A Comparative Study on the Influence of Al₂O₃-ZnO ALD Nanolaminates on the Properties of CrCN PVD Sputtered Coatings with Distinctive Morphologies and Microstructures

Elias Kaady 1,2,*; Syreina Sayegh 3, Mikhael Bechelany 3, Roland Habchi 2,4 and Akram Alhussein 1,*

Abstract: Chromium carbonitride (CrCN) coatings present the desired characteristics for improving the mechanical properties and the corrosion resistance of marine components. The purpose of this work is to investigate the effect of carbon insertion, using CH₄ gas flow as the carbon precursor in magnetron sputtering, on the mechanical and electrochemical properties of the CrN coating. Moreover, the influence of the Al₂O₃-ZnO nanolaminates sealing layers deposited by the atomic layer deposition (ALD) on the properties of distinctive CrCN sputtered coatings (dense and columnar) is investigated. Structural, morphological, and topographical analyses were performed using scanning electron microscopy, X-ray diffraction, and atomic force microscopy. The nanoindentation measurements determined the mechanical properties and the electrochemical behavior evaluated in a saline solution. The results revealed new important insights in the field of duplex treatment based on hybrid deposition using magnetron sputtering and ALD techniques.

Keywords: chromium carbonitride; thin film; atomic layer deposition; corrosion; physical vapor deposition; mechanical properties

1. Introduction

Marine equipment such as gears, bearings, propellers, as well as shafts are mainly essential materials in the field of marine engineering [1,2]. These components suffer from damages and a short lifetime service due to the synergistic effect of corrosion degradation and frictional wear in aggressive seawater environments [3]. Hence, it is imperative to guarantee the stability and the work reliability of these workpieces in a strong corrosive salt media [4]. Protective thin film technology is widely used as a good strategy to improve the surface properties of the materials used in harsh and severe environments [5]. Scientists and engineers are challenged to develop new coatings for ensuring the protection of metallic components from corrosive media and wear loss.

Among the used coatings in the marine related field, chromium carbonitrides CrCN are well reported [3,4,6–9] to present the well-desired characteristics for improving the mechanical properties and the corrosion resistance of the marine components. They have been paid more attention than chromium nitride CrN coatings [6], presenting higher hardness and lower friction coefficients. The good lubrication and wear-reduction effects observed in CrCN coatings are due to the amorphous carbon element [5]. Thus, the carbon incorporation into chromium nitride coatings influences their structural properties and
acts as a self-lubricated material reducing the friction coefficient [5]. Furthermore, it is well reported that complex carbides generated from the reaction of transition elements such as Cr with the interstitial carbon could form hard layers that improve the corrosion resistance of steels and ductile iron-based alloys as reported by Günen et al. [10]. Physical Vapor deposition (PVD) techniques are one of the most widely used thin-film deposition techniques. Several studies pointed out the optimization and the deposition of chromium carbonitride coatings using PVD techniques. Xu et al. [8] studied the structural, electrochemical, and tribocorrosion behavior of CrCN in a corrosive environment. They found that the dense CrCN deposited by magnetron sputtering exhibited more electrochemical performances than CrN. CrCN with 20.3% of carbon content presented the lowest wear rate of $3.85 \times 10^{-7}$ mm$^3$/N·m and the minimum open circuit potential (OCP) value of −0.19 V which revealed its excellent tribocorrosion properties. Liu et al. [5] found that the addition of carbon in the CrN matrix induced the formation of other phases of carbon and CN$. It improved the hardness from $17$ GPa to $19$ GPa with 6.3 at.% of carbon and the average friction coefficient decreased gradually from 0.62 to 0.40 with 23.7 at.% of carbon. Several studies pointed out the deposition of CrCN coatings using multi-arc ion plating or sputtering techniques using graphite target [5,11–13] or acetylene gas [3,4,6–9,14] as a source of the carbon element. However, there is no relevant detailed study on CrCN coatings deposited by magnetron sputtering using CH$_4$ gas as a carbon element source.

The last few years, intensive research was held to develop the PVD coatings, improve their properties, and achieve a higher performance in order to diversify their possible applications to meet the industrial requirements. Despite their high mechanical characteristics, the inherent defects [15] including columnar structures, pores, and discontinuities in PVD coatings significantly affect their corrosion resistance and toughness. Deposition of coatings in architectured multilayers [16] was applied as a suitable strategy to reduce the structural defects. These coatings exhibit strong mechanical properties and exceptional resistance to corrosion and oxidation, surpassing that of monolayer coatings. It may be due to the fact that the interlayer boundaries can restrain or change the direction of crack propagation [17]. Kong et al. [18] found that CrN/CrCN multilayered coatings had higher toughness and wear resistance than CrN monolayer coating, which can be attributed to the densification effect and characteristics of multilayer coating. Wang et al. [9] reported that the as-deposited CrN/CrCN multilayered coating could demonstrate significant improvement of tribocorrosion resistance compared to the CrN and CrCN monolayer coatings. Pogrebnjak et al. [19] studied MoN/CrN nanostructured coatings deposited by the Arc-PVD process. They noticed that the multilayer architecture approach with control of layer thickness and deposition parameters is an efficient method for transition metal nitrides fabrication.

