The effect of bilayer period and degree of unbalancing on magnetron sputtered Cr/CrN nano-multilayer wear and corrosion

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ABSTRACT

Cr/CrN nano-multilayers were grown on H13 steel and silicon (100), having different periods (Λ), at room temperature using the unbalanced magnetron sputtering technique by varying the degree of unbalancing (KC) to investigate the effect on multilayer properties. The multilayers’ total thickness was ~1 μm and the total number of layers varied from 10 (Λ = 200 nm), 20 (Λ = 100 nm) to 100 (Λ = 20 nm) layers. Film microstructure, hardness, wear and corrosion resistance were measured regarding bilayer period and degree of unbalancing. The results showed that wear resistance was lower for low KC values and that corrosion resistance was higher and hardness was improved. Nano-hardness was found to be higher for multilayers grown with Λ = 20 nm for all KC values, reaching a maximum 25 GPa value for KC = 0.87.

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1. Introduction

Transition metal nitride (TMN) coatings are of technological interest because their properties such as wear and corrosion resistance [1,2], low friction coefficient, good adhesion, extreme hardness [3,4] and good electrical conductivity [5] lead them to having ready applications in different fields, for instance as protective coatings for cutting tools, machine parts, molds for automotive piece production [6,7], diffusion barriers in electronic applications [8,9] and as decorative coatings for surface finishing due to their attractive colors [10]. CrN coatings have attracted special attention amongst TMN coatings due to their improved mechanical properties, oxidation resistance to high temperatures and better deposition rates [11,12]. CrN coatings have been proposed as replacements for electrolytic hard chromium due to their hardness and better corrosion resistance, such coating being deposited by electroplating involving carcinogenic hexavalent chromium vapors being released; they also represent a good alternative to the concomitant environmental contamination being produced by electrolytic hard chromium production [11,12].

Despite CrN coatings having such properties, some applications require improved properties which monolayers cannot fulfill, such as greater hardness or corrosion resistance. This is why structures combining several layers (multilayers) have been studied during the last decade to improve monolayer properties as they can combine different materials for producing a structure having improved properties. For instance, mechanical properties can be enhanced for reaching hardness values as high as 50 GPa [13]. Metal/ceramic multilayers (particularly chromium/chromium nitride ones) have aroused special attention as they have a number of advantages compared to their monolayer counterparts, such as greater hardness and resistance to wear and corrosion [14–18]. The period (the thickness where the multilayer composition is repeated) has also been shown to have an effect on multilayer properties [18]; this is usually attributed to the presence of a higher number of interfaces preventing the movement of dislocations as these produce plastic deformation in materials and the propagation of micro-cracks responsible for fractures in ceramics [19,20]. The re-nucleation process present in multilayer structures reduces the amount of pores, thereby resulting in better corrosion resistance [21–23].

A number of techniques have been used for producing Cr/CrN multilayers, such as cathodic arc [14,17,24–28], pulsed laser [18,29–31], DC magnetron sputtering [32–36], R.F. magnetron sputtering [16,37] and unbalanced magnetron sputtering [38–40]. The unbalanced magnetron (UBM) sputtering technique has gained importance amongst magnetron sputtering configurations for producing high quality coatings [11,41–44], due to its superior performance when
compared to conventional balanced magnetron sputtering [12]. The outer ring of magnets in a UBM configuration is strengthened in relation to the central pole causing the field lines to not become confined to the target region but also directed towards the substrate, thereby resulting in a high flux of coating atoms [41], contrary to a conventional configuration. Some secondary electrons (and therefore ions) are able to follow these field lines and high ion currents can be extracted from the plasma without the need for externally biasing the substrate [41] although applying a substrate bias voltage also increases ion current and therefore modifies coating structure and properties [45,46]. The ion current increases ion bombardment on the substrate surface, thereby improving adatom mobility [11]. It also allows to increase the relationship from the ion’s flux to the flux of condensing atoms, thereby changing the film’s structure [47]. The ion to atom flux ratio depends on the degree of magnetic field unbalancing (for a fixed substrate-target distance, pressure and power) [48].

Although the UBM technique has been widely used for producing different monolayer [49–53] and multilayer coatings [45,54–57], the influence of this degree of unbalancing on magnetron sputtered coating properties has been poorly studied. Olaya et al. [44,51,58] studied the influence of magnetic unbalanced) and the degree of magnetron unbalancing on CrN, TiN, ZrN, TaN and NbN monolayer properties while Flores et al. [59] studied the magnetic field’s effect on TiN/Ti multilayer plasma characteristics and corrosion properties by varying the degree of unbalancing through a concentric electromagnet coil around the magnetron. The present work has studied the effect of the degree of unbalancing and bilayer period on the hardness, wear and corrosion resistance of Cr/CrN nano-multilayer coatings produced by the UBM technique which, as far as the authors know, has not been done before.

