



Mechanical, tribological, and electrochemical behavior of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coatings deposited by r.f. reactive magnetron co-sputtering method

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ABSTRACT

Chromium aluminum nitride ($\text{Cr}_{1-x}\text{Al}_x\text{N}$) coatings were deposited onto AISI H13 steel and silicon substrates by r.f. reactive magnetron co-sputtering in (Ar/N_2) gas mixture from chromium and aluminum targets. Properties of deposited $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coatings such as compositional, structural, morphological, electrochemical, mechanical and tribological, were investigated as functions of aluminum content. X-ray diffraction patterns of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coatings with different atomic concentrations of aluminum ($0.51 < x < 0.69$) showed the presence and evolution of (1 1 1), (2 0 0), and (1 0 2) crystallographic orientations associated to the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ cubic and w-AlN phases, respectively. The rate of corrosion of the steel coated with $\text{Cr}_{1-x}\text{Al}_x\text{N}$ varied with the applied power; however, always being clearly lower when compared to the uncoated substrate. The behavior of the protective effect of the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coatings is based on the substitution of Cr for Al, when the power applied to the aluminum target increases. The mechanical properties were also sensitive to the power applied, leading to a maximum in hardness and a reduced elastic modulus of 30 and 303 GPa at 350 W and a monotonic decrease to 11 and 212 GPa at 450 W, respectively. Finally, the friction coefficient measured by pin-on disk revealed values between 0.45 and 0.70 in humid atmosphere.

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1. Introduction

For many years, binary transition metal nitride films like CrN and others have been widely used as protective and wear resistant hard coatings for cutting and forming tools, due to their superior mechanical and tribological properties [1,2]. However, in spite of their outstanding properties, binary systems are still inadequate for high-temperature applications. During operation at high temperatures (above 700 °C) [3], their mechanical properties degrade rapidly through the formation of porous oxides on film surface. To overcome these problems, different ternary nitride coating systems, such as Ti–Zr–N [4], Cr–Al–N [5], Zr–Al–N [6], and Si–Si–N [7] were developed. Among these ternary coatings, the Cr–Al–N films are probably the most promising coatings for high-temperature applications, because the addition of small

amounts of Al into the fcc structure of CrN results in the formation of a CrAlN metastable ternary solution, which exhibits improved hardness, as well as a high oxidation resistance due to the formation of complex aluminum and chromium oxides, which eventually suppress the oxygen diffusion into the bulk [8]. Sanjines et al. reported that a significant oxidation of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ occurs only at temperatures above 970 K while $\text{Cr}_{0.5}\text{Al}_{0.5}\text{N}$ remains stable up to 1170 K [9].

Different maximum hardness between 20 and 55 GPa, as well as different behaviors of oxidation resistance have been reported with the variation of Al concentration in the Cr–Al–N system [10,30]. However, by using different deposition techniques, no conclusions have been reached on the exact Al concentration in the Cr–Al–N films to obtain the maximum hardness and reduced elastic modulus, along with the best oxidation resistance and tribological properties [11,12]. For this reason, the aim of this work is to investigate the effect of aluminum concentration in the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films synthesized by r.f. reactive magnetron co-sputtering method from chromium and aluminum targets by varying the power applied to the aluminum target on the mechanical, tribological and electrochemical properties.

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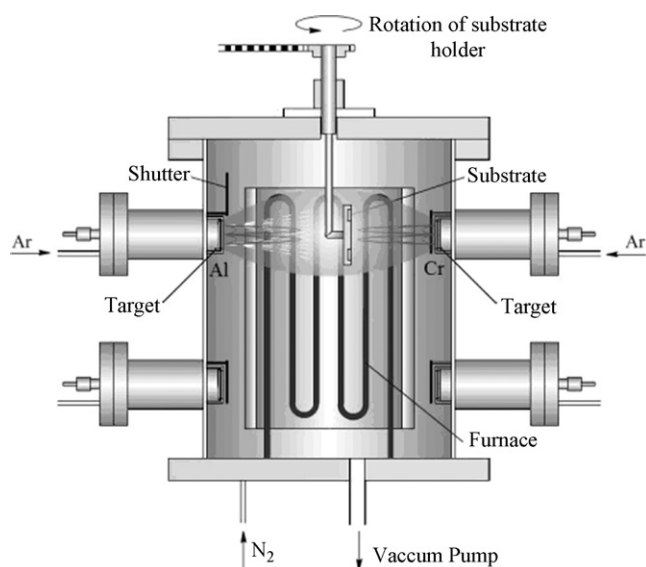


Fig. 1. Schematic diagram of the multitarget, r.f. magnetron sputtering system with horizontal magnetron sources.