Recently, duplex coatings combining PVD layers with atomic layer deposition (ALD) thin films presented more efficiency in mechanical and anti-corrosion properties than the as-deposited PVD coatings [20–24]. ALD is a powerful technique to deposit coatings with precise thickness control, excellent uniformity, conformity, and tunable composition [25,26]. The ALD process involves a unique mechanism of cyclic repetition, in which self-limiting surface reactions occur with two or more gaseous precursors injected in separate pulses [27,28]. Over the last few decades, ALD layers emerged as candidates in corrosive environment applications [29–33] due to their high quality permeation barrier properties and dense structures. Due to their insulating dielectric properties and the ability to well nucleate on metals surfaces, aluminum oxide (Al$_2$O$_3$) ALD films are the most readily studied ALD thin films for corrosion protection [31–34]. However, in moist environments, Al$_2$O$_3$ films eventually fail to provide long-term corrosion protection [35]. Facing that problem, the nucleation ability of Al$_2$O$_3$ was combined with the chemical stability of other oxides such as TiO$_2$: [36,37] and Ta$_2$O$_5$: [38] in nanolaminate architectures to provide an improvement in corrosion resistance, good barrier properties, and sufficient durability against chemical attacks. In our earlier study [39], we investigated the efficiency of Al$_2$O$_3$/ZnO nanolaminates in enhancing the mechanical and anticorrosion behavior of
chromium nitride CrN coatings. The studied architectured coating presents a great potential as an advanced coating for corrosive environment applications.

Several studies on the duplex coatings deposited by the combination of physical vapor deposition and atomic layer deposition techniques for corrosion protection have been reported. Dai et al. [20] studied the properties of Al2O/AlSiN hybrid ALD/PVD coatings in the multilayer design with various periods. Wan et al. [21] investigated the influence of the thickness and the position, where the Al2O ALD layer was inserted in the CrN PVD layer, on the microstructure, corrosion behavior, and mechanical properties of the coatings. Leppäniemi et al. [40] studied the effect of surface wear of ALD layers on the corrosion properties of the duplex coatings. They discovered that, despite removing the ALD nanolaminate completely from the top, the corrosion current density was still less than half that of the PVD CrN coating without surface wear. Staszuk et al. [41] investigated hybrid coatings produced using magnetron sputtering and ALD techniques, which consisted of layers of the same phase and were obtained through distinct surface treatment technologies.

In this study, a series of CrCN coatings was deposited by the pulsed magnetron sputtering technique using CH4 gas as a carbon precursor. The influence of the carbon insertion into CrN on the structural, mechanical, and electrochemical properties was investigated. Al2O/ZnO nanolaminates were deposited using the ALD technique on the distinctive CrCN coatings containing different carbon percentages. The main goal of this study is to investigate the way that the ALD layer could enhance the PVD layers’ properties, and its relationship with the PVD layer morphology and microstructure. The current work provides important insights for the advanced duplex PVD and ALD hybrid coatings.

2. Materials and Methods
2.1. Deposition of CrCN Coatings

The CrCN coatings were deposited on AISI 316L stainless steel disks (Φ 25 mm × 8 mm, purchased from the UGITECH company, Ugine, France) and Single crystalline Si (100) one sided polished wafers using a DEPHIS4 (Etupes, France) magnetron sputtering machine. The composition of 316L substrates, the samples’ preparation before deposition, and the sputtering system were described in our previous work [39]. The vacuum pressure in the sputtering chamber was reduced via mechanical and turbo-molecular pumps to 10⁻⁹ Pa. The chromium target (99.99% purity, Φ = 200 mm × 6 mm) was etched for 20 min with argon ions’ Ar⁺ bombardment prior to the deposition, in order to clean its surface from thin oxide layers and other impurities (0.30 Pa pressure, Argon flow rate = 100 sccm, discharge power of 1A). To improve the adhesion strength of CrCN coatings, a 0.5 μm pure Cr transition layer was pre-deposited on the substrates by sputtering a Cr target at 1.5 A for 35 min. The CrCN coatings were deposited in a mixed atmosphere (Ar, N₂, and CH₄). Subsequently, the sputtering current of the Cr target was set to 1.5 A, and the flow rates of Ar and N₂ gases injected in the chamber were fixed at 30 and 9 sccm, respectively, during the deposition. The substrate-holder rotation speed of 10 rpm was kept constant to obtain a homogeneous film in thickness and composition. During deposition, no bias on either substrates’ heating was performed. The CrCN coatings with different carbon contents were obtained by varying the flow rate of CH₄ gas (0, 2, 3, 4, and 5 sccm). The total deposition time was 300 min. CrCN coatings with various carbon contents obtained from different CH₄ gas flow rates (0, 2, 3, 4, and 5 sccm) were labeled as CrN, CrCN-2, CrCN-3, CrCN-4, and CrCN-5, respectively.

Al2O/ZnO nanolaminates were deposited using the atomic layer deposition technique following the procedure described in our previous study [39].

2.2. PVD/ALD/PVD Duplex Coatings Deposition

In order to compare between the duplex coatings and to well outline the influence of the Al2O/ZnO nanolaminates’ ALD insertion, the thickness should be the same for all the
coatings. Three CrCN compositions were chosen: CrCN-2, CrCN-4, and CrCN-5. A Cr adhesion layer was formerly deposited for 35 min as mentioned previously. Deposition times were adjusted in order to deposit 1.5 μm of the desired CrCN coatings. Al₂O₃/ZnO nanolaminates for a total 50 nm thickness were deposited as sealing layers on the top of the first 1.5 μm CrCN layer followed by the second 1μm CrCN layer. The coatings were labeled CrCN-2/ALD, CrCN-4/ALD, and CrCN-5/ALD.

