



Tribocorrosion behaviors of nc-TiC/a-C:H nanocomposite coatings: In-situ electrochemical response

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ABSTRACT

Tribocorrosion is a complex process coupled with wear and corrosion behaviors in aggressive solutions, which is closely related with in-situ electrochemical response in terms of the transient variation coefficient of friction (COF) and open circuit potential (OCP). Hence, in this work, nc-TiC/a-C:H nanocomposite coatings were deposited using filtered cathodic vacuum arc at various C₂H₂ flow rates ($f_{C_2H_2}$). With an increase of $f_{C_2H_2}$ from 20 to 70 sccm, the coatings exhibit the structure evolution from (111)-texture to random orientation along with the decreasing crystallinity degree. Dense microstructure and smooth morphology are obtained in nc-TiC/a-C:H nanocomposite coatings. The sp²/sp³ ratios show an initial increase from 2.2 to 2.8, then followed by a decrease to 2.5. Accordingly, the decrease of hardness(H), hardness and effective Young's modulus (E*) ratio (H/E*), and H³/E*² are obtained from 45.8 GPa, 0.12 and 0.67 at 20 sccm to 30.7 GPa, 0.11 and 0.38 at 70 sccm, respectively. Moreover, in potentiodynamic polarization tests, the coatings deposited at 70 sccm show the highest corrosion potential of 0.14 V and corrosion current density of $4.67 \times 10^{-8} \text{ Acm}^{-1}$, thanks to the contribution from amorphous carbon phase. During tribocorrosion tests in 3.5 wt.% NaCl aqueous solution, however, the coatings at 20 and 70 sccm exhibit mild abrasive wear with similar values of COF of 0.2, OCP of -0.025 V and specific wear rate of $1.03 \times 10^{-6} \text{ mm}^{-3} \text{ N}^{-1} \text{ m}^{-1}$. The enhanced tribocorrosion properties of the coating at 20 sccm are attributed to the high hardness, H/E* and H³/E*². The amorphous carbon phase in the coating at 70 sccm makes up for the deficiency of hardness, H/E* and H³/E*². Moreover, in cycling tribocorrosion tests, nc-TiC/a-C:H nanocomposite coatings reveal that passive films formed on sliding contact surface possess a strong ability of regeneration and self-repairation.

1. Introduction

Stainless steels are widely used in nuclear and marine engineering environment because of their good mechanical properties and high corrosion resistance [1–2]. The severe pitting corrosion and tribocorrosion damage occurring on the stainless steel surfaces in seawater limits its service life and reliability [3–6]. A strategy to solve this problem is to deposit a coating with excellent wear and corrosion resistance. The Ti doped into diamond-like carbon (DLC) to form nc-TiC/a-C:H nanocomposite coatings were found to enhance wear and corrosion resistance due to the reduction of defects and structural optimization [6–8]. nc-TiC/a-C:H nanocomposite coatings receive

immense attention for their ultrahigh hardness, wear and corrosion resistance [9,10]. However, there are limited researches on tribocorrosion behaviors of nc-TiC/a-C:H nanocomposite coatings, especially for its in-situ electrochemical response in the tribocorrosion process.

Tribocorrosion is characterized by the synergistic interaction of wear and corrosion [11–15]. In the majority of cases, the material damage caused by tribocorrosion is more serious than pure abrasion or corrosion [16,17]. The passive films will peel off under friction and be very difficult to recover. Meanwhile, corrosion also changes the hardness, roughness and microstructure of the contact surface, thus changing the wear process. It is suggested that the specific wear rates of Ti-Si-N coatings in seawater were higher than the specific wear rates in air

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[18]. While it is reported that the specific wear rates of TiN and TiCN coatings in seawater were higher than the specific wear rates in the air and distilled water [19]. The synergistic interaction mechanism between wear and corrosion is not yet clearly understood. The single experimental data obtained from electrochemical and tribological tests are not enough to evaluate the comprehensive performance of the coating in the actual practical application environment. It is necessary to use in-situ tribocorrosion tests to explore the synergistic effect of wear and corrosion in the tribocorrosion process.

The corrosion process often starts with the defects of the film. nc-TiC/a-C:H coatings deposited by filtered cathodic vacuum arc (FCVA) technique exhibit smooth morphology, homogenous and dense structure due to virtually magnetron filtered large particles [20]. Coatings with few micro defects can avoid accidental film damage in the process of corrosion and tribocorrosion. In this work, nc-TiC/a-C:H nanocomposite coatings were deposited by sputtering Ti target at various C_2H_2 flow rates ($f_{C_2H_2}$) on Si (100) and AISI 304L stainless steel substrates using FCVA. A Ti adhesion layer followed by nc-TiC/a-C:H nanocomposite coating was deposited between substrate and coatings to improve adhesion. The influence of $f_{C_2H_2}$ on chemical composition, mechanical properties, and corrosion and tribocorrosion resistance in 3.5 wt.% NaCl aqueous solution were studied in details to explore the related mechanisms.

2. Experimental details

Nc-TiC/a-C:H nanocomposite coatings were deposited on commercial Si(100) wafer (20 mm × 5 mm × 0.5 mm) and polished AISI 304L stainless steel (SS) (20 mm × 20 mm × 3 mm) substrates using filtered cathodic vacuum arc system (Fig. 1) at $f_{C_2H_2}$ in the range of 20–70 sccm. Before coating depositions, Si and AISI 304L stainless steel substrates were cleaned by ultrasonic cleaning in acetone, alcohol and deionized water for 15 min in turn, then drying in dry N_2 gas. After the cleaning process, the samples were fixed on the substrate holder in the middle of the chamber, and the chamber was evacuated to a base pressure of about 5×10^{-3} Pa. A Ti target ($\Phi 100$ mm, 99.99% purity) was used as an arc cathode. Ti plasma produced by a high current discharge of 120 A on the Ti target, while an exciting current of 2.5 A on the filter. Filter in the shape of a 90°-curved tube was used to filter the large and uncharged particles from the Ti plasma and formed as a plasma transport channel. Acetylene was ionized into plasma by colliding with Ti plasma in the vacuum chamber. Ion sputtering procedure without acetylene was firstly carried out with a negative bias voltage of 800 V for 2 min, then 600 V and 400 V for 30 s, removing the possible oxides on the substrate

surfaces. After that, a 200 nm thick Ti adhesion layer was grown under the negative bias voltage 100 V for 2 min. Finally, nc-TiC/a-C:H nanocomposite coatings were grown under the negative bias voltage 150 V for 30 min at $f_{C_2H_2}$ in the range of 20–70 sccm.

