



Surface Modification of SPK NL Steel: Relevance to Tribological and Electrochemical Potency

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ABSTRACT

SPK NL steel, as a hard and process-wise stable alloy, has myriad applications in sheet metal forming. However, to increase the quality of the products and decrease cost, applying a self-lubricant protective coating on the surface seems to be an efficacious strategy. The CrN and carbon-enriched CrN, i.e. (a-C: CrN), hybrid coatings are physically vapor-deposited on the SPK NL alloy surface. The C/N ratio on the morphology, tribological properties, mechanical characteristics, and anticorrosive features of the coated SPK NL substrates are studied. Results evidenced that high carbon inclusion increases the plastic hardness of the CrN coating up to about 35 GPa and significantly improves the plasticity index to ~0.2. The COF decreases from ~0.6 for CrN to ~0.1 for (a-C:CrN). Coatings with a high sp² fraction impart an excellent self-lubricant characteristic to SPK NL steel. Electrochemical impedance spectroscopy data approve that both coatings provide high corrosion resistance, and although CrN provides superior corrosion resistance nonetheless. As an outcome, (a-C:CrN) hybrid coatings with high carbon content, possessing high hardness, good tribological properties, and corrosion resistance seems to be a prospective candidate for surface protection of SPK NL steel. Prog. Color Colorants Coat. 15 (2022), 269-283© Institute for Color Science and Technology.

1. Introduction

Metal forming is a fundamental process of fashioning a specific shape of precise size through mechanical deformation. The metal is exposed to plastic deformation by applying tensile, compressive, bending, shear forces, or a mixture of them. This process is usually categorized into two main groups: i) bulk metal forming and ii) sheet metal forming. In the former, the raw materials have a low surface-to-volume ratio, while in the latter, sheets, plates, or strips with a larger aspect ratio are formed.

Sheet metal forming as an appropriate fabricating process has taken its place in automotive, aerospace, electronics, and building industries. The manufactured objects usually have high quality and possess accurate geometry. However, it is still of great importance for the manufacturers to increase the quality and durability of their products and simultaneously decrease cost by removing the present drawbacks of the process. For instance, in some metal forming processes such as deep drawing, wrinkle is a common fundamental problem.

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This is mainly originating from the friction between the blank surface and blank holder, punch, or die surfaces. The use of a liquid lubricant on the forming parts could be a solution, although issues arise. Lubricants may contain environmentally hazardous materials. It takes time, energy, and sometimes it is costly to remove the residual lubricant from the parts. Besides, the lubricants can be corrosive and damage the forming tools and the products. Therefore, considerable demands for the development of lubricant-free strategies in metal forming methods are growing. Some efforts have been made to omit lubricants in the deep drawing process. Self-lubricant coatings are recently exploited to avoid liquid lubricant usage [1, 2]. Therefore, improving the corrosion resistance of both the forming tools and the products seems to be of great significance. Hence, designing an approach through which both the desired attributions, i.e. self-lubrication and anticorrosion, are imparted to the metallic product seems reasonable and well-founded.

Amorphous carbon-based self-lubricant coatings have been used on sheet metal forming dies. The results demonstrate that the metal forming process has been significantly enhanced [1, 2]. Also, the chromium nitride, CrN, based protective coatings as highly hard, corrosion-resistant, and thermally stable coating materials have been widely applied on metal forming tools [3-6]. However, the high friction coefficient of CrN coatings is a disadvantage for processes under extreme conditions [7]. In consequence, finding a way to decrease the friction coefficient of the CrN coatings is of great necessity to broaden its industrial applications.

Notwithstanding, the CrN and amorphous carbon-based (a-C) protective coatings are still the most widely used protective coatings in actual productions. A combined hybrid coating of a-C and CrN coatings, which carries the advantages, i.e. highly anti-corrosive and low COF, and depletes the disadvantages, seems to be a smart strategy. a-C thin protective coatings fall into two main groups considering the chemical structure: (i) diamond-like carbon (DLC) thin coatings built up of high content of sp^3 hybridization and (ii) graphite-like carbon (GLC) coatings built up of high content of sp^2 hybridization [8-11]. High hardness and good tribological performance are attributions of the DLC coatings, while low friction coefficient, good wear resistance, and self-lubricating characteristics belong to GLC coatings [12-15]. It has been reported that the Cr and N incorporation into the a-C coating's structure

increases the anticorrosive properties, and mechanical strengths [16-22]. Guan et al. prepared Cr-doped GLC coatings and showed anticorrosion improvements [23]. Ming et al. reported that by the Cr incorporation into the a-C coating, the toughness and corrosion resistance enhance while internal stress decreases [24]. On the other hand, carbon impregnation into the CrN coatings improves the mechanical properties and lowers the coefficient of friction [25-27]. Apparently, incorporating a phase with a low friction coefficient, i.e. a-C, into the CrN coating reduces the friction coefficient of the final hybrid coating. Nevertheless, it should be noted that the situations governing the experiment are also of great importance. It is well accepted that there is a close correlation between the deposition condition and structure of the coatings. For instance, using various hydrocarbon gases as the carbon source in a plasma process results in coatings with different structures, and properties [28, 29]. It has been shown that when the hydrocarbon gases with more C-H bonds are used, a much denser a-C coating is formed on the substrate [28]. For the case in point, the a-C coatings prepared by CH_4 show higher density than the coatings prepared by C_2H_2 . Moreover, it has been demonstrated that the a-C coatings made by source gases of higher hydrogen to carbon ratios show outstanding high friction and wear performance and possess good performance in moist air [29].

Among the countless steel alloys, SPK NL, as a cold work tool steel simultaneously displays good wear resistance and high toughness, which give it exceptional cutting edge preservation. It has found its place in sheet metal forming such as mold plates, inserts, wear plates, and cutting dies. However, its low corrosion resistance decreases the lifetime of the forming tools and lowers final product quality. The dimension accuracy of the devices is also affected due to the forming defects such as wrinkles. Therefore, improving the alloy anti-corrosion properties and, in the meantime eliminating the process defects, i.e. crease, through using an appropriate coating seems to be necessary and reasonable. Carbon-enriched CrN hybrid coatings, i.e. (a-C:CrN), whose mechanical and electrochemical properties are optimized, may be a promising choice that simultaneously increases the anticorrosion and decreases the friction between the surfaces. Some studies report the microstructure and properties of (a-C:CrN) hybrid coatings prepared by C_2H_2 [30-32]. Notwithstanding, few studies investigate the coatings prepared using CH_4 as the carbon source in

the plasma process. Besides, there exist even fewer studies which provide sufficient knowledge of the electrochemical performance of these coatings in various environments. Carbon content is a crucial role that influences the anticorrosion properties of (a-C: CrN) hybrid coatings. Wang et al. synthesized CrCN coatings using graphite as a carbon source and evaluated the coatings' electrochemical performance in simulated body fluid (SBF) [33]. The results show that no carbide phase is formed as in Raman data D and G peaks did not emerge. Nevertheless, the CrCN coatings showed enhanced electrochemical performance compared to the CrN coating. In another study, the CrCN coatings with low carbon content (~ 12 at%) were prepared using C_2H_2 , and better corrosion resistance was obtained [25]. To assess and evaluate the effect of a new carbon source, i.e. CH_4 , on the microstructure and consequent mechanical and anti-corrosion properties alteration of the developed (a-C:CrN) hybrid coatings on SPK NL substrates, this study has been designed and conducted.