2.3. Characterization

A Hitachi (Tokyo, Japan) SU 8030 Scanning Electron Microscope (SEM) was used to investigate the coatings’ surfaces, thicknesses, and cross-sectional morphologies. The chemical composition was determined using scanning electron microscopy (SEM) Hitox (Tokyo, Japan) SH-4000 M equipped with an X ray energy dispersive spectroscopy (EDS). A Bruker (Billerica, MA, USA) atomic force microscopy AFM was used to evaluate the surface topography and roughness on 2 × 2 μm² scanning zones. The Rq roughness was calculated using NanoScope Analysis software (Bruker). An X-ray diffractometer (Bruker D8 advance, XRD) with a Cu-Kα radiation tube (λ = 1.5418 Å), operated at 40 kV and 40 mA, was employed to identify the microstructure and crystal phases. The crystallite size was determined using Scherrer’s formula and the texture coefficient (TC) for any reflection determined using the equations described in our previous study [39].

The hardness and reduced Young’s modulus of the coatings were determined using a TribolIndenter TI 980-Hysitron (Bruker) nanoindentation technique equipped with a Berkovich diamond tip (E indentation = 1140 GPa, v indentation = 0.07). To avoid any effect from substrate stiffness, the maximum penetration depth was restricted to less than 10% of the film thickness. Thirty indents were conducted for each sample, and the average values were recorded. The measurements’ uncertainty was determined from the standard deviation. A dataphysics OCA series machine based on the sessile drop method was used to measure the water contact angles on the films. Three measurements were carried out to ensure the reliability of the data. The electrochemical corrosion properties were evaluated using an Origalys potentiostat and a “Biologic” flat corrosion cell adapted to the samples’ dimensions as described in our previous study [39]. Pitting corrosion tests were performed at room temperature in a 3.5 wt.% (0.6 M) NaCl solution and pH ~ 6.3. To ensure system stability, the open circuit potential was measured for 60 min. The measurement range was set from ~150 mV/free to 1.3 V/ref. The scan rate and current threshold were both fixed at 0.5 mV/sec and 3 mA, respectively. The corrosion parameters were determined using the Tafel extrapolation method. The corrosion current density can be estimated by extrapolating the anodic branch of the polarization curve to the corrosion potential. The extrapolation involves fitting the anodic polarization curves to a straight line and extrapolating them to the corrosion potential. The point at which these lines intersect gives the corrosion current density. The polarization resistance Rp is calculated using the following equation:

$$R_p = \frac{\beta_a \beta_c}{(\beta_a + \beta_c)} \times \frac{1}{I_{corr}}$$

where βa and βc are the anodic and cathodic Tafel constants in V/decade, and Icorr is the corrosion current density in A/cm².

3. Results

3.1. Coatings Morphology and Surface Topography

Table 1 displays the chemical composition of the coatings. In order to compare the influence of the CH₄ gas flow on the carbon content, it was necessary to deposit all coatings, CrN to CrCN-5, for the same deposition time of 300 min. Cr, N, O, and C percentages were measured using the EDS technique. We noticed the presence of oxygen in the coatings that might be due to the residual oxygen impurities in the sputtering chamber and to the native oxidation of coatings after deposition and exposition to ambient air. The carbon content increased from 17 at.% to 28 at.% when the CH₄ flow was raised from 2 to 5 sccm.
The C/N and (C + N)/Cr ratios increased, which might be attributed to the existence of other phases such as CNx. Hybrid coatings have a higher oxygen content due to the insertion of the ALD oxide layer.

Table 1. Chemical composition of CrCN coatings.

<table>
<thead>
<tr>
<th>Coatings</th>
<th>CH4 Flow (sccm)</th>
<th>Er (C, N, O) ~ 5% Er (Cr) ~ 3%</th>
<th>C/N</th>
<th>(C+N)/Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN</td>
<td>-</td>
<td>58 38 - 4</td>
<td>- 0.7</td>
<td></td>
</tr>
<tr>
<td>CrCN-2</td>
<td>2</td>
<td>43 36 17 4</td>
<td>0.5</td>
<td>1.3</td>
</tr>
<tr>
<td>CrCN-3</td>
<td>3</td>
<td>36 36 21 7</td>
<td>0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>CrCN-4</td>
<td>4</td>
<td>34 34 27 5</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>CrCN-5</td>
<td>5</td>
<td>30 38 28 4</td>
<td>0.7</td>
<td>2.2</td>
</tr>
<tr>
<td>CrCN-2/ALD</td>
<td>2</td>
<td>22 45 22 11</td>
<td>0.5</td>
<td>3.1</td>
</tr>
<tr>
<td>CrCN-4/ALD</td>
<td>4</td>
<td>24 44 24 8</td>
<td>0.5</td>
<td>2.8</td>
</tr>
<tr>
<td>CrCN-5/ALD</td>
<td>5</td>
<td>28 38 29 5</td>
<td>0.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 1 shows the variation of the thickness and deposition rate versus the CH4 gas flow.

![Figure 1](image1.png)

**Figure 1.** Film thickness and deposition rate variation as a function of CH4 flow.

The thicknesses of CrN, CrCN-2, CrCN-3, CrCN-4, and CrCN-5 were 2.8, 3.1, 2.7, 2.4, and 2.5 μm, respectively. The deposition rate and film thickness increased with the addition of 2 sccm CH4; then, a linear decrease was observed with the increase of CH4 gas flow to 4 sccm. The highest deposition rate was obtained under a 2 sccm CH4 flow corresponding to 0.170 nm/s. The following decrease could be attributed to the carbon compounds adsorption on the chromium target surface. It is known that the sputtering rate of metals is different from that of compounds [42]. Furthermore, the sputtering efficiency using two reactive gases (N2 and CH4) is lower than that of one sputtering gas (N2 in CrN deposition) or inert gas (Ar), so the sputtering speed decreased with increasing the reactive gas’ volume. The increase in the deposition rate of CrCN-5 coating compared to CrCN-4 may be related to the formation of the CNx phase validated by the increase in C and N percentages and the decrease in the Cr content.