The degree of magnetron unbalancing was estimated by using the coefficient of geometrical unbalance \(K_c\), according to [60]:

\[
K_c = \frac{Z(B_g - B_r)}{2R}
\]

where \(R\) was average erosion zone radius and \(Z(B_g - B_r)\) the distance from the target surface to the point on the axis of the magnetron where the magnetic field changed its direction, i.e. where the \(B_r\) component had zero value. A high \(K_c\) value implied a low level of magnetron unbalance and vice versa. Different \(K_c\) values were obtained by varying the relative vertical position between the central magnet assembly and the target; a map of the magnetic field flux was derived for the different magnet arrangements as a function of both radial and axial distances.

2. Experimental details

2.1. Deposition system

Cr/CrN nano-multilayers were deposited in non-commercial equipment by the UBM technique; this consisted of a stainless-steel cylindrical chamber (1 m in diameter, 80 cm length) provided with a pumping system which consisted of a rotary vane mechanical pump and a turbo molecular pump having nominal 10 m³/h and 1800 m³/h pumping velocity, respectively. The system had an unbalanced magnetron Gencoa sputter VT 100 which allowed varying the discharge power (P), discharge current (I) and the sample surface in each interval to stabilize deposition conditions. The Cr/CrN multilayers were produced with 200 nm, 100 nm and 20 nm bilayer periods and deposition time was adjusted to set total thickness at about 1 μm for all cases. A floating substrate was used which had no external bias. The chromium layers were grown in an Ar atmosphere (99.99 purity) while N\(_2\) (99.99 purity) was used as substrates for CrN layers was blown at intervals corresponding to planned nitride layer. Ar and N\(_2\) flow rates were set at 9 standard cubic centimeter per second (sccm) and 3 sccm, respectively, and regulated with MKS mass flow controllers. The target was a 4 in. diameter and 0.125 in. thickness chromium disk (99.95% purity) which was sputtered using a MDX 1K DC power supply (Advanced Energy) working in 400 mA current regulation mode. A shutter was located between the target and the sample surface in each interval to stabilize deposition pressure before growing the corresponding layer. Base pressure was less than 1 × 10\(^{-5}\) Pa. All multilayers were grown at room temperature and the sample-target distance was set to 5 cm. Table 1 summarizes the experiments’ deposition conditions.

### Table 1: Deposition conditions

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<tr>
<th>Sample</th>
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<td>Cr/CrN-1</td>
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2.2. Magnetic field characterization

Three groups of multilayers (\(A=200, 100\) and 20 nm) were produced at three different magnetic field configurations (\(K_c = 0.87, 1.16\) and 1.32) that were measured by portable Phywe teslameter with a Hall effect probe. Both magnetic field components (\(B_g\) and \(B_r\)) were measured as a function of \(Z\) (axial distance), \(r\) (radial distance) and \(N_T\) (number of turns). An increase in \(N_T\) corresponded to enlarging the distance between the central magnet and the target, thereby modifying the magnetic field configuration.

2.3. Multilayer deposition

Commercial AISI H13 tool steel (composition: 0.32–0.45 C, 0.8–1.20 Si, 0.20–0.50 Mn, 4.75–5.5 Cr, 0.8–1.20 V, 1.10–1.75 Mo, Fe balance (wt.%)) and silicon (100) were used as substrates. The steel samples were polished using 100 to 1200 sandpaper, pretreated by quenching (1000 °C–1025 °C) and tempering (175 °C–15 °C) and mirror polished. The substrates were ultrasonically cleaned in acetone and alcohol in sequence and dried in flowing compressed air before being placed in the deposition chamber.

The Cr/CrN multilayers were produced with 200 nm, 100 nm and 20 nm bilayer periods and deposition time was adjusted to set total thickness at about 1 μm for all cases. A floating substrate was used which had no external bias. The chromium layers were grown in an Ar atmosphere (99.99 purity) while N\(_2\) (99.99 purity) was mixed with argon for CrN layers was blown at intervals corresponding to planned nitride layer. Ar and N\(_2\) flow rates were set at 9 standard cubic centimeter per second (sccm) and 3 sccm, respectively, and regulated with MKS mass flow controllers. The target was a 4 in. diameter and 0.125 in. thickness chromium disk (99.95% purity) which was sputtered using a MDX 1K DC power supply (Advanced Energy) working in 400 mA current regulation mode. A shutter was located between the target and the sample surface in each interval to stabilize deposition pressure before growing the corresponding layer. Base pressure was less than 1 × 10\(^{-5}\) Pa. All multilayers were grown at room temperature and the sample-target distance was set to 5 cm. Table 1 summarizes the experiments’ deposition conditions.

