

Article

Mechanical, Tribological, and Corrosive Properties of NbCrC_x and NbCrC_xN_y Coatings with Various Nitrogen and Carbon Contents

Yean-Liang Su ¹, Sung-Mao Chiu ², Wen-Hsien Kao ^{3,*}, Hsiang-Chun Hsueh ² and Tsung-Yen Hsieh ¹

¹ Department of Mechanical Engineering, National Cheng Kung University, Tainan 700, Taiwan; suyl@mail.ncku.edu.tw (Y.-L.S.); n16104961@gs.ncku.edu.tw (T.-Y.H.)

² Micro/Meso Mechanical Manufacturing R&D Department, Surface Engineering & Heat Treatment Section, Metal Industries Research and Development Centre, Kaohsiung 811, Taiwan; smchiu@mail.mirdc.org.tw (S.-M.C.); hchsueh@mail.mirdc.org.tw (H.-C.H.)

³ Department of Automation Engineering, Institute of Mechatronic Systems, Chienkuo Technology University, Changhua 500, Taiwan

* Correspondence: kaowh@ctu.edu.tw; Tel.: +886-4-7111111 (ext. 2414)

Abstract: CrC and NbC carbide coatings both have good mechanical properties, wear resistance, and corrosion resistance. The present study seeks to combine the two coating systems in order to further enhance their properties. NbCrC_x and NbCrC_xN_y coatings (where x and y denote the atomic percentages of carbon and nitrogen, respectively) were deposited on SKH51 substrates using a radio-frequency unbalanced magnetron sputtering system. The mechanical, tribological, and corrosive properties of the coatings were investigated and compared. Among the NbCrC_x coatings, the NbCrC₆₁ coating showed high levels of hardness, excellent adhesion strength, and good wear resistance. Among the NbCrC_xN_y coatings, the NbCrC₅₅N₅ coating showed high adhesion strength and hardness and excellent tribological properties. However, for nitrogen contents greater than 16 at%, the adhesion strength was dramatically reduced, resulting in poor tribological performance. Among all of the coatings, the NbCrC₄₉ coating showed the best corrosion resistance due to its enhanced crystallinity, high adhesion strength, moderate surface roughness, and high sp³ C-C bonding ratio.

Keywords: NbCrC; NbCrCN; coating; tribology; corrosion



Citation: Su, Y.-L.; Chiu, S.-M.; Kao, W.-H.; Hsueh, H.-C.; Hsieh, T.-Y. Mechanical, Tribological, and Corrosive Properties of NbCrC_x and NbCrC_xN_y Coatings with Various Nitrogen and Carbon Contents. *Metals* **2023**, *13*, 1488. <https://doi.org/10.3390/met13081488>

Academic Editors: Marcello Cabibbo, Frank Czerwinski and Mosab Kaseem

Received: 27 June 2023

Revised: 12 August 2023

Accepted: 16 August 2023

Published: 18 August 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Thin-film coatings provide an inexpensive yet effective means of protecting a wide range of industrial components and processing tools. They have thus attracted significant research attention in recent decades [1–6]. Transition metal carbide coatings are of particular interest due to their many outstanding properties, such as hardness, high wear resistance, good thermal stability, and superior chemical stability. For example, zirconium carbide (ZrC) and titanium carbide (TiC) coatings increase the wear resistance and reduce the friction coefficient of the underlying substrate [2], while TiC coatings also improve the corrosion resistance [3]. Niobium carbide (NbC) coatings have many favorable properties, including high levels of hardness [7], a high melting point, good corrosion resistance, excellent chemical stability [8], and good wear resistance [9]. Chromium carbide (CrC) coatings possess the similar advantages of high hardness [10], excellent tribological properties [11], and good resistance to corrosion [12].

The term “multimetallic cocktails” was first coined by Ranganathan [13] in 2003 to describe alloy systems consisting of two phases, three phases, or more, depending on the particular composition and processing conditions. The properties of such systems are determined by the overall contribution of the constituent phases, including their distributions, phase boundaries, and properties [14,15], and they are often very different from those of the individual phases themselves. However, adding elements with different characteristics

to the coating system invariably increases the corresponding characteristic in the final coating. For example, the addition of chromium, with its high corrosion resistance, increases the corrosion resistance of the coating [16], while the addition of vanadium increases the wear resistance [17]. As described above, NbC and CrC carbide coatings both have good tribological and corrosion properties. Based on the cocktail effect, it seems reasonable to assume that niobium chromium carbide (NbCrC) coatings may combine the advantages of NbC and CrC, resulting in yet better tribological and corrosion properties. Previous studies [18,19] have shown that carbon nitride (CN) and binary nitride [20] coatings, formed by introducing acetylene and nitrogen into the sputtering chamber during the deposition process, also have excellent tribological properties, together with high levels of hardness, high wear resistance, and a low friction coefficient. Thus, it is inferred that the mechanical properties and tribological performance of NbCrC coatings may be further improved by introducing nitrogen into the coating system to form niobium chromium carbide nitrogen (NbCrCN) coatings.

The literature already contains several studies on NbCrC coatings produced via thermal reactive deposition and diffusion [21,22], arc ion plating [23], or magnetron sputtering. Magnetron sputtering and thermal reactive diffusion are both widely used for the deposition of carbide coatings. Of the two techniques, magnetron sputtering has a lower formation temperature and tends to produce coatings with superior mechanical properties, wear resistance, and corrosion resistance [24]. Meanwhile, direct current sputtering systems have several disadvantages, including an inability to sputter insulators and the tendency to accumulate charges on the target surface, thereby leading to a lower sputtering yield [25]. By contrast, radio-frequency (RF) unbalanced magnetron sputtering provides a high deposition rate, good layer uniformity, and good adhesion to the substrate [26,27]. Consequently, in the present study, NbCrC and NbCrCN series coatings were deposited on SKH51 substrates using an RF unbalanced magnetron sputtering system. The coatings were prepared with various acetylene and nitrogen flux rates, and the mechanical, tribological, and corrosion performance of the resulting coatings were evaluated and compared. The effects of the carbon and nitrogen contents on the coating properties were examined. Finally, the NbCrC and NbCrCN series coatings with the optimal hardness, tribological properties, and corrosion resistance were identified.

2. Materials and Methods

2.1. Deposition Setup

The coatings were deposited on SKH51 substrates with a composition of 84.2 at% Fe, 4.3 at% C, 4.4 at% Cr, 3.0 at% Mo, 1.9 at% W, and 2.2 at% V using a radio-frequency unbalanced magnetron sputtering system (Teer-450C, Teer Coating, Droitwich, UK) with two niobium (Nb) targets and one chromium (Cr) target (see Figure 1). The targets were placed at a distance of 10 cm from the substrate holder, and the holder was rotated at a constant speed of 3 rpm throughout the deposition process. The SKH51 substrates had the form of discs with a diameter of 24 mm, a thickness of 8 mm, and a surface roughness of $R_a = 0.025 \pm 0.005 \mu\text{m}$. Due to instrument size restrictions, the coatings were also deposited on silicon wafers for X-ray diffraction spectrometry (XRD) and X-ray photoelectron spectrometry (XPS) analyses.

Prior to the deposition process, the targets were cleaned for 20 min with argon ions using a target current of 0.8 A, a negative bias of 280 V, and an argon atmosphere. The substrates were then bombarded with argon ions to remove surface contaminants using an Ar gas flow rate of 30 sccm for 10 min and a bias voltage of -280 V . To improve the adhesion between the substrate and the coatings, a Cr interlayer was deposited on the substrate surface using a Cr target current of 1.5 A, a sputtering time of 6 min, and a bias voltage of 150 V. The main coatings were all deposited using a Nb target current of 2.5 A, a Cr target current of 0.5 A, and a bias voltage of 35 V for 90 min. NbCrC_x coatings were prepared using three different acetylene fluxes of 10, 12, and 14 sccm. Among the NbCrC series of coatings, the NbCrC₆₀ coating (acetylene flux: 12 sccm) was found to have the

best tribological properties. Thus, in depositing the NbCrC_xN_y coatings, the acetylene and nitrogen flow rates were set in such a way that the total flux was equal to 12 sccm and the sum of the atomic percentages of carbon and nitrogen in the NbCrC_xN_y coatings was around 60 at%. The detailed deposition parameters for the NbCrC_x and NbCrC_xN_y coatings are listed in Table 1.

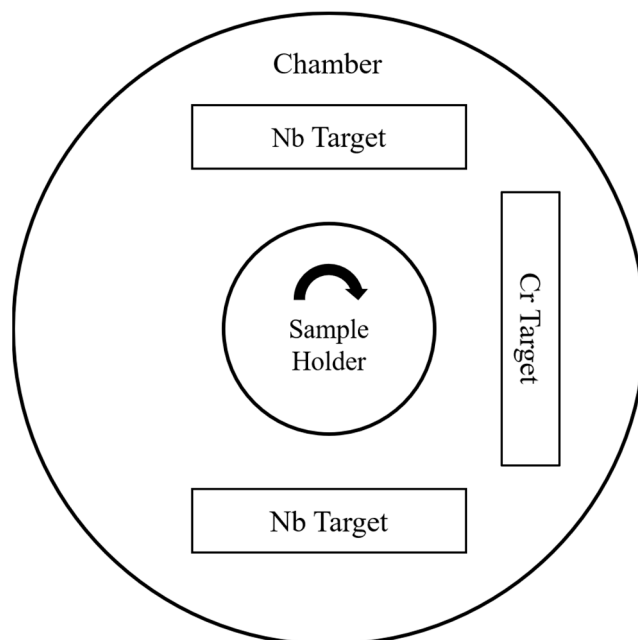


Figure 1. Schematic illustration of the sputtering chamber and target.

Table 1. Deposited parameters for each coating.

Coating Structure	Coating Code	C ₂ H ₂ Flux (sccm)	N ₂ Flux (sccm)	Fixed Parameters
Interlayer	Cr	0	0	Cr target current: 1.5 A Bias voltage: 150 V Time: 6 min
Main layer	NbCrC ₄₉	10	0	Nb target current: 2.5 A Cr target current: 0.5 A Bias voltage: 35 V Time: 90 min
	NbCrC ₆₁	12	0	
	NbCrC ₇₁	14	0	
	NbCrC ₃₄ N ₂₆	6	6	
	NbCrC ₄₃ N ₁₆	8	4	
	NbCrC ₅₅ N ₅	10	2	

Fixed parameters for the interlayer and the main layer: Ar gas: 20 sccm. Rotation speed: 3 cycle/min. Base pressure: 2.68×10^{-3} Pa. Working pressure: 3.6×10^{-1} Pa.

2.2. Coating Characterization

The cross-sectional microstructures, surface morphologies, coating thicknesses, scratch track characteristics, wear surface morphologies, and elemental compositions of the coatings were observed using a scanning electron microscope (SEM, SU5000, Hitachi, Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS). The crystalline structures of the coatings were identified using an X-ray diffractometer (XRD, D8-Discover, Bruker, Mannheim, Germany) with Cu-K α radiation at 40 kV and 100 mA. The chemical bonding states of the coatings were determined by an X-ray photoelectron spectroscope (XPS, PHI 5000 VersaProbe, ULVAC. Inc., Miyazaki, Japan) using Al K α as the X-ray source with a wavelength of 83.3 nm, an energy of 1486.6 eV, a scanning range of 0–1400 eV, and a step size of 0.2 eV. The coatings were etched with Ar ions to remove any surface contaminants prior to the XPS measurement process. The Raman spectra of the coatings were acquired

over the spectral range of 1000–2000 cm^{-1} using an HR800 spectrometer (Cambridge, MA, USA) with a 633 nm He-Ne laser source. The hardness and elastic modulus of the coatings were measured under a maximum load of 10 mN using a nanoindenter (UNAT-M, BMT, Dresden, Germany) with a diamond tip. The maximum indentation depth was controlled to be less than one-tenth of the coating thickness in order to avoid the substrate effect [28]. The adhesion strengths of the coatings were evaluated using a scratch tester equipped with a diamond indenter with a 0.3 mm diameter. In each test, the indenter was dragged across the coating surface for a distance of 10 mm as the load was increased from 0 to 100 N at a rate of 1 N/s. The coefficient of friction (C.O.F.) was recorded continuously throughout each test. The adhesion strength of the coatings was defined as the critical load (L_c) at which the coating first exhibited continuous removal from the scratch track as the indenter moved across the coating surface. To ensure the reliability of the measurement results, the critical load was taken as the average value of two measurements taken in different areas of the coating.