Figure 2 shows SEM and 2D AFM images of the surface and cross-section morphologies. This figure also presents the roughness values of CrN and the CrCN coatings.
Figure 2a shows the CrN coating as a “cauliflower” shaped surface. The insertion of carbon (17 at.%) into the CrN structure led to taper and “stars” faceted shape morphology (Figure 2b). The CrCN-2 coating SEM surface image shows the presence of intergranular voids and porosities that may form open paths and trajectories from the surface to the coating-substrate interface. The existence of those defects is related to the columnar growth of the coating as shown in the SEM cross-sectional image (Figure 2g). The CrCN-3 coating exhibited a granular surface morphology with an irregular shape and non-homogeneous grain size distribution (Figure 2c). In addition, less voids are observed as compared to CrCN-2, revealing that the increase in carbon content improves the compactness of the coating. Furthermore, the CrCN-4 and CrCN-5 surfaces became flat and fine, and no grain boundaries are visible. Meanwhile, the carbon led to a denser structure, which
could be related to the increase of the amount of the amorphous carbon phase. Furthermore, the cross-sectional images (Figure 2f–j) show that all the relative coatings grew continuously on the substrate within the Cr adhesion layer, and no obvious defects (such as cracks) are observed, which indicates a strong interface between the coatings and the substrates with no visible delamination. The CrN coating had a columnar compact structure in the upward direction. The CrCN-2 and CrCN-3 coatings exhibited columnar growth. The width of CrCN-3 columns decreased as compared to CrCN-2 and showed a compact structure with narrow intercolumnar boundaries. For the CrCN-4 and CrCN-5 coatings, the cross-sectional images showed a dense structure. Meanwhile, the carbon improved the microstructure density preventing the coating columnar growth. On the other hand, the roughness of the CrCN-2 coating increased as compared to the CrN coating. This increase in roughness is well explained by the change in the surface morphology of CrCN-2, where the “stars” grain-like shapes are well faceted compared to the flat “cauliflower” grain shapes’ flat and smoother CrN surface. Comparing the CrN coatings (Figure 2k–o), it was found that the surface roughness generally decreased with increasing CH₄ flow and carbon content. The CrCN-3 coating was more compact than CrCN-2, resulting in a surface roughness Rq = 20 ± 2 nm lower than that of CrCN-2 (Rq = 24 ± 3 nm). CrCN-4 and CrCN-5 presented the lowest surface roughness Rq = 9 ± 1 and 6 ± 1 nm, respectively. This is confirmed by the SEM images showing a smooth surface morphology and dense microstructure.

The morphology and surface topography of the hybrid CrCN/Al₂O₃-ZnO nanolaminate coatings were investigated. The SEM and AFM images as well as roughness values are presented in Figure 3. The ALD sealing layer was inserted within two CrCN PVD layers. Figure 3a–c shows the surface morphology of the top PVD layer. From Figure 3a, we can notice that the CrCN-2 top layer has a different surface morphology compared to that observed in Figure 2b. In fact, the change in the surface morphology and “stars” grains to “cauliflower” shape occurred due to the insertion of the ALD Al₂O₃/ZnO nanolaminates’ sealing layer. The observed morphology is more compact than that of the CrCN-2 coating. Furthermore, the intergranular narrow voids are visible. In fact, this surface morphology is quite similar to that of the CrCN-3 coating (Figure 2c), but the difference is observed in the homogeneous shape and particle size distribution (Figure 3a). Furthermore, the fineness in particle size pointed out the decrease in the columns’ size observed in the cross-sectional SEM images (Figure 2d). The fineness in particle size is also confirmed by the smoother surface with a lower surface roughness Rq = 17 ± 2 nm (Figure 3g), which is less than those observed in the CrCN-2 or even CrCN-3 coatings (24 ± 3 and 20 ± 2 nm, respectively). These results reveal that the ALD sealing layer interrupted the continuous columnar growth of the first PVD layer. However, there is no change in the growth form type and the second PVD layer grew through the columnar form but with finer columns. This interruption of the large columnar crystal growth is attributed to the ALD layer that creates a modified surface and allows more nucleation sites during the deposition of the top PVD layer, as discussed in our previous work [39].

On the other hand, the top PVD layer in CrCN-4/ALD and CrCN-5/ALD coatings revealed the same surface morphologies observed, respectively, in CrCN-4 and CrCN-5. The results pointed out that the ALD layer did not change the surface morphology. The dense growth type is maintained as well as it is observed in the cross-sectional images (Figure 3e,f). A slight decrease in the surface roughness was observed in CrCN-4/ALD (Rq = 8 ± 1 nm in Figure 3h) and a non-significant change in the surface roughness was noticed in the CrCN-5/ALD coating.
To sum up, the ALD layer inserted as a sealing layer did not provoke a change in the growth form type of the PVD layer. The top PVD layer follows the growth type (dense or columnar) of the inner PVD layer. The influence of the ALD layer is particularly significant on the columnar growth type where it causes columns refinement by creating more nucleation sites. This phenomenon could absolutely influence the surface topography relative to the summits of the columns, and smooth the surface resulting in the decrease of the surface roughness. However, these changes are less pronounced when the PVD layer follows the dense growth mode.