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Corrosion resistance was evaluated by electrochemical measurement using a PCI/300 Gamry potentiostat. A potentiodynamic anodic polarization test was carried out on a three-electrode cell where the specimen was connected to a working electrode. A saturated calomel electrode and graphite were used as reference and counter electrodes, respectively. The exposed area was 0.15 cm². After 1 h of immersion in a 3% NaCl solution, scans were conducted in the −300 to 1000 mV range, having a 20 mV/min potential sweep. Echem Analyst software was used for obtaining corrosion potential (Ecorr) and corrosion current (Icorr) by Tafel’s extrapolation. An electrochemical impedance spectroscopy (EIS) test was performed at open circuit potential using the same cell construction, area and potentiostat used in the polarization experiments. A 10 mV sinusoidal amplitude was applied in the 10⁻² to 10³ Hz frequency range for 1 h in a 3% NaCl solution. The impedance plots were interpreted based on the equivalent circuit using a suitable fitting procedure with the same software.

The films’ wear resistance was evaluated by using a ball cratering system (a microscale abrasion test). A hard steel 30 mm radius sphere was rotated in this test against the specimen in the presence of a slurry of fine abrasive particles (1 μm diamond suspension). The load used during the test was 2 N and the samples were evaluated at 100 rev min⁻¹ speed, corresponding to a 47.5 m sliding distance. The wear volume was then calculated by measuring crater dimensions, using the following equation [62]:

\[
V(\text{mm}^3) = \frac{\pi b^4}{64R^2} \left( R - \frac{b^3}{8R} \right).
\]

Where \( R \) was the radius of the sphere and \( b \) was the crater’s external diameter.

3. Results and discussion

3.1. Magnetic field configuration

Fig. 1 shows the magnetic field components \( B_r \) and \( B_z \) for the \( r-Z \) plane. Fig. 1(a) displays component \( B_r \) at \( Z=0 \) in function of radial distance (\( r \)) and number of turns (\( N_v \)). Magnetic field \( B_r \) decreased to minimum value at \( r=2 \) cm. This distance corresponded to the average radius of the erosion zone presented in Eq. (2) and it was observed for all variations in \( N_v \). Fig. 1(b) shows component \( B_z \) at \( r=0 \) in function of axial distance (\( Z \)) and \( N_v \). Magnetic field \( B_z \) had a maximum value at the center of the target (\( r=0 \) and \( Z=0 \)) decreasing to zero when \( Z \) increased and subsequently increasing but changing sign. Fig. 2 shows the coefficient of geometrical unbalance (\( K_C \)) which was calculated according to these data in function of \( N_v \). It can be seen that \( K_C \) became reduced when \( N_v \) increased. The coefficient of geometrical unbalance varied inversely to the degree of magnetron unbalancing; high \( K_C \) value implied a low degree of unbalancing and vice versa. Multilayer properties were evaluated for three different \( K_C \) values (\( K_C = 1.32, 1.16 \) and 0.87).

3.2. Structural characterization

Fig. 3 shows the results for high angle X-ray diffraction for the multilayers. All multilayers presented the cubic CrN phase (JCPDS 11-0065 card) with diffraction peaks in (111), (200), (220) and (311) planes and cubic Cr phase (JCPDS 06-0694 card). \( \text{Cr}_2\text{N} \) peaks were not observed. The deconvolution (not shown) of the peak located at around 44° indicated that this peak could be decomposed into two peaks for all \( K_C \) values, namely Cr and CrN. The peak corresponding to CrN (200) was always present and its intensity increased when decreasing \( K_C \) for all bilayer periods as CrN (111) peak intensity decreased. The deconvolution also showed that CrN (200) and Cr (110) peak positions shifted towards lower angle values when increasing the bilayer period for all \( K_C \) values, thereby indicating the presence of compressive stress, common for films produced by sputtering. For example, the CrN (200) peak position shifted from 43.6° for \( \Lambda = 200 \) nm to 42.92° for \( \Lambda = 20 \) nm as the Cr (110) peak shifted from 44.4° to 43.78°, respectively, for multilayers grown with \( K_C = 1.32 \). A similar pattern was observed for \( K_C = 1.16 \) and 0.87 and such results have also been obtained by other authors for multilayer coatings [37,63,64].
The level of unbalance had a different influence on the multilayers as shown in Fig. 3. CrN (200) and Cr (110) peak positions for the same bilayer period shifted to positions closer to the reference values when the magnetic field was increased (i.e. when reducing $K_G$), suggesting a decrease in compressive stress. For instance, the CrN (200) peak position shifted from 42.92° to 43.51° for multilayers grown with $\Lambda = 20$ nm; this could have been due to energetic bombarding with ions produced by the unbalanced configuration. Compressive stress may have arisen through atomic peening when bombarding a growing film with energetic atomic species ranging from a few to hundreds of electron volts [65].

