Nature in corrosion-erosion surface for [TiN/TiAlN]n nanometric multilayers growth on AISI 1045 steel

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Abstract

The aim of this work is to characterize the electrochemical behavior of [TiN/TiAIN]n multilayer coatings under corrosion-erosion condition. The multilayers with bilayer numbers (n) of 2, 6, 12, and 24 and/or bilayer period (Λ) of 1500 nm, 500 nm, 250 nm, 150 nm and 125 nm were deposited by magnetron sputtering technique on Si (100) and AISI 1045 steel substrates. Both, the TiN and the TiAIN structures for multilayer coatings were evaluated via X-ray diffraction (XRD) analysis. Mechanical and tribological properties were evaluated via nanoindentation measurements and scratch test, respectively. Silica particles were used as abrasive material on corrosion-erosion test in 0.5M of H₂SO₄ solution at impact angles of 30° and 90° over surface. The electrochemical characterization was carried out using the polarization resistance technique (Tafel), in order to observe changes in corrosion rate values of 359 mpy for uncoated steel substrate and 103 mpy for substrate coated with n = 24 (Λ = 125 nm) under an impact angle of 30° were found. On the other hand, for an impact angle of 90° the corrosion rate exhibited 646 mpy for uncoated steel substrate and 210 mpy for substrate coated with n = 24 (Λ = 125 nm). This behavior was correlated with the curves of mass loss for both coated samples and the surface damage was analyzed via SEM

images for the two different impact angles. These results indicate that TiN/TiAlN multilayer coatings deposited on AISI 1045 steel represent a practical solution for applications in corrosive-erosive environments.

Keywords: Hard coatings, wear, multilayers, Tafel, corrosion-erosion.

1. Introduction

The corrosion-erosion condition is an accelerated corrosion of metals due to a combination of chemical and abrasion attack by physical movement of fluids with suspended solids. Therefore, alloys that form a film surface under corrosive environment commonly have a corrosion speed limit, but this film is susceptible to delamination hence corrosion is accelerated rapidly. Corrosionerosion is associated with current induced by mechanical removal on the surface of the protective film that results in further increase of corrosion rate for chemical or electrochemical processes. Surface engineering of metallic substrates with protective coatings get unanimous attention from industry and researchers, as it produces a host of properties such as wear protection, erosion resistance, oxidation protection, and corrosion resistance. Moreover, hard coatings and multilayer coatings are highly functional if the interface between the coating and the substrate present good adherence [1]. The interest on Physical Vapor Deposition (PVD) at multilayers is based on their considerably enhanced mechanical properties [2-5] as shown by previous studies which have reported that the concept of multilayer coatings offers a potent solution for physical, tribological and chemical properties in hard coatings. The coatings deposited via PVD based on nitrides such as TiCN [6], AlCN [7], CrAlN [8], and oxides like YSZ [9], BiMnO₃ [10] provide high wear resistance, stability under high service temperature, oxidation resistance and low thermal conductivity. Furthermore, TiN/ZrN [11], TiCN/TiNbCN [12], CrN/NbN [13], CrN/AlN [14] and TiN/TiAlN multilayer coatings have been engineered on cutting tools yielding well mechanical and corrosion resistance [15]. Currently, the literature shows titanium aluminum nitride (TiAlN) as a material with better mechanical properties compared to monolithic TiN, due to the inclusion of aluminum atoms in the TiN crystalline structure which produces an increase in oxidation resistance by formation of the stable ternary material TiAlN [16]. In recent years, there have been considerable efforts for developing multilayer coatings to improve wear and oxidation resistance for many components. Some improvements have been presented by alternating the deposition of two or more different layers to avoid the fracture movement; therefore, the multilayer structure may act as nano-cracks inhibitors [17]. The aim of this work is to characterize the behavior of [TiN/TiAlN]n

multilayer coatings affected by erosion process without corrosive effect, corrosion without erosive effect, and multilayer coatings under corrosive-erosive fluid as function of bilayer number (n) and bilayer period ($\Lambda = t_{TiN} + t_{TiAIN}$) with changes in the impact angle in relation to wear particles, thus comparing with the behavior presented by the AISI 1045 steel uncoated substrate.

2. Experimental Details

[TiN/TiAlN]n multilayer coatings were grown onto Si (100) and AISI 1045 steel substrates using a multi-target magnetron sputtering system, with an r.f. source (13.56 MHz) and two Al and Ti stoichiometric targets with purity of 99.9%. The optimal deposition parameters were the following: sputtering power of 350 W for Al and 400 W for Ti targets, temperature of 300°C for the substrate under circular rotation with 60 RMP to facilitate the formation of the stoichiometric coatings, the sputtering gas was a mixture of Ar 93% and N_2 7% with total working pressure of 6.10⁻³ mbar under nitrogen gas flow of 3.7 sccm. An unbalanced r.f. bias voltage, which generates a constant voltage offset of -70 V, was applied. Additionally, the magnetron sputtering device has a positioning substrate system associated to the target spot which allows to vary the bilayer number (n) between 2, 6, 12 and 24, this way changing the bilayer period (Λ) from 1500 nm to 125 nm. The crystal structure of the coatings was determined by using a D8 Advance Bruker X'ray diffractometer with Cu-K α (λ = 1.5405 Å) radiation. Chemical composition of the coatings was assessed by energy dispersive X-ray (EDX) using a Philips XL 30 FEG; thus, a high-purity Ge EDX detector for the reliable acquisition of EDX spectra was used in this analysis. The structural assembly of the multilayers was analyzed by scanning electron microscopy (SEM) (Philips XL 30 FEG) equipped with a light optical magnification range: 525- 24.00X and height sensitivity backscatter electron detector (EDAX-EDX) system. Grain size was determined via atomic force microscopy (AFM-Asylum Research MFP-3D[®]) and calculated by a scanning probe image processor (SPIP[®]) that is the standard program for processing and presenting AFM data; such software has become the standard for image processing at nanoscale. The mechanical analyses were performed via nanoindentation by using an Ubil-Hysitron device and a diamond Berkovich tip at variable loads. Out of these measurements, load-penetration depth curves of the indentations of the multilayer coatings were obtained. These results were evaluated through the Oliver and Pharr method. Tribological characterization (adherence of the coatings) was studied by using a Scratch Test *Microtest MTR2* system; the parameters were a scratch length of 6 mm and a raising load of 0 N to 90 N. The analysis of the total mass loss by erosion damage as a function of bilayer number was