2. Experimental

2.1. Deposition process

A multi-arc ion plating deposition technique was utilized to deposit (a-C:CrN) hybrid coatings on the substrates. Before the deposition process, surface polishing treatment to attain a mirror-like appearance was applied on the substrates. Then, they were cleaned in an ultrasonic bath of deionized water, ethanol, and,

acetone for 15 minutes, respectively. The mirror-like cleaned substrates were consequently fixed in the multi-arc ion plating chamber. The base pressure of the chamber was dropped as low as 2.2×10^{-5} Torr. The mixtures of argon (Ar), nitrogen (N_2), and CH_4 flows were let in the chamber as the process atmosphere. The process was initiated by depositing a pure interlayer of chromium as thick as $0.3 \mu m$ on the substrates and accomplished by deposition of (a-C:CrN) hybrid layers in the next step. The concentration of the atmosphere compositions was controlled by adjusting the flow rate of gas. Detailed information on the process is given in Table 1.

2.2. Coatings characterization

The chemical composition of the coatings was analyzed by a JEOL JXA-8530 F field emission electron probe micro-analyzer. To investigate the crystalline structure of the deposited layers, a Phillips PW-1800 X-ray diffraction (XRD) analyzer was utilized. A $CuK\alpha$ rotating anode tube produces an X-ray with λ_{max} of 0.54 nm. The chemical structure was characterized by Raman spectroscopy using a Takram P50C0R10 device. A Lorentzian deconvolution method was employed to obtain the exact intensity and amplitude of the Raman peaks. The maximum deviation of two measured points multiplied by two was considered as the estimated experimental error.

Table 1: Detailed information on the deposition process.

Sample	Bias voltage & amperage	Arc current (A)	N_2 flow rate (sccm)	CH_4 flow rate (sccm)	Ar pressure (Pa)	CH_4/N_2
C-1	-70 V 65 A	100	60	0	0.3	0
C-2	-70 V 65 A	100	60	15	0.3	0.25
C-3	-70 V 65 A	100	60	20	0.3	0.33
C-4	-70 V 65 A	100	60	30	0.3	0.5
C-5	-70 V 65 A	100	60	30	0.3	1

2.3. Mechanical properties

A Hysitron TriboScopes® Nanomechanical device was used to measure the hardness and Young modulus. The coatings were indented by a Berkovich diamond indenter at ambient temperature. The indentation load was kept low enough that the deformation's depth was lower than 10 % of the thickness of the deposited layers. In this manner, the substrate interference with the mechanical properties of the coatings is sufficiently low to be ignored.

A universal mechanical tester tribometer (TSN.WTC 02) was used to measure the tribological properties. A ball-on-disk reciprocating sliding technique was exploited. The ball was made of Si_3N_4 , and the diameter was 3 mm. The measurement was conducted at room temperature. The sliding speed was 0.05 m/s, and the process was repeated at a frequency of 5 Hz. The load was fixed at 10 N.

2.4. Electrochemical properties

To assess the anti-corrosion attribution of the coatings, electrochemical impedance spectroscopy (EIS) was implemented in 3.5 % sodium chloride electrolyte employing an Ivium Compactstat device. A three-electrode cell configuration, Ag/AgCl (3 M KCl) as the referenced and graphite ($1 \times 1 \text{ cm}^2$) as the counter electrodes, was applied. A $1 \times 1 \text{ cm}^2$ area of the deposited coatings, as the working electrode, was exposed to the electrolyte. To isolate the remaining

area of the coatings, a barrier coating of beeswax-colophony was applied to the samples. The EIS measurements were conducted in an open circuit potential (OCP) armature at a ($\pm$) 10 mV sinusoidal potential perturbation across the frequency range of 10 kHz to 10 mHz. The measurement points were gathered after specific immersion durations (24 h) in 3.5 % NaCl solution.

3. Results and Discussion

Cr, N, and C contents of the deposited coatings are plotted versus the CH_4/N_2 ratio and is given in Figure 1a. As it is observed, Cr and N contents sharply decrease right after introducing CH_4 into the deposition chamber. As CH_4/N_2 goes up, the N content moderately decreases while Cr does not show any significant change. With methane incorporation, the surface of the Cr target is covered with organic compounds, which reduces the deposition rate of Cr. On the contrary, C content continually increases. To correlate the deposited coating's elemental composition to the composition of the plasma environment, the C/N ratio of the coatings is plotted versus the CH_4/N_2 ratio in Figure 1b. A nonlinear ascending correlation is seen, and C/N continuously increases as the CH_4/N_2 ratio increases. It can be concluded from these results that a-C impregnated CrN hybrid coatings, i.e. (a-C: CrN), with high amounts of carbon content have been successfully fabricated.