2.3. Tribology Testing

The tribological properties of the coatings were measured under unlubricated conditions using a ball-on-disk wear tester (KD-550U, Freeform, Kaohsiung, Taiwan) in air at room temperature (298 K) and a relative humidity of 45–55%. The tests were performed under normal loads of 5 and 8 N using a 6 mm diameter Si_3N_4 ball as the counterbody. The sliding speed was set as 200 mm/s, and a total of 3000 revolutions were performed. For each coating, the C.O.F. was recorded continuously throughout the test, and, on completion of the test, the wear width and wear depth were measured using a white light interferometer (Contour GT-K, Bruker, Billerica, MA, USA). The wear surface was measured at three points around the wear track, separated by intervals of approximately 120° . Three wear depth measurements were acquired at each point, and the nine values were then averaged to obtain the average wear depth for the coating. The wear rate (WR) was evaluated as $\text{WR} = 2\pi RA / (N \times m)$, where R is the wear track radius, A is the cross-sectional wear area, N is the normal load, and m is the total sliding distance. Finally, the morphologies and element compositions of the wear tracks and scars on the coating surface were analyzed using SEM and EDS.

2.4. Corrosion Testing

The corrosion resistance of the coatings was tested using a commercial electrochemical workstation (ECW-5000, Jiehan, Taichung, Taiwan) with a three-electrode system consisting of a saturated calomel electrode as the reference electrode, the coated sample as the working electrode, and a platinum sheet as the counter electrode. The tests were performed in a corrosive environment consisting of 0.5 M H_2SO_4 solution. The coatings were scanned at a rate of 1 mV/s over the range of -0.5 V to 1.0 V.

3. Results and Discussion

3.1. Composition, Microstructure, Morphology

Table 2 lists the elemental compositions of the various NbCrC_x and NbCrC_xN_y coatings. All of the coatings have low O content (4.3–7.7 at%) due to the presence of residual oxygen or water in the sputtering chamber and environmental oxidation following the removal of the coatings from the chamber. For the NbCrC_x coatings, the C content increases from 49.1 to 70.6 at% as the acetylene flux increases from 10 to 14 sccm. In contrast, the Nb content decreases from 30.3 to 19.8 at% and the Cr content decreases from 12.9 to 5.3 at%. In preparing the NbCrC_xN_y coatings, the Nb (24 at. %) to Cr (9.5 at. %) ratio was fixed at around 5:2 for all of the coatings, and the acetylene flux was increased from 6 to 10 sccm, while the N flux was decreased from 6 to 2 sccm to maintain a total flux of 12 sccm for each coating. The results presented in Table 2 show that, as the C content increases from 34.1 to 55.3 at%, the N content decreases from 26.0 to 4.5 at%, and the C/N ratio increases from 1.3 to 12.3.

Table 2. Elemental composition (at. %) of each coating.

Coating Code	Nb	Cr	C	N	O
NbCrC ₄₉	30.3 ± 0.3	12.9 ± 0.3	49.1 ± 0.5	0	7.7 ± 0.3
NbCrC ₆₁	25.1 ± 0.2	8.0 ± 0.5	60.5 ± 0.2	0	6.4 ± 0.4
NbCrC ₇₁	19.8 ± 0.2	5.3 ± 0.1	70.6 ± 0.1	0	4.3 ± 0.1
NbCrC ₃₄ N ₂₆	23.9 ± 0.2	9.9 ± 0.1	34.1 ± 0.1	26.0 ± 0.2	6.1 ± 0.1
NbCrC ₄₃ N ₁₆	24.0 ± 0.1	9.7 ± 0.2	43.3 ± 0.1	16.1 ± 0.1	6.9 ± 0.1
NbCrC ₅₅ N ₅	24.5 ± 0.1	9.4 ± 0.1	55.3 ± 0.1	4.5 ± 0.3	6.3 ± 0.2

The XRD patterns in Figure 2a show that the NbCrC_x coatings contain NbC (cubic, Joint Committee on Powder Diffraction Standards (JCPDS) No. 38-1364) and Cr₂₃C₆ (cubic, JCPDS No. 35-0783) phases, which indicates that the coating has the preferred (111) orientation of NbC. Moreover, as the C content increases, the intensity of the peaks decreases and the peaks become broader. In other words, the NbCrC_x coatings consist predominantly of crystalline phases; however, the crystallinity is degraded as the C content increases, and the structures contain a greater quantity of amorphous phases. The results are thus consistent with those of [29], which show that NbC coatings tend toward an amorphous structure with increasing C content.

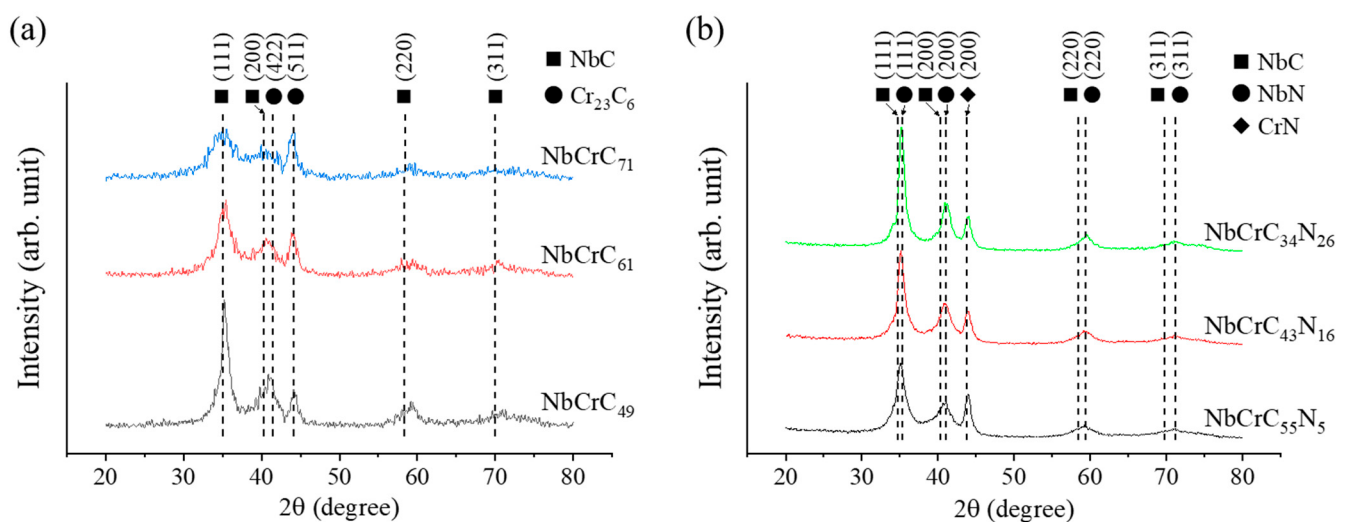
**Figure 2.** XRD patterns of: (a) NbCrC_x coatings, and (b) NbCrC_xN_y coatings.

Figure 2b shows the XRD patterns of the NbCrC_xN_y coatings. The peaks in the XRD patterns indicate that the coatings contain NbC and NbN phases (cubic, JCPDS No. 38-1155) and a CrN phase (cubic, JCPDS No. 11-0065). The NbC and NbN phases are solid solution phases, in which the C and N atoms substitute one another in the crystalline lattice. The XRD patterns show that, for the NbCrC₃₄N₂₆ coating, with the lowest C content and highest N content of the three coatings, the diffraction peak of the solid solution phase is closer to that of NbN. However, as the C content increases, the N atoms are partially replaced by C atoms in the NbN phase; hence, the diffraction peak of the solid solution phase shifts slightly to a lower angle and approaches that of NbC. The study reported in [30] also indicated that a higher C content causes the diffraction peak of CrCN films to gradually shift to a smaller angle. Zhang et al. [31] detected the presence of NbC and NbN solid solution phases in NbCN coatings, and found that, as the C content of the coating increased, a partial substitution of the N atoms in the crystalline lattice by C atoms occurred, which resulted in a continuous shift of the XRD peak to lower 2θ values in the range of 41.21° to 40.84°. For the present NbCrC_xN_y coatings, the XRD patterns show the presence of a CrN phase but not a CrC phase. This finding is reasonable, since the Gibbs energy of formation of CrN is lower than that of CrC, meaning that CrN is more likely to be generated [32].

A Raman analysis was performed to examine the structural properties of the C-C bonds in the two series of coatings. As shown in Figure 3, all of the coatings exhibit an asymmetric Raman band between 1000 and 1700 cm^{-1} . The band can be fitted to two peaks, namely, the D peak and the G peak, located at 1380 and 1570 cm^{-1} , respectively. It was shown in [33] that a higher I_D-I_G ratio (i.e., a higher intensity ratio of the two peaks) indicates a higher proportion of sp^2 carbon bonds in the coating structure. Figure 3a shows that the I_D-I_G ratio of the NbCrC_x coatings increases significantly with an increasing C content. The I_D-I_G ratios of the NbCrC_xN_y coatings also increase with an increasing C content (Figure 3b); however, the effect is not as pronounced due to the relatively low C content (<55.3 at%) and the presence of NbC, NbN, and CrN crystalline phases (Figure 2b). Figure 4 shows the XPS results for the C1s spectra of all the coatings. For convenience, the corresponding bond ratios are tabulated in Table 3. For the NbCrC_x coatings, the sp^2 C-C bond content increases from 37.3% to 55.1% as the C content increases from 49.1 at% to 70.6 at%. For the NbCrC_xN_y coatings, the sp^2 C-C bond content also increases (from 19.9% to 41.5%) as the C content increases; however, the C=N bond content decreases from 63.5% to 29.6%.

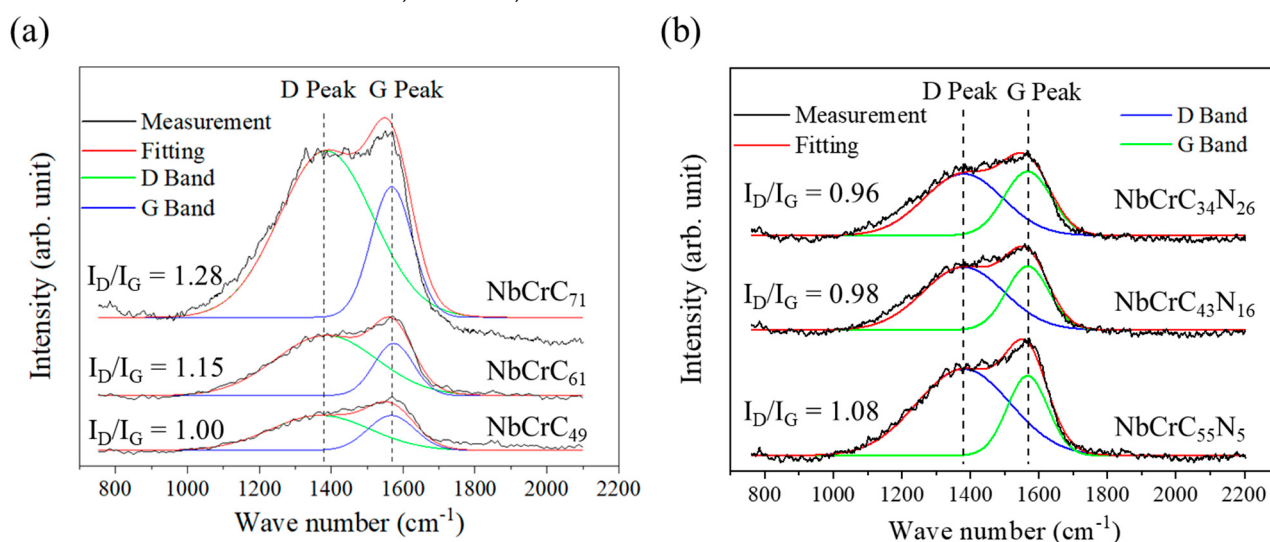


Figure 3. (a) NbCrC_x coatings and (b) NbCrC_xN_y coatings.