The elemental compositions and chemical bondings of the coatings were analyzed by laser confocal Raman spectroscopy (LabRAM Aramis) and X-ray photoelectron spectroscopy (XPS, ESCALAB250) equipped with a monochromatized source of Al K α X-rays. The Al K α X-ray source was operated at 320 W power and the pressure in the analysis chamber was lower than 5×10^{-7} Pa during spectral acquisition. All spectra were calibrated using the adventitious carbon C 1s peak at 284.6 eV. The raw data processing was performed by Thermo Advantage software. The Ti 2p and C 1s spectra were deconvoluted after a Smart-Shirley type background subtraction. Deconvolution was performed using mixed Lorentzian-Gaussian (L/G 30%) function for each fitting component. The Raman spectra were measured in the range of 100–2500 cm^{-1} with an Ar-Kr laser by using a wavelength of 532 nm laser. The crystallographic structures of nc-TiC/a-C:H nanocomposite coatings were detected using X-ray diffraction (XRD, X pert pro MPD) in θ –2 θ configuration with the Cu K α radiation. The microstructure of nc-TiC/a-C:H nanocomposite coatings deposited at various $f_{C_2H_2}$ by FCVA were investigated by both field emission scanning electron microscope (FESEM, S4800) and transmission electron microscope (TEM, TF20). Cross-sectional morphologies of coatings were carried out at 10 kV operating voltage up to 20000x magnification levels by FESEM, While the accelerating voltage of 20 kV and the working distance of 15 mm were used for energy dispersive spectrometer (EDS) analyses. The nanohardness of the coatings was measured by continuous stiffness method, and the maximum indentation depth was 200 nm. HR-TEM images were obtained at 100 kV. Focused ion beam technique was used for the preparation of HR-TEM specimens. The hardness and Young's modulus of the nc-TiC/a-C:H nanocomposite coatings were tested by a nanoindenter (Keysight G200). Indentation depth was set as below 10 % of coating thickness to minimize the substrate effect. H/E^* and H^3/E^{*2} ratios were calculated using hardness (H) and effective Young's modulus (E^*), where $E^* = E/(1-\nu^2)$, ν is the Poisson ratio of the coating material. Residual stress in the coating deposited on Si substrates at various $f_{C_2H_2}$ was measured by Stoney equation as follow [20]:

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

Where E_s , ν_s , t_s , R_0 and R_n are Young's modulus, Poisson ratio, Si substrate thickness, coating thickness, curvature radii of Si substrate and coatings, respectively. Thus, residual compressive stress in the coatings deposited at 20, 40 and 70 sccm are -1.3, -2.2 and -2.7 GPa, respectively.

The corrosion resistance of the nc-TiC/a-C:H nanocomposite coatings was explored by an electrochemical workstation (ParStat 2273). Tribological and tribocorrosion properties of nc-TiC/a-C:H nanocomposite coatings were studied using in-situ reciprocating electrochemical corrosion tribometer (MFT-EC4000) equipped with a three-electrode electrochemical test system in a reciprocating configuration against Si_3N_4 ball (6 mm in diameter) under a normal load of 1 N at 1 Hz for a reciprocating sliding time of 40 minutes. The cross-section profiles of wear tracks were examined using a surface profilometer (Taylor Hobson) to calculate a specific wear rate using the integration function in Origin software. Besides, worn surface morphologies were analyzed by FESEM and EDS to study wear mechanisms.

3. Results and discussion

3.1. Deposition rate, crystallographic structure and morphologies

Fig. 2 shows XRD patterns of nc-TiC/a-C:H nanocomposite coatings deposited on AISI 304L stainless steel by FCVA at a $f_{C_2H_2}$ of 20–70 sccm. It is clearly seen in XRD diffraction patterns that (111) and (220) peaks

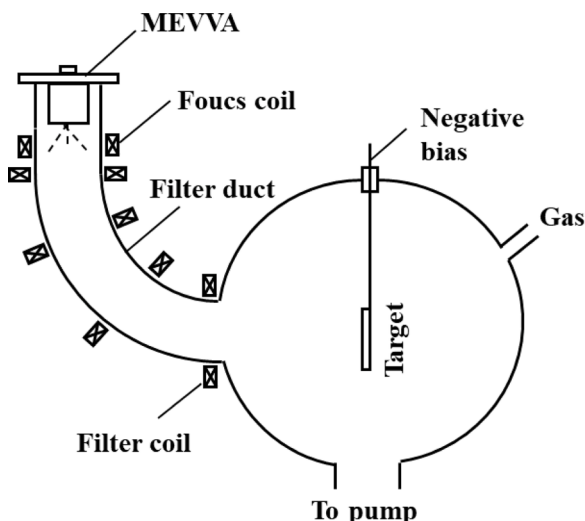


Fig. 1. Diagram of FCVA deposition system.

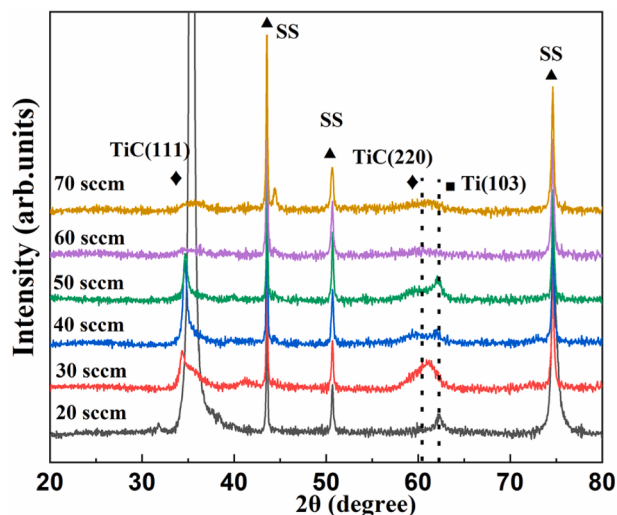


Fig. 2. XRD patterns of nc-TiC/a-C:H nanocomposite films deposited at various $f_{C_2H_2}$.

from face-centered cubic (fcc) structure assigned to TiC phase (JCPDS 71-0298) are detected except for diffraction peaks of 304L austenitic stainless steel substrates (labeled as SS) and Ti (JCPDS44-1294) transition layer. The decreasing intensity and broadening width of TiC(111) peak are gradually obtained with $f_{C_2H_2}$ increasing from 20 to 70 sccm probably due to refined grains. It is suggested that the growth of grains is interrupted by the amorphous coating structure formed by the increases of C content, accomplished with a transform from polycrystalline to amorphous coated nanocrystalline structure [21]. TiC (220) peak of nc-TiC/a-C:H nanocomposite coatings show a slight shifting to a lower diffraction angle along with increasing peak width, which is possibly related to the change of residual stress state in the range of -1.3 to -2.7 GPa.

