0.37	0.27
	S-3	1.98×10^{-8}	-0.36	0.23
Tribocorrosion	Ti-6Al-4V	1.86×10^{-5}	-0.53	218.12
	S-1	2.58×10^{-7}	-0.44	3.01
	S-2	1.99×10^{-7}	-0.38	2.34
	S-3	1.39×10^{-7}	-0.56	1.63

tribocorrosion performance under a dynamic polarization condition in artificial seawater.

3.3.3 Discussion

The material loss caused by the joint action of wear and corrosion during tribocorrosion has been extensively studied in detail [48, 49]. During tribocorrosion, it was assumed that (1) corrosion only occurred within the wear track area during the tribocorrosion tests and (2) no corrosion occurred during the pure wear tests. Consequently, the total material wear loss volume (T) during the tribocorrosion test could be divided into the following parts: (1) the loss volume caused by pure wear behaviors (W); (2) the loss volume caused by pure corrosion behaviors (C_o); (3) the loss volume caused by the joint action (ΔT), which includes two parts: the loss volume caused by wear contribution to corrosion (C_w); and the loss volume owing to the corrosion contribution to wear (W_c). Therefore, the total material loss volume can be described by the following formula:

$$T = W + C_o + \Delta T \quad (1)$$

$$\Delta T = C_w + W_c \quad (2)$$

The total loss volumes (T) of the Ti-6Al-4V alloy and the resultant coatings could be calculated by the corresponding 2D cross-sectional profile of the wear tracks shown in Fig. 10(d). Similarly, the loss volume owing to the pure wear behavior (W) was calculated using the same method according to the pure wear test in Fig. 10(c). According to Faraday's law in Eq. (3), the loss volumes owing to pure corrosion (C_o) could be calculated from the polarization curve (without performing wear tests) in Fig. 10(a). Additionally, $C_o + C_w$ was obtained from the polarization curve during the tribocorrosion test in Fig. 10(b).

$$C_o = itM / (nF\rho) \quad (3)$$

where t is the test time (s), i is the average current (A), which can be obtained from the polarization curve data, M is the relative molecular mass (g/mol), ρ is the material density (g/cm³), n is the charge transfer number during the tribocorrosion test, and F is Faraday's constant (C/mol). Subsequently, the loss volume caused by the corrosion contribution to wear (W_c) was calculated as follows:

$$W_c = T - W - C_o - C_w \quad (4)$$

Figure 11 shows the contributions of the tribocorrosion components for the Ti-6Al-4V alloy, S-1, S-2, and S-3 coatings sliding against the SiC balls under polarization conditions in seawater. For the Ti-6Al-4V alloy, the main causes of material loss were owing to three aspects: pure wear behaviors (W , 41.12%), the corrosion contribution to wear (W_c , 47.17%), and the wear contribution to corrosion (C_w , 11.63%). The total material loss volume caused by the synergistic effect accounted for 58.8%, indicating that the synergy of wear and corrosion dominated the entire tribocorrosion process for the Ti-6Al-4V alloy in artificial seawater. For all the resultant coatings, it was clear that the wear behaviors were the primary reason for the coating degradation. The loss volume owing to pure wear behaviors accounted for 86.14% for the S-1 coating and decreased to 76.80% for the S-3 coating. This phenomenon indicated that the impact of W was weakened for a high Mo content. In contrast, the loss volume caused by the corrosion contribution to wear (W_c) increased from 12.8 % for the S-1 coating to 21.13% for the S-3 coating, indicating that the impact of W_c became more significant. This phenomenon could be explained by the fact that a higher Mo content increased the impact of the wear behavior caused by corrosion [22]. The loss volumes caused by the wear contribution to corrosion (C_w) accounted for only a small proportion (less than 1.95%); however, the loss volumes caused by pure corrosion behaviors (C_o) were negligible with a proportion of less than 0.12% for the three coatings. The small proportions of C_o and C_w

Fig. 11 Contributions of tribocorrosion components for Ti-6Al-4V alloy and CrMoSiCN coatings sliding against SiC balls under polarization condition in seawater.

indicated that the corrosion-related behaviors had a weak effect on the material loss of the CrMoSiCN nanocomposite coating. Moreover, the compact nanocomposite structure and the semi-conductive passive layer containing Cr_2O_3 and MoO_3 [32] contributed to the enhancement of the tribocorrosion performance of CrMoSiCN coatings in artificial seawater.