3.2. Phase Composition and Microstructure Analysis

In order to investigate the effect of carbon insertion on the CrN microstructure and the influence of ALD nanolaminates on the microstructure of the top CrCN PVD layer, XRD experiments were performed. The XRD patterns and the texture coefficients of the different coatings are shown in Figure 4. The XRD pattern of the CrN thin film shows the peaks corresponding to (111), (200), (220), and (311) crystallographic orientation. All the peaks shift towards higher two theta values. The peaks broadening could be ascribed to the coating non-uniform residual internal stress or to the existence of an amorphous CrN phase. CrN coatings exhibiting (111) preferential orientation were reported in our previous study [39], but in this case, the chromium nitride does not exhibit a preferential orientation. As shown in Figure 4d, the texture coefficients of (111) and (200) orientations are very close, and those of (220) and (311) are not negligible. The (200) orientation of CrN is associated with lower surface free energy, whereas the (111) orientation is expected when films present high compressive stress and dominant strain energy [43]. In this study, the (200) orientation is more pronounced. Meanwhile, the surface free energy dominates in
the coating instead of the strain energy and the compressive stress. This could be attributed to the compact structure of the film with a small crystallite size (9 ± 1 nm), as compared to the pyramidal columnar structure of the CrN coating in the previous study [39], showing a high crystallite size (52 ± 1 nm).

Figure 4. XRD diffractograms and texture coefficient variations of (a,b,d) CrN, CrCN-2, to CrCN-5 and (c,e) CrCN/ALD duplex coatings. (f) Raman spectra of CrN and CrCN-2 to CrCN-5 coatings.

The XRD patterns of all the coatings in Figure 4a,c show the presence of the peaks at 44.36° and 81.69° corresponding, respectively, to the (110) and (211) planes of the Cr adhesion layer compared to the standard reference file provided by the Joint Committee on Powder Diffraction (JCPDS, 01–085–1336). In Figure 4a, the CrCN-2, CrCN-3, and CrCN-4 coatings present two diffraction peaks at 2θ = 37.53° and 80.05° corresponding, respectively, to (111) and (222) planes of the CrN (JCPDS, 00–11–0065). From Figure 4d, we notice the increase of the texture coefficients calculated for the (111) and (222) orientations for the CrCN-2, CrCN-3, and CrCN-4 coatings while the other orientations are negligible as compared to the CrN coating. Thereby, the carbon insertion in the CrN coating led to the change in its texture, and promoted the (111) plane growth tendency. The Cr2N phase was not detected. For the CrCN-5 coating, the corresponding XRD pattern revealed, in addition to (111) and (222) corresponding peaks, the presence of peaks at 2θ = 43.73°, 63.53°,
and 76.15° relative to (200), (220), and (311) planes of CrN, respectively (JCPDS, 00–11–0065). The texture coefficient variation shown in Figure 4d confirms this observation where the TC of the (111) orientation decreased while the TC of the other orientations increased. The magnified zone on the (111) orientation peaks of the various coatings is represented in Figure 4b. By increasing the CH₄ gas flow and the carbon content in the coatings, the (111) corresponding peak of the coatings shifted towards lesser two theta values which indicates a possible increase in the residual stress [8].

For more investigation on the effect of carbon insertion in the CrN coating, the lattice parameter was calculated and displayed in Table 2.

No Cr₃C₄ phase or carbides crystalline phase peaks are detected in the XRD patterns. The carbon may exist as an amorphous carbon or an amorphous CN₃ phase, or inserted as a solid solution in the CrN lattice. The lattice parameter gradually increased with increasing the CH₄ flow rate to reach its higher value of 4.17 Å at 5 sccm. Since the C atom has a larger atomic radius than that of N, the carbon substitutes N atoms in the CrN lattice and distorts it, resulting in a larger interplanar space distance and lattice parameter. Typically, the shift in the diffraction angles is due to the lattice parameter increase with increasing the C concentration. Furthermore, as it can be seen in Figure 4b, with the increase of the CH₄ flow, a slight broadening and reduced intensity in the (111) XRD peak was observed. The (111) FWHM of the coatings was calculated and the crystallite size was estimated using the Scherrer equation (Table 2). The crystallite size increased from 9 ±1 nm to 46 ±1 nm with 17 at.% carbon insertion. The 17.4 at.% carbon addition could interrupt the formation of the CrN amorphous phase that may exist in the CrN coating, and thus promote the crystalline state and the crystallite size increase. With increasing the CH₄ flow rate from 2 to 5 sccm, the crystallite size decreased to reach 14 ± 1 nm. This indicates that the CrN crystals became finer with the increase of the amorphous carbon or CN₃ phases. Other studies [8,44] reported a similar decrease in the grain size due to the increase of carbon content. Hence, as reported in [18], the carbon addition changes the texture of the CrN crystal in the coating and interrupts the normal crystal arrangement of chromium nitride. It forms nucleation centers and limits the excessive growth of CrN grains [44].

Figure 4c shows the XRD patterns of the hybrid coatings CrCN/ALD. No new peaks corresponding to phases different of those than of the CrN phase were detected. The insertion of the Al₂O₃/ZnO ALD sealing layer did not provoke any phase transformation in the CrCN top layer of the three hybrid coatings. To further investigate the effect of the ALD layer, the texture coefficient was calculated and represented in Figure 4e. This allows the comparison of hybrid CrCN/ALD coatings with their relative CrCN PVD monolayer ones. The results revealed that there is no major texture variation despite the slight decrease in the TC of the (111) orientation in CrCN-4/ALD and CrCN-5/ALD coatings. The CrCN-2/ALD coating showed a decrease in the crystallite size (39 ± 1 nm) as compared to the CrCN-2 coating (46 ± 1 nm). The observed decrease in the crystallite size is due to the ALD layer that creates more nucleation sites that could suppress the large columnar crystal growth and contribute to crystal refinement as discussed in our previous work [39]. The CrCN-4/ALD and CrCN-5/ALD coatings showed no major variation in the crystallite size which means that the ALD layer has no effect on the PVD crystallite size when the PVD layer exhibits a dense microstructure.

