An analysis on tribological performance of CrCN coatings with different carbon contents in seawater

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1. Introduction

With a “blue revolution” of exploiting the ocean springing up all over the world, more and more people have focused on the application performance of materials in the ocean environment, and developed new materials suitable to the ocean environment [1]. Some mechanical components such as piston pumps, seal rings and slide or thrust bearings working in water or seawater conditions lead to severe damage during running-in period, frequent starting/stopping, over-loading and over-speeding, which result in the ever-stringent requirements for protective and lubricating surfaces [2]. CrN coating has been demonstrated a good protective coating candidate for aqueous hydraulic system applications due to its high hardness, good wear resistance and corrosion resistance in the past years [3–9]. However, sometimes CrN coating cannot satisfy the application in some conditions, especially under extreme conditions because of its high friction coefficient [10,11]. Therefore, research of CrN coatings that retain its own merits, but have a lower friction coefficient has become an academic focus in the self-lubricating coating field in recent years. Carbon as self-lubricated solid materials can significantly reduce the friction coefficient of hard coatings [12–15]. Besides, the addition of carbon into chromium nitride has an important effect on the microstructure and mechanical properties of the coatings. Almer et al. [16] found that the carbon content in CrCN structure was closely related to the stress, hardness and critical load of the coatings. Choi et al. [17] indicated that CrCN coatings with 20 at% C revealed high hardness and residual stress than that of CrN coating. Cekada et al. [18] indicated that adhesion force between substrate and CrCN coating was lower than CrN and CrC coatings. Moreover, friction coefficient and wear rate of CrCN coatings were significantly depend on their carbon content [19]. Tong et al. [20] pointed out that CrCN coatings with 1.5 at% C showed the lowest friction coefficient when the carbon content was less than 5 at%. When the carbon content in CrCN coating up to 27 at%, the coefficients of friction and wear rate were decreased [21]. Therefore, the excellent tribological properties of CrCN coatings reveal its potential application as a protective coating in water hydraulic systems.

However, there is little investigation carried out on the tribological behavior of CrCN coatings with different carbon contents in seawater. Based on this, CrCN coatings with different carbon contents were deposited on 316L stainless steel and silicon (100) wafer using a multi-arc ion plating deposition technique via adjusting the C2H2 flow rate, and then the composition, microstructure, mechanical properties and tribological properties of CrCN coatings in seawater were investigated systematically to outline the influence of microstructure on the friction and wear properties of CrCN coatings in seawater.

2. Experimental detail

2.1. Deposition

The CrCN coatings were deposited on both Si (100) wafers and 316L stainless steel (24 mm × 12 mm × 2 mm) substrates using...
the multi-arc ion plating deposition technique. Before the deposition, all substrates were cleaned ultrasonically in deionized water for 15 min and in ethanol for 20 min, respectively. After loading the substrates on substrate holder, the deposition chamber was pumped down to a background pressure less than $4 \times 10^{-3}$ Pa, then the substrates were cleaned by Ar $^+$ bombardments for 2 min with negative bias voltages of $-900$ V, $-1100$ V and $-1200$ V, respectively, to remove the thin oxide layer and other adherent impurities. A pure Cr adhesive layer was first deposited onto the substrates for 30 min, followed by the deposition of CrCN coatings. During deposition, the working gas pressure was maintained at 0.3 Pa. The substrate holder was rotated at a speed of 3 rpm. The CrCN coatings were prepared using a chromium target (purity > 99.5 wt%) in N$_2$ (purity 99.99%) and C$_2$H$_2$ (purity 99.99%) mixed atmosphere. The relative concentration of C element in the coatings was controlled by adjusting the C$_2$H$_2$ flow rate. The bias voltage and current were kept at $-70$ V and 65 A, the deposition temperature and time were kept at 350 °C and 120 min, the flow rate of N$_2$ was kept at 400 sccm, while the flow rate of C$_2$H$_2$ was adjusted in the range of 0–30 sccm (0, 5, 10, 15, 20, 30 sccm). The pure CrN coating for comparison was obtained at 0 sccm, and the CrCN coatings deposited at 5, 10, 15, 20 and 30 sccm will be denoted in the next section as C$_2$H$_2$-0, C$_2$H$_2$-5, C$_2$H$_2$-10, C$_2$H$_2$-15, C$_2$H$_2$-20 and C$_2$H$_2$-30 sccm.