SEM results showed a clearly defined layered structure for $\Lambda = 200$ nm and $\Lambda = 100$ nm multilayers for all $K_G$ values (Fig. 4). A clear image could not be obtained for $\Lambda = 20$ nm multilayers due to the resolution of the microscope being used (not shown).

### 3.3. Nano-hardness measurement

Fig. 5 shows the nano-hardness profiles for the multilayers grown with different $K_G$ values. As can be seen, nano-hardness was found to be higher for multilayers grown with $\Lambda = 20$ nm for all $K_G$ values, i.e. the multilayer having the highest number of interfaces, reaching a maximum 25 GPa value for $K_G = 0.87$. This value was higher than the value predicted by the rule of mixtures for Cr and CrN hardness and it was also higher than the values obtained for CrN multilayers produced by different DC magnetron sputtering techniques [66–69]. Such increased hardness could have been attributed to the presence of interfaces which would have blocked dislocation movement [70]. The bilayer period has also been shown to be the most critical parameter in enhancing hardness [16,37,71–74] and, according to Hall and Petch [75] and Lehoczky’s [76] theories, multilayer hardness increases when bilayer period decreases. Higher hardness values were obtained for low $K_G$ values, i.e. a higher level of unbalance. This could have been attributed to the increase in ion bombardment on substrate surface increasing adatom mobility and producing denser films and the effect on hardness of compressive stresses present in these films [77].

### 3.4. Wear pattern

Two body grooving abrasion was the wear mechanism observed for all multilayers (not shown), probably due to the micro-cutting action of abrasive particles which were dragged across the ball, basically remaining fixed to the ball surface during the test [78]. Fig. 6 shows the results of wear measurements for all multilayers as a function of $K_G$. Wear volume was lower for multilayers grown with $\Lambda = 20$ nm and, in this case, it decreased for $K_G = 1.32$. This could be
explained by the decreased period size causing the presence of interfaces acting as barriers against crack propagation [79]. Similar results have been obtained in other studies for Cr/CrN [74] and Ti/TiN [63] multilayers. Unlike other composite types, the interfaces were orientated parallel to the direction of abrasion and, if the wear resistance of the zones close to the interface differed from the rest, this would have influenced composite wear resistance [33]. Increased wear resistance in these multilayers could also have been explained by the combination of a hard (CrN) and a soft (Cr) substrate where low Cr hardness allowed the abrasives to penetrate easily, thereby producing deep scratches; however, high ductility kept the amount of material removed small compared to the size of the scratch, and high CrN hardness limited penetration [33]. The increased wear resistance for the coatings grown with \( \Lambda = 20 \text{ nm} \) was associated with a decrease in coating hardness. Such hardness pattern could have been explained by possible weak interface bonding strength and residual stress presence [80].

3.5. Corrosion pattern

Figs. 7 and 8 show the impedance and phase angle values between the harmonic signal of applied voltage and circulating current vs. the logarithm of frequency for the substrate and Cr/CrN-4 sample, respectively (Bode diagram). The equivalent circuits for data fitting are also shown.

As can be observed, electrolyte–substrate interface impedance could be associated with a Randles circuit transfer function [81,82], formed by electrolyte resistance \( (R_E) \) in series with a parallel circuit \( (R_{TC}, Q_{DL}) \). \( Q_{DL} \) was a constant phase element, whose impedance, \( Z_{Q} = [j\omega Y]^{-n} \), depended on angular frequency \( \omega \), an exponent \( n \) whose value was generally between 0.5 and 1, and a pseudo capacitive constant \( Y \) (\( j \) was the imaginary number). When \( n = 0.5 \) the constant phase element was called Warburg impedance, and when \( n = 1 \) it was equivalent to a condenser. Within the electrolyte, ion circulation found a resistance \( (R_g) \); a resistance to charge

**Fig. 4.** Cross-section SEM micrographs of multilayers grown with (a) \( \Lambda = 200 \text{ nm}, K_G = 1.32 \), (b) \( \Lambda = 200 \text{ nm}, K_G = 1.16 \), (c) \( \Lambda = 200 \text{ nm}, K_G = 0.87 \), (d) \( \Lambda = 100 \text{ nm}, K_G = 1.32 \), (e) \( \Lambda = 100 \text{ nm}, K_G = 1.16 \), and (f) \( \Lambda = 100 \text{ nm}, K_G = 0.87 \).