Here, we defined ΔW as equal to the sum of W and W_c and ΔC represents the total material loss caused by C_o and C_w . Accordingly, ΔW and ΔC can be defined as follows:

$$\Delta W = W + W_c \quad (5)$$

$$\Delta C = C_o + C_w \quad (6)$$

Stack et al. [50–52] developed erosion–corrosion mechanism maps to identify the transformations between the erosion and corrosion regimes as a function of testing parameters during the tribocorrosion test. These results presented the contributions of the tribocorrosion component to material loss, and the contribution of the synergistic effect was also contained in the regime map. These maps may help to analyze the components required to improve the resistance by highlighting whether wear or corrosion aspects need to be inhibited. Likewise, the regime map with the total corrosion loss volume proportion (ΔC) versus the total wear loss volume proportion (ΔW) in Fig. 12 was used to analyze the contribution to material loss during the tribocorrosion test in artificial seawater. The wear–corrosion regimes can be defined as follows [50–52]:

$$\Delta W / \Delta C \leq 0.1$$

$$\text{Pure corrosion } (C_o) \text{ dominated} \quad (7)$$

$$0.1 < \Delta W / \Delta C \leq 1$$

$$\text{Wear contribution to corrosion } (C_w) \text{ dominated} \quad (8)$$

$$1 < \Delta W / \Delta C \leq 10$$

$$\text{Corrosion contribution to wear } (W_c) \text{ dominated} \quad (9)$$

$$\Delta W / \Delta C > 10$$

$$\text{Pure wear } (W) \text{ dominated} \quad (10)$$

As shown in Fig. 12, the point of Ti–6Al–4V appeared in the corrosion contribution to wear (W_c) dominated regime, indicating the significant effect of the corrosion contribution to wear loss during the tribocorrosion

Fig. 12 Wear–corrosion regime map with corrosion material loss proportion versus wear material loss proportion for tribocorrosion of Ti–6Al–4V and S-1, S-2, and S-3 coatings in artificial seawater.

test. However, all points of the CrMoSiCN coatings emerged in the pure wear dominated region. This revealed that the wear behaviors were the primary reason for the degradation of the CrMoSiCN coatings in the tribocorrosion test conducted under dynamic polarization test conditions in seawater. This was because the nanocomposite coating with the multi-component possessed a better electrochemical response than the Ti–6Al–4V alloy. Furthermore, the MoO_3 passive layer that formed on the wear track could effectively slow down the corrosion rate during tribocorrosion tests in artificial seawater [49].

To elaborate on the tribocorrosion mechanism of CrMoSiCN coatings in artificial seawater, the wear track was investigated using a white-light interferometer and SEM. Figure 13(a) shows the wear track for the Ti–6Al–4V alloy during the tribocorrosion test under polarization conditions. It can be observed that the severe peeling-off phenomenon occurred on the wear track in Fig. 13(a2). In contrast, all the wear tracks were clear and presented no obvious worn-through phenomena for the CrMoSiCN coating in Figs. 13 (b1)–13(d1). However, the abrasive wear occurred on the wear track of the S-1 coating in Fig. 13(b1). After magnifying the local area of the wear track, many wear debris and obvious furrows along the sliding direction were observed inside the wear track (Fig. 13(b2)). These plow grooves were caused by the surface roughness of tribopairs and abrasive particles that existed in the interface during the sliding

Fig. 13 3D profile images, SEM images of wear track and the corresponding EDS results of Ti-6Al-4V alloy and prepared coatings during tribocorrosion tests in artificial seawater: (a–a3) Ti-6Al-4V; (b–b3) S-1; (c–c3) S-2; and (d–d3) S-3.

contact. The primary tribocorrosion mechanism was dominated by abrasion wear. For the S-2 coating, it was clear that the plow grooves phenomenon on the wear track of the S-2 coating was significantly alleviated (Fig. 13(c1)). It can be observed that more wear debris adhered to the wear track in Fig. 13(c2). The wear track of the S-3 coating was relatively smooth with no clear plow grooves detected (Fig. 13(d1)), and a large quantity of wear debris was observed on the wear track (Fig. 13(d2)). Therefore, the tribocorrosion mechanism transferred from abrasion wear to tribochemical wear.