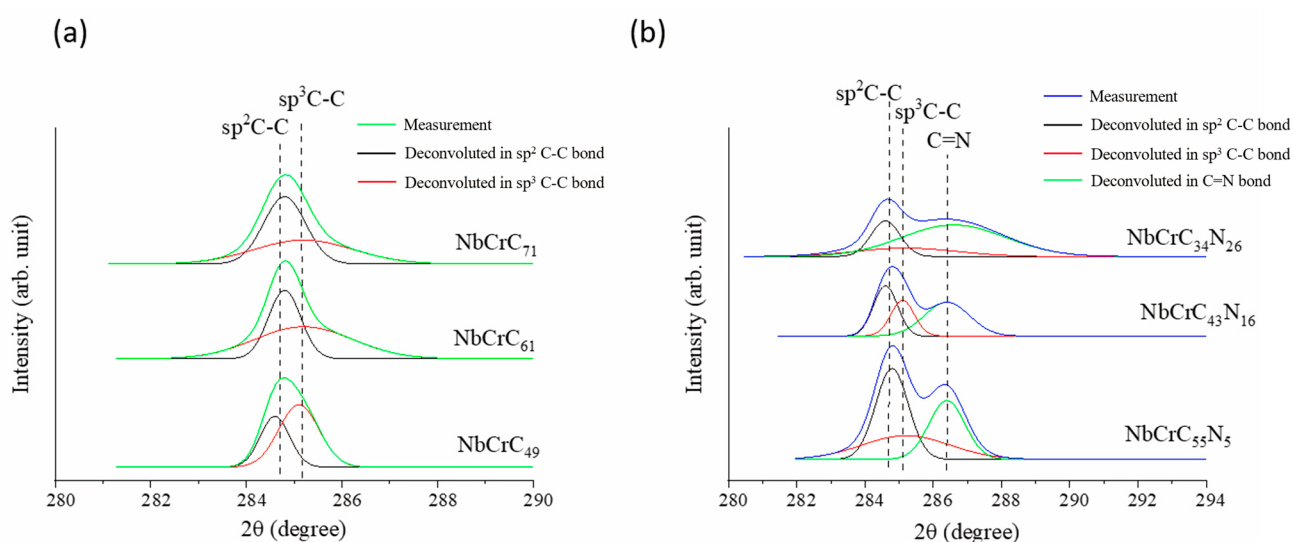


Figure 4. XPS results for C1s spectra of: (a) NbCrC_x and (b) NbCrC_xN_y coatings.

Table 3. Chemical bond ratios of C1s spectra for all coatings.

Coating Code	sp ² C-C, %	sp ³ C-C, %	C=N, %
NbCrC ₄₉	37.3	62.7	-
NbCrC ₆₁	41.5	58.5	-
NbCrC ₇₁	55.1	44.9	-
NbCrC ₃₄ N ₂₆	19.9	16.6	63.5
NbCrC ₄₃ N ₁₆	34.4	23.2	42.4
NbCrC ₅₅ N ₅	41.5	28.9	29.6

Figure 5 shows cross-sectional SEM images of the NbCrC_x and NbCrC_xN_y coatings. The images presented in Figure 5a–c show that the NbCrC₄₉, NbCrC₆₁, and NbCrC₇₁ coatings all have distinct columnar structures. This columnar morphology arises from the anisotropic growth rate of different crystal planes, which leads to the preferential overgrowth of certain grains [34]. The NbCrC₃₄N₂₆, NbCrC₄₃N₁₆, and NbCrC₅₅N₅ coatings also have a columnar structure, as shown in Figure 5d–f. Hence, it is inferred that the N content has no significant effect on the cross-sectional structure of the coatings.

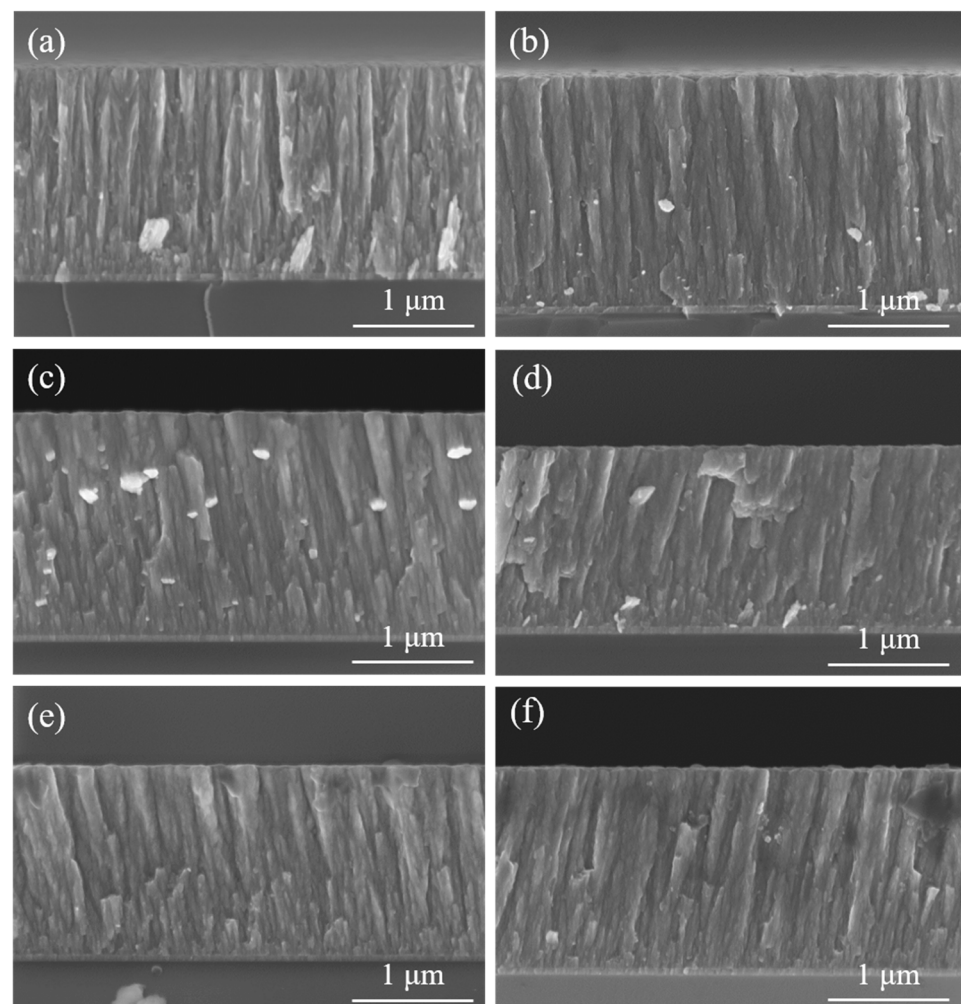
**Figure 5.** Cross-sectional SEM images of NbCrC_x series coatings: (a) NbCrC₄₉, (b) NbCrC₆₁, (c) NbCrC₇₁; and of NbCrC_xN_y series coatings: (d) NbCrC₃₄N₂₆, (e) NbCrC₄₃N₁₆, (f) NbCrC₅₅N₅.

Figure 6 shows the surface morphologies and cluster sizes of the various coatings. All of the coating surfaces have an earth-cracking-type feature. Moreover, the cluster size reduces as C content increases. For example, the NbCrC₄₉, NbCrC₆₁, and NbCrC₇₁ coatings have cluster sizes of 186.0, 175.2, and 172.2 nm, respectively, while the NbCrC₃₄N₂₆,

NbCrC₄₃N₁₆, and NbCrC₅₅N₅ coatings have cluster sizes of 177.4, 167.9, and 162.5 nm. As described in [35], grain clusters are essentially an assembly of twin-related grains that are formed by a multiple-twinning process. As the C content increases, the amorphous carbon phase also increases, and this inhibits grain growth and makes the crystals less likely to bond together to form larger clusters.

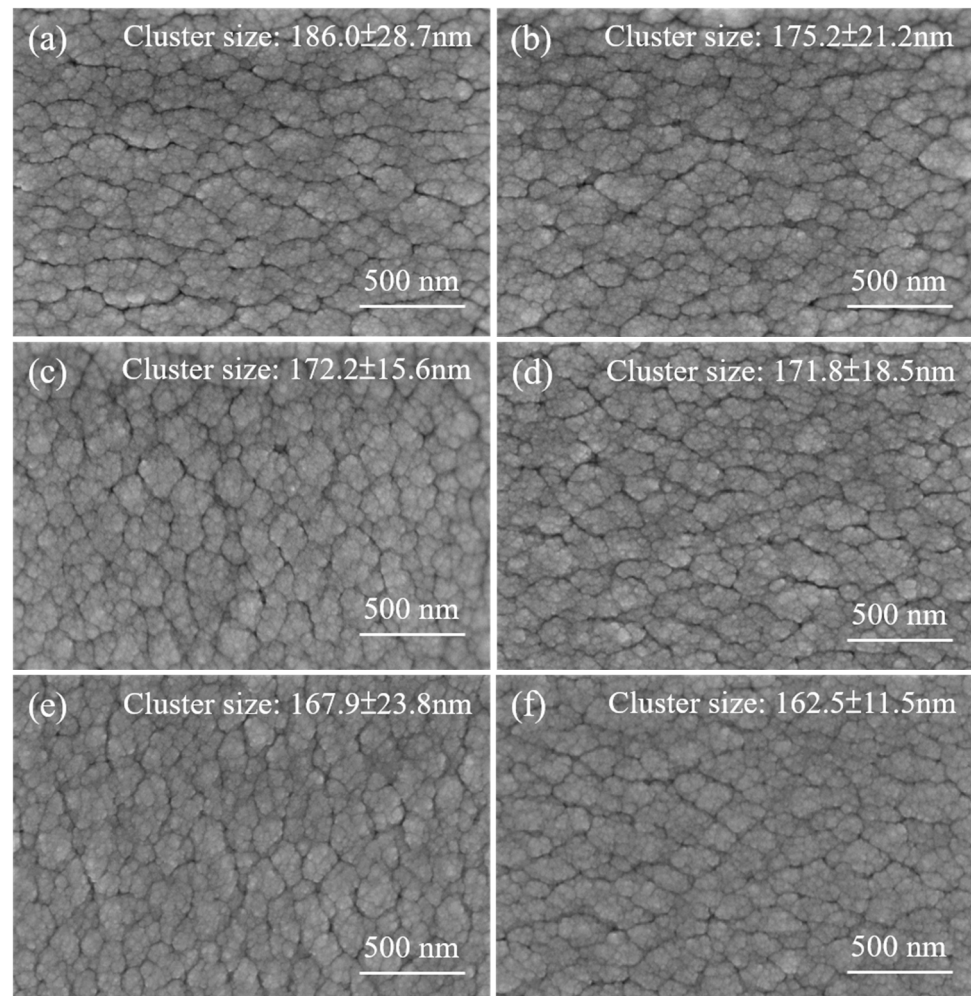


Figure 6. The surface morphology and cluster size of NbCrC_x series coatings: (a) NbCrC₄₉, (b) NbCrC₆₁, and (c) NbCrC₇₁; and of NbCrC_xN_y series coatings: (d) NbCrC₃₄N₂₆, (e) NbCrC₄₃N₁₆ and (f) NbCrC₅₅N₅.

3.2. Grain Size, Thickness, Surface Roughness, Hardness, and Adhesive Strength

Table 4 shows the crystal grain size, thickness, surface roughness, hardness, Hertz stress, and adhesive properties of the various coatings. The grain size (D) was calculated using the Scherrer equation, i.e., $D = K\lambda/(\beta \cos \theta)$, for the most intense peak located at $2\theta = 35^\circ$, where K is a dimensionless shape factor with a value of 0.94, λ is the X-ray wavelength, θ is the Bragg angle, and β is the line broadening at half the maximum intensity [36]. For the NbCrC_x coatings, the grain size is significantly reduced from 11.01 (NbCrC₄₉) to 5.79 nm (NbCrC₇₁) as the C content increases. The result is thus consistent with the finding of [29] that NbC coatings with a greater C content have a smaller grain size. For the NbCrC_xN_y coatings, the crystal grain sizes of the NbCrC₃₄N₂₆, NbCrC₄₃N₁₆, and NbCrC₅₅N₅ coatings are 11.78, 10.03, and 9.13 nm, respectively. Thus, the grain size is slightly reduced as the C content increases and the N content decreases.

Table 4. Grain size, thickness, surface roughness (Ra), hardness, Hertz stress, and adhesive strength (Lc) of each coating.