Cross-sectional images of nc-TiC/a-C:H nanocomposite coatings deposited on Si(100) substrates at various $f_{C_2H_2}$ are presented in Fig. 3. As $f_{C_2H_2}$ is increased from 20 to 70 sccm, the deposition rate of the coatings accordingly increases from 0.07 to 0.12 $\mu\text{m}/\text{min}$ due to the increasing concentration of carbon ions to promote the growth of the coatings. Cross-sectional morphologies of the coatings deposited at $f_{C_2H_2}$ of 20, 40 and 70 sccm show homogeneous and dense microstructure features. Moreover, it is noted that there are no visible micro-particles or coarse grain is observed throughout the nc-TiC/a-C:H coatings sections attributed to the high-efficiency magnetic filter. An adhesion Ti layer with a thickness of about 300 nm is detected. Also, there is a dense interface without a distinct boundary between the Ti layer and nc-TiC/a-C:H nanocomposite coatings.

Fig. 4 presents the high-resolution TEM micrographs with selected area electron diffraction (SAED) patterns inserted of nc-TiC/a-C:H nanocomposite coating deposited at 70 sccm. It is observed that the

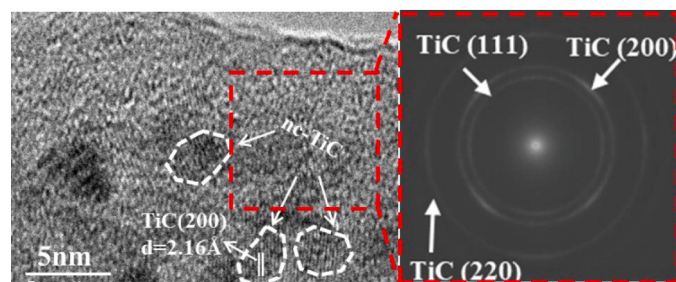


Fig. 4. High resolution TEM micrograph with selected area electron diffraction (SAED) patterns of the nc-TiC/a-C:H nanocomposite films deposited at 70sccm.

nc-TiC/a-C:H nanocomposite coating exhibit an amorphous coated TiC nanocrystalline structure. The grain sizes of TiC are about 3–5 nm. The SAED patterns show distinct diffraction rings assigned to (111), (200) and (220) reflections from the fcc crystal TiC structure of nc-TiC/a-C:H nanocomposite coatings.

3.2. Chemical bonding structure

Chemical bonding structure of nc-TiC/a-C:H nanocomposite coatings was investigated by XPS. Ar^+ ion etching of 30 s at 800 V was carried out before the XPS test to remove surface contaminants. The atomic percentage of each element of coatings calculated by XPS are provided in Fig. 5(a). The carbon content in nc-TiC/a-C:H nanocomposite coatings increases from 44.7 to 87.9 at.%, while the titanium content decreases from 50 to 9.8 at.% with the $f_{C_2H_2}$ increase from 20 to 70 sccm. The oxygen content remains virtually unchanged, about 1.5 ~5.3 at.%.

Fig. 5(b) presents the C1s spectra of nc-TiC/a-C:H nanocomposite coatings deposited at different $f_{C_2H_2}$. The asymmetric C1s peak can be fitted to 281.8 ± 0.1 eV, 282.8 ± 0.1 eV, 284.3 ± 0.1 eV, 285.2 ± 0.1 eV and 286.5 ± 0.2 eV peaks originated from C-Ti, $\text{C}^*\text{-Ti}$, $\text{sp}^2\text{-C}$, $\text{sp}^3\text{-C}$ and C-O/C=O [22–29], as shown in Fig. 5(a). The high-intensity peaks of $\text{sp}^2\text{-C}$ in samples of 30–70 sccm indicating carbon is mainly present as an amorphous phase. Besides, it is generally accepted that the $\text{C}^*\text{-Ti}$ bond belongs to non-stoichiometric TiCx [25,29,30] which located at the interface between TiC grains and amorphous DLC phase. It is seen that C-Ti and $\text{C}^*\text{-Ti}$ bond intensity gradually decreases with the $f_{C_2H_2}$ increases from 20–70 sccm, while $\text{C}^*\text{-Ti}/\text{C-Ti}$ ratios show a sharp increase with the $f_{C_2H_2}$ increases from 20–50 sccm because of the grain refinement. The increases of $\text{sp}^2\text{-C}$ and $\text{sp}^3\text{-C}$ bonds intensity reveals that the excess carbon in high $f_{C_2H_2}$ conditions would exist as the form of amorphous carbon in the nc-TiC/a-C:H nanocomposite coating.

Fig. 5(c) presents the Ti2p spectra of nc-TiC/a-C:H nanocomposite coatings deposited at different $f_{C_2H_2}$. The Ti2p peak composes of three pairs double peaks at a binding energy of 454.7 ± 0.2 eV and 460.6 ± 0.2 eV, 455.4 ± 0.2 eV and 461.4 ± 0.2 eV, 456.8 ± 0.2 eV and 462.5 ± 0.2 eV. The peaks at 454.7 eV and 456.8 eV are attributed to TiC and Titanium oxide [23–25,29]. There are two broad Ti-C* peaks at 455.4 eV

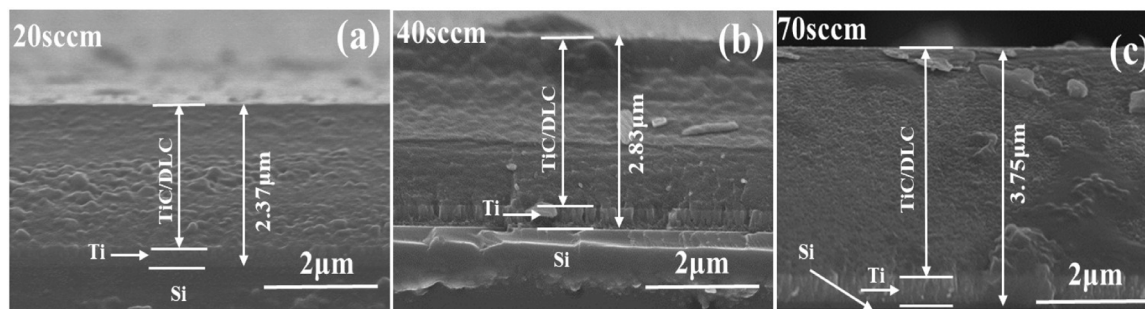


Fig. 3. Cross-sectional images of nc-TiC/a-C:H nanocomposite coatings deposited at various $f_{C_2H_2}$: (a) 20sccm (b) 40sccm (c) 70sccm.