### 2.2. Characterization

The surface cross-sectional images of the coatings were investigated by using a field emission scanning electron microscope (FE-SEM) (FEI Quanta FEG 250) equipped with EDS (OXFORD X-Max). Crystal phase of the as-deposited coatings was investigated by X-ray diffraction (Bruker D8 X-ray facility) using Cu K$_\alpha$ radiation ($\lambda_\alpha$=0.154 nm), which was operated at 40 kV and 40 mA with grazing incidence angle of 2°. The scanning angle ranged from 20° to 90° at a scanning speed of 4°/min with 0.02° step size. The XPS spectra was measured by X-ray photoelectron spectroscopy (AXIS Ultra DLD) using an Al(mono) K$_\alpha$ X-ray source which was operated at 12 kV and 10 mA. Raman spectra of the transfer layers were obtained by a Raman spectrometer (HR800) measurement using an Ar$^+$ laser of 532 nm with a resolution of 1 cm$^{-1}$. The typical data acquisition time was in the range of 60 s and the spectrum was recorded in the range of 1000–1800 cm$^{-1}$ in order to allow reliable fitting.

The adhesion force of the total coating was determined by a scratch tester (CSM Revetest) with a conical diamond tip of 0.2 mm radius and 120° taper angle. The measurement parameters are as follows: table speed of 5 mm/min, loading rate of 118 N/min, loading scale of 0–100 N and scratch length of 5 mm under ambient condition. The damage of the scratch track was examined by a JSM-5600 SEM. LC1 corresponding to the ambient condition. The damage of the scratch track was examined with the measurement parameters from 0 to 15 sccm, however, they are constant when the C$_2$H$_2$ flow rate increases to high level. Fig. 1 shows the cross-sectional FE-SEM micrographs of the coatings deposited at various C$_2$H$_2$ flow rates. The typical columnar structure can be found on Fig. 1a. By increasing the C$_2$H$_2$ flow rate to 30 sccm, a dense and compact structure is revealed. This structure change is related to the phase structure of the coatings.

In order to know the phase structure of CrCN coatings, the XRD spectra of the CrCN coatings deposited at various C$_2$H$_2$ flow rates were performed to have reliable statistics. The corrosion behavior of CrCN coatings was evaluated by polarization tests (EG&C 273) in artificial seawater. The artificial seawater is prepared according to Standard ASTM D 1141-98. The chemical composition of artificial seawater is listed in Table 1. The contact area in all cases was 1 cm$^2$ and the tests were carried out at ambient temperature (16 ± 5 °C). The electrode potential was raised from $-1.5$ to 1.0 V at a scanning rate of 1 mV/s.

### 2.3. Tribological test

Wear tests were performed with a ball-on-disc in sliding contact with a steel ball at room temperature of about 22 ± 2 °C and relative humidity of 62 ± 5%. The WC balls (94% WC + 6% Co) with a diameter of 3 mm were used as the counterparts. The tests were also conducted in artificial seawater. UMT-3MT tribometer (CETR, USA) was used in order to evaluate the friction and wear characteristics of the sliding couples. A sliding speed of 300 rpm, a constant normal load of 5 N and a sliding stroke of 5 mm were used in the experiments and the friction coefficient was continuously recorded during testing. Based on the wear track depth profiles detected by an Alpha-Step IQ profilometer, the wear losses of the coatings were calculated. Then use the formula $K=V/S$ to calculate the wear ratio. $V$ is the wear loss of coating, $S$ is the sliding distance and $F$ is the normal load applied.

### 3. Results and discussion

#### 3.1. Composition, bonding structure and morphology of the coatings

Table 2 shows the chemical composition of the CrCN coatings deposited at different C$_2$H$_2$ flow rates. With the increase of C$_2$H$_2$ flow rates, the carbon content in the coating increases significantly from 0% to 21.32%, while the contents of Cr, N decrease from 46.51% to 33.17%, 53.25% to 28.07%, respectively. These indicate that the C$_2$H$_2$ flow rate exhibited a great effect on the carbon content of the coatings.