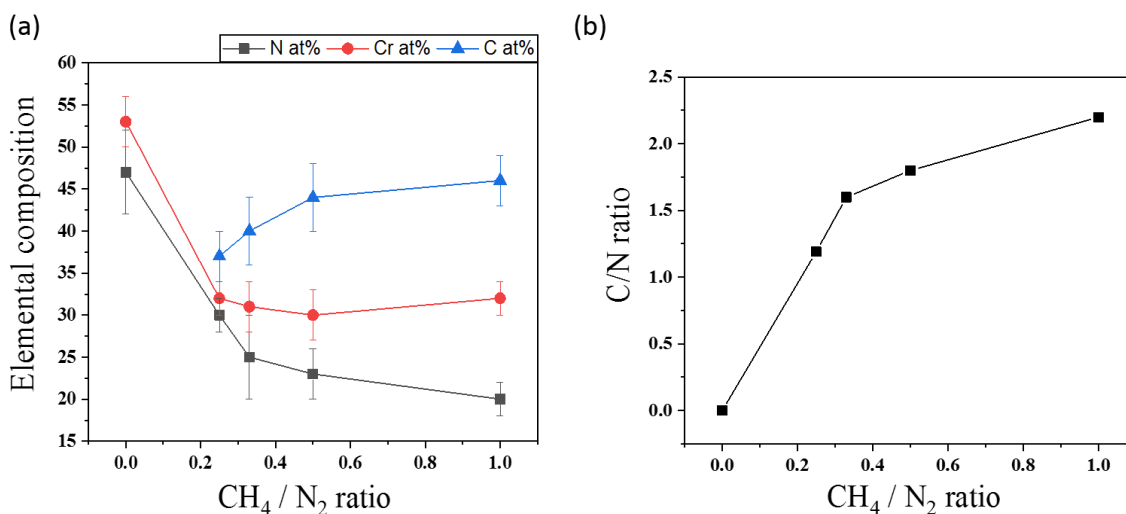


Figure 1: Chemical composition and C/N ratio of (a-C: CrN) hybrid coatings versus CH_4/N_2 .

XRD and Raman analyses give ideas about the crystalline and chemical structures of the coatings; hence a better understanding of the microstructure can be gained. The coatings' XRD spectra are presented in Figure 2. There are two short diffracted peaks at around 41° and 65° for the coatings prepared at lower C/N ratios that are attributed to the Cr phase of the Cr droplets [26]. These peaks disappeared in the coatings with higher C/N ratios, i.e. C/N=1.83. Three diffracted peaks corresponding to (111), (200), and (220) planes of face-centered cubic, fcc, phase formed in CrN coating, i.e. C-1, can be seen. Nonetheless, a mixed structure of fcc-CrN and (220) orientation along with orthorhombic-Cr₃C₂ phases, is formed in all the hybrid coatings, i.e. C-2 to 5. It should be noted that the peak at around 43° , which is attributed to the (200) plane of CrN phase, almost disappears in (a-C: CrN) hybrid coatings while a weak peak at about 63° exists in all samples, which is correlated to the (220) plane of CrN. However, this peak becomes broader at higher C/N ratios, indicating that its crystallinity and grain size are decreased [34]. Other distinctive peaks that are correlated to the Cr₃C₂ phase can be seen at around 44.2° , and 75° in (a-C: CrN) hybrid coatings. These two diffracted peaks are respectively related to the

(240) and (271) planes of the Cr₃C₂ phase and as it can be seen, the intensity increases upon increasing the C/N ratio. The results confirm that the CH₄ incorporation leads to a higher density of carbon species in plasma and encourages carbide phase formation in (a-C: CrN) hybrid coatings [30]. The crystal grain size in the coatings can be quantitatively estimated considering the peak broadening through Scherrer's equation. The output of this equation is, in fact, the thickness of the crystal planes parallel to the normal direction. The CrN and Cr₃C₂ crystal grain size of the coatings as a function of C/N is given in Figure 2c. The crystal grain size of the CrN phase significantly drops from ~ 275 nm for C-1 to ~ 10 nm for C-4. However, the crystal grain size of the (271) plane of Cr₃C₂ phase shows an increment from ~ 70 to ~ 190 nm as C/N increases. According to Figure 1, the coatings' nitrogen content decreases with increasing CH₄ flow rate, which results in lower CrN content of the coatings. It seems that with increasing C/N ratio, solid solution hardening of the carbon phase in the CrN phase takes place and leads to nucleation and growth of hard carbide, i.e. Cr₃C₂, phase in the coatings [26, 30]. It can be concluded that carbon incorporation increases the abundance and grain size of the Cr₃C₂ phase in (a-C: CrN) hybrid coatings.

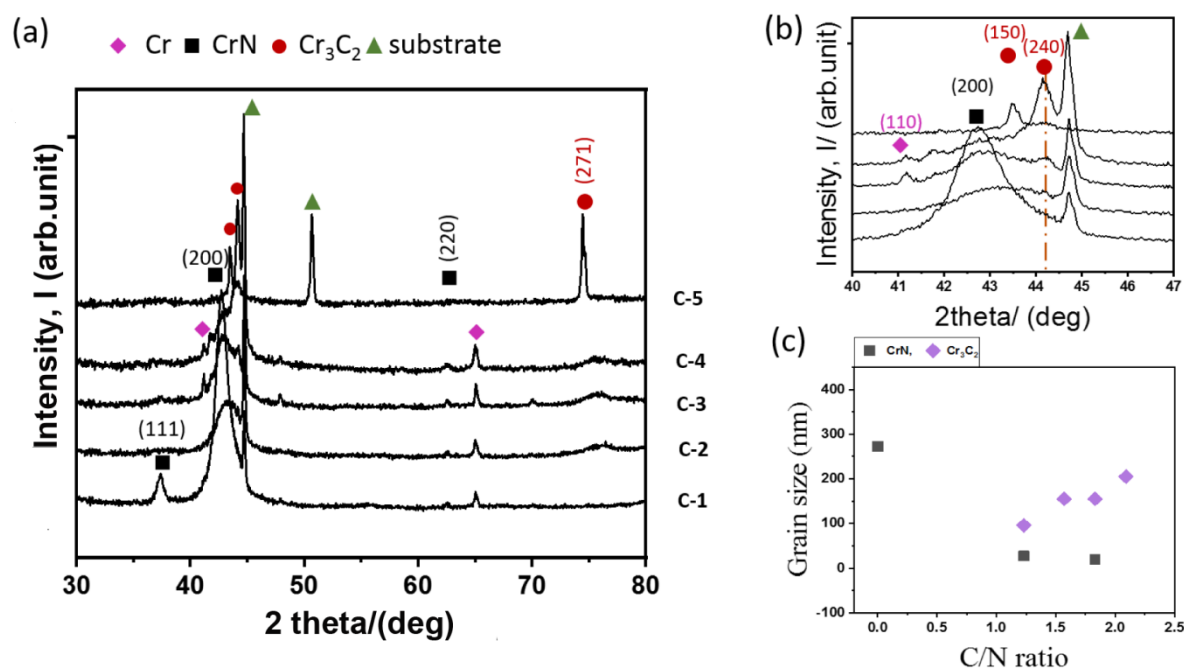


Figure 2: X-ray diffraction patterns (a), magnified section (b), and grain size (c) of the coatings.

