Characterization of mechanical properties and electrochemical behaviour in a Hank’s solution of 316L/Cr$_{1-x}$Al$_x$N system

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Abstract. Cr$_{1-x}$Al$_x$N hard coatings were successfully deposited by R.F. reactive magnetron co-sputtering in an Ar/N$_2$ gas mixture using chromium and aluminium targets on 316L stainless steel substrates. Crystallographic orientations associated to the Cr$_{1-x}$Al$_x$N FCC based in the conjugate complex of CrN and w-AlN phases, with ao=4.18Å lattice parameter for the ternary Cr$_{1-x}$Al$_x$N compound were identified by X-Ray diffraction. The thickness and roughness of the deposited coatings are 1.00±0.05nm and 2.65±0.6nm, respectively. The mechanical properties were determined by nanoindentation leading to a hardness of 27.8±2.6GPa and elastic modulus of 346GPa. The corrosion resistance of the coated 316L/Cr$_{1-x}$Al$_x$N system under simulated body fluid (SBF, Hank’s solution) was determined via electrochemical impedance spectroscopy. A reduction in the corrosion rate of 99% in relation to uncoated 316L stainless steel substrate was found by Tafel. Thus, these coatings seem to be excellent candidates to be used in biomedical applications.

1. Introduction

CrAlN protective coatings have been studied for decades due to their excellent mechanical, tribological and electrochemical properties. Some of the first contributions were reported by Okimiya, et al. [1] and Makino et.al. [2]. It is well established that the aluminium addition to the CrN coatings contributes to a significant increase in hardness, wear and corrosion resistance [3–6], especially for high temperature applications. The properties of the CrAlN coatings are from five to six times better than the CrN or AlN coatings deposited at the same conditions [7].

For biomedical applications, the surface properties of a device play an important role. For instance, for surgically implanted biomaterials, the important reactions take place at the interface between the materials and tissues/body fluids determine their suitability[8,9]. The most frequently used methods to improve the surface properties of a component, are based in the use of biocompatible coatings, such as DLC, ZrO2, TiAlV, TiO2, HA, among others [10]. In general, the mechanical and electrochemical properties of hard coatings such as CrAlN improve the mechanical behaviour of steels exposed to wear conditions leading to an increase in their useful life [10–12]. However, there is a lack of information in the literature about the use of CrAlN as coating materials on materials for biomedical
applications, such as of 316L stainless steel, considering that it has also lower cost compared to Ti and Ti alloys. The most determinant factor to be addressed is the electrochemical behaviour of the hard coatings when exposed to simulated body fluid (SBF) as a first biocompatibility test.

That is why the main goal of this work is to determine the functionality of these films exposed to simulated body fluids such as Hank’s solution related to the mechanical and morphological properties of the top CrAlN protective layer.

2. Experimental Procedure

AISI 316L stainless steel coupons were polished and cleaned in an ultrasonic acetone bath prior to deposition. Additionally, silicon substrates with a (111) preferential orientation were used as control samples during deposition process. Cr$_{1-x}$Al$_x$N films were deposited by R.F. (13.56MHz) magnetron sputtering on a rotating substrate holder at a constant velocity of 23rpm. Chromium and aluminium targets (99.99% of purity and 100mm of diameter) were used keeping deposition temperature constant at 250°C for 2h. Power applied to the Cr and Al targets was 200W and 350W, respectively. Other parameters were kept constant during deposition process as total pressure of 2.1 × 10$^{-2}$mbar, an Ar/N$_2$ (90/10) gas mixture with a -50V of applied bias voltage to the substrate. A schematic description of the experimental set up has been reported elsewhere [5]. To improve the bonding between the CrAlN ternary compounds to the substrate and reduce the misfit a system of two buffer layers was carried out by depositing Cr and then CrN on top (8 minutes deposition for each layer).

2.1. Films characterization

The Cr$_{1-x}$Al$_x$N samples deposited on silicon substrate were characterized by using grazing incidence X-ray diffraction (GIXRD) at angles less than 1, with a RIGAKU (Dmax2100) diffractometer and using a Cu Kα radiation (λ=1.5418Å, 30kV and 20mA), to determine the main characteristics of crystalline structure and residual stresses of the films. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis, were done in a JEOL JSM9450LB at 13kV to determine the thickness and elemental composition, respectively. Additionally, the roughness and grain size of the CrAlN top layer, an MFP-3D, Asylum Research atomic force microscope (AFM) was used. The nanohardness and reduced elastic modulus were obtained by nanoindentation, in an Ubi-Hysitron Inc. device. The tests were carried out with a diamond Berkovich tip in a variable load test. The results were evaluated by the Oliver and Pharr method [13]. Particularly the elastic modulus of the film was obtained from the reduced elastic modulus considering the elastic constants (Young modulus, E and Poisson ratio, ν) of the diamond tip (E=1070GPa and ν=0.07)[14] and the CrAlN coatings (ν=0.25) [15]. Finally, electrochemical impedance spectroscopy (EIS) and Tafel polarization curves techniques were performed at room temperature, using a 300ml cell with a working electrode of CrAlN sample and an exposed area of 1cm$^2$, an Ag/AgCl as a reference electrode, and a platinum wire counter-electrode immersed in a Hank’s solution as a simulated body fluid. From EIS measurements the Nyquist diagrams were obtained conducting frequency sweeps in the range 100kHz to 0.001Hz with a sinusoidal voltage perturbation and a signal amplitude of 10mV.