Surface roughness and thickness of the coatings are also listed in Table 2. Generally, the surface roughness decreases with increasing carbon content [21]. However, some macro-particles and pin holes are also formed on the surface, which always affect the roughness of coating [23]. At the same time, the thickness decreases from 3.98 to 3.02 µm with increasing the C$_2$H$_2$ flow rates from 0 to 15 sccm, however, they are constant when the C$_2$H$_2$ flow rate increases to high level. Fig. 1 shows the cross-sectional FE-SEM micrographs of the coatings deposited at various C$_2$H$_2$ flow rates. The typical columnar structure can be found on Fig. 1a. By increasing the C$_2$H$_2$ flow rate to 30 sccm, a dense and compact structure is revealed. This structure change is related to the phase structure of the coatings.

In order to know the phase structure of CrCN coatings, the XRD spectra of the CrCN coatings deposited at various C$_2$H$_2$ flow rates were obtained in the experiments.

### Table 2

<table>
<thead>
<tr>
<th>Coating</th>
<th>Cr (at%)</th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
<th>Thickness (µm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_2$-0</td>
<td>46.51</td>
<td>0</td>
<td>53.25</td>
<td>2.74</td>
<td>3.98</td>
<td>74.29</td>
</tr>
<tr>
<td>C$_2$H$_2$-5</td>
<td>42.32</td>
<td>5.72</td>
<td>49.55</td>
<td>2.41</td>
<td>3.35</td>
<td>71.18</td>
</tr>
<tr>
<td>C$_2$H$_2$-10</td>
<td>41.43</td>
<td>12.84</td>
<td>43.06</td>
<td>2.68</td>
<td>3.34</td>
<td>65.52</td>
</tr>
<tr>
<td>C$_2$H$_2$-15</td>
<td>38.07</td>
<td>16.83</td>
<td>42.65</td>
<td>2.45</td>
<td>3.02</td>
<td>66.46</td>
</tr>
<tr>
<td>C$_2$H$_2$-20</td>
<td>35.88</td>
<td>18.72</td>
<td>42.01</td>
<td>3.39</td>
<td>3.13</td>
<td>67.17</td>
</tr>
<tr>
<td>C$_2$H$_2$-30</td>
<td>33.17</td>
<td>21.32</td>
<td>41.07</td>
<td>4.44</td>
<td>3.45</td>
<td>67.12</td>
</tr>
</tbody>
</table>
are shown in Fig. 2. The CrN (111), CrN (200), Cr7C3 (151), CrN (220), Cr2N (113) and Cr2N (302) diffraction peaks can be observed in the image. As the C2H2 flow rate increases, CrN (111) and CrN (200) preferential orientations become weaker and broader. However, Cr7C3 (151) and CrN (220) preferential orientations become stronger with the increase of flow rates in the lower range, and then they are constant for higher values, but these phases are stable and have no obvious change. This is due to the difference in crystal structures of carbon simple substance, chromium carbide and chromium nitride. The carbon atoms can replace the nitrogen atom in chromium nitride crystal structure to form chromium carbon, which crystal is different from chromium nitride. Thus the carbon element disturbs the normal crystal arrangement of chromium nitride, the coatings transform from crystalline state to amorphous state [21,24].