The raman spectra of the CrN and CrCN coatings are shown in Figure 4e. The observed peak can be deconvoluted into two Gaussian peaks, the D and G bands’ characteristics of amorphous carbon at 1350 cm⁻¹ and 1550 cm⁻¹. The D peak corresponds to the

<table>
<thead>
<tr>
<th>Sample</th>
<th>CrN</th>
<th>CrCN-2</th>
<th>CrCN-3</th>
<th>CrCN-4</th>
<th>CrCN-5</th>
<th>CrCN-2/ALD</th>
<th>CrCN-4/ALD</th>
<th>CrCN-5/ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite Size (nm)</td>
<td>9 ± 1</td>
<td>46 ± 1</td>
<td>49 ± 1</td>
<td>30 ± 1</td>
<td>14 ± 1</td>
<td>39 ± 1</td>
<td>30 ± 1</td>
<td>15 ± 1</td>
</tr>
</tbody>
</table>
disordered graphite vibration [18] and the G peak corresponds to the bond stretching vibration of the atoms at sp² sites [8]. The D and G bands are absent in the CrN coating. With increasing the carbon content, these two peaks are raised, suggesting that the amorphous carbon increased which is consistent with the XRD analysis. The D and G peaks’ intensities are much higher in CrCN-5 than other coatings. Meanwhile, it confirms the role of amorphous carbon in densifying the structure of the CrCN-5 coating and decreasing its crystallite size. The peak observed around 540 cm⁻¹ in the CrCN-5 coating spectrum is attributed to the Cr₂O₃ phase.

3.3. Hardness and Young’s Modulus

Figure 5 presents the hardness (H) and reduced Young’s modulus (Er) of coatings. H and Er values are shown in Table 3.

![Figure 5](image)

**Figure 5.** Hardness and reduced Young’s modulus: (a) as a function of CH₄ flow rate and (b) for different coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CrN</th>
<th>CrCN-2</th>
<th>CrCN-3</th>
<th>CrCN-4</th>
<th>CrCN-5</th>
<th>CrCN-2/ALD</th>
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</tr>
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<tbody>
<tr>
<td>H (GPa)</td>
<td>19 ± 1</td>
<td>11 ± 1</td>
<td>15 ± 2</td>
<td>20 ± 2</td>
<td>19 ± 1</td>
<td>14 ± 1</td>
<td>19 ± 1</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>Er (GPa)</td>
<td>220 ± 5</td>
<td>172 ± 8</td>
<td>160 ± 10</td>
<td>181 ± 8</td>
<td>167 ± 3</td>
<td>158 ± 4</td>
<td>192 ± 8</td>
<td>170 ± 5</td>
</tr>
</tbody>
</table>

The hardness of the CrN coating was ~19 GPa higher than that already obtained in our previous work (5.4 GPa) [39]. The compact structure and the small crystallite size of the CrN coating are the most important parameters for the hardness improvement. With the 2 sccm CH₄ gas flow rate, the hardness of the CrCN containing 17 at.% C decreased to ~11 GPa which is due to the coating columnar structure and the increase in the crystallite size according to the Hall–Petch relation [45]. As the CH₄ gas flow increased, the density of the coatings increased significantly, and the roughness and the crystallite size decreased. The morphological and microstructural results are in accordance with nanoindentation measurements where the hardness increased with the increasing CH₄ gas flow and thus the carbon content in the coatings. However, the CrCN-4 presented the highest hardness of ~20 GPa. The CrCN-5 coating hardness is slightly smaller than that of CrCN-4, which may be attributed to the increase of the amorphous carbon phase in the CrCN-5 coating observed in Raman spectra and correspondingly reducing the crystal phase in the coating. In this case, the cohesion energy decreased between the crystalline phase and amorphous carbon, which results in the decrease of the hardness [5,8]. Moreover, the Cr₂O₃ further decreased the hardness by breaking the continuity of amorphous carbon [13,46]. The reduced Young’s modulus of all the CrCN coatings is less than that of CrN, which means that the carbon increased the elasticity in the coatings. Figure 5b shows the effect of the ALD nanolaminate layer insertion on the mechanical properties of the
duplex coatings as compared to their relative CrCN PVD monolayers. The ALD layer increased the hardness of the CrCN-2 coating to ~14 GPa and decreased the Er ~158 GPa. Such an improvement in the hardness is due to the decrease of the crystallite size (39 ± 1 nm) according to the Hall–Petch relation [45]. Similar improvement in the mechanical properties was discussed in the literature [20,22,39]. As the CrCN-2 coating exhibited a columnar morphology, the dense ALD layer blocked the defects proliferation and dislocations motion in the CrCN layer during the indentation, and resisted shear sliding between vertically aligned columnar grains [39]. On the other hand, the ALD layer did not enhance the hardness of the dense CrCN-4 and CrCN-5 coatings. The hardness of the duplex coatings CrCN-4/ALD and CrCN-5/ALD was in the same range as those of CrCN-4 and CrCN-5 PVD monolayer coatings. These results are in accordance with the microstructural and morphological observations discussed in Sections 3.1 and 3.2 where the crystallite size remained constant and the morphology did not change with the ALD sealing layer insertion. However, a slight increase in the reduced Young’s modulus was observed.

3.4. Wettability Behavior

The interaction between the surface of the films and water was studied using contact angle (CA) measurements at room temperature. These measurements were also used to investigate the coating behavior in a humid environment. The contact angles of water droplets on the coatings’ surface are presented in Figure 6.