3. Results and Discussion

The electrochemical behaviour of the prepared coatings as well as their mechanical behaviour strongly depends on the chemical composition, crystalline structure as well as roughness.

3.1. Chemical composition and crystalline structure

The concentrations of Al, Cr and N were measured by EDS on the Cr$_{1-x}$Al$_x$N film and are listed in Table 1. In the film, impurities, such as carbon and oxygen, were less than 3%, and the Al content (defined as the metal ratio x=Al/(Al+Cr)) and the nitrogen-to-metal atomic ratio of nitrogen (N/(Cr+Al)), are 0.29 and 0.45, respectively. Figure 1 presents a typical cross section SEM micrograph of the Cr$_{1-x}$Al$_x$N coating, where it was observed the homogeneity of the coating with a thickness around of 1μm.
Table 1. Atomic concentration of CrAlN top layer determined by EDS.

|       | Al   | Cr   | N    |
|-------|------|------|------|
| Wt. % | 20±1 | 49±2 | 31±1 |

Figure 1. Cross section SEM micrograph of Cr\textsubscript{x}Al\textsubscript{1-x}N coating.

Figure 2 shows the X-ray diffraction patterns of Cr\textsubscript{1-x}Al\textsubscript{x}N sample at 1 grazing angle, where we can see that the films crystallized in the rocksalt structure (B1), with the preferential direction (111) perpendicular to the substrate, in accordance to JCPDF 00-003-1157 and 00-025-1495 card. Particularly, the diffraction peaks with the highest intensity observed at 38, 44, 63 and 76 correspond to both CrN and AlN of (111), (200), (220), (311) crystallographic planes [16]. An additional peak is observed at 33 that correspond to AlN (100).

The Cr\textsubscript{1-x}Al\textsubscript{x}N ternary compound is formed when the AlN phase is incorporated into the CrN FCC structure, where the Al atoms are substituting Cr atoms leading to a variation in the lattice parameter, due to its atom size[6,17]. In this sense, it is clear that the (111), (200) and (220) diffraction planes have a shoulder on the left side, which indicates the FCC-(Cr, Al)N solid-solution phase formation [5,6,16].

Figure 2. GIXRD pattern of Cr\textsubscript{1-x}Al\textsubscript{x}N sample at 1 incidence angle.

3.2. Morphological analysis by AFM

Figure 3 shows the AFM image for CrAlN coating deposited on Si substrate with a scan area of 1µm\textsuperscript{2}. The surface roughness and grain size were obtained from AFM image with 2.7±0.6nm and 41±2nm,
respectively, indicating that the deposited coating exhibits a homogeneous surface. Moreover, it is possible to evaluate the electrochemical behaviour compared with the uncoated substrate since the electrical conduction in EIS depends on the conductivity of the electrolyte and microstructural characteristics of the Cr$_{1-x}$Al$_x$N constituents including roughness, thickness, grain size, porosity, etc. Our focus is on the damage of the electrolyte to the coating depth.

![Image of Cr$_{1-x}$Al$_x$N coating surface at 1µm×1µm window.](image_url)

**Figure 3.** Image of Cr$_{1-x}$Al$_x$N coating surface at 1µm×1µm window.

### 3.3. Mechanical properties of Cr$_{1-x}$Al$_x$N films

The hardness and reduced elastic modulus measured by nanoindentation were evaluated with the Oliver and Pharr equation[13]. Figure 4 plots the applied load during the nanoindentation test as a function of penetration depth. From it, can be seen that for all tests, the maximal penetration depth does not exceed 10% total coating thickness (~1µm). For this reason, the hardness was determined as the average of the experimental points (27.8±2.6GPa). Furthermore, the reduced elastic modulus was obtained following the principle of springs in series, where a linear fit in the graph of elastic modulus as a function of contact radius/film thickness ratio, was carried out to obtain the value of reduced elastic modulus. The Young modulus of the film was obtained from the reduced elastic modulus considering the elastic constants of the diamond tip and the CrAlN coatings leading to a value of (346GPa). These hardness and elastic modulus values are in the range of those reported previously by O. M. Sanchéz et.al.[5] Under similar deposition conditions, depending on the concentration of aluminium in the Cr$_{1-x}$Al$_x$N sample.