Raman spectra of the coatings are given in Figure 3a. Two distinctive peaks, commonly known as D- and G-bands, as a typical feature of a-C coatings, are seen. Alteration in their relative intensity, i.e. I_D/I_G , and broadening, i.e. FWHM, can be attributed to the structure and properties of the coating. For example, in carbon-based films, FWHM of the D- and G-band peaks determine crystallinity [11, 19]. It has been shown that when most of the carbon-based coating is amorphous, broad and diffuse peaks appear. Sharp peaks emerge when the carbon coating is more crystalline [11]. I_D/I_G is obtained through curve area integration of D- and G-band peaks using a Gaussian curve fitting. I_D/I_G and FWHM are plotted as a function of C/N and presented in Figure 3 b and c. Both values continuously decrease as C/N increases. Hence, (a-C: CrN) hybrid coatings prepared at higher C/N ratios contain a more significant amount of sp^3 hybridized carbon and a lower degree of sp^2 ones. Furthermore, since FWHM reduces as C/N increases, these coatings are more crystalline.

It is ostensibly concluded from the microstructural analyses, i.e. XRD and Raman, that (a-C: CrN) hybrid coatings are composed of a two-phase amorphous carbon and CrN or Cr_3C_2 nanograins. Besides, the carbon incorporation encourages chromium carbide (Cr_3C_2 phase) formation in the coatings, and carbide content increases by increasing C/N. Moreover, the (a-C: CrN) hybrid coatings prepared at higher C/N ratios contain greater extents of sp^3 carbon, and the structural order is enhanced. Therefore, to pursue the changes in structure and morphology alteration mentioned above, the FE-SEM technique was exploited. The images are given in Figure 4. A honeycomb-like co-continuous structure has been developed in all coatings. This was previously reported in Arc PVD synthesized coatings [25]. The metal droplets of Cr can be seen on the surface, and the number of these droplets is maximum at medium C/N ratios (Figures 4c and d). This is in good agreement with the XRD analysis of the coatings. The thickness of the Cr interlayer in CrN and (a-C: CrN) hybrid coatings are about 0.3 and 2.2 μm , respectively.

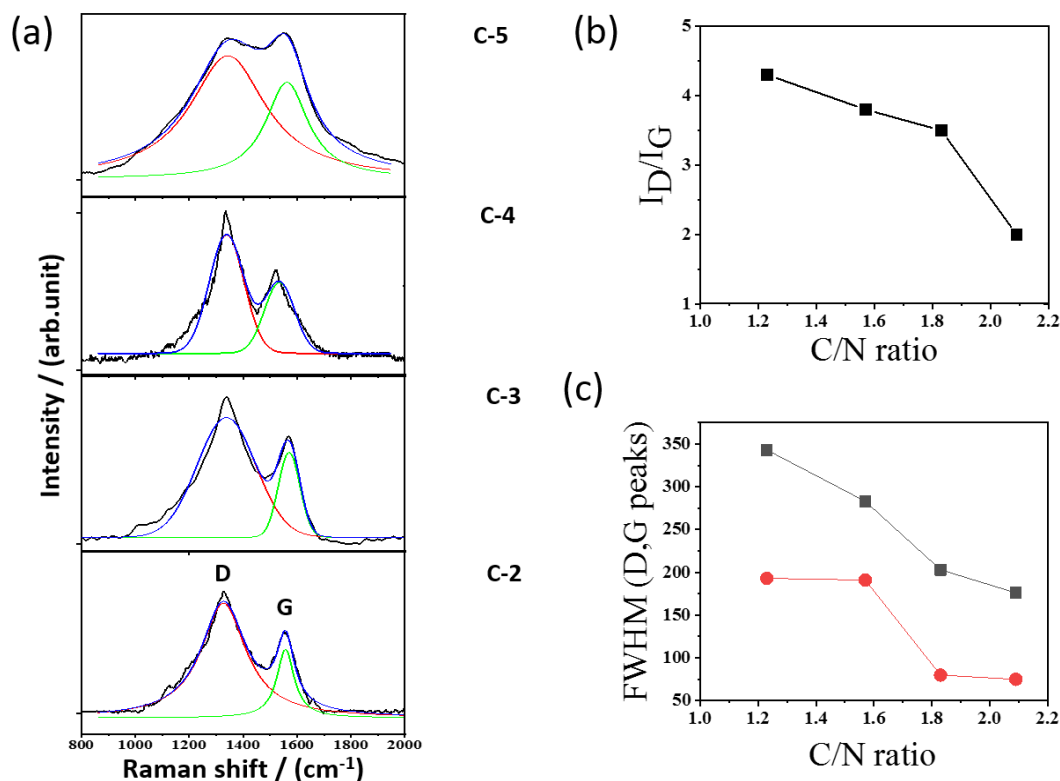


Figure 3: Raman spectra (a), I_D/I_G (b) and FWHM (c) versus C/N ratio.

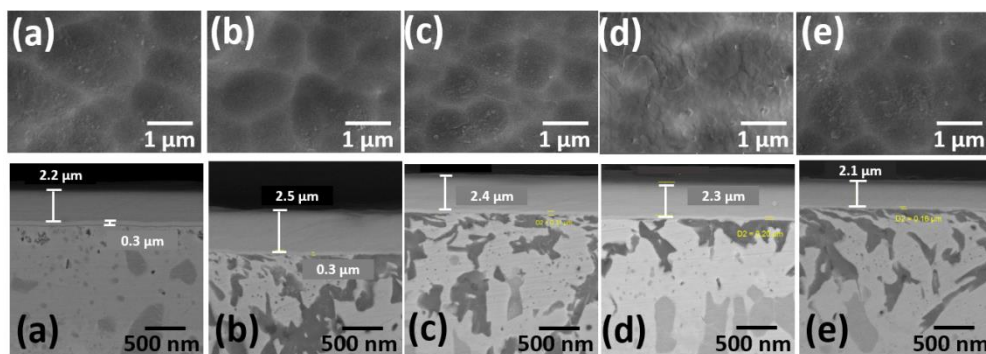


Figure 4: Plane view FE-SEM images of (a-C: CrN) hybrid coatings, i.e. C-1 to C-5 (a-f).