![Figure 6. Water contact angles of (a) CrN; (b) CrCN-3; (c) CrCN-2; (d) CrN-4; (e) CrCN-5; (f) CrCN-2/ALD; (g) CrCN-4/ALD; and (h) CrCN-5/ALD coatings.](image)

We can notice that the CrN coating exhibited a hydrophilic character with $\theta = 86 \pm 1^\circ$. The addition of 17 at.% of carbon did not change the wettability behavior of the CrCN coating where the water contact angle was $\theta = 85^\circ$. As the CH$_4$ gas flow and the carbon content in the coatings increased, the hydrophobic character was promoted with a CA higher than 90°. The surface smoothing, the decrease in voids and surface defects, and the dense microstructure are all parameters promoting the coating hydrophobic character. The contact angles between the water droplets and the films’ surfaces deposited at different CH$_4$ gas flow rates 2, 3, 4, and 5 sccm were 85°, 96°, 98°, and 90°, respectively. Meanwhile, the contact angle and thus the hydrophobicity character increased gradually then
decreased, with an increasing carbon content in the coatings. The results reveal that carbon promoted the hydrophobicity character by smoothing the surface appearance and densifying the microstructure of the coatings. However, the decrease of the CA on the CrCN-5 coating could be due to the increase of the amorphous carbon phase and to the existence of the Cr₂O₃ phase detected by the Raman spectroscopy. The influence of the ALD sealing layer insertion on the wettability character of the coatings is studied. The CrCN-2/ALD, CrCN-4/ALD, and CrCN-5/ALD contact angles' measurements are presented in Figure 6f–h, respectively. They show an increase in the contact angle and they are all hydrophobic. Meanwhile, the Al₂O₃/ZnO nanolaminates’ ALD sealing layers through the smoothing of the surface appearance of the top PVD layer, and decreasing the microstructural voids and defects, led to the increase of the contact angles in the 106°–113° range.

3.5. Corrosion Behavior of the Coatings

The corrosion behavior of the coatings was investigated in an NaCl solution. The Tafel plots are presented in Figure 7. The electrochemical parameters were determined and listed in Table 4.

![Cyclic polarization curves of coatings tested in a 3.5 wt.% NaCl solution.](image)

**Figure 7.** (a–d) Cyclic polarization curves of coatings tested in a 3.5 wt.% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CrN</th>
<th>CrCN-2</th>
<th>CrCN-3</th>
<th>CrCN-4</th>
<th>CrCN-5</th>
<th>CrCN-2/ALD</th>
<th>CrCN-4/ALD</th>
<th>CrCN-5/ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₉₀₉ (mV/SCE)</td>
<td>−238</td>
<td>−8</td>
<td>26</td>
<td>−59</td>
<td>−207</td>
<td>4</td>
<td>−56</td>
<td>−50</td>
</tr>
<tr>
<td>J₀₉₀ (×10⁻⁸ A.cm⁻²)</td>
<td>79</td>
<td>60</td>
<td>48</td>
<td>2.5</td>
<td>5</td>
<td>43</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>βc (mV/decade)</td>
<td>28</td>
<td>23</td>
<td>56</td>
<td>83</td>
<td>119</td>
<td>12</td>
<td>56</td>
<td>38</td>
</tr>
<tr>
<td>βa (mV/decade)</td>
<td>300</td>
<td>385</td>
<td>234</td>
<td>190</td>
<td>130</td>
<td>500</td>
<td>148</td>
<td>370</td>
</tr>
<tr>
<td>Rp (kΩ·cm²)</td>
<td>32</td>
<td>36</td>
<td>95</td>
<td>2283</td>
<td>1230</td>
<td>27</td>
<td>2655</td>
<td>2945</td>
</tr>
<tr>
<td>Eₚₚ (mV/SCE)</td>
<td>122</td>
<td>285</td>
<td>763</td>
<td>224</td>
<td>8</td>
<td>918</td>
<td>666</td>
<td>662</td>
</tr>
</tbody>
</table>

**Table 4.** Electrochemical parameters of the different coatings.
The CrN coating exhibited an $E_{\text{corr}} = -238$ mV/SCE, $J_{\text{corr}} = 79 \times 10^{-8}$ A.cm$^{-2}$, and $E_{\text{pit}} = 122$ mV/SCE. In comparison to the CrN studied in our previous study [39], the CrN in this work was less noble since $E_{\text{corr}}$ is lower and the pitting corrosion occurred at a lower potential of 122 mV/SCE. The reduced anticorrosion behavior of the CrN could be due to the decrease in the TC of the (111) crystallographic orientation, since the preferential orientation in the (111) direction exhibits a good anticorrosive behavior [47]. However, the CrN in this work exhibited an improvement in the mechanical properties. The aim of the carbon insertion is to maintain the good mechanical characteristics of the CrN coating with enhancing its corrosion behavior. The corrosion potential of the CrCN coatings gradually increased to $-68$ and $26$ mV/SCE for CrCN-2 and CrCN-3 coatings respectively, and then decreased to $-59$ and $-207$ mV/SCE for CrCN-4 and CrCN-5 respectively. However, the corrosion rate is well defined by the corrosion current density. As it can be seen, the corrosion current density decreased from $79 \times 10^{-8}$ A.cm$^{-2}$ for CrN to reach a minimum value of $2.5 \times 10^{-8}$ A.cm$^{-2}$ for the CrCN-4 coating. The $J_{\text{corr}}$ of the CrCN-5 coating showed a slight increase to $5 \times 10^{-8}$ A.cm$^{-2}$, which can be due to the increase of the TC of the (200) orientation as observed in Figure 4d and to the slight decrease in the water contact angle to 90°, reducing the hydrophobic character. However, this slight increase in the corrosion current density does not indicate that the CrCN-5 coating exhibited a high current corrosion density. The lower corrosion density observed in CrCN-4 and CrCN-5 can be attributed to their dense microstructure, which exhibited fewer voids and defects. Although, the lower roughness value leads to a better anticorrosion behavior. Liao et al. [48] found that Anjanthopanax senticosus leaf extracts as eco-friendly can act as an eco-friendly novel corrosion inhibitor for carbon steel in a HCl solution. The SEM, XPS, and water contact angle results presented in their study showed that the dense hydrophobic film can effectively retard the invasion of aggressive ions and inhibit the corrosion of carbon steel. Meanwhile, the hydrophobicity character of the CrCN coatings also leads to better anticorrosion behavior. The polarization resistance of CrN, CrCN-2, and CrCN-3 coatings was weak, while the CrCN-5 had a moderate Rp. The CrCN-4 had the highest Rp = 2283 kΩ.cm$^{-2}$. The CrCN-2 and CrCN-3 presented a wide stage of passivation as shown in Figure 7a. All the coatings exhibited a pitting corrosion potential less than that of the 316L stainless steel (415 mV/SCE) except the CrCN-3 coating with an extended pitting potential of 763 mV/SCE. The passive region increased with increasing the carbon content to 21 at.% and then decreased. The obtained results could be explained by the increase of the amorphous carbon content in the CrCN-4 and CrCN-5 coatings that could limit the stability of the passive film. Despite the good enhancement in the corrosion resistance of the CrCN-4 and CrCN-5 coatings, validated by their low corrosion current density and high polarization resistance, the stability of their passive region was weak. Meanwhile, a stable pitting corrosion occurred at lower potentials, limiting their protection efficiency for steels against pitting corrosion.