For further analyze the change of bonding structure for CrCN coatings, the C1s, Cr2p and N1s spectra in the XPS analysis of CrCN coatings were detected. Since there was no obvious difference between CrCN coatings, just the deconvolved C1s, Cr2p and N1s XPS spectra of CrCN coatings deposited at 15 sccm are shown in Fig. 3. The Cr2p XPS spectra (Fig. 3a) can be fitted with different binding energies of 574.2 eV, 575.7 eV, 576.3 eV, 583.6 eV, 585.4 eV and 586.4 eV, which corresponds to Cr7C3, CrN, Cr2N, Cr2O3, Cr2O3 and Cr2O3, respectively [25–29]. As shown in Fig. 3b, the C1s peak can be fitted by four components, which center around 282.8 eV, 284.6 eV, 286 eV and 288.1 eV, corresponding to C–Cr, sp2C–C, sp3C–C and C–O, respectively [30–33]. The total volume fraction of each bond is calculated and listed in Table 3. In general, the hardness is closely related with sp3 fraction. In the other words, higher sp3 fraction, higher hardness. The friction coefficient is closely related with sp2 fraction i.e. higher sp2 fraction, lower friction coefficient. Thus, the CrCN coating (10 sccm) may possess the highest hardness and lowest friction coefficient among these coatings. Fig. 3c illustrates the N1s core level spectra and the fitting curves of the coating, where the N1s peak is deconvolved into three peaks with binding energies of 397.8 eV, 399.3 eV and 400.5 eV, which corresponds to Cr–N, N–C, N–C, respectively [34–36]. This indicates that the amorphous CNx is formed in the CrCN coatings after carbon atoms were incorporated. To sum up, it can be seen from the image there exist CrN, Cr2N, Cr7C3 and Cr2O3 phase in the CrCN coating, which are consistent with the XRD analysis.
The HRTEM results of these coatings are shown in Fig. 4. When the 
C2H2 flow rate was 0 sccm, Fig. 4a shows the high-resolution TEM and 
SAED pattern of the CrN coating. The discrete (111), (200), (220) and 
(113) diffraction spots were observed in the selected-area electron 
diffraction (SAED) pattern. Combined with the XRD and the SAED 
pattern, it can be concluded that the CrN coating consists of a CrN 
phase with a cubic crystal system and a Cr2N phase with a trigonal 
system. As shown in Fig. 4b, when the C2H2 flow rate increased to 
10 sccm, the discrete (151) diffraction spots were observed in the 
selected-area electron diffraction (SAED) pattern, which corresponding 
to the XRD analysis. It is significantly that the coating was composed 
by crystalline and amorphous region. These indicated that the CrCN 
coating exhibits a nanocrystalline/amorphous microstructure. Similar 
results are observed in Fig. 4c and d. Fig. 4c also shows that a twinning 
structure that consists of (200) planes of the CrN phase, which plays 
an important role in hindering of the movement of dislocations and 
improving the toughness of the coating [37]. It is worth to mention 
that the grain size decreased with the increase of C2H2 flow rates from 
0 to 10 sccm, whereas, it was contrary when the C2H2 flow rates 
increased to the high level. The grain size is a key factor to affect the 
performances of coating [20].

### 3.2. Mechanical properties of the coatings

Fig. 5 shows the critical loads (LC1 and LC2) of CrCN coatings 
deposited at various C2H2 flow rates. As for LC1, the value first 
increases to 36 N at 15 sccm and then decreases to 28 N at 30 sccm. 
The LC1 is gained by an acoustic signal which arises from the broken 
 micro-particle on the coating surface. The micro-particle consisting of 
Cr is easier to break than CrN and Cr7C3, which may be attributed to a 
lower hardness of the Cr micro-particle. Meanwhile, some acoustic 
signals are formed by the crack propagating during the sliding process, 
cause by the conical diamond tip extruding pin holes. As to LC2, the 
value first increases to 86 N at 10 sccm and then decreases to the 
lowest value of 63 N at 30 sccm. This is due to the amount of carbon 
causing refinement of structure, increase of compressive stress and 
decrease of critical load [38]. On the other hand, scratch results are 
influenced by substrate and coating hardness, surface roughness, 
coefficient of friction between coating and the scratch stylus, elastic 
properties of the substrate, coating thickness [4,39]. The substrate 
hardness, scratch stylus and elastic properties of the substrate are 
constant, the surface roughness and coating thickness are listed in 
Table 2, thus the coating hardness and coefficient of friction are tested. 
The hardness, elastic modulus, H/E and H3/E2 of the CrCN coatings are shown in Fig. 6. The hardness, H/E and H3/E2 show a 
similar tendency with respect to the C2H2 flow rates. The hardness first increases to 32 GPa at 10 sccm and then decreases to 22 GPa 
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content is attributed to the solid solution hardening effect of 
carbon atoms. Meanwhile, Lim [41] and Jung [42] found that the 
hardness increased with decreasing grain size. Thus, when the 
C2H2 flow rate increased to 10 sccm, the hardness of coating is the 
highest. As is known, the H/E or H3/E2 ratios relate to the durability 
and plastic deformation resistance of the coatings, respectively, 
which provide close correlation with relative wear resistance [43]. 
As seen in Fig. 6, the CrCN coating deposited at 10 sccm shows the 
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### 3.3. Corrosion properties of the coatings