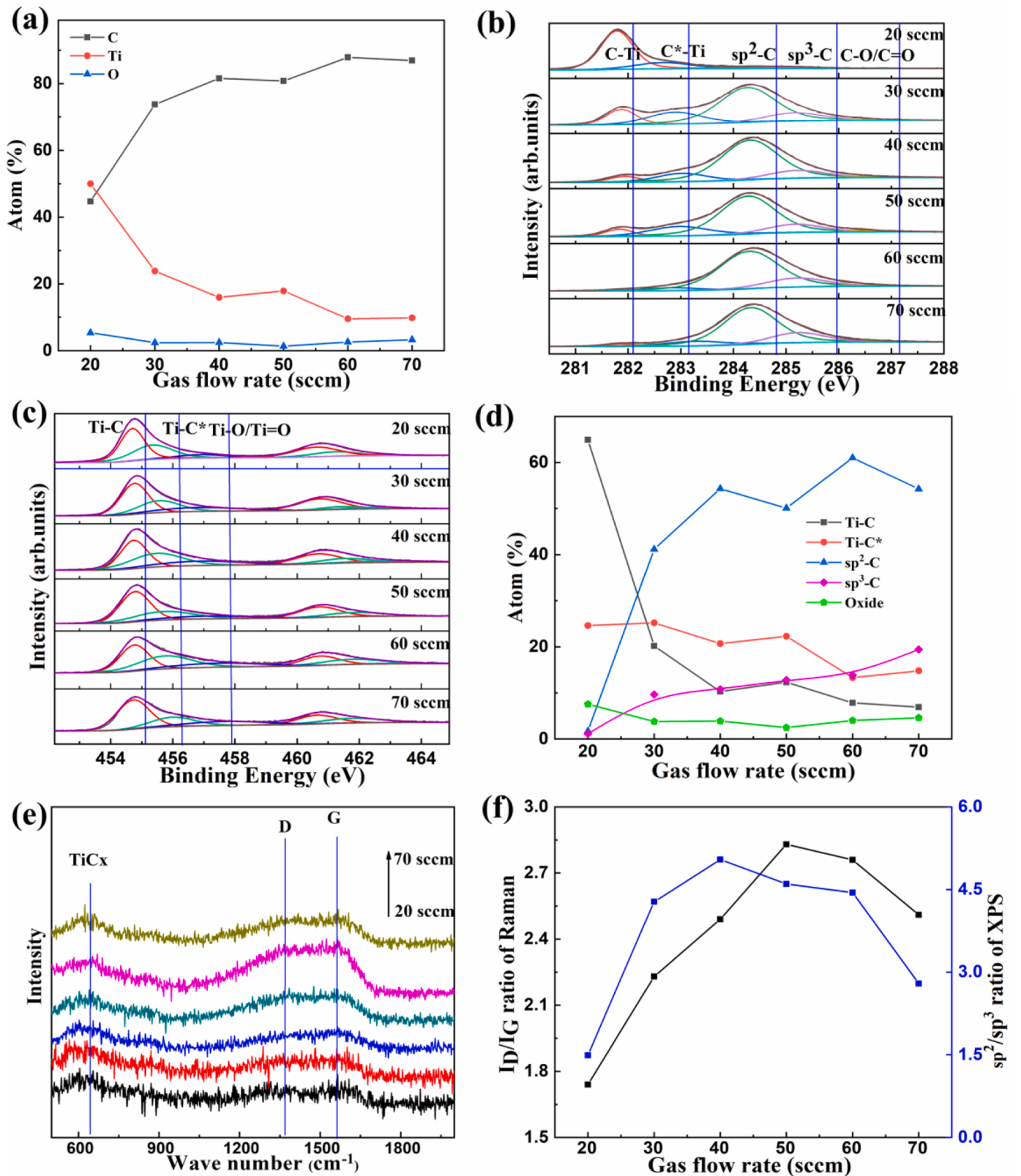


Fig. 5. Composition patterns of TiC / DLC nanocomposite films under various $f_{C_2H_2}$: (a) C1s XPS fitted spectra (b) Ti2p XPS fitted spectra (c) Raman spectra (d) I_D/I_G ratio of Raman spectrum and sp^2/sp^3 ratio of XPS.

and 461.4 eV, which can be assigned to non-stoichiometric TiC in the nc-TiC boundary [25,30,31]. Valence charge transfer on the interface between nc-TiC and amorphous carbon leads to the Ti-C binding energy shifts to higher energy [23,32]. It was also mentioned in nc-CrC/a-C:H,

nc-ZrC/a-C:H and other metal carbide/DLC nanocomposite systems [25, 33–37].

Fig. 5(d) presents the change of component contents in nc-TiC/a-C:H nanocomposite coatings deposited at different $f_{C_2H_2}$. The XPS fitting

results in the following components: TiC, TiC*, sp²-C, sp³-C and oxide. It can be seen from Fig. 5(d) that the TiC content in the coatings decreases rapidly from 64.9 at.% to 6.9 at.%, the TiC* content first increase from 24.6 at.% to 25.1 at.% and then decreases slowly to 13.3 at.%, the sp²-C content increase quickly from 1.7 at.% to 54.3 at.%, the sp³-C content increase gradually from 1.1 at.% to 19.44 at.%, while the oxide content remains virtually unchanged from 2.5 at.% to 7.5 at.% with the increase of acetylene flow rate from 20 sccm to 70 sccm.

Fig. 5(e) presents the Raman spectra of nc-TiC/a-C:H nanocomposite coatings deposited at different $f_{C_2H_2}$. Broaden peaks at 500–800 cm⁻¹ were originated from TiC [38–42]. S. Pellegrino's research on Au⁺ implant TiC coatings investigated that two well-separated optical bands located at 580 cm⁻¹ and 670 cm⁻¹ of TiC increase and broaden continuously with the increasing number of vacancies created by irradiation [43]. It is proved that the atom distribution at the nc-TiC/a-C:H interfaces is different from the internal structure of TiC nanocrystals. The existence of peaks at about 1100–1700 cm⁻¹ proves the existence of amorphous carbon in nc-TiC/a-C:H coatings. The Raman spectra of nc-TiC/a-C:H nanocomposite coatings peaks have been curve-fitted with Gaussian-Lorentzian to estimates I_D/I_G ratios (Fig. 5(d)). Peaks around 1370 cm⁻¹ is assigned for D peak, which corresponds to highly disordered graphitic structures [44], and peaks around 1550 cm⁻¹ for G peak, which are sp²-C hybrid bond. The calculated ratios of sp²/sp³ by XPS as a function of $f_{C_2H_2}$ is also shown in Fig. 5(f). The I_D/I_G ratios exhibit the degree of disorder in the carbon network.