As mentioned previously, the mechanical characterization was carried out by analyzing the hardness, and Young modulus of the obtained coatings. The variation of hardness, Young modulus, and H^3/E^2 of the (a-C: CrN) hybrid coatings as a function of C/N are presented in Figure 5. It can be seen that the hardness value of SPK NL substrate increased via its surface modification and all coated substrates showed higher hardness values. Seemingly, hardness has an ascending trend as C/N increases and reaches a maximum value of ~ 35 GPa for CrCN-5 and all the (a-C: CrN) hybrid coatings are harder than CrN. However, the Young modulus demonstrates a second-degree parabolic trend with a minimum at $C/N=1.8$ and a maximum at $C/N=2.09$. These behaviors might be explained through the microstructure of the coatings. According to the XRD results, all (a-C: CrN) hybrid coatings contained a mixed structure of amorphous C, CrN, and Cr_3C_2 phases yet at various concentrations. One reason causes the higher hardness for (a-C: CrN) hybrid coatings compared to CrN might be the solid solution hardening effects of the carbon phase on the CrN phase that leads to nucleation and growth of hard carbide, i.e. Cr_3C_2 , phase in the coatings [26, 30]. This effect is even enhanced as C/N increases. Moreover, Raman outcomes showed that (a-C: CrN) hybrid coatings prepared at higher C/N contain a-C structure, which is composed of a higher share of sp^3 hybridization or the so-called diamond-like carbon. This phase can increase the hardness of the whole structure, hence (a-C: CrN) the hybrid coatings prepared at a higher C/N ratio are harder (Figure 3). Although it is an accepted term that a-C based coatings which contain a higher amount of sp^3 hybridization are harder [35], in some related studies that (a-C: CrN)

hybrid coatings prepared using C_2H_2 gas as the carbon source, the coatings showed lower carbon content and lower hardness values compared to the results of the current study [25, 26, 30, 31]. The results of the present study show that (a-C: CrN) hybrid coatings with higher carbon content and higher hardness can be obtained using CH_4 gas as the carbon source in the plasma environment and this coating is a good candidate for surface protection of SPK NL.

The plasticity index, i.e. H^3/E^2 , of the coatings, has been presented in Figure 5c as a function of C/N. This index represents the coating resistance against plastic deformation. This applied parameter is an indicator of evaluating the coatings' tribological properties [36–38]. As the diagram depicts, the plasticity index continuously increases as C/N rises. Higher plasticity index and at the same time, higher hardness indicate a hard nanocomposite coating. As an accepted knowledge, the existence of two phases, one continuous amorphous phase, and one nano-grains dispersed phase, together improves the mechanical properties of the nanocomposite coatings [39, 40]. According to the microstructural analysis of the coatings, i.e. XRD and Raman, (a-C: CrN) hybrid coatings are composed of a mixed structure of Cr_3C_2 and CrN nano-grain phases dispersed in a continuous a-C phase which in turn is comprised of different contents of sp^2 and sp^3 hybridizations. Hence, the structure is quite resembling a nanocomposite material [36–38]. This structure is responsible for the increases in the plasticity index of the coatings and enhanced mechanical properties [36–40]. From the above mentioned results it can be concluded that surface treatment of SPK NL substrate has a great impact on mechanical and tribological properties.

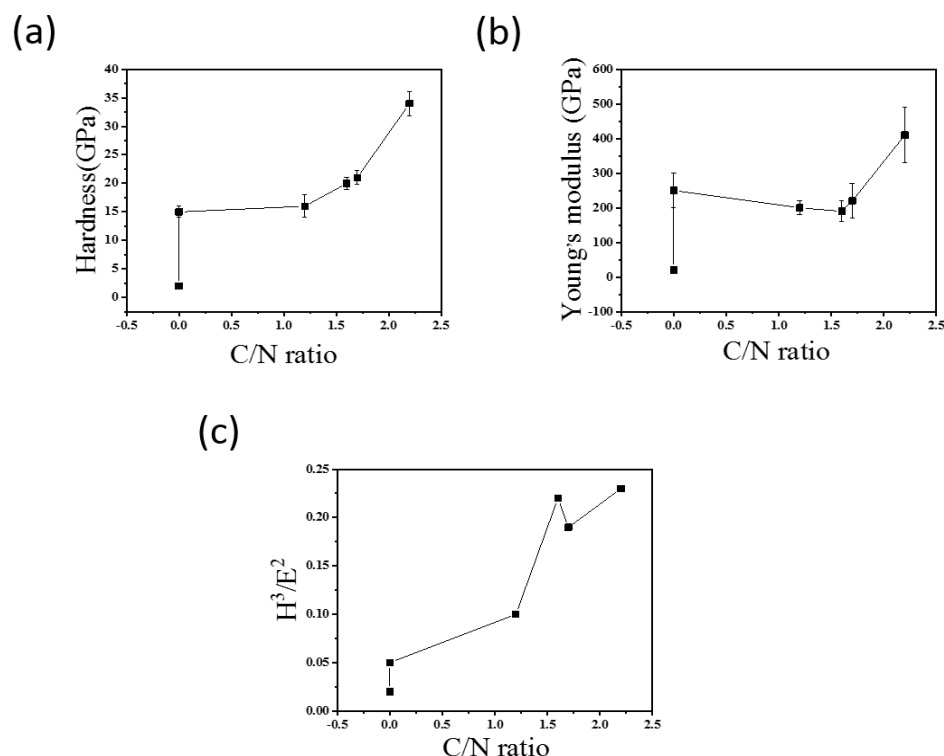


Figure 5: Variation of hardness (a), Young modulus (b), and H^3/E^2 (c) of CrN and (a-C: CrN) hybrid coatings as a function of C/N.

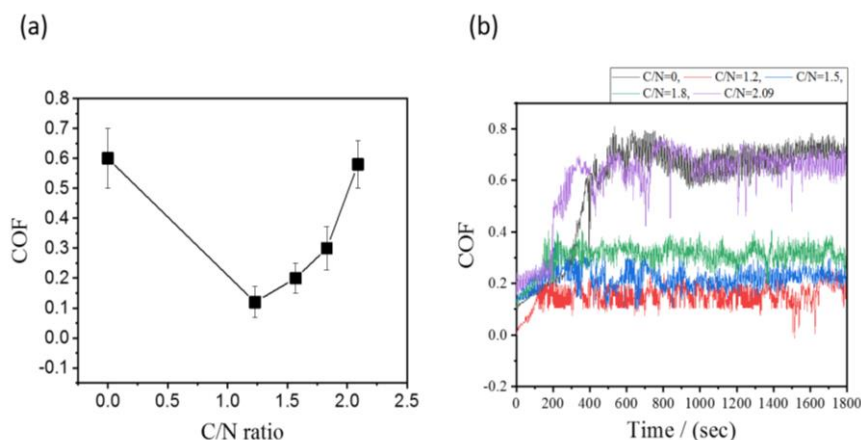


Figure 6: Variation of COF value (a) and friction behaviors (b) of CrN and (a-C: CrN) hybrid coatings.