In order to evaluate the anodic dissolution of the coatings during 
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**Table 2** Calculated concentration of different bonds from C1s XPS results at different C2H2 flow rates.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Cr–C (%)</th>
<th>sp2C–C/C–N (%)</th>
<th>sp3C–C/C–N (%)</th>
<th>C–O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H2-5</td>
<td>41.62</td>
<td>44.94</td>
<td>6.5</td>
<td>6.94</td>
</tr>
<tr>
<td>C2H2-10</td>
<td>40.22</td>
<td>47.65</td>
<td>9.49</td>
<td>2.64</td>
</tr>
<tr>
<td>C2H2-15</td>
<td>41.91</td>
<td>46.63</td>
<td>8.21</td>
<td>3.25</td>
</tr>
<tr>
<td>C2H2-20</td>
<td>41.02</td>
<td>46.51</td>
<td>8.39</td>
<td>6.08</td>
</tr>
<tr>
<td>C2H2-30</td>
<td>42.48</td>
<td>43.98</td>
<td>5.42</td>
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### 3.3. Corrosion properties of the coatings

In order to evaluate the anodic dissolution of the coatings during 
cycle sliding process, the polarization tests are investigated in
artificial seawater. As shown in Fig. 7 and Table 4, it is observed that the corrosion current density value ($i_{corr}$) of the CrN coating is low. With the increase of $C_2H_2$ flow rate, the corrosion current density value shows a descending trend until 10–15 sccm, which is the lowest corrosion current density value at about $7.27 	imes 10^{-7}$ A/cm$^2$. It may be attributed to the small grain size, dense structure and defect of the coatings, which is consistent with the result of TEM, SEM and roughness. Qin [44] and Aung [45] pointed out that the corrosion
rate significantly increased as the grain size increased. This is due to smaller grain size have higher density of nucleation sites for passive film, which leads to a higher fraction of passive layer, and thus a lower passive current density. Dense structure can effectively prevent seawater permeate into coating, enhancing the corrosion resistance of coating. What is more, the defect can accelerate the corrosion speed \[46\]. The distinct defect such as pin holes are not detected inside the as-fabricated coatings, the microcracks would grow under cyclic stress in combination with the erosion of water molecules, resulting in delaminations or spallations around these weak points. When the flow rates further increase, the corrosion current densities show an ascending trend to 30 sccm, where the corrosion current density reaches at about \(8.31 \times 10^{-7}\) A/cm². In addition, there is a passivation phenomenon when the polarization potential increases from \(-0.2\) to \(0.2\) V, which illustrates that the passivation layer is formed on the surface of the coatings, and then prevents the substrate exposure to surrounding environment for a short time. Thus, the CrCN coatings exhibit good corrosion resistance (Table 4).

### 3.4. Tribological properties of the coatings

Fig. 8a shows the friction behaviors of CrCN coatings deposited on 316 L sliding against WC balls in artificial seawater. The friction curve of CrN coating in seawater possess a features: first increase rapidly and then reach the relative steady-state wear stage after about 300 s. Whereas for the CrCN coatings, as a whole, the friction curves possess similar features: the first part increase rapidly, and the second part is obvious decrease of the value after about 150 s, and then decrease to the relative steady-state wear stage. The decrease after the run-in period attributed to the counterface become smoother. Moreover, the continuous water provides a certain degree hydrodynamic lubrication \[47,48\]. At the same time, Ca\(^{2+}\) and Mg\(^{2+}\) will be deposited on the counterface in the form of Mg(OH)\(_2\) and CaCO\(_3\), which played a certain degree in lubrication \[49\]. This is due to Mg(OH)\(_2\) and CaCO\(_3\) with sludge-like matters deposited on the sliding surfaces have some lubricating effects in cycle sliding process \[50\].