obtained by means of stopping the system at intervals of 10 minutes, with a total time of 2 hours for two different impact angles $(30^{\circ} \text{ and } 90^{\circ})$. As for the analysis of the erosive, corrosive and erosivecorrosive effects, a device built for the evaluation of chemical attack in metallic materials was used, Fig. 1. The erosive-corrosive testing device consists of a tribometer with a glass container for erosive-corrosive storage, one reference and one counter electrode, an acrylic cover that is available in the sample holder and electrodes, a impeller of High Ultra Molecular Weight Polyethylene (HUMWPE) which rests on the teflon shaft that is attached to the main motor shaft that provides fluid motion. The lid of the container allows locating two different samples exposed under angles for corrosive fluid action (30° and 90°). The fluid movement is caused by a shaft driver of the motor. The speed motor was fixed to 1930 RPM, the tangential speed applied to the fluid was fixed to 11.12 m/s. The electrochemical study was carried out with a *Gamry* unit, model PCI 4 with D.C. and A.C. signal which generates Tafel polarization curves. These curves were obtained at room temperature using a cell that supports one working electrode within an exposed area (1 cm^2) , a reference electrode (Cu/CuSO₄) and a graphite counter electrode in a 3.5% NaCl + 0.5 M-H₂SO₄ solution with distilled water. The resting potential was measured during 30 minutes to ensure repeatability of results. The Tafel curves were taken about 1 hour in the test, this time was necessary for the anodic and cathodic sweep potentials. Tafel polarization curves were obtained at a sweep speed of 0.138 mV/s within a voltage range from -0.2 V to 0.8 V with an exposed area of 1 cm². In this work, silica (SiO₂) was used as an abrasive agent with a particle size between 210 µm and 300 µm. This chemical solution was chosen since it has been shown that it can be used to study steel as it facilities the observation of chemical attack at defined anodic region and chloride addition guaranteed the effective attack. The weight of the work electrode (E_w) for all test was around 55.847g/mol taking into account the Fe (pure) as reference since this material (Fe) present low carbon content. Finally, the process of surface corrosion was analyzed and the superficial morphology was characterized by using a High-Resolution Scanning Electron Microscope (SEM) (Philips XL 30 FEG).



Figure 1. Schematic of the device used in the corrosion-erosion wear test. Auxiliary electrode (AE), working electrode (WE), reference electrode (RE) [18].

3. Results and discussion

3.1. X-ray diffraction analysis

The measurements of the thickness of the deposited monolithic multilayers, i.e. TiN, ternary TiAlN, and [TiN/TiAlN]n were found to be approximately 3 μ m for each of them. The X-ray diffraction (XRD) patterns of the Ti–N and Ti-Al–N single layer coatings deposited on Si (100) with a r.f. negative bias voltage of -70 V (Fig. 2) indicate that both coatings have a cubic structure with two strong Bragg peaks corresponding to the TiN(200) and TiAlN(220) planes, showing a light textured growth along these orientations. The other weak peaks correspond to diffractions of TiN (202), TiN (220), TiN (311), and TiN (222) [19], and for TiAlN was found TiAlN (140), AlN (422) and TiAlN (311) planes of the FCC structure [20].

Regarding the lattice parameter, the value of a0 (\pm 0.0001 nm) was obtained for TiAlN coatings, where the *Nelson-Riley* function was employed in the refinement procedure, see Table 1. This result shows an expansion of the cell unit with respect to the value reported in the literature for Ti_{1-x}Al_xN_y powder (Ti_{0.1}Al_{0.1}N_{0.8}) [21], compared to the TiAlN coating deposited with a r.f. negative bias voltage of -70 V. Which creates a mismatch effect with the TiN layer since the latter has a lattice parameter of 0.4240 nm. The presence of the TiAlN (220) obtained on the TiAlN layer is associated to a substitution mechanism where Al atoms replace Ti atoms resulting in a Ti-ordered and Al-N disordered FCC NaCl-type structure. In such atomic arrangement Ti and Al atoms are placed at the *Wyckoff* site 4a, while N atoms occupy randomly the *Wyckoff* site 4b [21]. This means that the FCC structure is determined by a partially ordered structure with Ti atoms, creating vacancies in non-metallic sublattice [18, 20].



Figure 2. XRD pattern for TiN and TiAlN single layer coatings deposited with a negative bias voltage of -70 V.