Figure 6a gives the average coefficients of friction versus C/N, and Figure 6b shows the friction behaviors as a function of time while the normal load is applied on the CrN and (a-C: CrN) hybrid coatings. The coatings slide against Si_3N_4 balls in ambient air. The CrN friction curve shows a rapid increase within the first 400 s and then becomes steady-state with a relatively small amplitude of fluctuations. However, the (a-C: CrN) hybrid coatings offer different behavior. Their trend can be divided into two distinguished

sections: An abrupt increase across the first 300 s and then a relatively steady-state region. Notwithstanding, the C-5 shows friction coefficients as significant as CrN yet smaller fluctuations. For other (a-C: CrN) hybrid coatings with lower C/N ratios, the first stage is less abrupt than is accomplished within the early 200 s and the steady-state region, which is distinctively shorter compared to C-1 and C-5. It can be concluded from the COF diagram that the average COF of the coatings prepared at lower C/N ratios is less than CrN.

Obviously, (a-C: CrN) hybrid coatings possess improved wear resistance. To explain this behavior, a flashback to the structural results is required. The Raman outcomes showed that (a-C: CrN) hybrid coatings prepared at lower C/N composed of a higher fraction of sp^2 hybridization or graphite-like carbon. This smooth structure shows a self-lubricant effect during the friction measurement and significantly reduces friction. The planar 2D structure of sp^2 carbon at the interface minimizes swinging effects of σ bonds at the contacted surfaces and attenuates the strong

adhesion between contacted surfaces. This results in low surface energy either [41]. The same explanation justifies elevated COF for C-5. The lower fraction of sp^2 carbon in (a-C: CrN) hybrid coatings prepared at higher C/N weakens the anti-wear capacity.

EIS analyses have been carried out at various time intervals, i.e. 1, 4, and 24 h, of immersion in 3.5% NaCl electrolyte to evaluate the corrosion protection of the coatings on the SPK NL substrates. The Bode-phase and Nyquist diagrams for these as-prepared coatings are illustrated in Figures 7 and 8.

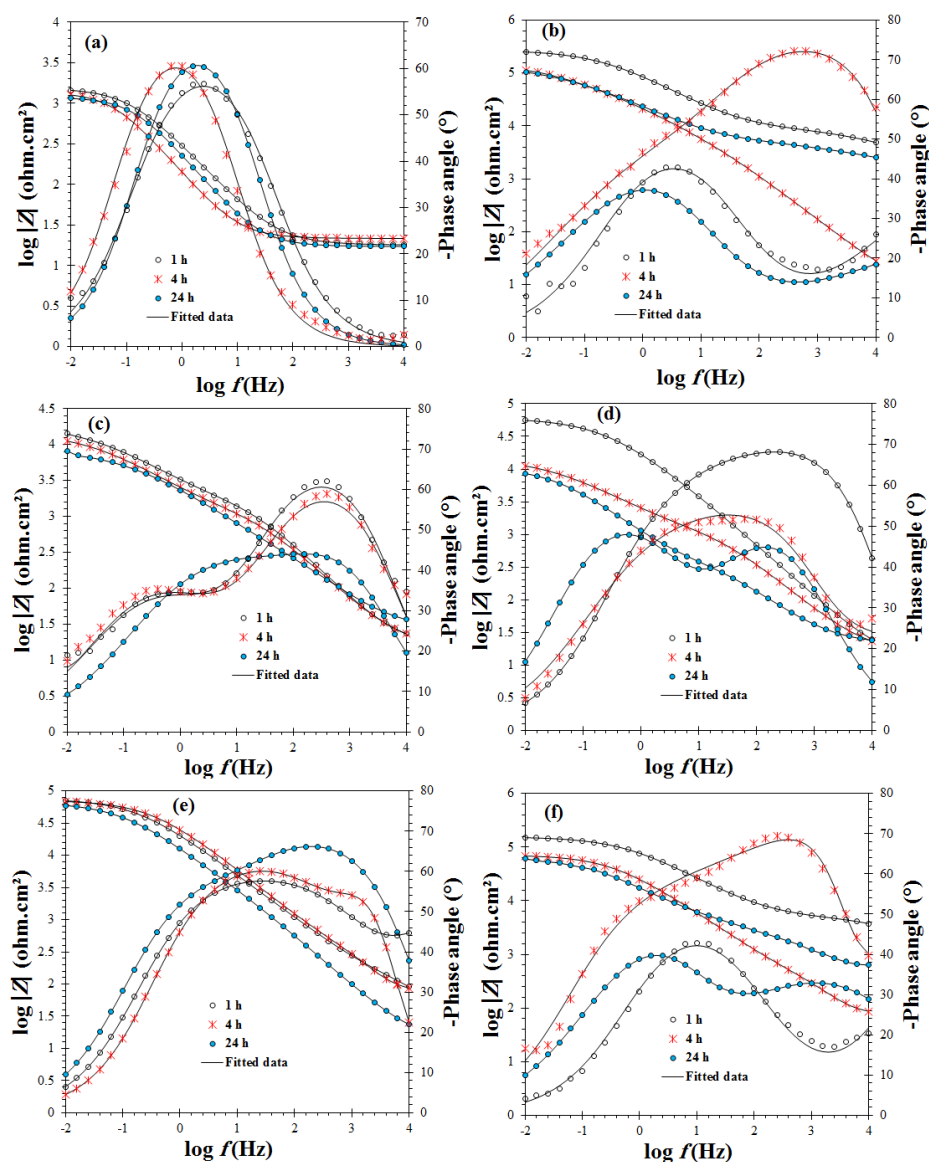


Figure 7: Impedance modulus and phase angle as functions of frequency at various intervals (Bode-Phase angle) diagrams: (a) blank, (b) C-1, (c) C-2, (d) C-3, (e) C-4 and (f) C-5.