**Fig. 5.** Nano-hardness values for multilayers regarding level of unbalance \( (K_G) \).

**Fig. 6.** Multilayer wear pattern regarding bilayer period and \( K_G \).
transference between the metal and ions \( (RT_C) \) appeared in the interface with the substrate and some ions temporarily located on the metal surface induced opposite sign charges, forming a double charge layer \( (Q_{DL}) \). The following values for the substrate were obtained from data fitting to transfer function (shown by a solid continuous line in Fig. 7): 
\[
R_E = (23.57 \pm 0.20) \ \Omega, \quad R_{CT} = (4044 \pm 74) \ \Omega, \quad Y_{DL} = (3.27 \pm 0.05) \times 10^{-4} \ \text{s/\Omega} \quad \text{and} \quad n = 0.791 \pm 0.004.
\]

Fig. 8 shows the Bode diagram for Cr/CrN-4. The other multilayers’ electrochemical impedance curves were very similar to the one shown. Two relaxation points appeared in the phase angle vs. frequency logarithm curves, suggesting the presence of two constant phase elements corresponding to two electrolyte–electrode interfaces. The results were then fitted to the transfer function of the equivalent circuit shown in Fig. 8. This circuit is commonly used in interpreting EIS diagrams, particularly when the interface of a metal having porous coatings in contact with an electrolyte is being analyzed. The electrolyte penetrates through pores and pinholes of the coating and makes contact with the metallic substrate. \( R_p \) represented electrolyte resistance through these porosities and parallel circuit \( R_{CT}Q_{DL} \) represented the interface formed by the electrolyte and the substrate. The ions located on the coating induced opposite sign charges on the metallic substrate and this is why one constant phase element for the coating \( (Q_{C}) \) was included.

Figs. 9 and 10 show that pore resistance plus charge transfer resistance \( (R_P + R_{CT}) \) increased with bilayer period and with \( K_C \), whereas the double layer pseudo capacitance \( (Y_{DL}) \) decreased. Increased porosity and coating defects would imply an increase in pores’ total cross-section and the contact area between the electrolyte and the substrate which would cause a decrease in pore resistance and charge transfer resistance and an increase in double layer pseudo capacitance \[83–85].

\[
\begin{align*}
\text{Fig. 7.} & \quad \text{Bode diagram of substrate H13.} \\
\text{Fig. 8.} & \quad \text{Bode diagram of sample Cr/CrN-4.} \\
\text{Fig. 9.} & \quad R_P + R_{CT} \text{ as a function of bilayer period and } K_C. \\
\text{Fig. 10.} & \quad \text{Double layer pseudo capacitance } Y_{DL} \text{ as a function of bilayer period and } K_C. \\
\text{Fig. 11.} & \quad \text{Corrosion potential as a function of bilayer period and } K_C.
\end{align*}
\]
multilayers grown with different bilayer periods. It was found that formation, wear, hardness and corrosion pattern of nanometric

4. Conclusions

This work studied the influence of the level of unbalance on phase formation, wear, hardness and corrosion pattern of nanometric multilayers grown with different bilayer periods. It was found that the level of unbalance ($K_C$) had a strong influence on these properties, showing that hardness was higher for lower $K_C$ values as higher wear volume was obtained. All the multilayers were shown to improve substrate corrosion resistance, probably due to the interfaces blocking the propagation of cracks and dislocations and avoiding the continuity of pinholes and pores.

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References


Fig. 12. Corrosion current as a function of bilayer period and $K_C$.

Figs. 11 and 12 give the corrosion potential and corrosion current results. Corrosion potentials were generally more positive than those for the substrate ($V_{CORR} = -713 mV$); the corrosion currents were less than those for the substrate. Fig. 11 shows a more positive potential for a higher level of unbalance ($K_C = 0.87$) and for coatings having the highest period thickness while Fig. 12 shows the opposite pattern for corrosion currents: lower currents having the highest degree of unbalance and the largest period thickness.

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