In the case of the TiN/TiAlN multilayer, the individual thickness was varied as a function of the bilayer number from n = 2 to n = 24, producing bilayer periods (A) from 1500 nm to 125 nm. Hence, Fig. 3a shows the XRD pattern of TiN/TiAlN coatings deposited with n = 2, $\Lambda = 1500$ nm; n = 12, $\Lambda = 250$ nm and n = 24, $\Lambda = 125$ nm onto a Si (100) substrate, at a r.f. negative bias voltage of -70 V. The XRD pattern represents a cubic structure where the strongest peak (220) corresponds to the TiAlN (220) plane, indicating a light textured growth along this orientation. The other weak peaks correspond to diffractions of TiN (220), TiN (311), TiAlN (311), and TiAlN (222) planes of the FCC structure. Moreover, the AlN (422) peak for the AlN within Ti-Al-N material is also exhibited, except at n = 24 due to spatial periodicity reduction that prevents the nucleation of AlN crystals. On the other hand, it was observed that the Ti-Al-N (220) peak position presents a significant deviation from the bulk value indicating a possible stress evolution of TiN/TiAIN layers with the bilayer period (Fig. 3b). The quasi-relaxed position observed for thinner bilayer periods was progressively shifted to higher compressive stress values as the bilayer period is reduced until the $\Lambda = 125$ nm, therefore, this compressive effect is reached due to a multilayer mechanism actuating on TiN/TiAlN coatings. For the multilayer with bilayer number equal to 24, an abrupt change at the Ti-Al-N (220) peak was observed, the peak moved towards higher angles compared to other thinner multilayers - but close to bulk value (63.60°)- indicating a stress relief due to the shift. The stress evolution at the Ti-Al-N (220) peak position comes together with a progressive and intense symmetric broadening and an increase in its intensity. Furthermore, it was also clearly shown on these XRD patterns that there is not presence of satellite peaks with the increase of the bilayer number and the reduction of the thickness of individual layers, which indicates that there is low structural coherency in relation to the lowest bilayer period ($\Lambda = 125$ nm) [20].



Figure 3. XRD patterns for TiN/TiAlN multilayers: (a) multilayer set displayed at increasing bilayer number grown with n = 2, n = 12 and n = 24. Dashed lines indicate the position of the peaks obtained out of JCPDF 462553 and 01-080-2286 files from ICCD cards and (b) maximum Ti-Al-N (220) peak with shift toward high angles in relationship to increasing bilayer number (n).

It is worth mentioning that a careful correction has to be done in all stoichiometric analysis because energy-dispersive X-ray spectroscopy (EDX) has low reliability for nitrogen concentration. Therefore, EDX elemental concentrations were obtained using the ZAF correction method because certain factors related to the sample composition can affect the X-ray spectrum produced during the analysis of electron microprobe. These factors, called matrix effects, are associated with the atomic number (Z), the absorption (A), and the fluorescence (F). In other to ensure the development of an appropriate analysis, such factors should be corrected. The correction factors for a standard specimen of known compositions were determined initially by the ZAF routine. The relative intensity of the peak K was determined by dead time corrections and a referent correction for the X-ray measured. Thus, before each quantitative analysis of an EDX spectrum was done, a manual background correction and an automated ZAF correction was carried out [11]. Thus, Table 1 shows the EDX values of $Ti_{1-x}N_x$ ($Ti_{0.22}N_{0.78.}$) single layers [19] and $Ti_{1-x}Al_xN_y$ ($Ti_{0.22}Al_{0.20}N_{0.58}$) single layers [22, 23], deposited with an r.f. negative bias voltage of -70 V. All samples were observed via SEM and chemical analyses were done with an amplification of 20000X.

Table 1. Stoichiometric relation analyzed by EDX with subtractions of oxygen contribution and lattice parameter of Ti-N and Ti-Al-N single layer coatings.

Negative r.f. bias	Binary	a ₀ (nm) FCC	Ternary	a ₀ (nm) FCC (220)
voltage (V)	coatings	(111) (Ti _{1-x} N _x)	coatings	$(Ti_{1-x}Al_xN_y)$
	$(Ti_{1-x}N_x)$		$(Ti_{1-x}Al_xN_y)$	
-70	Ti _{0.22} N _{0.78.}	0.4240	$Ti_{0.22}Al_{0.20}N_{0.58}$	0.4175

3.2 Stress analysis

The presence of residual stress in the coatings was initially shown in our XRD results (Fig. 3b). For TiN/TiAlN multilayer coatings, as the bilayer number (n) was increased, a slight shift of the maximum peak towards higher angles (lower lattice parameter) was observed. A reasonable explanation for this behavior is that previously observed peaks were shifted to higher 2θ values and broadened due to compressive stresses caused by multilayer effect when the bilayer period (Λ) was reduced. Each of the PVD methods had their own strengths and weaknesses; nevertheless, they presented different traits in common that promoted their use in hard coating deposition: all four techniques can be reactive processes, i.e. it is possible to combine the vaporized material with a reacting gas in order to create compounds with high multilayer numbers and well-adhered coatings. This latter ability modifies the interface number within a multilayer system (multilayer effect), which gives significant relevance on final coating properties [24-27]. Therefore, an important parameter on coating properties is the residual stresses, since some limiting factors on increased service life of metal nitride coatings arise from their limited adhesion strength and thermal stability issues. The high stresses observed in XRD results, can also be attributed to microstructural transformations produced during the transition from crystalline binary TiN and ternary TiAlN materials to overstoichiometric Ti-Al-N coatings. On the other hand, biasing may imply some changes on the stress and the microstructure, and probably it is somehow reflected on the mechanical and tribological properties of TiN/TiAlN multilayer coatings.