Since most of the C atoms in the 20 sccm sample are formed as TiC and TiC*, it will not be discussed here. The I_D/I_G ratios and sp²/sp³ ratios of nc-TiC/a-C:H nanocomposite coatings are more or less similar, and its first increase then decreases with an increase of $f_{C_2H_2}$. The I_D/I_G ratios are in a small extent between 2.49 and 2.83. However, the ratio increases up to 2.83 with an increase of $f_{C_2H_2}$ at 50 sccm then decreases to 2.51, and therefore suggests that the disorder in the material first increase and then decrease with increasing $f_{C_2H_2}$ in the nc-TiC/a-C:H nanocomposite coatings. Both XPS and Raman results show that non-stoichiometric TiCx exists at the interface between TiC nanocrystalline and amorphous carbon matrix. It is generally believed that C exists in the form of metallic carbides and amorphous in me-c (me = Ti, Cr, Zr, etc.) coatings [34,45–46]. The XRD diffraction peaks of C are not found in Figure 2, so sp²-C and sp³-C in nc-TiC/a-C:H coating exists as amorphous. XRD and XPS results show that coating deposited at $f_{C_2H_2}$ =20sccm have a good crystallization TiC structure, the total contents of TiC and TiC* as high as 89.5 at.%; The content of TiC decreases rapidly to 20.2 at.%, TiC* increases slightly to 25.1 at.%, the total

content of sp²-C and sp³-C increases to 50.8 at.%, while the XRD diffraction patterns peaks of TiC confirm the grains size decreases with the increases of $f_{C_2H_2}$ to 30 sccm; As the $f_{C_2H_2}$ increases to 70 sccm, the total content of TiC and TiC* in the coating decrease to 21.7 at.%, and the total content of sp²-C and sp³-C increases to 71.7 at.%, meanwhile, TEM graphs show that the coating is amorphous coated nanocrystalline TiC composite structure. The peak of TiC* in Ti2p shifts to higher binding energy with the increases of $f_{C_2H_2}$, which confirmed that the boundary of TiC nanocrystals was transformed from Ti-rich TiCx to C rich TiCx. In summary, it can be concluded that the coatings transform from well-crystallized TiC to nc-TiC/a-C:H nanocomposite coating with the increasing acetylene gas flow from 20 to 70 sccm.

3.3. Mechanical properties

Fig. 6 exhibits hardness, Young's modulus, H/E* and H³/E*² of nc-TiC/a-C:H nanocomposite coatings. It is defined that material toughness refers to the ability of materials to absorb energy in the process of deformation to fracture. H/E* and H³/E*² ratios of hard coatings are concerned with the resistance of elastic strain to failure and plastic deformation. Thus, H/E* and H³/E*² are factors to evaluate the toughness of the film [47–49]. As shown in Fig. 6(a), hardness and Young's modulus decrease from 45.8 GPa and 378.6 GPa at 20 sccm to 30.7 GPa and 272.7 GPa at 70 sccm. The hardness and Young's modulus decrease with the carbon content increased from 44.7 at.% to 87.9 at.%, which also matches with the results of Zhao et al [50]. However, H/E* and H³/E*² show similar trends with hardness from 0.12 and 0.67 at 20 sccm to 0.11 and 0.38 at 70 sccm (Fig. 6(b)). The decrease of hardness, H/E* and H³/E*² are related to the change of nanocrystalline size and amorphous structure.

3.4. Corrosion properties

Potentiodynamic polarization curves of the nc-TiC/a-C:H nanocomposite coatings were measured by the electrochemical measuring system in 3.5 wt.% NaCl solution with a scan rate of 2 mV/s. Free corrosion potential (E_{corr}), corrosion current density (I_{corr}) and polarization resistance (R_p) were calculated by Tafel extrapolation, as shown in Table 1. The corrosion current density is an electrochemical kinetic parameter, indicating the rate of corrosion, while free corrosion potential indicating the corrosion tendency.

Fig. 7(a) presents potentiodynamic polarization curves of nc-TiC/a-C:H nanocomposite coatings deposited at different $f_{C_2H_2}$. Fig. 7(b)

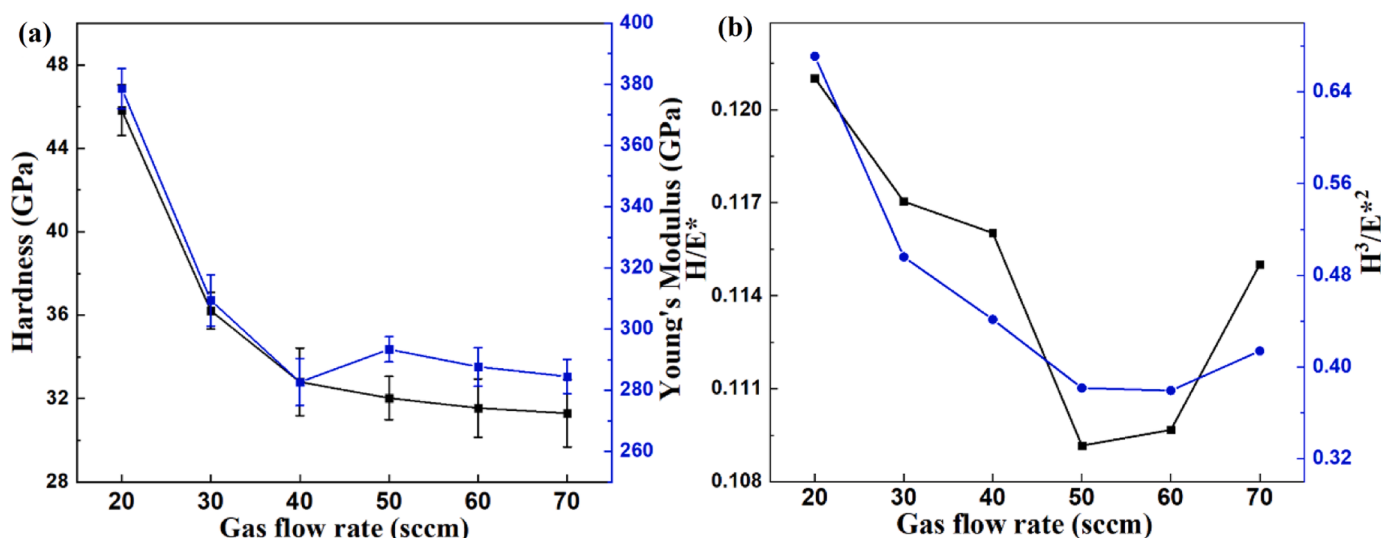


Fig. 6. (a) Hardness, Young's modulus and (b) H/E*, H³/E*² of nc-TiC/a-C:H nanocomposite films with various $f_{C_2H_2}$.