For further investigation, and in order to enhance the stability of the passive film in the CrCN-4 and CrCN-5 coating while maintaining the benefit of their low corrosion densities, the AlO-ZrO ALD nanolaminates were deposited as sealing layers. The corrosion polarization plots with a reverse scan of the CrCN-2/ALD, CrCN-4/ALD, and the CrCN-5/ALD are plotted in Figure 7b–d, respectively.

From Figure 7b, we can notice that the ALD layer insertion shifted the $E_{\text{corr}}$ of the CrCN-2 from $-68$ to 4 mV/SCE and decreased the corrosion current density from $60 \times 10^{-8}$ to $43 \times 10^{-8}$ A.cm$^{-2}$. In addition, it extended the stability of the passive film. This later exhibited a slow rhythm of depassivation, where the stable pitting occurred at 918 mV/SCE. However, the reverse scan of the CrCN-2/ALD coating showed no ability for repassivation that can limit the efficiency of the coating for pitting protection even with the good enhancement in the electrochemical parameters and the anticorrosion behavior.

From Figure 7c, we notice, in comparison to the CrCN-4 coating, that the CrCN-4/ALD duplex coating showed a slight shift of the $E_{\text{corr}}$ to $-56$ mV/SCE and a slight de-
crease in the corrosion density to $1.5 \times 10^{-8} \text{ A.cm}^{-2}$. An increase in the polarization resistance to 2655 kΩ cm$^{-2}$ was noticed and the pitting corrosion shifted to 666 mV/SCE. The passive region was wider, indicating the improvement in the stability of the passive film. The CrCN-4/ALD film showed the ability for re-passivation in the reverse scan where the re-passivation occurred at 638 mV/SCE. The potential of re-passivation was very close to the pitting potential, which confirmed the difficulty for stabilizing the pitting and to maintain the efficiency of the CrCN-4/ALD for the protection against pitting corrosion.

Figure 7d shows the corrosion behavior of the CrCN-5/ALD coating compared to CrCN-5. It is obvious that the corrosion potential presented a high shift from −207 to −50 mV/SCE. The corrosion current density of the CrCN-5/ALD coating ~1.2 × 10^{-6} \text{ A.cm}^{-2} presented the lowest value as compared to all other coatings. Similarly, the Rp increased to reach the highest value of 2945 kΩ cm$^{-2}$. The reverse scan showed the ability of the coating for re-passivation without the existence of the pitting hysteresis loop. Meanwhile, the CrCN-5/ALD was the most efficient coating providing pitting corrosion protection. The Al$_2$O$_3$-ZnO nanolaminates’ ALD layer constituted a good barrier for preventing the diffusion of corrosive substances towards the coating-substrate interface [39].

4. Conclusions

In this work, we investigated the effect of carbon insertion on the structural, mechanical, and electrochemical properties of CrCN coatings deposited by magnetron sputtering. As the carbon content increased in the CrCN coating, the structure transformed from columnar to dense. The carbon existed as an amorphous phase in the coatings, reduced the crystallite size, decreased the intergranular voids, and enhanced surface smoothing. The hardness of the CrCN coating was enhanced with the carbon addition due to crystallite size refinement. Furthermore, the corrosion resistance of the coating was also enhanced where the lowest corrosion current density was found for the CrCN-4 coating (30 times less than that of CrN).

We also evaluated the effect of the Al$_2$O$_3$-ZnO nanolaminate layer (50 nm thick) deposited by the ALD technique on the properties of the CrCN coating. The ALD nanolaminates’ sealing layer insertion decreased the particles’ size and created more nucleation species in the columnar structure growth, while it had no significant effect on the dense coatings. The ALD sealing layer improved the hardness of the columnar CrCN coating while it has no significant effect on the dense coatings. The ALD sealing layer enhanced the pitting corrosion resistance of the CrCN coatings, extended their service lifetime, and improved the stability of their passive films with the capacity for re-passivation. The CrCN-4/ALD and the CrCN-5/ALD coatings presented excellent mechanical and anticorrosion properties. They can be used to ensure the protection of stainless steels against pitting corrosion.

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References


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