In this work the stress phenomenon was analyzed from XRD results, taking into account that Fig. 3b shows the behavior of the lattice parameter of 3 μ m-thick TiN/TiAlN multilayers deposited on Si substrates, as a function of increasing bilayer number (n = 2, n = 12 and n = 24). The lattice parameters corresponding to preferential orientation TiAlN (220) were determined using the Bragg law written in terms of the lattice parameter (a₀):

$$n\lambda = 2\sin(\theta) \cdot \left(\frac{a_0}{\sqrt{h^2 + k^2 + l^2}}\right) \tag{1}$$

where *n* is an integer determined by the order given, λ is the wavelength of the X-rays (and moving electrons, protons and neutrons) (1.5406 Å), (*hkl*) is the reciprocal lattice vector, θ is the angle between the incident ray and the scattering planes, and (*a*₀) is the lattice parameter [12]. The lattice parameters for TiN/TiAlN multilayer with Ti-Al-N layer at (220) direction are shown in Fig. 4. Regarding the lattice parameter *a*₀ (±0.0001 nm) for TiN/TiAlN multilayer, where the *Nelson–Riley* function was employed in the refinement procedure, the results showed (Fig. 4) a strain of the cell unit related to the value reported in the literature for Ti-Al-N powder (0.4112 nm), compared to the TiN/TiAlN multilayer deposited at a different bilayer number. In this sense, it can be observed that the lattice parameter (*a*₀) decreases as a function of the increasing bilayer number (n) or with the reduction of bilayer period (Λ); therefore, when the negative bilayer number is increased, the TiN/TiAlN multilayer suffers a compressive stress relief due to the interface effect.



Figure 4. Lattice parameter of the TiN/TiAlN multilayer at TiAlN(220) preferential orientation as a function of the bilayer number (n = 2, n = 12 and n = 24).

3.3. Scanning electron microscopy analysis (SEM)

A first glimpse on TiN/TiAlN multilayers modulation and microstructure was accomplished by scanning electron microscopy (SEM) micrographs. Fig. 5 shows the cross-sectional image of a TiN/TiAlN coating with n = 24 ($\Lambda = 125$ nm). The darkest contrast of the TiAlN layers with respect to the TiN ones allowed a clear determination of the structure of the layers. These TiN/TiAlN coatings presented a well-defined and uniform periodicity. All the multilayer stacks were resolved by SEM and confirmed quite precisely the previously designed values of bilayer thickness, as well as the total thicknesses. The only slight deviation observed by SEM imaging was on relative nanometric thicknesses. In this specific sample, the TiAlN layers seem a little bit thicker than the TiN ones. These deviations are difficult to evaluate because of the poor resolution of the TiN/TiAlN interfaces with this technique.

Additionally, the effect of the wave-like interfaces upon the built-in strain in TiN/TiAlN wavy multilayer was observed in Fig.5. In this micrograph, the monolithic TiN layers evolve from a planar morphology at the ternary TiAlN to TiN interface into a wavy morphology as more material is deposited. The TiAlN spacer layers suppress this undulation and a planar morphology is recovered by the time the next TiN layer is deposited. This is shown in more detail in the right panel of Fig. 5. Two additional observations can be made from the micrographs of Fig. 5. First, the TiN undulations from layer to layer are aligned vertically. This suggests that contrary to a planar multilayer, the TiAlN lattice in the spacer layers is strained. The expansion of the TiAlN lattice above the TiN crests favors nucleation and lateral migration within the next TiAlN layer above the previous crests and results in vertical alignment of the undulations, as observed. The second observation is some flattening at the top of the TiN mounds, as it is clearly seen in the right panel of Fig. 5. A similar phenomenon has been observed in $Si_{1-x}Ge_x/Si$ superlattice and InAs quantum dots on GaAs, where the flattening of the dots has been attributed to lateral diffusion of In from the InAs dots to the GaAs spacer surface [26, 27], as was reported by H.K. Shin et al. [26] where Ge is known that segregates towards the surface of SiGe epitaxy on Si. Al in our case possibly also segregates towards the surface of TiN, and it is possible that a similar mechanism is in effect here.



Figure 5. Scanning electron microscope cross-section of a [TiN/TiAlN]n multilayer with $\Lambda = 125$ nm (left panel) and magnified view of the central section (right panel) showing details of the interface morphology.

3.4 Mechanical properties

3.4.1 Hardness and Elastic modulus

In the literature it is reported that the thickness period for many multilayer systems is between 5 nm and 20 nm, which is relevant for mechanical properties [12, 14, 28]. However, in industrial applications, as mentioned in the introduction, it is necessary to obtain coatings with thicknesses of \sim 3.0 µm; therefore, TiN and TiAlN single layer and multilayer coatings where deposited achieving a total thickness about 3.0 µm. In this sense, the TiN/TiAlN multilayer with bilayer period (Λ) below 20 nm implies a complex and extended number of multilayers; consequently, this study was carried out with a minimum period bilayer of 125 nm. In this regard, the typical load-displacement indentation curves of multilayer coatings were carried out by using the standard *Berkovich* indenter and indentation matrix image by atomic force microscopy (AFM) shown in Fig. 6b. Values of hardness, H, and elasticity modulus E, (Fig. 6a) were obtained by using the *Oliver and Pharr's* method with load-unload micro-cycles to strain the material on the indentation track, which is relevant to determine the maximum load value.[12, 29].



Figure 6. Nanoindentation results with (a) load-displacement indentation curves for all coatings and (b) indentation matrix images via AFM for multilayers with a bilayer period (Λ) of 125 nm and n = 24.

Figure 6b shows a 14 µm×14 µm image of a TiN/TiAlN multilayer deposited with a bilayer period $(\Lambda) = 125$ nm, n = 24, and a negative bias voltage of -70 V. The general trend in the TiN/TiAlN multilayer, below different bilayer periods, exhibits a decrease of the grain size when the bilayer number (n) is increased. Fig. 6b also shows the pyramidal traces (nanoindentation matrix) generated on the surface of the TiN/TiAlN multilayer by the indentation method with their corresponding indentation depth. Moreover, Fig. 6b shows the quantitative data extracted from the AFM images. Each data point in the plots represents an average over 3 AFM images. The corresponding error bar was obtained by a standard deviation of the values. Therefore, in the Fig. 7 it is possible to compare the grain size values of the TiN/TiAlN multilayer coatings; accordingly, in this study a decreasing tendency on the measurements of surface was observed when the bilayer period was reduced. The lower grain size value obtained in this study by the [TiN/TiAlN]₂₄ multilayer (Fig. 7) represented a decrease of grain size around 77%, 83% and 94%, compared to those obtained for the [TiN/TiAlN]₁ bilayer, TiN, and TiAlN single layer, respectively. This observation is relevant since the continuity of the surface is important for fabricating tools and mechanical devices under wear and corrosive environment. The variation of grain size (Fig. 7) obtained for the TiN/TiAlN multilayer suggests that coatings with (n = 1) grow more disordered than coatings with (n = 24). The grains of the multilayered coatings are smaller than those of the coatings with a low bilayer period, because the Ar^+ ion bombardment on coatings stimulates a greater number of nucleation places, which is due to the reduction of individual thicknesses for each layer when the bilayer period is reduced and bilayer numbers are increased; this implicates a decrease in the entire surface roughness [12].