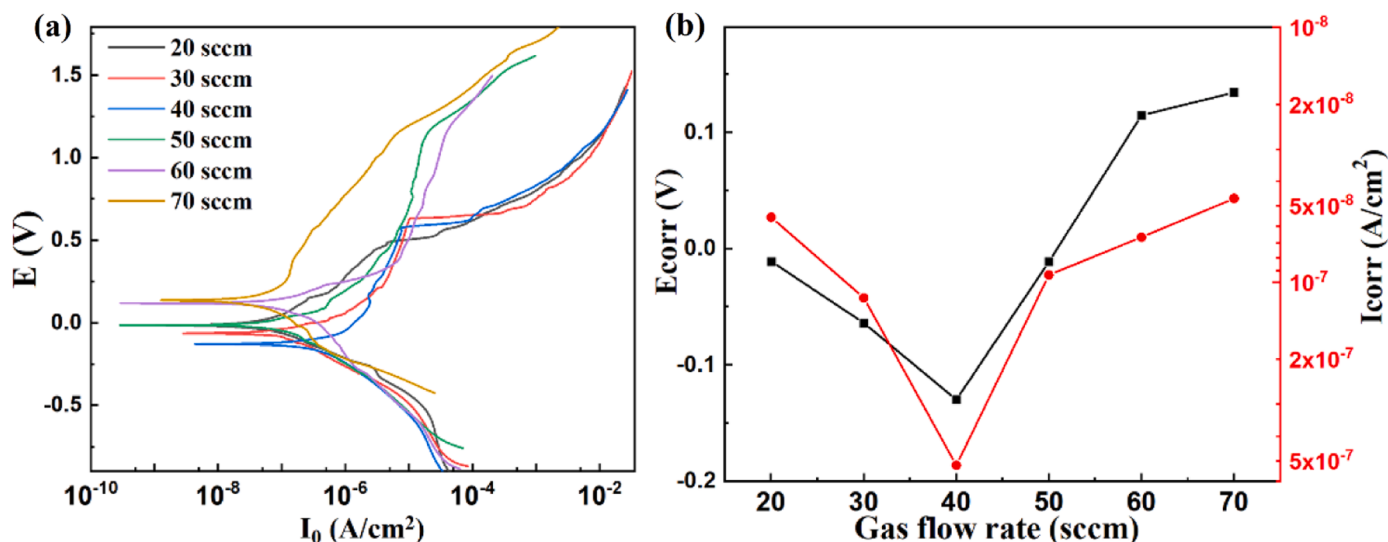


Fig. 7. (a) Potentiodynamic polarization curves of nc-TiC/a-C:H nanocomposite films in 3.5wt.% NaCl solution with different acetylene gas flow rates, (b) E_{corr} and I_{corr} of nc-TiC/a-C:H nanocomposite films in 3.5wt.% NaCl solution with various $f_{C_2H_2}$.

plots the E_{corr} and I_{corr} as a function of $f_{C_2H_2}$ for nc-TiC/a-C:H nanocomposite coatings. The E_{corr} of nc-TiC/a-C:H nanocomposite coatings range from -0.15 to 0.14 V. The E_{corr} of nc-TiC/a-C:H nanocomposite coatings show a decreasing trend and then increased with an increase of $f_{C_2H_2}$. Moreover, the I_{corr} shows an opposite trend. nc-TiC/a-C:H nanocomposite coatings deposited at 70 sccm have the best corrosion, while the E_{corr} is 0.14 V and the I_{corr} is $4.67 \times 10^{-8} \text{ A/cm}^2$.

At present, there is no unified conclusion about the influence of doping treatment on the corrosion resistance of DLC. A few transition metal elements doping can improve the corrosion resistance of DLC [51, 52], but high doping leads to the descend of corrosion resistance [53]. The enhanced corrosion resistance of amorphous is attributed to the chemical homogeneity and lack of structural defects [54]. There are only a few defects or grain boundaries in the amorphous that can provide ion transport channels, which can slow down the ion transport in the corrosion process to a certain extent [55], thus providing excellent corrosion resistance.

Nanostructured materials have high crystal boundary density. On the one hand, high crystal boundary density can provide more active sites to rapidly form a continuous protective passive film [56,57]. On the other hand, the decrease of electronic work function leads to the increase of electrochemical activity at the boundary of nanocrystalline [58]. Also, higher grain boundary density will form more micro electrochemical cells between a large number of grain boundaries and the matrix, and improve the electrochemical reactivity during the corrosion process, thus accelerating the corrosion, which is consistent with the classical corrosion theory [59-61].

The corrosion resistance of nc-TiC/a-C:H nanocomposite coatings firstly decreases and then increases with the increasing acetylene gas flow rates mainly due to the influence of composition and structure distribution of nanocrystalline boundary in nc-TiC/a-C:H nanocomposite coatings. The boundary of TiC nanocrystals is transformed from Ti-rich TiCx to C-rich TiCx, and finally separated by the amorphous DLC to form a DLC coated nc-TiC/a-C:H amorphous nanocrystalline coating structure with the increasing C contents. Furthermore, the grain refinement caused by the increase of C contents leads to the increase of grain boundary density in the film, then a DLC coating layer is formed on the surface of TiC nanocrystals with a further increase of C contents. The grain boundary density decreases with the increase of DLC coating thickness, which was proved by TiC* contents in Fig. 5(d). Thus, the density of continuous grain boundary first increases and then decreases with the increasing acetylene gas flow rate from 20 to 70 sccm. The

corrosion resistance of the film increases with the decrease of continuous grain boundary density.

3.5. Tribocorrosion behaviors

Tribocorrosion is a complex process coupled with wear and corrosion behaviors in 3.5 wt.% NaCl solution, which is closely related with an in-situ electrochemical response in terms of the transient variation coefficient of friction (COF) and open circuit potential (OCP) during in-situ tribocorrosion tests. The COF, OCP and worn surface of nc-TiC/a-C:H nanocomposite coatings deposited at various $f_{C_2H_2}$ were shown in Fig. 8(a-e). The fluctuate of OCP value is related to the combining action between various factors, such as the electrochemical condition of working electrode, sliding contact surface, mass transfer, and competitive effects of applied potential and film dissolution rate [62-64].

It is suggested that the continuous formation and breaking-up of passive films continue to endure the sliding wear in 3.5 wt.% NaCl aqueous solution, which has a close correlation with the transient change of COF and OCP, corresponding to tribocorrosion mechanism [49]. As shown in Fig. 8(a), a large amount of black debris covered on wear track with 754 μm in width. The COF of AISI 304L stainless steel dramatically changes in the process of abrasion owing to the synergistic effects of corrosion damage and abrasive wear. Moreover, the deep wear crack increases the contact area between the grinding ball and stainless steel, resulting in the expansion of corrosion active zone, which also can lead to the decrease of OCP [65]. The values of OCP, COF and specific wear rate are -0.20 V, 0.7 and $2.12 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, respectively.

It is observed that there are three stages, a rapid ascent section, a relatively stable section and rapid rise to stability, in the transient change of OCP for nc-TiC/a-C:H nanocomposite coatings in tribocorrosion process, as shown in Fig. 8(b-d). The three stages of OCP are identified to correspond to the breakdown of the passive film, the dynamic equilibrium between the destruction of the passive film and electrochemical repassivation and repair of the passive film, respectively. Otherwise, compared with the depth of wear marks and the change of OCP in Fig. 7(b,d), it can be found that the decrease of OCP in the relatively stable section is related to the increase of active area caused by the increase of contact area.