Fig. 8b shows the average friction coefficients and wear rates of the coatings. For friction coefficient, when the \(\text{C}_2\text{H}_2\) flow rate is 0 sccm, the average friction coefficient is about 0.31, which is the highest value among these coatings. The higher friction coefficient of the CrN coating can be attributed to three reasons. To begin with, the Cr phase in the CrN coating is softer than the WC ball and easily flakes off during the sliding. Furthermore, the loose columnar structure of the CrN coating is another reason. The columnar structure is easy to form the through-film channels, which accelerates the initiation and propagation of crack during sliding and thus causes the higher friction coefficient \[51\]. Finally, the carbon dope into the CrN coating can form the self-lubricating amorphous carbon phase, which can sharply reduce the friction coefficient of CrCN coatings. With the increase of \(\text{C}_2\text{H}_2\) flow rate, the friction coefficients first slight decrease and reach its lowest value at 10 sccm, then show an ascending trend. These phenomena are closely related to the roughness of the coatings. Higher roughness reduces the actual contact area between the ball and coating, which result in the load only focusing on the contact areas and then enhance the friction coefficient of the coating \[52\]. For wear rates, as a whole, it is obvious that the wear rates of CrCN coatings in seawater are lower than CrN coating, which can be attributed to the presence of sp\(^2\)-hybridized carbon in the CrCN coatings. Since the graphite-like structure with sp\(^2\)-hybridized carbon forms an interface layer and reduces the frictional shear resistance during the cycle friction process, it dramatically reduces the friction. With the increase of \(\text{C}_2\text{H}_2\) flow rates, the wear rates show a descending trend until 10 sccm, where the wear rate reaches its lowest value at about \(7.686 \times 10^{-7}\) mm\(^3\) N\(^{-1}\). This is due to the high content of sp\(^2\)-hybridized carbon and good toughness of the coating. When the flow rates further increase, the wear rates show an ascending trend to 30 sccm, where the wear rate reaches its highest value at

<table>
<thead>
<tr>
<th>(\text{C}_2\text{H}_2) (sccm)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i_{\text{corr}}) ((10^{-7}) A/cm²)</td>
<td>9.86</td>
<td>9.78</td>
<td>7.32</td>
<td>7.27</td>
<td>7.65</td>
<td>8.31</td>
</tr>
</tbody>
</table>

Fig. 7. Polarization curves of CrCN coatings deposited at different \(\text{C}_2\text{H}_2\) flow rates.
about $1.9519 \times 10^{-6} \text{ mm}^3 \text{ N m}^{-1}$. Shan [46] points out that water can have an ambiguous effect on wear rates; it can aggravate wear loss by accelerating crack growth and micro-fracture, or reduce wear loss by the formation of extremely smooth lubricant tribo-layers formed by tribo-chemical reactions. Seawater is a typical tribo-corrosion environment, in which corrosion and wear degrade materials by both mechanical and chemical processes, and then aggravate wear rate [53]. At the same time, the wear rate is also related to the adhesion force between coating and substrate. Low adhesion force means to the poor combination between coating and substrate, which indicates the chipping and spalling are easy to form in the friction process, corresponding to serious wear.

Fig. 9 shows the cross-sectional profiles of wear tracks on the CrCN coatings with different C$_2$H$_2$ flow rates in seawater. At the C$_2$H$_2$ flow rate of 0 sccm, the maximum depth of wear track is about 0.6 μm, which is a relatively higher value among these coatings. With the increased C$_2$H$_2$ flow rates, the maximum depths show a descending trend until 15 sccm, where the maximum depth reaches its lowest value at about 0.3 μm. However, when the C$_2$H$_2$ flow rates further increase, the maximum depths show an ascending trend to 30 sccm, where the value is about 1 μm. The maximum wear depth of the coating for 30 sccm is higher than others in seawater, which may arise from the corrosion and tribo-corrosion reaction in seawater. However, the maximum wear depth of CrN coating is relatively higher value among these coatings, which is attributed to the low hardness and columnar structure. The columnar structure with more pin holes provides straight diffusion channels for corrosive medium, which may weaken the bonding of compound and accelerate the wear [54].

Fig. 10. The morphologies of wear tracks on CrCN coatings in seawater.
Combined with the thickness of the coatings, it is observed that all coatings are not worn out in the process of friction, which means tribo-balls and substrates have no direct contact occurred during sliding process.