Figure 7. Grain size as a function of bilayer number (n) showing different bilayer periods (Λ).

Fig. 8a-b shows the hardness and elastic modulus of the binary nitride single layers such as monolithic TiN with H = 18 GPa, Er = 210 GPa, ternary nitride single layers TilAN with H = 20 GPa, Er = 223 GPa and multilayer coatings depending on the bilayer numbers (n) or bilayer periods (Λ). According to the figures, the properties of the multilayer coatings are strongly affected by the bilayer period, Λ . The hardness and elastic modulus of TiN/TiAlN multilayer coatings ranged from approximately 22 GPa to 32 GPa and 235 GPa to 290 GPa respectively, having found the maximum value for both properties for n = 24, which corresponded to Λ = 125 nm. These values represented an increase of 31 % and 19 % of the hardness and elastic modulus with respect to the multilayer system with n = 2 (Λ = 1.5 µm) and an increase of hardness (44 %, 37 %) and elastic modulus (27 %, 23 %) in relation to monolithic TiN and ternary TiAlN single layer respectively.



Figure 8. Mechanical properties: (a) Hardness and (b) Elastic modulus for TiN/TiAlN coatings as a function of bilayer number (n) showing different bilayer periods (Λ).

Taking into account the densification of the interface between layers by the decrease of grain size previously analyzed in Fig. 7 and the decrease of surface roughness as the multilayer periods decrease, it is evident that the proximity of the interfaces is reduced as the bilayer period. Also, the dereference in crystalline structure of the constituent layers of the multilayer system contribute to impeding micro-crack motions across the layer interfaces, increasing in this way the multilayer hardness [30, 31]. Another explanation was proposed by *Anderson* and coworkers [32] where the mechanical behavior was modeled for multilayer materials with layer thicknesses as low as 1-100 nm, using a *Hall-Petch* approach which is shown in the next equation presented by *J. C. Caicedo et al.* [12].

$$H_m = H_{(f1+f2)} + k_{(IM)} D_{(t)}^{-\frac{1}{2}}$$
(2)

where H_M is the multilayer hardness, $H_{(f1+f2)}$ is the hardness from layers 1 and 2, K_{IM} is the interface parameter between layers 1 and 2, and $D_{(i)}$ is the bilayer period (Λ). This model predicts the overall behavior of the hardness on Λ that is observed in most multilayer systems. According to this model, each interface in the multilayer system works like a grain boundary, such that dislocations pile-up at the interfaces and harden the layer by strain [12, 33, 34]. The enhancement of mechanical properties for TiN/TiAlN multilayers is in accordance with the increase in hardness as it has been shown in multilayer-type coatings for diverse material systems (*e.g.*, TiCN/TiNbCN [12], CrN/AlN [35], TiN/VN, TiN/TiAlN and TiN[BCN/BN]n/c-BN [34, 36, 37]. Furthermore, a dependence of the elasticity with the bilayer number (n) or bilayer period (Λ) was observed, the highest bilayer number corresponds to the highest elastic modulus. Therefore, it is possible to conclude that the elasticity of the multilayer coatings is improved by increasing the interface number. Hence, from the nanoindentation measurement, the typical values of elastic modulus, *Er*, and hardness, *H* were obtained by using the *Oliver and Pharr's* method [29].

In another way, according to Kim et al. [38] there is a relationship between elastic modulus and hardness named plastic deformation resistance (H^3/E^2 ratio), this relation was calculated for all multilayered coatings in function of the bilayer number or bilayer period. Fig. 8b shows a considerable increase of the resistance to the plastic deformation (H^3/E^2) as the bilayer number (n) increases, this fact is due to the hardness and also the increase of the elastic modulus as the interface number increased for all multilayer coatings. This enhancement in plastic deformation resistance occurs when the bilayer period (Λ) decreases, this way increasing the interface number for coatings with total thickness. As a result, crystallite refinement, point defect formations and increase of interface number are achieved, which improves the hardness of the TiN/TiAlN multilayer coatings. As shown in Fig. 8, the [TiN/TiAlN]n multilayer coatings increased the plastic deformation resistance and the elastic recovery with respect to coatings deposited with lower bilayer number. The maximum value was reached for the bilayer number (n = 25) and the bilayer period $(\Lambda = 125 \text{ nm})$, i.e. the plastic deformation due to the applied load is more markedly reduced than that of other multilayered systems with fewer bilayer numbers. This effect is clearly correlated to the reduction of grain size, increasing coating density, and hardness [12]. In general the bilayer number (n) or bilayer period (Λ) has some effects on multilayer that has been shown to exhibit very

high hardness in multilayers composed of a binary nitride (*e.g.* TiN) and a ternary nitride (*e.g.* TiAlN). Binary nitride is used to provide significant ductility while the ternary nitride gives the high hardness. In this binary-nitride/ternary-nitride multilayer system, dislocation motion across layer interfaces should be unlikely to happen since the layers typically have different crystal structures showing the increase in the mechanical properties.