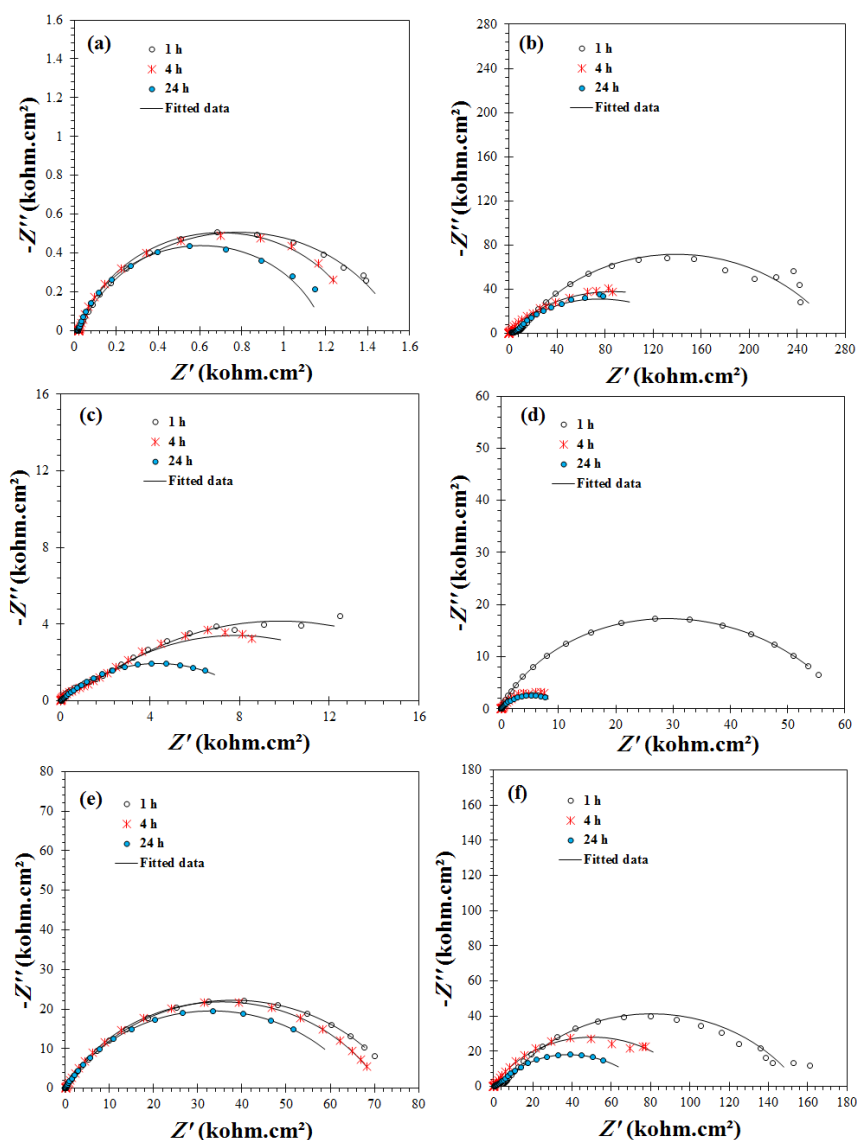


Figure 8: Nyquist diagrams for: (a) blank, (b) C-1, (c) C-2, (d) C-3, (e) C-4 and (f) C-5.

The low-frequency impedance modulus can be considered as a precise ruler, which evaluates the corrosion protection of the coatings [42, 43]. Moreover, the high-frequency phase angle values provide accurate information on the barrier performance of the coatings [44, 45]. As it is obtainable from the Bode-Phase diagrams, the uncoated (bare) sample has the lowest low-frequency impedance modulus. The most positive high-frequency phase angle also belongs to the bare substrate at different immersion intervals. In other words, the capacitive-loop size is enlarged as the coatings are applied on the surface. The capacitive-loop size in the Nyquist diagrams is associated with the total resistance of the coated samples [46]. These results confirm that the SPK NL surface has become immune by a protecting layer. The low-frequency impedance

modulus of the CrN (C-1) coating is higher than that for the (a-C: CrN) (C-2 to 5) hybrid coatings at the end of the immersion time. This is confirmed by the lowest capacitive-loop size of this sample in the Nyquist diagrams (Figure 8). The (a-C: CrN) hybrid coatings show similar impedance modulus values at around $10^4 \Omega \cdot \text{cm}^2$ at the early stage of the immersion; however, the resistance abruptly decreases as time passes. Seemingly, these coatings are initially protecting the surface, yet the breaks due to the continuous exposure to the harsh and aggressive environment. The best performance among these hybrid coatings belongs to the C-5. Using the Bode-Phase diagrams, it is also possible to describe the type of electrochemical reactions occurring at the coating and metal-solution interface. These reactions are directly correlated to the corrosion resistance [47, 48].

These diagrams also depict two-time constants for the coated substrates at each immersion interval. These high-frequency and low-frequency time constants are correlated to the deposition of the coating, and the formation of corrosion products at the exposed surface, respectively [49].

An equivalent circuit (two-time constant equivalence) was modeled using the impedance results (Figure 9) for CrN and (a-C: CrN) hybrid coatings. As it is depicted in Figure 9a, the modeled circuit for the bare metal reveals three moduli; (i) a resistance (R_s) associated with the solution or electrolyte, (ii) a resistance (R_{ct}) assigned to the charge transfer resistance of the reactions, which happen at the metal/solution interface, and (iii) a double layer constant phase element created at the mentioned interface (CPE_{dl}). In Figure 9b, two other moduli, namely R_c (coating resistance) and CPE_c (coating constant phase element), are given. The quantitative outcomes are presented in Table 2. In this table, Y_0 and n are the admittance and index of the surface irregularity, respectively. It is clear from the data that as the immersion time increases, the R_{ct} decreases while $Y_{0,dl}$ increases. These are solid proofs that the SPK NL corrosion has initiated in the corrosive electrolyte, and low corrosion resistance is observed. However, the deposition of CrN and (a-C: CrN) hybrid coatings on the surface causes R_{ct} to improve, and a new resistance emerges for all of the immersion periods. The increment of R_{ct} is mainly due to the protecting layer of the coatings that hinders electrolyte access to the surface [50]. Moreover, R_p (collection of R_{ct} and R_c) for CrN is higher than that for the (a-C: CrN) hybrid coatings across the whole immersion durations. Also, this modulus increases as the immersion time goes by. The latter is vice versa for the (a-C: CrN) hybrid coatings meaning that the R_p decreases as the immersion time increases. Accordingly, $Y_{0,dl}$ for CrN is lower than that for the (a-C: CrN) hybrid coatings and decreases as the immersion prolongs. This behavior can be attributed to the alteration of the chemical composition of CrN. It is well accepted that the changes in the chemical composition of the layer lead to changes in the double-layer properties of the coated substrate. Altogether, the electrochemical behavior of CrN concludes that an active/protecting performance mechanism governs the coatings.

Changes in R_c give information on the barrier performance of the coating [51]. R_c for CrN is higher than that for (a-C: CrN) hybrid coatings across the whole immersion durations, although they all relatively

decrease as the immersion prolongs. This decrease in R_c of the (a-C: CrN) hybrid coatings may be correlated to the accumulation of conducting species of the corrosion products into the coating porosity. Also, C_c for CrN is lower than that for the (a-C: CrN) hybrid coatings meaning that a relative deterioration in corrosion resistance has occurred by impregnating carbon into the structure. Nevertheless, the absolute measure of the corrosion moduli for these coatings is still significant. This reduction could be attributed to the higher concentration of Cr in CrN than the (a-C: CrN) ones. Among the hybrid coatings, CrCN-5 demonstrates the best corrosion protection. They can be ordered as $CrCN-5 < CrCN-4 < CrCN-3 < CrCN-2$. This is mainly attributed to the chromium carbide (Cr_3C_2) phase formed in (a-C:CrN) hybrid coatings. The corrosion resistance enhances as the concentration of this phase increases and the highest concentration of Cr_3C_2 phase belongs to C-5.