Coating Code	Grain Size (nm)	Thickness (μm)	Surface Roughness Ra (nm)	Hardness (GPa)	Hertz Stress (5 N) (MPa)	Hertz Stress (8 N) (MPa)	Adhesive Strength Lc (N)
NbCrC ₄₉	11.01	1.75 $\pm$ 0.01	31.1 $\pm$ 2.9	18.8 $\pm$ 2.0	1540.7	1802.0	>100
NbCrC ₆₁	9.12	1.93 $\pm$ 0.02	21.8 $\pm$ 0.9	21.0 $\pm$ 1.5	1488.3	1740.8	>100
NbCrC ₇₁	5.79	1.86 $\pm$ 0.01	21.1 $\pm$ 1.6	17.7 $\pm$ 1.2	1375.1	1608.3	90.2 $\pm$ 1.2
NbCrC ₃₄ N ₂₆	11.78	1.52 $\pm$ 0.01	44.8 $\pm$ 3.5	21.5 $\pm$ 1.6	1516.0	1773.1	18.0 $\pm$ 0.7
NbCrC ₄₃ N ₁₆	10.03	1.57 $\pm$ 0.01	43.6 $\pm$ 3.2	24.4 $\pm$ 1.8	1527.5	1786.5	19.9 $\pm$ 0.4
NbCrC ₅₅ N ₅	9.13	1.68 $\pm$ 0.01	29.9 $\pm$ 2.9	24.5 $\pm$ 1.7	1513.6	1770.3	>100

The NbCrC₄₉, NbCrC₆₁, and NbCrC₇₁ coatings have thicknesses of 1.75, 1.93, and 1.86 μm , respectively. The reduction in the coating thickness for the sample with the highest C content can most likely be attributed to a poisoning of the Nb and Cr targets under high acetylene fluxes, which leads to a lower deposition rate [37,38]. The thicknesses of the NbCrC₅₅N₅, NbCrC₄₃N₁₆, and NbCrC₃₄N₂₆ coatings are further reduced to 1.68, 1.57, and 1.52 μm , respectively. The reduction in thickness can again be attributed to a target poisoning effect. In particular, as the nitrogen concentration in the chamber increases, the nitrogen atoms react with the niobium and chromium targets, resulting in the formation of nitrides on their surfaces. The sputtering rate of nitrides is lower than that of pure metal targets; hence, the coating thickness reduces [39].

As shown in Table 3, the percentage of sp^2 C-C bonds in the NbCrC_x coatings increases from 37.3% to 55.1% as the C content increases. Meanwhile, the surface roughness (Ra) decreases from 31.1 (NbCrC₄₉) to 21.1 (NbCrC₇₁) nm, as shown in Table 4. In other words, the surface roughness of the NbCrC_x coatings is reduced with an increasing proportion of sp^2 C-C bonds. Zhang et al. [40] similarly showed that the presence of an amorphous carbon phase in NbCN coatings results in a smoother surface. For the NbCrC_xN_y coatings, the NbCrC₅₅N₅ coating has a surface roughness of 29.9 nm. However, as the N content increases beyond 16 at%, the surface roughness increases to 43.6 nm (NbCrC₄₃N₁₆) and 44.8 nm (NbCrC₃₄N₂₆).

The NbCrC₄₉, NbCrC₆₁, and NbCrC₇₁ coatings have hardness values of 18.8, 21.0, and 17.7 GPa, respectively. As the C content increases, the proportion of soft sp^2 C-C bonds also increases; hence, the NbCrC₇₁ coating, with the greatest number of sp^2 C-C bonds (55.1%), has the lowest hardness. The results are thus consistent with those of [41], which showed that the hardness of diamond-like carbon (DLC) coatings decreases with an increasing proportion of sp^2 C-C bonds. Furthermore, the grain size of the NbCrC₄₉ and NbCrC₆₁ coatings decreases from 11.01 nm to 9.12 nm as the C content increases, resulting in a fine-grain strengthening effect. However, as the C content continues to increase, and the grain size is further reduced to 5.79 nm (NbCrC₇₁), the inverse Hall–Petch effect occurs, and the hardness decreases. It was shown in [42] that NbC exhibits a maximum hardness for a grain size of approximately 8 nm. This finding is in line with the present results, which show that, for the NbCrC_x coatings, the maximum hardness occurs in the coating with a grain size of 9.12 nm.

The NbCrC_xN_y coatings exhibit a higher hardness than the NbCrC_x coatings, with hardness values of 21.5 (NbCrC₃₄N₂₆), 24.4 (NbCrC₄₃N₁₆), and 24.5 (NbCrC₅₅N₅) GPa for N contents of 26.0, 16.1, and 4.5 at%, respectively. Among the NbCrC_xN_y coatings, some are harder than the single NbC coatings reported in [43]. For example, the single NbC coatings have hardness values in the range of 15–22 GPa, whereas the present NbCrC₄₃N₁₆ and NbCrC₅₅N₅ coatings have hardnesses of 24.4 GPa and 24.5 GPa, respectively. The hardness of the NbCrC_xN_y coatings increases significantly compared to that of the NbCrC₆₁ coating, since the nitrogen atoms dissolve into the NbC lattice and form an interstitial solid solution, which results in a solid-solution strengthening effect. The study reported in [40] similarly showed that the addition of nitrogen to NbCN coatings leads to improved hardness as the result of the formation of an interstitial solid solution. However, the study also showed that excessive nitrogen content reduced the hardness. According to [44], at higher nitrogen

pressures, the higher frequency of the collisions between the nitrogen species and the growing coating may promote the formation of molecular nitrogen that becomes trapped in the film and forms microscopic voids. These voids increase the porosity of the coating and therefore decrease its hardness. The grain size of the present NbCrC₅₅N₅ and NbCrC₄₃N₁₆ coatings increases from 9.13 nm to 10.03 nm as the N content increases; however, the hardness values show almost no change (i.e., 24.5 and 24.4 GPa, respectively). As the N content is further increased, the grain size increases further to 11.78 nm; this is accompanied by a significant Hall–Petch effect, which reduces the hardness (21.5 GPa). The greater N content leads to the generation of more nitrides, which may also contribute to the decrease in hardness. For example, it was shown in [40] that the hardness of NbCN coatings reduces as the quantity of NbN phases increases. As discussed above, the presence of solid-solution strengthening contributes to a higher hardness in the NbCrC_xN_y coatings compared to the NbCrC_x coatings. However, in the NbCrC_xN_y coatings, an excessive N content leads to the formation of voids, a reduction in the fine grain size strengthening effect, and an increased generation of nitrides. Consequently, the NbCrC₃₄N₂₆ coating has the lowest hardness (21.5 GPa) among all the NbCrC_xN_y coatings.

As shown in Table 4, the NbCrC₄₉ and NbCrC₆₁ coatings have an excellent adhesive strength with a critical load of more than 100 N. Accordingly, the SEM image presented in Figure 7a shows that the NbCrC₄₉ coating remains fully intact under the maximum normal load of 100 N in the scratch test. For the NbCrC₇₁ coating, with the highest C content of 70.6 at%, the critical load is reduced slightly to $L_c = 90.2$ N. However, in general, all of the NbCrC_x coatings show a good adhesive performance due to their low roughness ($R_a < 31.1$ nm) and low C.O.F. (< 0.27) during the scratch test. Among the NbCrC_xN_y coatings, the NbCrC₅₅N₅ coating also has excellent adhesive properties ($L_c > 100$ N) due to its smooth surface ($R_a = 29.9$ nm) and low friction coefficient (0.25). However, the NbCrC₄₃N₁₆ and NbCrC₃₄N₂₆ coatings both have extremely poor adhesion performance, with critical strength values lower than 20 N. Figure 7b presents a typical SEM image of the NbCrC₃₄N₂₆ scratch track, showing that the coating is already completely removed from the substrate under a low applied load of just 18 N. The poor adhesive strength of the two coatings can be attributed to their high surface roughness (more than $R_a = 43.6$ nm). In particular, the high surface roughness results in high C.O.F. values (0.415 and 0.359, respectively) during the scratch test, which increases the magnitude of the lateral force acting on the coating and reduces the adhesion strength as a result.

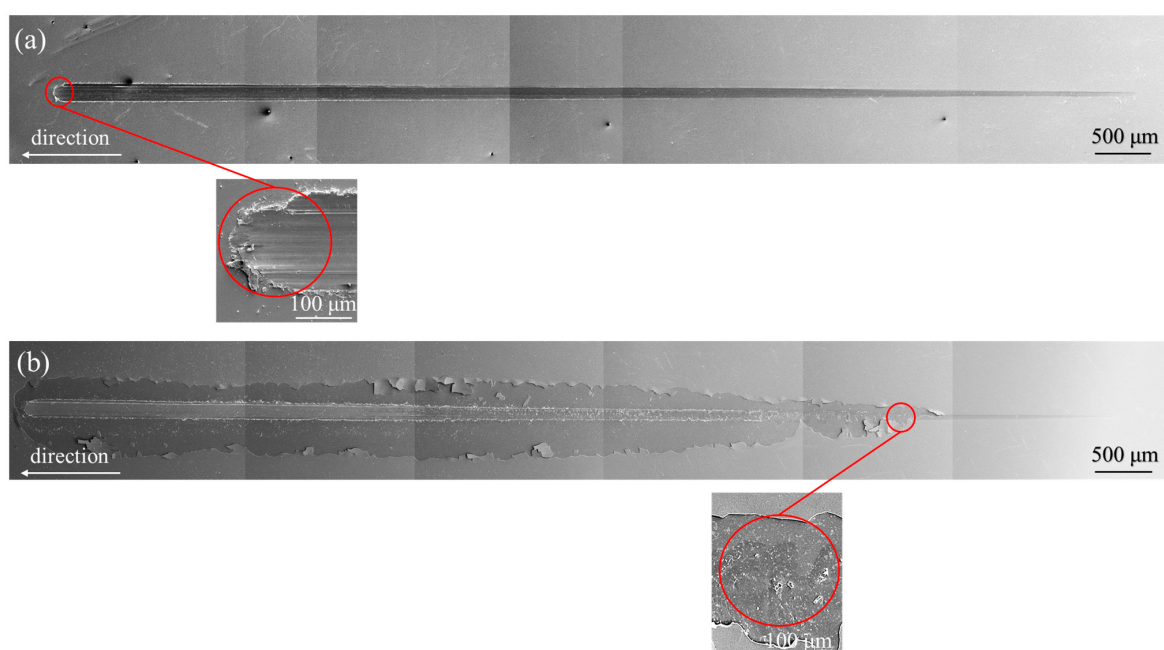


Figure 7. SEM images of the scratch test for the (a) NbCrC₄₉ and (b) NbCrC₃₄N₂₆ coatings.

3.3. Coefficient of Friction, Wear Depth, and Wear Rate

3.3.1. Coefficient of Friction

Table 5 shows the average friction coefficients, wear rates, wear depths, and wear widths of the NbCrC_x and NbCrC_xN_y coatings and the SKH51 substrate under normal loads of 5 N and 8 N. The friction coefficients of the coatings are lower than those of the substrate under both loads. The carbon content of the coatings reduces their coefficient of friction, whereas the uncoated substrate suffers from severe adhesion wear, which increases the friction coefficient. Compared with the uncoated substrate, the coated samples experience less severe adhesion wear; hence, the friction coefficient is correspondingly reduced. Overall, the results in Table 5 indicate that all of the coatings have a friction-reducing effect.

Table 5. Average friction coefficient, wear rate, wear depth, and wear width of each coating at normal load of 5 and 8 N.