Figure 9. Elasto-plastic properties with plastic deformation resistance for TiN/TiAlN multilayer coatings with bilayer period from $\Lambda = 1.5 \ \mu m$ to 120 nm.

3.4 Tribological properties

3.4.1 Scratch test

The scratch test technique was carried out to characterize coating adherence strength. The adhesion properties of monolithic TiN, TiAlN single layers and TiN/TiAlN multilayer coatings can be characterized by using the upper critical load, which is the load where the first delamination occurred at the edge of the scratch track (adhesion failure) [39].

The critical loads in adhesive failure values for the different coatings are summarized in Fig. 10. In this figure, it is clearly showed the increased adhesion properties of TiN/TiAIN multilayer coatings as a function of the decrease in the bilayer period (Λ). Since performing quantitative adhesion measurements between layers and substrates is a complex process even for single layer coatings in agreement with some authors [40], a qualitative characterization is necessary to evaluate the adhesion behavior for all multilayer systems, i.e. in terms of critical loads. Therefore, for the purpose of ensuring a fair comparison between the different coating systems, it was assumed that the adhesion between the substrate and the first layer of the multilayer system remains constant, because the conditioning of samples and the parameters for coating depositions used in this study were the same. Besides, in all cases it was verified that the parameters of the scratch test for all samples were also the same. According to the latter, it was expected that the response to the applied

load would only be depending on the coating properties, due to the effect of each layer and the interfaces that conform the entire multilayer system.

From Fig. 10, it was observed that the critical load increased when the bilayer period (Λ) was reduced and the bilayer number (n) was increased, this improvement is in part due to the increase on the coating/substrate deformation resistance and enhancement of mechanical properties (Fig. 8) (Hardness and Elastic modulus). In this mechanism each interface serves as crack tip deflector, which changes the direction of the initial crack when it penetrates deep into the coating and strengthens the coating systems. Moreover, by decreasing the bilayer period ($\Lambda = t_{TiN} + t_{TiAIN}$), the dislocations that are among the layers find a major impediment to moving, therefore, TiN/TiAIN multilayer will require a higher critical shear stress to move and spread through the whole coating and allow the delaminating of the coating [34, 41]. This means that multilayer coatings can fail in a laminar manner by particle impact effect. In consequence, multilayers as well as multiple structures as studied in this research work can enhance the resistance of coatings against crack propagation, resistance to particle impact and thus, preserve the integrity of the coatings under punctual and dynamical loads [42, 43]. In this study, it was observed that an increase of 40 % on the critical loads, on adhesive failure for multilayer systems with n = 24 and $\Lambda = 125$ nm with lowest stress observed by XRD (Fig. 3b), results in relation to multilayers deposited with n = 2 and $\Lambda = 1500$ nm. Moreover, it was found an increase of 53 % and 46 % on the critical loads on adhesive failure for [TiN/TiAlN]₂₄ multilayer in relation to TiN and TiAlN single layer respectively.



Figure 10. Critical loads (adhesive failure) correlation with the bilayer number (n) showing different bilayer periods (Λ).

Erosion analysis without corrosive effect can be associated to the wear indicator. For instance, mass loss related to erosive mechanisms without corrosive effect as a function of exposure time for different multilayer numbers under two impact angles (30° and 90°). In this work, it was noted that the decrease in wear rate is in relationship to an enhancement in the physical properties provided by multilayer coatings, which is due to two cooperative effects. First, multilayer coatings with preferential orientation TiAlN (220) and a decrease in the residual compressive stress shown by XRD results (Fig 3b) exhibits the highest hardness (Fig 8a), because the impact energy provided from wear particles is absorbed and distributed in a better way across the interfaces between different materials like TiN and TiAlN [44], generating an increase in the mechanical toughness of multilayer coatings. Fig. 11 shows the mass loss as a function of bilayer number or bilayer period (Λ) for one similar exposure time (120 min) without corrosive effect. In this figure, it is possible to observe the effects of bilayer number (n) or bilayer period (Λ) on mass loss; since the interface number offers wear resistance by the increase of mechanical properties (hardness and elastic modulus) and an improvement of the tribological properties (critical load). Furthermore, it was confirmed that erosion strongly depended on bilayer period modulation, such as that accomplished by SEM micrographs, microstructure, plastic deformation resistance (Fig. 9) and critical load (Fig. 10). On the other hand, the change in impact angle produces an increase in mass loss, as this effect (high impact angle, 90°) increases the impact energy of the particles which generates more erosive wear.



Figure 11. Mass loss without corrosive effect as function of bilayer number for two impact differents angles (30° and 90°) showing different bilayer periods (Λ).

3.6 Corrosion analysis without erosive effect

Figure 12 shows Tafel polarization curves and the corrosion potential as a function of the corrosion current density for monolithic Ti-N and Ti-Al-N single layers coatings without erosive effect for two impact angles, Fig. 12a (30°) and Fig. 12b (90°). In these results, it is possible to observe that TiAlN single layer presents the lowest corrosion potential for both angles, which indicates that ternary nitride is more protective compared to binary TiN, the last effect can be attributed to Al ion incorporation. Moreover, the changes in the impact angle generate a small displacement of the corrosion potential, thus evidencing the damage caused by increase of the impact energy.



Figure 12. Tafel curves of corrosion without erosive effect for TIN and TiAlN single layer coatings with two different impact angles: (a) 30° and (b) 90°.

Also, Tafel polarization curves and the corrosion potential as a function of the density of corrosion current for the TiN/TiAlN multilayers coating at different bilayers number (n) without erosive effect for two impact angles 30° and 90° are shown in Fig. 13a and Fig. 13b respectively. Tafel polarization curves have been used to calculate surface corrosion rate without erosive effect, these curves are strongly dependent on the Λ and n, indicating the influence of interfaces present within the multilayers. The curves allow finding anodic and cathodic slope values in each case, which are necessary to calculate a correct value of the corrosion rate for all systems, confirming the protective effects of the coatings [45]. So, this protective effect is characteristic of multilayer structures; as a consequence of increasing bilayer number (n) or increasing interface number whit the reduction of bilayer period (Λ).