It is evident from the EIS results that, CrN and (a-C: CrN) hybrid coatings can provide the SPK NL substrate with relatively significant corrosion resistance. Besides, the anti-corrosion performance of CrN itself is superior to the (a-C:CrN) hybrid coatings. According to Figure 4, all the coatings show the same honey-comb-like morphology. It seems that the surface morphology does not affect the corrosion resistance. However, the Cr content of the CrN coating is the highest. It is well known that Cr forms a passive chromium oxide or chromium hydroxide layer at the interface that hinders the substrate contact with corrosive species [52, 53]. The efficient formation of such a layer is most probable for CrN compared to (a-C: CrN) the hybrid coatings. An interesting correlation can be found between the carbon content and anticorrosion properties of the hybrid coatings. The resistance improves as the carbon content increases.

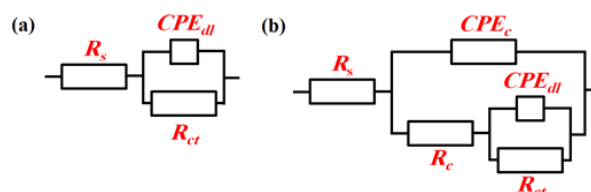


Figure 9: Electrical equivalent circuits used for modeling of impedance data; (a) one-time constant and (b) two-times constants.

According to XRD analyses outcomes (Figure 2), the chromium carbide (Cr_3C_2) phase formed in (a-C: CrN) hybrid coatings structure increases by increasing the C/N ratio. The crystalline chromium carbide can effectively isolate the structural defects of (a-C: CrN) hybrid coatings resulting in an improvement in corrosion resistance [54]. Also, the chromium carbide with higher carbon content offers superior corrosion resistance [55]. Accordingly, the higher availability of the chromium carbide (Cr_3C_2) phase in the structure might be the main reason for the improvement of the corrosion resistance. Wang et al. evaluated bio-corrosion resistance of CrCN coatings in SBF solution. They showed that when the coating's carbon content is less than ~52 at%, the coatings contain a stable N-C bond, which is challenging to be broken in the corrosive media (SBF for that research) [33], leading to

better corrosion resistance. However, the current study results somehow contradict some of the others; for instance, the studies of Ye et al. [25] and Wang et al. [33]. There are two probable reasons for these differences; (i) carbon content of the coatings prepared by Ye et al. was ~12 at%, which is much lower than in this paper, i.e. 47%. As mentioned above, there is a strong correlation between the carbon content and corrosion resistance of the hybrid coatings [55], and (ii) in Wang et al. study; they used SBF as the electrolyte, which is a much weaker corrosive medium compared to the solution of 3.5 wt% NaCl. The current study results show that the carbon does not positively impact the corrosion resistance of CrN notwithstanding, (a-C: CrN) hybrid coatings with higher carbon contents demonstrate sufficiently enough anticorrosion performance in 3.5 wt% NaCl.

Table 2: Electrochemical parameters extracted from EIS data for the prepared samples at various exposure times.

Sample	Time (h)	R_{ct}^a (ohm.cm^2)	CPE_{dl}		R_c^a (ohm.cm^2)	CPE_c	
			Y_0^b ($\mu\text{s}^n.\text{ohm}^{-1}.\text{cm}^2$)	n^c		Y_0^b ($\mu\text{s}^n.\text{ohm}^{-1}.\text{cm}^2$)	n^c
Blank (without coating)	1	1531	197.7	0.74	-	-	-
	4	1358	263	0.81	-	-	-
	24	1178	299.4	0.81	-	-	-
C-1	1	263800	3.7	0.66	9698	0.5	0.49
	4	174800	9.6	0.48	6467	5.5	0.68
	24	158900	10.6	0.63	6319	4.5	0.34
C-2	1	16830	133.1	0.56	1731	14.9	0.78
	4	13580	161.8	0.56	1391	20.1	0.75
	24	8331	169.2	0.52	379.9	33.6	0.69
C-3	1	37630	14.5	0.78	2900	9.0	0.79
	4	10600	128.9	0.74	37.9	99.1	0.53
	24	10200	141.9	0.69	484.6	78	0.70
C-4	1	75620	7.8	0.67	304.5	4.2	0.69
	4	71260	8.5	0.68	431.4	0.5	0.89
	24	61200	13.5	0.78	5979	0.8	0.78
C-5	1	151300	3.7	0.63	4995	0.60	0.66
	4	101600	4.8	0.96	4050	18.9	0.63
	24	70570	8.1	0.69	6577	10.3	0.49

^a The standard deviation range for resistance values is between 2.1% and 9.4%.

^b The standard deviation range for admittance values is between 1.3% and 5.6%.

^c The standard deviation range for n values is between 0.8% and 1.2%.

4. Conclusions

In the current study, the SPK NL substrates were surface treated via deposition of CrN and carbon enriched CrN, i.e. (a-C:CrN) hybrid coatings, by the aid of a multi-arc ion plating device. The improvement in the mechanical properties and enhancement of the wear and corrosion resistance were considered. The influence of the C/N ratio on the microstructure, mechanical properties, COF, and electrochemical characteristics of the coatings was investigated. The results showed that the carbon incorporation improves the mechanical properties of CrN coatings however; it relatively deteriorates the corrosion resistance. Notwithstanding, (a-C:CrN) hybrid coatings still possess significant corrosion resistance and protect the surface of SPK NL substrates against corrosive species. Moreover, the results confirmed the

self-lubricant characteristic of the (a-C:CrN) hybrid coatings, and the vital role of the sp^2 fraction on the COF was approved. In conclusion, it is possible to protect the surface of SPK NL alloy against wear, and corrosion using (a-C:CrN) hybrid coatings prepared by CH_4 as the carbon source. These coatings contain higher carbon content and show higher hardness than the reports in which C_2H_2 had been used as the carbon source. From the viewpoint of the coatings applications on metal forming parts, (a-C:CrN) hybrid coatings having an average C/N ratio are promising candidates that have enhanced mechanical and tribological properties, low COF, and good corrosion resistance. The results of the current study clarified the vital role of protective coatings on mechanical, tribological and electrochemical performance of SPK NL substrates.

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