Coating Code	Load: 5 N				Load: 8 N			
	COF	Wear Depth (μm)	Wear Width (mm)	Wear Rate 10 ^{−6} mm ³ /Nm	COF	Wear Depth (μm)	Wear Width (mm)	Wear Rate 10 ^{−6} mm ³ /Nm
NbCrC ₄₉	0.18	0.22 ± 0.03	0.09 ± 0.01	1.29 ± 0.13	0.17	0.29 ± 0.04	0.13 ± 0.01	1.63 ± 0.19
NbCrC ₆₁	0.16	0.16 ± 0.01	0.12 ± 0.01	1.20 ± 0.09	0.15	0.24 ± 0.01	0.16 ± 0.01	1.57 ± 0.09
NbCrC ₇₁	0.15	0.28 ± 0.03	0.12 ± 0.01	2.12 ± 0.19	0.15	0.42 ± 0.09	0.16 ± 0.01	2.70 ± 0.57
NbCrC ₃₄ N ₂₆	0.34	0.87 ± 0.03	0.34 ± 0.03	20.1 ± 1.74	0.38	1.11 ± 0.09	0.48 ± 0.06	22.0 ± 2.96
NbCrC ₄₃ N ₁₆	0.36	0.82 ± 0.06	0.36 ± 0.02	19.7 ± 1.69	0.43	1.10 ± 0.09	0.44 ± 0.03	20.3 ± 1.21
NbCrC ₅₅ N ₅	0.13	0.13 ± 0.01	0.11 ± 0.01	0.96 ± 0.04	0.13	0.20 ± 0.02	0.14 ± 0.01	1.18 ± 0.09
SKH51	0.47	0.39 ± 0.04	0.31 ± 0.06	8.11 ± 1.05	0.50	0.43 ± 0.01	0.46 ± 0.02	8.33 ± 0.52

Figure 8a,b shows the friction coefficient curves of the coatings and uncoated substrate under loads of 5 N and 8 N, respectively. All of the NbCrC_x coatings, as well as the NbCrC₅₅N₅ coating, show low and stable friction coefficient curves due to their good adhesion strength ($L_c > 90.2$ N) and high sp² carbon bond ratio (more than 37.3%, as shown in Table 3). In general, sp² carbon bonds comprise weak interplanar van der Waals bonds, which are easily sheared between layers, resulting in a solid lubricant effect. In addition, the study in [45] reported that carbon with an sp² configuration forms a graphitic structure with a low coefficient of friction. The friction coefficient curves of the coatings show similar tendencies under the two loads; hence, it is inferred that they possess good anti-friction properties under both loads. However, as the C content in the NbCrC₅₅N₅ coatings is reduced to below 43 at%, the coefficients of friction of the NbCrC₄₃N₁₆ and NbCrC₃₄N₂₆ coatings increase to more than 0.34 under a load of 5 N. This can be attributed to the low sp² carbon bond ratios of the two coatings (<34.4%) and the significant reduction in the adhesion strength ($L_c < 19.9$ N), which collectively cause the coatings to fracture and peel away from the substrate during sliding. Moreover, as the coatings break down and flake away from the substrate, they produce abrasive debris, which can lead to three-body wear. This further increases both the magnitude of the C.O.F and the amplitude of the oscillations of the friction coefficient curves. Under an 8 N load, the impact of a poor adhesion strength on the friction coefficient curve is more apparent, as shown in Figure 8b, in which the friction coefficient curves for the NbCrC₃₄N₂₆ and NbCrC₄₃N₁₆ coatings and SKH51 substrate are not only higher, but also more unstable than those under a load of 5 N. In summary, the NbCrC₃₄N₂₆ and NbCrC₄₃N₁₆ coatings, with low critical loads ($L_c < 19.9$ N) and low sp² carbon bond ratios (<34.4%), show a higher-amplitude friction coefficient curve. By contrast, the other coatings, with high critical loads ($L_c > 90.2$ N) and high sp² carbon bond ratios (>37.3%), maintain a low and stable friction coefficient curve throughout the entire wear test.

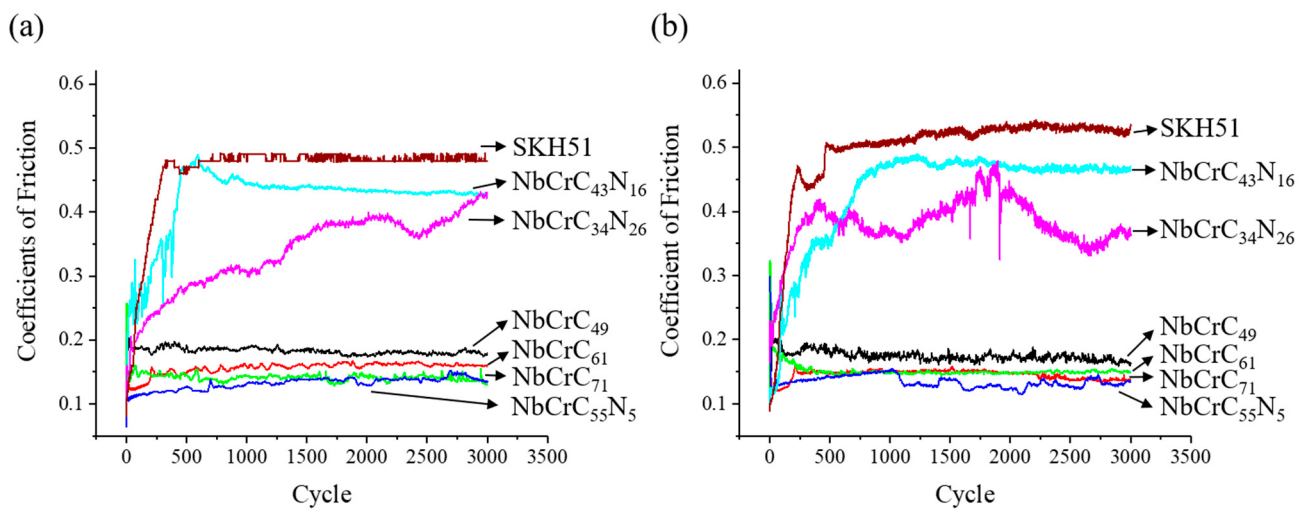


Figure 8. Coefficient of friction of all coatings and the substrate under (a) a 5 N load and (b) an 8 N load after the wear test.

3.3.2. Wear Depth and Wear rate

The average wear depths of the NbCrC₄₉, NbCrC₆₁, and NbCrC₇₁ coatings under a load of 5 N are 0.22, 0.16, and 0.28 μm , respectively (see Table 5); the corresponding wear rates are 1.29×10^{-6} , 1.20×10^{-6} , and 2.12×10^{-6} mm^3/Nm . The NbCrC₆₁ coating has the highest hardness (21.0 GPa) of the NbCrC_x coatings and excellent adhesion strength ($L_c > 100$ N). It therefore has the lowest wear rate and average wear depth of the three coatings. By contrast, the NbCrC₇₁ coating has the highest wear rate and wear depth (0.28 μm) due to its low hardness (17.7 GPa) and adhesion strength ($L_c = 90.2$). Among the NbCrC_xN_y coatings, the NbCrC₅₅N₅ coating has the lowest wear depth (0.13 μm) and wear rate (0.96×10^{-6} mm^3/Nm) due to its high hardness (24.5 GPa) and adhesion strength ($L_c > 100$ N). The NbCrC₄₉, NbCrC₆₁, NbCrC₇₁, and NbCrC₅₅N₅ coatings all have a wear depth and wear rate lower than those of the uncoated SKH51 substrate (i.e., 0.39 and 8.11×10^{-6} mm^3/Nm , respectively). However, as the N content increases, the NbCrC₄₃N₁₆ and NbCrC₃₄N₂₆ coatings show significantly higher wear depths (0.82 and 0.87 μm , respectively) and wear rates (19.7×10^{-6} and 20.1×10^{-6} mm^3/Nm , respectively) due to their lower adhesion strengths ($L_c = 19.9$ and 18.0 N, respectively).

As shown in Table 4, all of the coatings exhibit a higher Hertz stress (i.e., maximum contact stress under static conditions) under the 8 N load (greater than 1608 MPa) than under the 5 N load (less than 1540 MPa). In other words, for all of the coatings, the wear depth, wear width, and wear rate increase as the load increases to 8 N (Table 5). Among the NbCrC_x coatings, the NbCrC₆₁ coating again possesses the lowest wear depth and wear rate. Compared with the load of 5 N, the wear depths and wear rates increase only slightly from 0.16 to 0.24 μm and 1.20 to 1.57×10^{-6} mm^3/Nm , respectively. For the NbCrC₅₅N₅ coating, the wear depth and wear rate similarly increase slightly from 0.13 to 0.20 μm and 0.96 to 1.18×10^{-6} mm^3/Nm , respectively. The NbCrC₅₅N₅ coating possesses the best wear resistance among all the coatings under both loads. Compared with the SKH51 substrate, the NbCrC₅₅N₅ coating reduces the wear depth and wear rate by three times and eight times, respectively, under a load of 5 N, and two times and seven times under a load of 8 N.

In conclusion, the coatings' properties, including the adhesion strength, hardness, and structural composition, all have an effect on the wear resistance. Poor adhesion strength results in a high wear depth and wear rate, which may even exceed those of the uncoated substrate. By contrast, the coatings with high adhesion strength and hardness and large number of sp^2 carbon bonds demonstrate significantly improved tribological properties. Among all of the tested coatings, the NbCrC₅₅N₅ coating showed the highest hardness (24.5 GPa), adhesive strength ($L_c > 100$ N), and sp^2 carbon bond ratio (41.5%), and thus

exhibits the best tribological performance, including the lowest friction coefficient, wear depth, and wear rate under loads of both 5 N and 8 N.

3.4. Wear Surface and Mechanisms

Figure 9a,b shows the wear tracks on the NbCrC₄₉ coating following sliding under 5 N and 8 N loads, respectively. In Figure 9a, Region 1 of the wear track has a similar elemental composition to the original coating, but also contains a very small quantity of Si (0.4 at%) transferred from the counterbody. The wear track has a smooth appearance with only mild and wide scratches. However, oxidized chips can be seen on either side of the wear track. Compared to the main wear track region, the O and Si elements of these oxidized clumps (Region 2) are increased from 7.6 to 21.9 at% and 0.4 to 0.7 at%, respectively. The wear surface in Figure 9b is similar to that in Figure 9a; however, the O and Si elements in Region 3 are both higher (i.e., 10.5 at% and 0.7 at%, respectively). The O and Si contents of the oxidized chips (Region 4) are also higher than those under the lower load of 5 N (46.8 at% and 1.0%). As discussed in Section 3.2, the NbCrC₄₉ coating remained intact after the wear test (i.e., $L_c > 100$ N, Table 4). Thus, it is inferred that, for both loads (5 N and 8 N), the NbCrC₄₉ coating undergoes only minor abrasion and oxidative wear, with oxide accumulation at the sides of the wear track during sliding against the Si₃N₄ ball.

Figure 9c,d shows the wear tracks on the NbCrC₆₁ coating under loads of 5 N and 8 N, respectively. As shown in Figure 9c, the wear track has a smooth surface with only some minor scratches in the central region following sliding under a 5 N load. Region 5 of the wear track contains 24.5 at% Nb, 6.6 at% Cr, 61.9 at% C, and 6.5 at% O, and thus has a composition similar to that of the original coating. Under the higher load of 8 N, the wear track has a greater width and contains more scratches (Figure 9d). Moreover, the oxygen content is increased to 10.5 at%. Regions 5 and 6 of the wear track have low Si contents of 0.3 at% and 0.5 at%, respectively. Overall, the results indicate that the coating remains intact during sliding under both loads, and only minimal material transfer from the counterbody occurs. In other words, the NbCrC₆₁ coating has excellent wear resistance and experiences only minor abrasion wear during sliding.

Figure 9e,f shows the wear tracks on the NbCrC₇₁ coating under 5 N and 8 N loads, respectively. Figure 9e shows that the wear surface comprises a smooth area (Region 7) and a dark area with scratches (Region 8). The EDS analysis results show that the smooth region has a composition similar to that of the original coating. The element composition of the dark area is also similar to that of the original coating; however, the oxygen content is increased to 25.4 at%, which indicates the occurrence of slight oxidation. Under the 8 N load, the wear track also comprises two different areas, namely, a smooth region with scratches (Region 9) and a rough dark region (Region 10). The element composition of the smooth region is again similar to that of the original coating. However, the number of scratches is increased compared to that under a lower load of 5 N. Moreover, in Region 10, the O content is increased to 37.3 at% and the coating exhibits more severe damage. Thus, overall, the wear mechanism of the NbCrC₇₁ coating is inferred to be one of abrasive wear, oxidative wear, and partial coating fracture.

Figure 10a,b shows the wear tracks on the NbCrC₅₅N₅ coatings under normal loads of 5 N and 8 N, respectively. The wear track in Figure 10a has a smooth surface with only two noticeable scratches in the central region. Region 1 of the wear track has an element composition similar to that of the original coating and shows almost no signs of oxidation. However, under the higher load of 8 N, the wear track displays multiple scratches, and the EDS analysis results for Region 2 reveal evidence of mild oxidation (O content 11.8 at%). The EDS analysis results further reveal that the Si contents of the wear track are around 0.5 and 0.7 at%, respectively, under loads of 5 N and 8 N. Overall, the results suggest that the coating remains intact under both loads, and the wear mechanism is limited to minimal abrasive wear.