To investigate the reaction during the tribocorrosion test, energy dispersive X-ray spectroscopy (EDS) analyses were conducted on the selected points A, B, C, and D on the wear tracks of the Ti-6Al-4V, S-1, S-2, and S-3 coatings (Table 5), respectively. The EDS analysis of the Ti-6Al-4V alloy wear track showed that Ti, O, Al, and V were detected on point A inside the wear track, indicating that oxidation occurred during the friction process. By comparing the EDS results of the three points B, C, and D, it was determined that the Mo contents inside the wear tracks of the S-1, S-2, and S-3 coatings were higher than those of the respective untreated coatings. In addition, large amounts of O were detected inside the wear track

with contents of 10.1, 19.7, and 32.4 at% for the S-1, S-2, and S-3 coatings, respectively, proving the occurrence of a tribochemical reaction during the tribocorrosion test. In addition, different amounts of Cr were detected inside the wear track for the three coatings, indicating the formation of Cr_2O_3 on the wear track. The reaction can be defined by Eq. (11) [22, 37, 53]:

Based on this result, the obvious abrasion phenomena on the wear tracks of the S-1 and S-2 coatings could be explained by the low Mo content in the coatings. The MoO_3 content was insufficient to form good lubrication during the tribocorrosion test. The tribopairs slid against each other under poor lubrication conditions, and the severe furrow along the sliding direction subsequently appeared. When the Mo content was 10.3 at% (S-3 coating), the increased formation of MoO_3 contributed to forming a good lubrication condition and improving the corrosion resistance [49]. Finally, the plow groove phenomenon gradually disappeared at a Mo content of 10.3 at%. For this reason, the S-3 coating exhibited the best wear resistance with the lowest friction coefficient and wear loss volume during the tribocorrosion test. Consequently, the

Table 5 EDS results of selected points on the wear tracks during the tribocorrosion test.

Points	Si	N	C	Cr	Mo	O	Ti	Al	V
A	—	—	—	—	—	9.3	79.1	9.1	2.5
B	1.9	27.3	18.0	35.4	7.3	10.1	—	—	—
C	1.4	22.2	15.0	32.3	9.4	19.7	—	—	—
D	1.0	13.0	12.3	26.1	15.2	32.4	—	—	—

tribocorrosion performance was enhanced for the CrMoSiCN coating with a high doped Mo content.

4 Conclusions

CrMoSiCN coatings with nanocomposite microstructures were prepared on a Ti-6Al-4V alloy using an unbalanced magnetron sputtering system. These coatings are an ideal alternative protective coating against wear corrosion in artificial seawater. The results of this study can be summarized as follows:

1) The cubic phases of CrN and Mo₂N were randomly distributed in the amorphous matrix consisting of a-C, SiN_x, SiCN, and a-CN_x to configure the nanocomposite structure of the CrMoSiCN coating. In addition, a (Cr,Mo)N substitutional solid solution was formed in the CrMoSiCN nanocomposite coating.

2) The CrMoSiCN nanocomposite coating with a 10.3 at% Mo content exhibited good coating adhesion strength, and the mechanical performance of the coating was enhanced, owing to the solid solution strengthening effect.

3) During the tribocorrosion test, the CrMoSiCN nanocomposite coating exhibited a favorable tribocorrosion performance compared with the Ti-6Al-4V alloy in artificial seawater. The main tribocorrosion mechanism for Ti-6Al-4V was dominated by the corrosion contribution to wear behaviors (synergistic effect) in artificial seawater, while that of the CrMoSiCN coating effectively prevented the material loss caused by the joint action of wear and corrosion behaviors. The primary reason for the failure of the CrMoSiCN coating was owing to pure wear behaviors.

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