In order to further analysis the wear mechanism, the morphologies of wear tracks on CrCN coatings in seawater are shown in Fig. 10. In a cycle sliding process, some micro-particles on the surface of the CrCN coating are sufficiently deformed to form a smoother interface and seawater will accelerate the corrosion. Thus plastic deformation and corrosion of seawater are contributed to the wear-loss. It is clear that some wear pits are found in Fig. 10a. The wear pits are formed by the micro-particles spalling from the surface of coating during repetitive sliding. Meanwhile, seawater can accelerate the corrosion, which is advantage to aggravate the spalling of coating [55]. In addition, the flake pits are also observed in Fig. 10c and d, which show the morphologies of wear tracks on the coating deposited at 20 and 30 sccm. The large flake pits are formed by the crack propagating during cycle sliding process due to the low hardness and poor adhesion. As plastic deformation accumulates, cracks are preferentially formed under the surface, this is due to a highly compressive stress exists below the contact region. If the cracks are formed, further deformation will cause the cracks to extend, and then result in the delamination of large flake pits [56]. However, no obvious flake pits and wear pits are found on the coating at 10 sccm, which can be attributed to the high hardness and good corrosion resistance. The EDS analysis on the wear tracks reveals the similar features, thus only the coating deposited at 10 sccm and the EDS analysis of non wear region are presented, as shown in Fig. 11. The result shows that the Na, S and Cl elements are observed on the coating surface (Fig. 11a) and wear track (Fig. 11b), which indicates that a transfer of elements from artificial seawater to coating occurred. The signal of Na and Cl elements in wear track are stronger than in non wear region. This is due to the wear track can store more artificial seawater. Meanwhile, a few of W elements are also observed on the wear track, which indicates that a transfer of elements from friction pair to coating occurred during sliding. Furthermore, the wear track mainly contains Cr, C, N and O elements, which indicate that oxidation occurred. Similar results were reported by Refs. [46].

The low friction can be attributed to the graphitization effect or tribolayers formed on the contact surfaces during cycle sliding process. The graphite character of each tribolayer was identified by the Raman spectrum as shown in Fig. 12. Under seawater-sliding conditions, a peak centered at 1580 cm$^{-1}$ can be seen, which indicated that sp$^2$-hybridized carbon existed on the contact surface of the mating ball. The planar 2D graphite-like structure of sp$^2$-hybridized carbon in the surface will reduce dangling σ bonds on the contact surface, thus it can avoid the adhesive interaction between WC ball and coating [56]. At the C$_2$H$_2$ flow rate of 0 sccm, there is not obvious graphite character on the contact surface. With the increase of C$_2$H$_2$ flow rate, the peak intensity shows an ascending trend until 10 sccm, where the peak intensity reaches its highest value. These results are consistent with the content of sp$^2$ fraction. As discussed in the above, the wear behaviors of the CrCN coatings are closely relate to the carbon content, and it is obvious that the CrCN coatings deposited at the C$_2$H$_2$ flow rate of 10–15 sccm reveal a comprehensive value, indicating their potential applications as protective coating for tribo-components in seawater.

4. Conclusions

The CrCN coatings were deposited by multi-arc ion plating with different C$_2$H$_2$ flow rates. The effect of carbon content on micro-structure, mechanical properties and tribological properties in seawater has been investigated. The conclusions are summarized as follows:

(1) With the increase of C$_2$H$_2$ flow rate, the concentration of C atom increased gradually from 0 to 21.32 at%. The carbon element mainly exists as Cr–C, sp$^2$ and sp$^3$ bonds.

(2) The friction coefficients of the coatings at varied C$_2$H$_2$ flow rates show an apparent difference in seawater. The lowest friction coefficient is gained at 10 sccm and highest at 0 sccm, which are closed relate to the fraction of sp$^2$ bond and columnar structure of the coating. The graphite carbon exists as sp$^2$ bond in the coatings can greatly reduce the friction coefficient. The columnar structure contributes to the more micro-fracture during sliding in seawater.

(3) The lowest wear rate is gained at 10 sccm, where the maximum depth of wear track is also lowest. This arises from the high hardness, excellent toughness and better corrosion resistance.
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