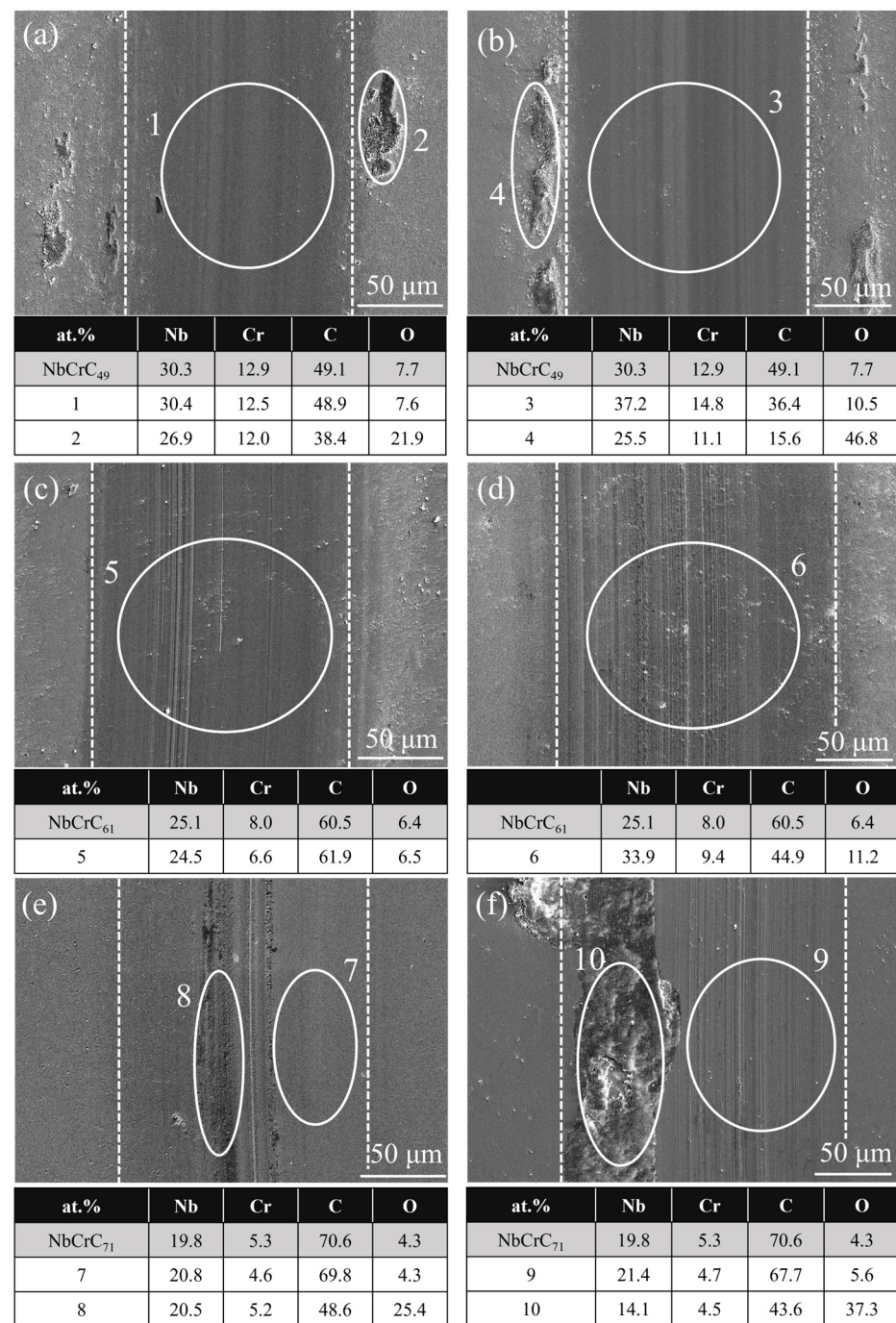


Figure 9. SEM images and EDS element composition results for wear tracks under 5 N and 8 N loads on (a) NbCrC₄₉-5N, (b) NbCrC₄₉-8N, (c) NbCrC₆₁-5N, (d) NbCrC₆₁-8N, (e) NbCrC₇₁-5N and (f) NbCrC₇₁-8N. (Note: dotted lines represented wear track boundaries).

Since the wear surfaces and mechanisms of the NbCrC₄₃N₁₆ and NbCrC₃₄N₂₆ coatings are similar under both loading conditions, the following discussions consider only the wear mechanism of the NbCrC₃₄N₂₆ coating. Figure 10c,d shows the wear tracks on the NbCrC₃₄N₂₆ coating under loads of 5 N and 8 N, respectively. The wear tracks comprise dark areas (Regions 3 and 5) and bright areas (Regions 4 and 6). For the wear track produced under a load of 5 N, the dark region (Region 3) contains 51.6 at% O, while the bright region (Region 4) contains 64.7 at% Fe. Similarly, for the wear track produced under a load of 8 N, the dark region (Region 5) contains 42.6 at% O, while the bright region (Region 6) contains 58.9 at% Fe. The high Fe contents in Regions 4 and 6 indicate that most of the coating

is destroyed during sliding, while the high O contents in Regions 3 and 5 suggest the occurrence of severe oxidative wear. Furthermore, both wear surfaces exhibit a relatively high Si content (4.7–6.8 at%), which indicates that material transfer occurred from the counterbody to the coating during the wear test, prompting the severe adhesive wear of the coatings.

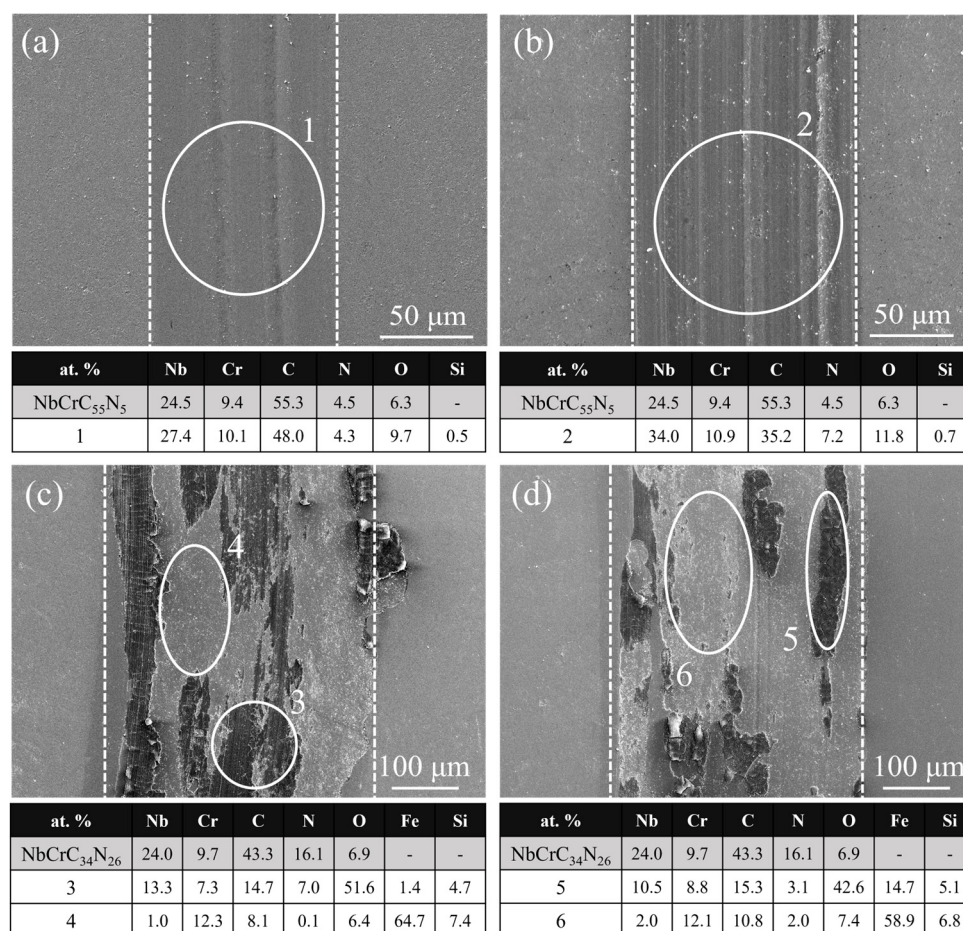


Figure 10. SEM images and EDS element composition results for wear tracks under 5 N and 8 N loads on (a) NbCrC₅₅N₅-5N, (b) NbCrC₅₅N₅-8N, (c) NbCrC₃₄N₂₆-5N, and (d) NbCrC₃₄N₂₆-8N. (Note: dotted lines represented wear track boundaries).

The SEM images show that the NbCrC_xN_y coatings are partially removed from the substrate during sliding. However, the wear depth values in Table 5 suggest that the coatings are not in fact completely worn through (i.e., the wear depths are lower than the corresponding coating thicknesses shown in Table 4). However, the wear depth values are average values obtained over nine separate measurements (see Section 2.3). Figure 11a shows the wear scar morphology of the NbCrC₃₄N₂₆ coating after sliding under a 5 N load. Figure 11b,c shows the cross-sectional profiles of the wear track corresponding to Line 1 in Figure 11a, with two different methods used to calculate the wear depth. Specifically, ΔZ_1 ($-0.8548 \mu\text{m}$) in Figure 11b represents the average wear depth calculated as the difference in height between the average height at marker R (red area) and the average height at marker M (green area). By contrast, ΔZ_2 ($-1.5113 \mu\text{m}$) in Figure 11c shows the wear depth at marker M and is calculated as the difference between the average height at marker R (red area) and the average height at marker M (green line). The value of ΔZ_2 is close to the thickness of the coating ($1.52 \mu\text{m}$, Table 4), which suggests that the NbCrC₃₄N₂₆ is partially worn down to the substrate under a 5 N load. Overall, therefore, it can be inferred that the presence of adhesive wear and severe oxidative wear degrades the wear resistance of

the NbCrC₃₄N₂₆ coating and results in the highest wear depth (0.87 μm) and wear rate ($20.1 \times 10^{-6} \text{ mm}^3/\text{Nm}$) among all the NbCrC_xN_y coatings.

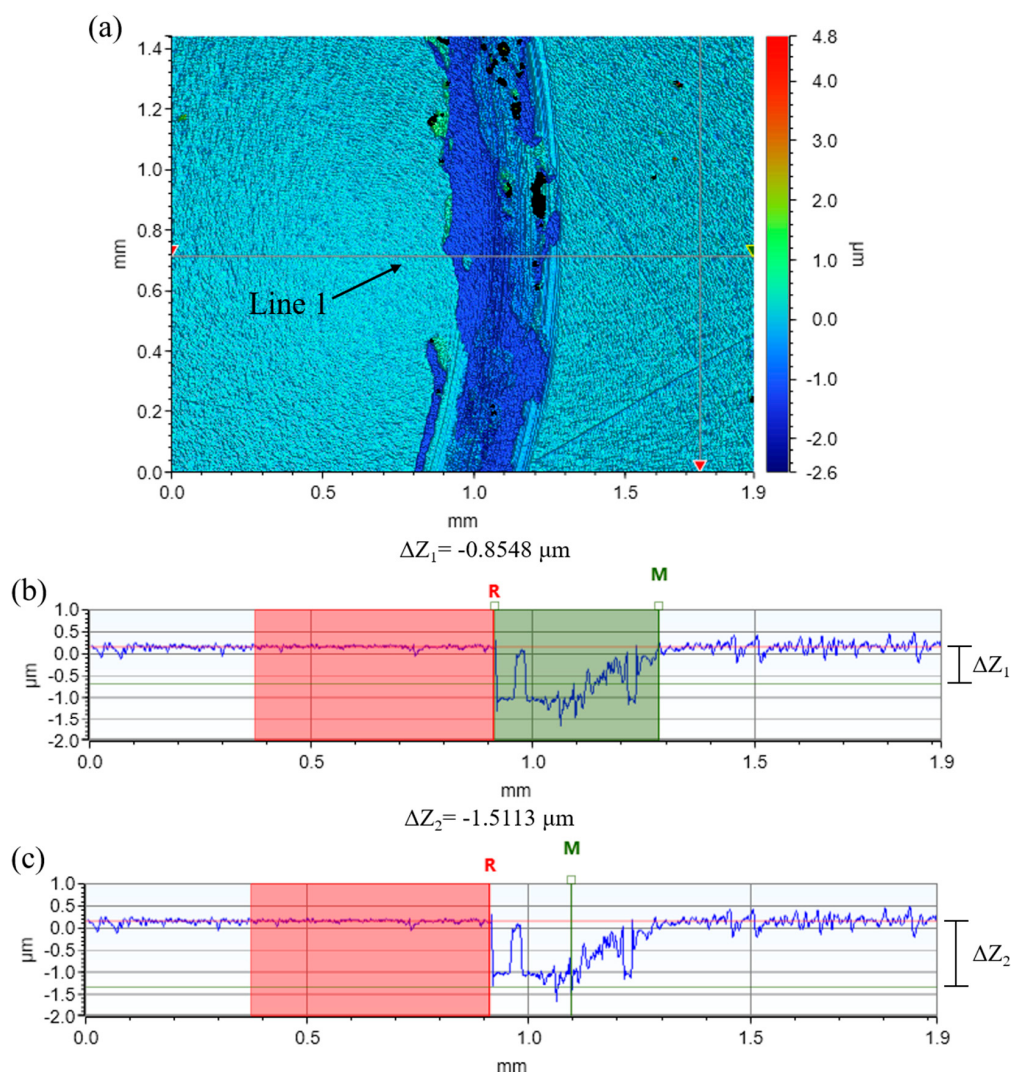


Figure 11. Schematic illustrations of the 2D wear scar patterns of the NbCrC₃₄N₂₆ coating under a 5N load: (a) wear scar (marked line 1 is the wear measurement location shown in figures (b) and (c)), (b) cross-sectional profile of the wear scar with average wear depth and (c) cross-sectional profile of the wear scar with wear depth at the marker M position.