Figure 13. Tafel curves of corrosion without erosive effect with two different impact angles: (a) 30° and (b) 90°.

Taking into account the erosion analysis without corrosive effect and the corrosion analysis without erosive effect, it is possible to observe that corrosive failure of nitride coatings (single layer or multilayers) under the action of a corrosive medium occurs at structural defects (pin holes, pores, micro-cracks, etc.). Therefore, the corrosion resistance of multilayer nitride coatings (TiN/TiAIN) is higher than that of single-layer coatings, which may be explained by their greater interface number and features of their microstructure, including the absence of circular crystals characteristic of single-layer coatings [46].

In this work, it was observed that the corrosion potentials of the coated steel are more electropositive when the bilayer number is increased in relationship to the uncoated steel, confirming the protective effects of the coatings [45]. This behavior is characteristic of multilayer structures; as a consequence of an increase on bilayer number (n) or interface number and reduction on bilayer period (Λ), the density and the interface number are also increased uniformly thorough the thickness of the multilayer system, thus, the number of pores is reduced. This leads to that the energy required for Cl⁻ ions movement across the coating/substrate interface when freedom is higher; therefore, fewer ions arrive to the substrate due to the change of direction experienced by Cl⁻ ions when these find a new interface [47].

In this study, for an impact angle of 30°, it was observed an increase of 26 % and 19 % on the corrosion potential without erosive effect for multilayer systems with n = 24 and Λ = 125 nm in relation to TiN and TiAlN single layer, respectively. Additionally, for an the impact angle of 90°, it was found an increase of 21 % and 14 % on the corrosion potential for [TiN/TiAlN]₂₄ multilayer in relation to TiN and TiAlN single layer, respectively. Thus, the aforementioned results indicate that

multilayer coatings present more corrosive protection than that binary and ternary nitride, due to interface effect generated by increase of bilayer number.

3.7. Corrosion-erosion analysis

For the corrosion rate analysis, the corrosion velocity was calculated after determining the density of the current corrosion, j_{corr} , by using the *Stern – Geary* equation:

$$j_{corr} = \frac{\beta_a \cdot \beta_c}{2.303 R_t^T (\beta_a + \beta_c)}$$
(3)

where $R^T t$ is the polarization resistance, and βa and βc are the anodic and cathodic Tafel slopes, respectively. To determine βa and βc , a potenciodynamic sweeping was conducted by using the Tafel technique. Finally, the corrosion velocity, *Vcorr*, can be expressed as:

$$V_{corr} = \frac{j_{corr} \cdot K \cdot E_w}{A \cdot d} \tag{4}$$

where *K* is a proportionality constant, and *Ew* is the weight of the work electrode [48]. The general results of corrosion rate in multilayer coatings with impact angles of 30° and 90° are showed in Table 2.

30°								
	Steel	n = 2	n = 6	n = 12	n = 24			
Corrosion Potential (mV)	-799.23	-589.41	-459.48	-266.17	-132.99			
$\beta_a(mV/decade)$	0.378	0.270	0.243	0.223	0.169			
$\beta_c(mV/decade)$	-0.343	-0.280	-0.289	-0.212	-0.174			
$j_{corr}(\mu A/cm^2)$	791.9	604.1	545.0	329.8	228.0			
V _{corr} (mpy)	359.17	274.01	247.2	149.59	103.42			
90°								
	Steel	n = 2	n = 6	n = 12	n = 24			
Corrosion Potential (mV)	-0.474	-0.463	-0.421	-0.375	-0.328			
$\beta_a(mV/decade)$	0.422	0.347	0.314	0.295	0.241			
$\beta_c(mV/decade)$	-0.412	-0.321	-0.312	-0.265	-0.217			
j_{corr} (μ A/cm ²)	1420.0	738.6	573.4	505.3	465.0			
V _{corr} (mpy)	646.28	335.00	260.09	229.17	210.91			

Table 2. Parameters used to calculate the corrosion rate with different impact angles (30° and 90°).

Tafel polarization curves are shown in Fig. 14a and 14b. These curves allowed determining the values of the anodic and cathodic Tafel slopes, which are necessary to calculate an accurate value of the corrosion rate. For two different impact angles, 30° and 90° , a passive behavior was observed in all analyzed samples. The coatings generated a displacement of the curves towards lower values of the current density and potentials more nobles than those observed for steel substrate. This behavior is related to the increase of bilayer number (n) and decrease of bilayer period (Λ) period, showing that larger bilayer numbers and lower bilayer periods in multilayer coatings enhance the response against the corrosive erosive effects [49].



Figure 14. Tafel curves of corrosion- erosion with two differents impact angles (a) 30° and (b) 90°.

Fig. 15 shows the values of the corrosion rate as a function of the bilayer number (n) and bilayer period (Λ), in corrosion-erosion conditions for two different impact angles, 30° and 90°. The curves show a tendency towards lower values when the bilayer number increases and the bilayer period decreases. These type of coatings generate a great number of interfaces such those showed by SEM results, which are regions that presents structural disorder and marked changes in crystallographic orientation. The interfaces can act as dispersion points preventing that electrolyte spread towards the substrate which cause damage in the surface. Fig. 15, shows higher corrosion rate for the impact angle of 90° than those for an impact angle of 30°, this phenomenon was observed in samples that exhibited twice corrosion rate compared to those multilayer coatings attacked with an angle of 30°. The reason for this observation is that because of the normal angle, the particles hit the surface with great energy causing significant wear of the material. In that sense, it was found that the coating deposited with n = 24 (Λ = 125 nm) under an impact angle of 90° provides a corrosion rate two times higher than that of coating deposited with n = 24 (Λ = 125 nm) for lower impact angle of 30°.