The OCP values in a relatively stable section of nc-TiC/a-C:H nanocomposite coatings firstly decreases and then increases with increasing $f_{C_2H_2}$, consistent with the change of corrosion potential. Fig. 8(a-d) present that nc-TiC/a-C:H nanocomposite coatings deposited at 70 sccm

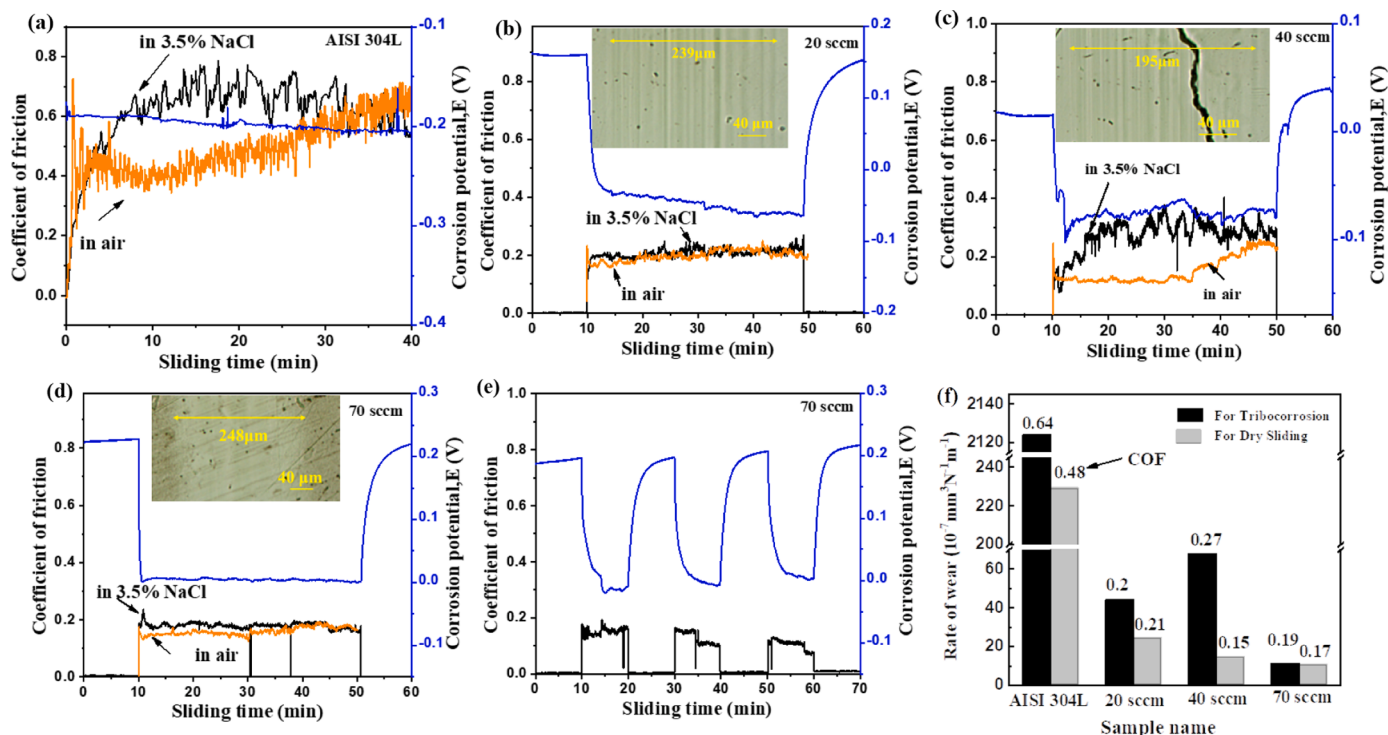


Fig. 8. COF, OCP and specific wear rates of nc-TiC/a-C:H nanocomposite coatings deposited at 20, 40 and 70 sccm in 3.5 wt.% NaCl aqueous solution and air, as well as the images of worn surface inserted, as compared with those of AISI 304L stainless steel.

have the highest value (-0.01 V) of OCP in relatively stable sections and the shallowest wear scars, which implies the highest tribocorrosion resistance. Moreover, the sharp fluctuation OCP of nc-TiC/a-C:H nanocomposite coatings deposited at 40 sccm is due to crack initiation and propagation in the tribocorrosion process. Periodic sliding tests were used to further analyze the passivation and depassivation behavior of coatings in tribocorrosion (Fig. 8(e)). The variation of OCP exhibits periodic fluctuations due to the breaking-up and reparation of the passivation film. Also, OCP rapidly gets back to the initial value once the slider stops, indicating the excellent passivation recovery ability of nc-TiC/a-C:H nanocomposite coatings.

The comparison of friction coefficient and specific wear rate in air and 3.5 wt.% NaCl aqueous solution of nc-TiC/a-C:H nanocomposite coatings and AISI 304L stainless steel were shown in Fig. 8(a-d,f). It can be seen that the friction coefficient of nc-TiC/a-C:H nanocomposite coatings deposited at 20 and 70 sccm in the air are similar to that in 3.5 wt.% NaCl aqueous solution. The value of COF of 20 sccm and 70 sccm sample is about 0.2. However, the value of COF of 40 sccm sample shows a drastic change, up to 0.35, due to the rapid crack initiation and propagation, accompanied by the micro-cutting action in deep plough grooves.

Nc-TiC/a-C:H nanocomposite coatings deposited at 20 sccm have the highest specific wear rate of $1.03 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ in 3.5 wt.% NaCl aqueous solution, as compared to $1.13 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ at 70 sccm, $1.7 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ at 40 sccm and $2.12 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for AISI 304L stainless steel. The increased hardness, H/E^* and H^3/E^{*2} of the coatings with lower residual stress are responsible for low COF, low specific wear rate and high OCP. In addition, it is noted that the amorphous carbon phase in the coatings deposited at 70 sccm makes up for the deficiency of hardness, H/E^* and H^3/E^{*2} .

The surface morphology and elements distribution of wear track are investigated using FESEM images and EDS to explore tribocorrosion mechanisms of nc-TiC/a-C:H nanocomposite coatings deposited at various $f_{C_2H_2}$, as shown in Fig. 9. The nubby oxides uniformly covered on the worn surface of sample 20 sccm and 70 sccm are attributed to the transfer of some wear debris, which has a function as a tribo layer to

reduce friction and wear. At 40 sccm, a lot of cracks and corrosion pits are observed on the worn surface. Furthermore, no Cl element accumulation is detected around cracks probably induced by corrosion, revealing that ploughing and mechanical micro-cutting resulted in coating adhesion failure.