In summary, the wear performance of the NbCrC_x and NbCrC_xN_y coatings is determined primarily by their adhesive properties and hardness. In particular, the NbCrC₆₁ coating, with the highest hardness and critical load, shows only minor abrasive wear and mild oxidative wear and has the best wear resistance among all the NbCrC_x coatings. For the NbCrC_xN_y coatings, the wear performance is dominated by the adhesive strength. Thus, the NbCrC₅₅N₅ coating, with the highest critical load (>100 N), shows the best wear resistance, with only slight abrasive and oxidative wear. Conversely, the NbCrC₄₃N₁₆ and NbCrC₃₄N₂₆ coatings, both with low critical loads, suffer extreme damage during sliding, which results in severe adhesive and oxidative wear and poor wear resistance.

3.5. Electrochemical Properties

Figure 12 shows the potentiodynamic polarization curves of all the coatings and the SKH51 substrate. The corrosion current density (I_{corr}), corrosion potential (E_{corr}), and Tafel slopes (β_a and β_c) of each coating (and substrate) were fitted via the Tafel interpolation

method using CView software (version: 2.6b). Specifically, the intersection point of the Tafel slopes of the cathode and anode polarization curves was determined and taken as the current density, I_{corr} , and corrosion potential, E_{corr} , respectively. In general, a higher corrosion potential indicates a later onset of corrosion but does not necessarily mean a slower corrosion rate, I_{corr} . The calculated I_{corr} , E_{corr} , and Tafel slope values for each coating are shown in Table 6, where a higher value of I_{corr} indicates a faster corrosion rate and hence a poorer corrosion resistance.

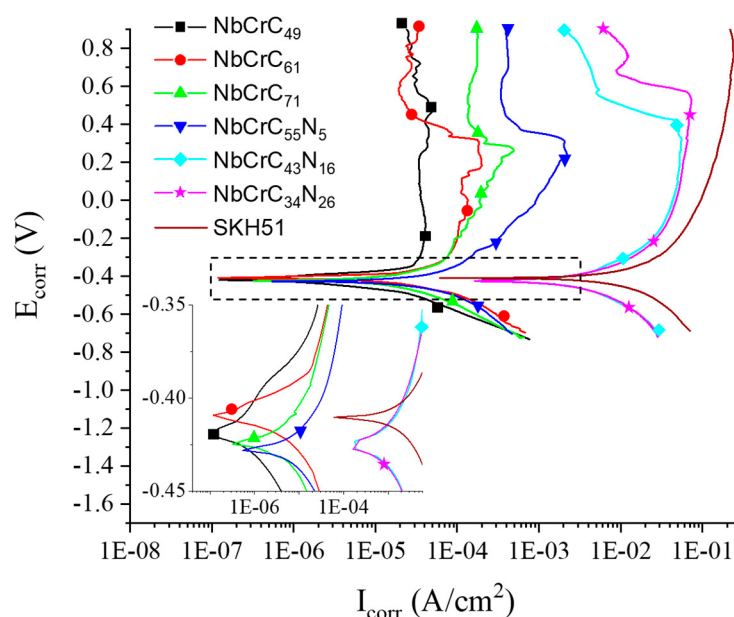


Figure 12. The potentiodynamic polarization curves of all coatings and the SKH51 substrate.

Table 6. Electrochemical parameters of each coating and the SKH51 substrate.

Coating Code	I_{corr} , A/cm ²	E_{corr} , V	β_a , mv/dec	β_c , mv/dec
NbCrC ₄₉	1.40×10^{-6}	−0.416	89.54	78.71
NbCrC ₆₁	7.86×10^{-6}	−0.410	123.02	95.76
NbCrC ₇₁	2.90×10^{-5}	−0.424	269.94	227.50
NbCrC ₃₄ N ₂₆	5.36×10^{-3}	−0.425	262.97	327.61
NbCrC ₄₃ N ₁₆	4.94×10^{-3}	−0.425	288.14	309.18
NbCrC ₅₅ N ₅	7.65×10^{-5}	−0.428	353.79	298.23
SKH51	2.16×10^{-2}	−0.410	407.36	456.01

As shown in Figure 12, all of the coatings exhibit a lower I_{corr} value than the substrate (2.16×10^{-2} A/cm²). It is speculated that the improved corrosion resistance stems from the formation of a stable passive film on the coated surface. Notably, all of the curves show a relatively stable or decreasing corrosion current density as the potential increases, which indicates that they display good anti-corrosion performance. By contrast, the surface of the SKH51 substrate does not produce a stable passive film; hence, its anti-corrosion performance is degraded. The I_{corr} values of the NbCrC₄₉, NbCrC₆₁, and NbCrC₇₁ coatings are 1.40×10^{-6} , 7.86×10^{-6} , and 2.90×10^{-5} A/cm², respectively. In other words, the corrosion resistance of the NbCrC_x coatings is reduced as the C content increases, which can be attributed to a reduction in the crystallinity of the NbC and CrC phases under higher C concentrations (Figure 2a). It was shown in [10,14] that both NbC and CrC exhibit good corrosion resistance, but this resistance decreases as their crystallinity is reduced. The corrosion resistance of the NbCrC_x coatings is also affected by the sp^3 C-C bond ratio. Specifically, as the C content increases, the ratio of sp^3 C-C bonds decreases from 62.7% to 44.9% (Table 3), which leads to lower corrosion resistance [46].

The NbCrC₅₅N₅, NbCrC₄₃N₁₆, and NbCrC₃₄N₂₆ coatings have I_{corr} values of 7.65×10^{-5} , 4.94×10^{-3} , and 5.36×10^{-3} A/cm², respectively, which are all higher than those of the NbCrC_x series coatings. In other words, the incorporation of nitrogen into the NbCrC coating reduces the corrosion resistance. Moreover, the degradation of the corrosion resistance increases as the N content increases. The present results are thus consistent with those of [47], which also showed that excessive nitrogen doping can reduce the corrosion resistance of carbon materials (graphene). The poorer corrosion resistance of the NbCrC₄₃N₁₆ and NbCrC₃₄N₂₆ coatings relative to that of the NbCrC₅₅N₅ coating can also be attributed to their poor adhesion strength ($L_c < 19.9$ N), which causes the coating to peel away from the substrate during the corrosion process, thereby allowing the corrosive solution to come into direct contact with the substrate. In addition, both coatings have a higher surface roughness ($R_a = 43.6$ and 44.8 nm) than the NbCrC₅₅N₅ coating ($R_a = 29.9$ nm), which increases the surface area that is in contact with the corrosive solution. Finally, higher N content decreases the percentage of sp³ C-C bonds in the NbCrC_xN_y coatings, and this too contributes to a reduction in the corrosion resistance [48].

In summary, the NbCrC₄₉ coating has the best corrosion resistance among all the coatings due to its excellent crystallinity, moderate surface roughness, high sp³ C-C bonding ratio, and high adhesion strength. The corrosion rate of the I_{corr} is around 15,000 times lower than that of the substrate, thereby highlighting its excellent protection performance.

4. Conclusions

A radio-frequency unbalanced magnetron sputtering system was used to deposit NbCrC_x and NbCrC_xN_y coatings with different atomic percentages of carbon (x) and nitrogen (y) on SHK51 substrates. The effects of the carbon and nitrogen contents on the mechanical, tribological, and corrosive properties of the coatings were investigated and compared. The results indicate that, among the NbCrC_x coatings, the NbCrC₆₁ coating has a high sp³ C-C content and a fine grain structure, which collectively result in the high hardness level of 21 GPa. Among the NbCrC_xN_y coatings, the NbCrC₅₅N₅ coating exhibited highest hardness level (24.5 GPa) due to the solid-solution strengthening effect induced by the addition of nitrogen. The NbCrC₅₅N₅ coating exhibited the highest adhesion strength and hardness of all the tested coatings (both NbCrC_x and NbCrC_xN_y). As a result, it displayed the best tribological properties, including the lowest friction coefficient, wear depth, and wear rate under loads of both 5 N and 8 N. Moreover, compared with the uncoated SKH51 substrate, the NbCrC₅₅N₅ coating reduced the wear rate by 8 times and 7 times under loads of 5 N and 8 N, respectively. Among all of the coatings, the NbCrC₄₉ coating exhibited the best corrosion resistance as a result of its excellent crystallinity, moderate surface roughness, high sp³ C-C bonding ratio, and high adhesion strength. The corrosion current rate of the sample was shown to be 1.40×10^{-6} A/cm². Notably, the corrosion rate of the NbCrC₄₉ coating is around 15,000 times lower than that of the substrate. Thus, the feasibility of using the NbCrC₄₉ coating as a protective material for substrates exposed to corrosive environments in real-world applications is confirmed.

Author Contributions: Conceptualization, Y.-L.S. and S.-M.C.; methodology, Y.-L.S., W.-H.K. and H.-C.H.; software, T.-Y.H. and H.-C.H.; validation, W.-H.K. and T.-Y.H.; formal analysis, Y.-L.S. and W.-H.K.; investigation, W.-H.K. and T.-Y.H.; resources, S.-M.C. and H.-C.H.; data curation, W.-H.K. and T.-Y.H.; writing—original draft preparation, W.-H.K. and T.-Y.H.; writing—review and editing, W.-H.K.; visualization, H.-C.H.; supervision, Y.-L.S. and S.-M.C. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support provided to this study by the Ministry of Science and Technology of Taiwan under Contract No. MOST 111-2221-E-006-135-MY2.

Data Availability Statement: Data sharing is not applicable to this article.