![Graph of load-depth penetration curves obtained under variable load tests of samples coatings.](image_url)

**Figure 4.** Summary of load-depth penetration curves obtained under variable load tests of samples coatings.
Nyquist plots (imaginary impedance \( Z_{\text{imag}} \) vs real impedance \( Z_{\text{real}} \)) for uncoated 316L stainless steel and coated with Cr\(_{1-x}\)Al\(_x\)N exposed to electrochemical evaluation in presence of a Hank’s solution as a simulated body fluid, are shown in Figure 5, where an equivalent circuit modelling of EIS data is used to extract physically meaningful properties of the electrochemical system by modelling the impedance data in terms of an electrical circuit composed of ideal resistors (R), capacitors (C), and inductors (L). To test a coating via EIS, it is necessary to fit a model data.

![Nyquist plots](image)

**Figure 5.** Nyquist plots for uncoated stainless steel 316L substrate and coated with Cr\(_{1-x}\)Al\(_x\)N.

The EIS data were interpreted based on proposed equivalent electrical circuits using a suitable fitting procedure elaborated with Echem Analyst™ software. Therefore, for the equivalent circuits, \( R_{\text{soln}} \), \( R_{\text{po}} \) and \( R_{\text{corr}} \) are the ohmic resistance of the Hank’s solution, the polarization resistance of the coating/metal interface and the resistance between the solution and coating, respectively; and \( C_c \), \( C_{\text{corr}} \) represent the capacitance of the intact coating and the double layer capacitance at electrolyte/coating interface.

![Tafel polarization curves](image)

**Figure 6.** Tafel polarization curves for uncoated 316L SS and coated with Cr\(_{1-x}\)Al\(_x\)N.
On the other hand, Figure 6 shows Tafel polarization curves (corrosion potential as a function of the corrosion current density) for uncoated and coated with Cr1-xAlxN 316L stainless steel. The corrosion resistance for protective materials in the polarization curve is determined by low current densities when the electric potential is increased. Therefore, the Tafel analysis is used to determine quantitatively the corrosion potential (Ecorr), and the corrosion current density (icorr). If the polarization or charge-transfer resistance is known, it is possible to calculate the electrochemical reaction rates. The corrosion current, icorr, is related to the slope of the plot through the Stern–Geary Equation (1) [18]:

$$i_{corr} = \frac{B}{R_{po}}$$

Where: $B$ and $R_{po}$ are a constant and the polarization resistance, respectively. Thus, in addition to requiring a prior knowledge of $B$, the determination of $i_{corr}$ requires the measurement of $R_{po}$ obtained from EIS measurements. Moreover the B constant is defined by the equation (2):

$$B = \frac{\beta_a \beta_b}{2 \beta_a + \beta_b}$$

Where $\beta_a$ and $\beta_b$ are the anodic and cathodic Tafel slopes, respectively, generated by the potentiodynamic polarization curves performed at the end of the experiment. Corrosion current can be related directly to corrosion rate through the equation (3):

$$\text{Corrosion rate (mpy)} = \frac{0.131i_{corr} (E.W.)}{d}$$

Where, E.W., d and $i_{corr}$ are the equivalent weight of the corroding species (g), their densities (g/cm²) and the corrosion current density (µA/cm²), respectively. The electrochemical parameters evaluated from potentiodynamic polarization measurements for the 316L stainless steel substrate and the substrate with the system, are shown in Table 2, where the estimated $i_{corr}$ values, from the $R_{po}$ measurements using the Stern–Geary equation, are presented. As can see the values of corrosion rate are inversely proportional to the value of the polarization resistances ($R_{po}$) in the Nyquist diagrams, where 316L stainless steel substrate coated with the CrAlN is 99% more resistant to electrochemical attack than steel alone, increasing the polarization resistance of the system.

| Sample          | $R_{po}$ (Ω cm²) | Vc (mmy) |
|-----------------|-----------------|---------|
| 316L            | 3.31 x10⁻³      | 1.97    |
| 316L/CrAlN      | 9.15 x10⁻⁴      | 9.17 x10⁻³ |

4. Conclusions
Cr1-xAlxN coatings were successfully deposited by R.F. reactive magnetron co-sputtering on 316L substrates and its mechanical properties were in the range of values reported previously under similar deposition conditions on other substrates. Therefore, is possible to observe the enhancement in the corrosion resistance for 316L stainless steel coated with Cr1-xAlxN when it is exposed to simulate body fluids, particularly (Hank's solution), where the corrosion rate was reduced by 99% and the
polarization resistance increased in six orders of magnitude compared with uncoated 316L stainless steel substrate ($9.15 \times 10^4 \Omega \cdot \text{cm}^2$ coated to $3.31 \times 10^3 \Omega \cdot \text{cm}^2$ uncoated). Finally, it is important to notice that as a material to be employed in biomedical applications strongly requires exhaustive biocompatibility analysis using in-vitro tests such as MTT, genotoxicity, hemotoxicity, or even in-vivo testing. However, the current encouraging biocompatibility analysis with SBF allows us to consider Cr$_{1-x}$Al$_x$N coatings as good candidates for this purpose.

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