In the process of friction and wear in corrosion solution, corrosion behaviors preferentially would be activated along the grain boundary. Intergranular corrosion leads to the separation of TiC nanocrystals in the coating, leading to abrasive wear due to hard abrasive particles cutting the film surface. The rapid expansion of the weak area caused by corrosion leads to the rupture and failure of the film in the process of erosion, which leads to the accelerated destruction of the films in the coupled process of corrosion and wear.

The improvement of tribocorrosion resistance of nc-TiC/a-C:H nanocomposite coatings mainly depends on the increased hardness, H/E^* and H^3/E^{*2} of the coatings with lower residual stress. The periodic sliding test shows that the passivation films of nc-TiC/a-C:H nanocomposite coatings has strong regeneration and reparability on the sliding contact surface, which can protect the coating from the further influence of corrosion solutions.

4. Conclusions

Nc-TiC/a-C:H nanocomposite coatings with dense microstructure and smooth morphology were deposited using filtered cathodic vacuum arc at various C_2H_2 flow rates ($f_{C_2H_2}$). With an increase of $f_{C_2H_2}$ from 20 to 70 sccm, highly (111)-textured coatings changes to randomly orientated coatings along with the decreased crystallinity degree. The highest hardness of 45.8 GPa, H/E^* of 0.12, H^3/E^{*2} of 0.67 are achieved at 20 sccm, and then decrease to the hardness of 30.7 GPa, H/E^* of 0.11, H^3/E^{*2} of 0.38 at 70 sccm. The coating deposited at 70 sccm shows the highest corrosion potential of 0.14 V and corrosion current density of $4.67 \times 10^{-8} \text{ A cm}^{-2}$ than those of other coatings thanks to the contribution from amorphous carbon phase. During tribocorrosion tests in 3.5 wt.% NaCl aqueous solution, however, the coatings deposited at 20 and 70 sccm exhibits mild abrasive wear with similar values of COF of 0.2,

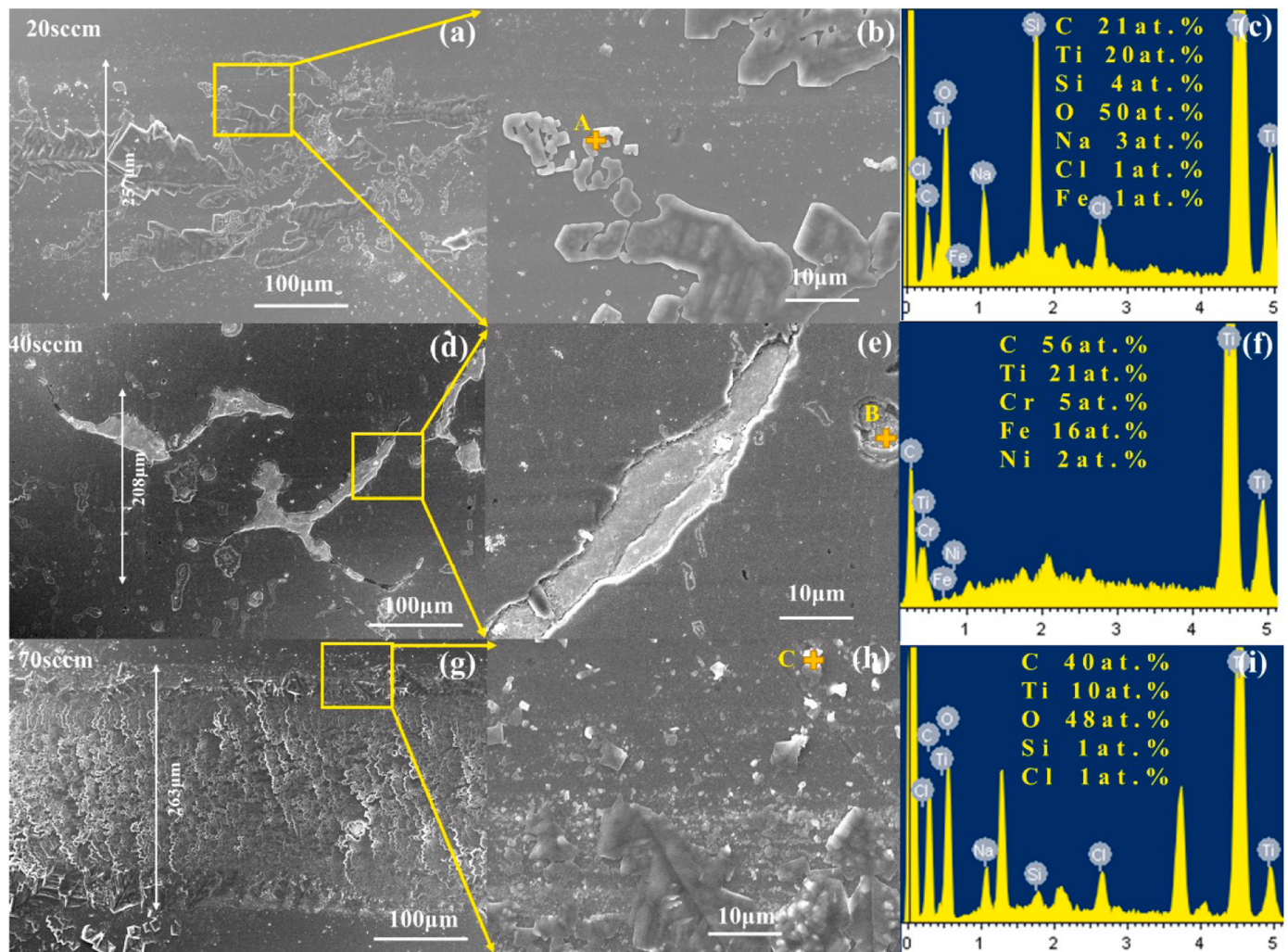


Fig. 9. SEM images and EDS results of wear tracks of nc-TiC/a-C:H nanocomposite coatings.

OCP of -0.025 V and specific wear rate of $1.03 \times 10^{-6} \text{ mm}^{-3} \text{ N}^{-1} \text{ m}^{-1}$. The enhanced tribocorrosion properties of the coatings deposited at 20 sccm are attributed to the high hardness, H/E^* and H^3/E^{*2} . The amorphous carbon phase in the coatings deposited at 70 sccm makes up for the deficiency of hardness, H/E^* and H^3/E^{*2} . Moreover, nc-TiC/a-C:H nanocomposite coatings in cycling tribocorrosion tests revealed that passive films formed on sliding contact surface possessed a strong ability of regeneration and self-repairment.

Declaration of Competing Interest

We confirm that the submitted paper is original and has not been or is not being submitted to the peer review process to any other journal.

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