Acknowledgments: The authors also wish to thank the Core Facility Center of National Cheng Kung University, Taiwan, for the access provided to EM000600, EM000700, ESCA000200, OTHER002200, and XRD001900 of No. NSTC 111-2740-M-006-001.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Mayrhofer, P.H.; Mitterer, C.; Hultman, L.; Clemens, H. Microstructural design of hard coatings. *Prog. Mater. Sci.* **2006**, *51*, 1032–1114. [\[CrossRef\]](#)
- Kumar, D.D.; Kumar, N.; Kalaiselvam, S.; Radhika, R.; Rabel, A.M.; Jayavel, R. Tribo-mechanical properties of reactive magnetron sputtered transition metal carbide coating. *Tribol. Int.* **2017**, *114*, 234–244. [\[CrossRef\]](#)
- Günen, A.; Soylu, B.; Karakas, O. Titanium carbide coating to improve surface characteristic, wear and corrosion resistance of spheroidal graphite cast irons. *Surf. Coat. Technol.* **2022**, *437*, 128280. [\[CrossRef\]](#)
- Cai, F.; Zhou, Q.; Chen, J.; Zhang, S. Effect of inserting the Zr layers on the tribo-corrosion behavior of Zr/ZrN multilayer coatings on titanium alloys. *Corros. Sci.* **2023**, *213*, 111002. [\[CrossRef\]](#)
- Shao, Y.X.; Yang, Y.; Wang, L.; Zhao, C.C.; Wang, Y.W.; Ma, Y.D.; Cui, Y.H.; Sun, W.W.; Wang, X.Y.; Wang, L.; et al. Microstructure characterization of in-situ ZrC composite coating with graceful toughness and improved tribological properties prepared by plasma spraying. *Mater. Charact.* **2021**, *179*, 111382. [\[CrossRef\]](#)
- Alam, M.S.; Das, A.K. Advancement in cermet based coating on steel substrate: A review. *Mater. Today Proc.* **2022**, *56*, 805–810. [\[CrossRef\]](#)
- Wu, J.; Zhu, W.; Yu, W.; Ma, H.; Shao, Y. Effect of TiC additions on the microstructure, mechanical and tribological properties of NbC-CoCrFeNiMn high entropy alloys cermets. *Int. J. Refract. Met. Hard Mater.* **2023**, *112*, 106141. [\[CrossRef\]](#)
- Zhang, P.; Hao, C.; Han, Y.; Du, F.; Wang, H.; Wang, X.; Sun, J. Electrochemical behavior and surface conductivity of NbC modified Tibipolar plate for proton exchange membrane fuel cell. *Surf. Coat. Technol.* **2020**, *397*, 126064. [\[CrossRef\]](#)
- Nedfors, N.; Tengstrand, O.; Flink, A.; Andersson, A.M.; Eklund, P.; Hultman, L.; Jansson, U. Reactive sputtering of NbCx-based nanocomposite coatings An up-scaling study. *Surf. Coat. Technol.* **2014**, *253*, 100–108. [\[CrossRef\]](#)
- Kot, M.; Major, L.; Chronowska-Przywara, K.; Lackner, J.M.; Waldhauser, W.; Rakowski, W. The advantages of incorporating CrxC nanograins into an a-C:H matrix in tribological coatings. *Mater. Des.* **2014**, *56*, 981–989. [\[CrossRef\]](#)
- Zhao, D.; Jiang, X.; Wang, Y.; Duan, W.; Wang, L. Microstructure evolution, wear and corrosion resistance of CrC nanocomposite coatings in seawater. *Appl. Surf. Sci.* **2018**, *457*, 914–924. [\[CrossRef\]](#)
- Liu, R.; Jia, Q.; Zhang, B.; Lai, Z.; Chen, L. Protective coatings for metal bipolar plates of fuel cells: A review. *Int. J. Hydrog. Energy* **2022**, *47*, 22915–22937. [\[CrossRef\]](#)
- Ranganathan, S. Alloyed pleasures: Multimetalllic cocktails. *Curr. Sci.* **2003**, *85*, 1404–1406.
- Yeh, J.W. Alloy Design Strategies and Future Trends in High-Entropy Alloys. *JOM* **2013**, *65*, 1759–1771. [\[CrossRef\]](#)
- Pogrebnjak, A.D. Hard and superhard nanostructured and nanocomposite coatings. In *Nanomaterials-Based Coatings*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 237–337.
- Zhao, S.; He, L.X.; Fan, X.X.; Liu, C.H.; Long, J.P.; Wang, L.; Chang, H.; Wang, J.; Zhang, W. Microstructure and chloride corrosion property of nanocrystalline AlTiCrNiTa high entropy alloy coating on X80 pipeline steel. *Surf. Coat. Technol.* **2019**, *375*, 215–220. [\[CrossRef\]](#)
- Voevodin, A.A.; Muratore, C.; Aouadi, S.M. Hard coatings with high temperature adaptive lubrication and contact thermal management. *Surf. Coat. Technol.* **2014**, *257*, 247–265. [\[CrossRef\]](#)
- Wang, P.; Takeno, T.; Fontaine, J.; Aono, M.; Adachi, K.; Miki, H.; Takagi, T. Effects of substrate bias voltage and target sputtering power on the structural and tribological properties of carbon nitride coatings. *Mater. Chem. Phys.* **2014**, *145*, 430–440. [\[CrossRef\]](#)
- Sánchez-López, J.C.; Donnet, C.; Belin, M.; Le Mogne, T.; Fernández Ramos, C.; Sayagués, M.J.; Fernández, A. Tribochemical effects on CNx films. *Surf. Coat. Technol.* **2000**, *133*, 430–436. [\[CrossRef\]](#)
- Pogrebnjak, A.; Smyrnova, K.; Bondar, O. Nanocomposite multilayer binary nitride coatings based on transition and refractory metals: Structure and properties. *Coatings* **2019**, *9*, 155. [\[CrossRef\]](#)
- Wu, Z.; Qing, H.; Guo, H.; Chen, Y. Growth and mechanical properties of Nb–Cr carbide coatings on graphite by TRD technique. *Int. J. Refract. Hard Met.* **2021**, *101*, 105660. [\[CrossRef\]](#)
- Castillejo, F.E.; Marulanda, D.M.; Olaya, J.J.; Alfonso, J.E. Wear and corrosion resistance of niobium–chromium carbide coatings on AISI D2 produced through TRD. *Surf. Coat. Technol.* **2014**, *254*, 104–111. [\[CrossRef\]](#)
- Gou, Y.; Chen, H.; Li, R.; Geng, J.; Shao, Z. Nb–Cr–C coated titanium as bipolar plates for proton exchange membrane fuel cells. *J. Power Sources* **2022**, *520*, 230797. [\[CrossRef\]](#)
- Emamverdian, A.A.; Sun, Y.; Cao, C.; Pruncu, C.; Wang, Y. Current failure mechanisms and treatment methods of hot forging tools (dies)—A review. *Eng. Fail. Anal.* **2021**, *129*, 105678. [\[CrossRef\]](#)
- Jehn, H.A. Improvement of the corrosion resistance of PVD hard coating–substrate systems. *Surf. Coat. Technol.* **2000**, *125*, 212–217. [\[CrossRef\]](#)
- Swann, S. Magnetron sputtering. *Phys. Technol.* **1988**, *19*, 67–75. [\[CrossRef\]](#)

27. Xiang, Y.; Chengbiao, W.; Yang, L.; Deyang, Y.; Tingyan, X. Recent Developments in Magnetron Sputtering. *Plasma Sci. Technol.* **2006**, *8*, 337. [\[CrossRef\]](#)
28. Buckle, H. *The Science of Hardness Testing and Its Research Applications*; Westbrook, J.H., Conrad, H., Eds.; American Society for Metals: Materials Park, OH, USA, 1973; p. 453.
29. Nedfors, N.; Tengstrand, O.; Lewin, E.; Furlan, A.; Eklund, P.; Hultman, L.; Jansson, U. Structural, mechanical and electrical-contact properties of nanocrystalline-NbC/amorphous-C coatings deposited by magnetron sputtering. *Surf. Coat. Technol.* **2011**, *206*, 354–359. [\[CrossRef\]](#)
30. Liu, C.; Ju, H.; Han, P.; Quan, C.; Mo, C.; Zhao, Y.; Geng, Y.; Xu, J.; Yu, L. The influence of carbon content on the microstructure, mechanical and frictional property of chromium carbon nitride composite films. *Vacuum* **2020**, *178*, 109368. [\[CrossRef\]](#)
31. Zhang, K.; Balasubramanian, K.; Ozsdolay, B.D.; Mulligan, C.P.; Khare, S.V.; Zheng, W.T.; Gall, D. Epitaxial NbC $\times$ N $_{1-x}$ (001) layers: Growth, mechanical properties, and electrical resistivity. *Surf. Coat. Technol.* **2015**, *277*, 136–143. [\[CrossRef\]](#)
32. Christiansen, T.; Somers, M.A.J. Low temperature gaseous nitriding and carburising of stainless steel. *Surf. Eng.* **2005**, *21*, 445–455. [\[CrossRef\]](#)
33. Santiago, J.A.; Fernández-Martínez, I.; Sánchez-López, J.C.; Rojas, T.C.; Wennberg, A.; Bellido-González, V.; Molina-Aldareguia, J.M.; Monclús, M.A.; González-Arrabal, R. Tribomechanical properties of hard Cr-doped DLC coatings deposited by low-frequency HiPIMS. *Surf. Coat. Technol.* **2020**, *382*, 124899. [\[CrossRef\]](#)
34. Liang, S.C.; Tsai, D.C.; Chang, Z.C.; Sung, H.S.; Lin, Y.C.; Yeh, Y.J.; Deng, M.J.; Shieu, F.S. Structural and mechanical properties of multi-element (TiVCrZrHf)N coatings by reactive magnetron sputtering. *Appl. Surf. Sci.* **2011**, *258*, 399–403. [\[CrossRef\]](#)
35. Liu, T.; Xia, S.; Bai, Q.; Zhou, B.; Lu, Y.; Shoji, T. Evaluation of Grain Boundary Network and Improvement of Intergranular Cracking Resistance in 316L Stainless Steel after Grain Boundary Engineering. *Materials* **2019**, *12*, 242. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Scherrer, P. Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachr. Ges. Wiss. Goettingen Math.-Phys. Kl.* **1918**, *2*, 98–100.
37. Bouabibsa, I.; Lamri, S.; Alhussein, A.; Minea, T.; Sanchette, F. Plasma investigations and deposition of Me-DLC (Me = Al, Ti or Nb) obtained by a magnetron sputtering-RFPECVD hybrid process. *Surf. Coat. Technol.* **2018**, *354*, 351–359. [\[CrossRef\]](#)
38. Cheng, H.Y.; Wu, W.Y.; Ting, J.M. Microstructure and optical properties of chromium containing amorphous hydrogenated carbon thin films (a-C:H/Cr). *Thin Solid Films* **2009**, *517*, 4724–4727. [\[CrossRef\]](#)
39. Brčka, J.; Hotový, I. Processes on the target, discharge and NbN film behaviour in reactive dc magnetron deposition. *Vacuum* **1995**, *46*, 1407–1412. [\[CrossRef\]](#)
40. Zhang, K.; Wen, M.; Wang, S.; Deng, R.P.; Gall, D.; Zheng, W.T. Sputter deposited NbC $_x$ N $_y$ films: Effect of nitrogen content on structure and mechanical and tribological properties. *Surf. Coat. Technol.* **2014**, *258*, 746–753. [\[CrossRef\]](#)
41. Savvides, N.; Bell, T.J. Hardness and elastic modulus of diamond and diamond-like carbon films. *Thin Solid Films* **1993**, *228*, 289–292. [\[CrossRef\]](#)
42. Yate, L.; Coy, L.E.; Wang, G.; Beltrán, M.; Díaz-Barriga, E.; Saucedo, E.M.; Cenicerros, M.A.; Załęski, K.; Llarena, I.; Möllera, M.; et al. Tailoring mechanical properties and electrical conductivity of flexible niobium carbide nanocomposite thin films. *RSC Adv.* **2014**, *4*, 61355. [\[CrossRef\]](#)
43. Günen, A.; Açıkgöz, H.H.; Keddām, M.; Karahan, I.H. Characterizations and Kinetics of Refractory Niobium Carbide Coatings on AISI D3 Steel. *J. Mater. Eng. Perform.* **2022**, *31*, 365–378. [\[CrossRef\]](#)
44. Li, D.; Chung, Y.W. Mechanical properties of amorphous carbon nitride thin films prepared by reactive magnetron sputter-deposition. *Tribol. Lett.* **1995**, *1*, 87–93. [\[CrossRef\]](#)
45. Umada, N.; Kanda, K.; Niibe, M.; Hirata, Y.; Ohtake, N.; Akasaka, H. Oriented sp² bonded carbon structure of hydrogenated amorphous carbon films. *Diam. Relat. Mater.* **2023**, *131*, 109533. [\[CrossRef\]](#)
46. Han, B.B.; Ju, D.Y.; Chai, M.R.; Zhao, H.J.; Sato, S. Corrosion Resistance of DLC Film-Coated SUS316L Steel Prepared by Ion Beam Enhanced Deposition. *Adv. Mater. Sci. Eng.* **2019**, *2019*, 7480618. [\[CrossRef\]](#)
47. Li, Y.; Li, J.; Wang, Y.G.; Chen, X.; Liu, M.; Zheng, Z.; Peng, X. Carbon corrosion mechanism on nitrogen-doped carbon support d A density functional theory study. *Int. J. Hydrog. Energy* **2021**, *46*, 13273–13282. [\[CrossRef\]](#)
48. Dong, H.; He, S.; Wang, X.; Zhang, C.; Sun, D. Study on conductivity and corrosion resistance of N-doped and Cr/N co-doped DLC films on bipolar plates for PEMFC. *Diam. Relat. Mater.* **2020**, *110*, 108156. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.