The general trend was to reduce the corrosion rate when the interface number is increased because of increasing the bilayer number (n) and reducing the bilayer period (Λ). Also, in Fig. 15 it is seen that the highest impact angle (90°) exhibited a dramatic increase in corrosion rate in all cases.



Figure 15. Corrosion rate as a function of bilayer number for two differents impact angles (30° and 90°).

A wear indicator such as mass loss related to corrosive-erosive system is showed Fig. 16. In this study it was noted that the decrease in wear rate is related to passivation provided by multilayer coatings. An increase of 41 % and 38 % was observed on the mass loss with erosive effect for multilayer systems with n = 24 and $\Lambda = 125$ nm in relation to TiN and TiAlN single layer, respectively, for a impact angle of 30°. Moreover, when the impact angle is 90°, it was found an increase of 50 % and 47 % on the mass loss with erosive effect for [TiN/TiAlN]₂₄ multilayer in relation to TiN and TiAlN single layer, respectively.

These results are due to two cooperative effects. First, multilayer coatings exhibit a higher hardness because the load is absorbed and distributed in a better way across the interfaces between different materials such as monolithic TiN and TiAlN layers [44], gendering an increase in mechanical toughness of multilayer coating. Thus, on uncoated samples (steel AISI 1045), it was observed delamination in punctual zones on the surface of the steel substrate, because of the poor mechanical and anticorrosive properties compared with [TiN/TiAlN]n multilayers. Second, the mass loss decreases for both angles measured on steels coated with increment of bilayer number (n) and reduction of bilayer period (Λ) in relation of steel uncoated, indicating well performance for these multilayer coatings under corrosive-erosive conditions. On the whole, it was confirmed that corrosion-erosion strongly depends of the impact angle. On the other hand, the mass loss under

corrosive-erosive effect is higher than that mass loss without corrosive effect or without erosive effect due to the presence of synergistic critical wear.



Figure 16. Mass loss vs. Bilayer number for two different impact angles (30° and 90°).

4. Surface analysis after erosive-corrosive attack

Scanning electron microscopy (SEM) micrographs are shown in Fig. 17 and 18 for the uncoated steel substrate and [TiN/TiAlN]n nanometric multilayer deposited with n = 24 ($\Lambda = 125$ nm) on steel substrate under corrosion-erosion processes for two impact angles. When the impact angle is 30°, Fig. 17a shows the uncoated steel where a crack is generated by wear mechanism. The white areas reflect the surface damage caused by corrosion attack. Fig. 17b shows a surface without fracture which exhibit the protection afforded by multilayer coating on steel substrate.



Figure 17. SEM micrographs for samples under corrosion-erosion processes (a) uncoated steel, (b) steel/[TiN/TiAIN]₂₄ with impact angle of 30°.

For impact angles of 90°, Fig. 18a shows the surface of the uncoated steel substrate evidencing a more aggressive attack than that of impact angles of 30°, producing in this way a high corrosive wear. Fig. 18b shows a fractured surface where the coating has been delaminated due to abrasion phenomenon caused by energetic particles that impact in normal angle of 90° on the surface of [TiN/TiAlN]n, showing in this way a large aggressive effect.



Figure 18. SEM micrographs for samples under corrosion-erosion processes: (a) uncoated steel, (b) steel/[TiN/TiAlN]₂₄ with impact angle of 90°.

Conclusions

[TiN/TiAlN]n multilayer coatings were deposited by reactive r.f. magnetron sputtering using simultaneous deposition from Al and Ti targets in N₂+Ar mixture. The X-ray diffraction pattern confirmed the formation of the Ti-N binary and Ti-Al-N ternary phase in nanostructured multilayers coatings. Mechanical and tribological properties exhibited an improvement as a function of increase of bilayer number due to multilayer effect. Therefore, these values represented an increase in hardness (44 %, 37 %) and elastic modulus (27 %, 23 %) in relation to monolithic TiN and ternary TiAlN single layer respectively. Moreover, the mechanical results showed that there was an increase of 46 % on the H^3/Er^2 for [TiN/TiAlN]₂₄ ($\Lambda = 125$ nm) with the lowest stress, as was observed by XRD results in relation to multilayers deposited with n [TiN/TiAlN]₂ and ($\Lambda = 1.5 \mu m$).

The erosive effect and corrosive effect are smaller when multilayers are without corrosive-erosive effect, as the synergistic effect between corrosion and erosion have a bigger impact while decreasing the wear resistance of a material. [TiN/TiAlN]n multilayer coatings improves the performance for AISI 1045 steel under corrosion-erosion processes, as it was shown on Tafel curves for two different impact angles. Moreover, for a impact angle of 30°, it was found an increase of 26 % and 19 % on the corrosion potential without erosive effect for multilayer systems with n = 24 and Λ = 125 nm in relation to TiN and TiAlN single layer, respectively. Additionally, when the impact angle is 90°, it was found an increase of 21 % and 14 % on the corrosion potential for [TiN/TiAlN]₂₄ multilayer in relation to TiN and TiAlN single layer, respectively.

On the other hand, wear corrosion mechanisms, found after corrosion-erosion tests, were microcutting and micro-plow for an impact angle of 30° . Finally, as observed by SEM micrographs, generation of craters and surface cracking for impact an angle of 90° were shown to pose higher aggressive effect than wear produced for an impact angle of 30° .

The increase of bilayer number (n) and decrease of bilayer period (Λ) in the nanometric multilayer coatings allow the improving of resistance corrosion under corrosive-erosive conditions.

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