2. Experimental details

Chromium aluminum nitride ($\text{Cr}_{1-x}\text{Al}_x\text{N}$) coatings were deposited onto AISI H13 steel and silicon substrates by r.f. (13.56 MHz) reactive horizontal magnetron co-sputtering method in (Ar/N_2) gas mixture, from metallic 99.99% chromium and aluminum targets (diameter: 100 mm), under circular rotation of substrate with 23 rpm in front of the targets to facilitate the formation of the stoichiometric films. The multitarget, r.f. magnetron sputtering system used in this work is shown in Fig. 1.

Prior to film deposition, the sputtering chamber was evacuated to 6.0×10^{-6} mbar and a pre-sputtering process at an Ar pressure of 2.1×10^{-2} mbar was carried out by placing a shutter between the targets and the substrate for 20 min to clean the target surface. After target cleaning, two buffer layers of Cr and CrN were deposited for 8 min to improve the adhesion of the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films to the substrate. $\text{Cr}_{1-x}\text{Al}_x\text{N}$ film deposition was performed for 2 h at a constant temperature (250 °C) and total pressure (2.1×10^{-2} mbar), in an Ar/N_2 (90/10) gas mixture and at -50 V of applied bias voltage to the substrate.

As it is well known, at low Ar^+ ion energies, the Cr sputtering yield (Y_{Cr}) is higher than that for Al (Y_{Al}), approximately $Y_{\text{Cr}}/Y_{\text{Al}} = 3$ or 2 [13]. For this reason, and in order to study the influence of the atomic concentrations of Cr and Al on the properties of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coatings, the power applied to the chromium target was kept constant at 200 W, and for the aluminum target it was systematically varied between 300 and 450 W.

The crystal structure of the films was determined by using glancing incident X-ray diffraction (GIXRD) at 2° incidence angle with a RIGAKU (Dmax2100) diffractometer using $\text{Co K}\alpha$ radiation ($\lambda = 1.78899 \text{ \AA}$, 30 kV and 16 mA). The chemical composition of deposited films was performed in a Philips XL30 ESEM with an EDAX microprobe for chemical analysis (12 kV), equipped with a window for the detection of light elements. The thickness of the films was measured by means of profilometry. The nanohardness and reduced elastic modulus were obtained from nanoindentation method, using at variable load Ubi1-Hysitron device with a diamond Berkovich tip. The results were evaluated by the Oliver and Pharr method [14] and the hardness curves as functions of penetration depth were fitted by Korsunsky's model [15]. The electrochemical study was carried out with a GAMRY Model PCI 4 unit used for DC and AC measurements, through Electrochemical

Impedance Spectroscopy (EIS) and Tafel polarization curve techniques at room temperature, using a cell (volume of 300 ml) with a working electrode of a $\text{Cr}_{1-x}\text{Al}_x\text{N}$ sample within an exposed area (1 cm^2), a reference electrode (Ag/AgCl), and a platinum wire counter-electrode under 3.5% NaCl solution with distilled water. The electrochemical behavior of the electrolyte was studied by using Electrochemical Impedance Spectroscopy (EIS) at the Open Circuit Potential for 30 min to establish stable Open Circuit Potential values at which the EIS measurements were initiated. For Nyquist diagrams, frequency sweeps were conducted in the range 100 kHz to 0.001 Hz, using sinusoidal voltage perturbation with signal amplitude of 10 mV. Diagrams for Tafel polarization curves were obtained at a sweep speed of 0.166 mV/s in voltage ranging from -0.25 to 0.75 V. On the other hand, IR compensation was applied by using the interrupted current method, and noise reduction was carried out by the GAMRY Model PCI 4 software provided. Finally, to evaluate the tribological properties of the CrAlN coatings, sliding wear tests were carried out using a MicroTest pin-on-disc tribometer. The tests were performed at a normal load of 5 N using a steel-chromium ball (100Cr6) with 6 mm in diameter as the wear counterpart. The sliding linear speed and total sliding distance were set at 0.10 m/s and 1000 m, respectively.

3. Results and discussion

3.1. Chemical composition and crystalline structure

In Table 1, the atomic concentrations of Al, Cr and N as determined by EDS on the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films are listed as functions of the discharge power applied to the aluminum target. In all films, impurities, such as carbon and oxygen, were less than 3 at.% and the Al content, defined as the metal ratio $x = \text{Al}/(\text{Al} + \text{Cr})$, increased monotonically from 0.51 to 0.69 with increasing Al target power; whereas, the nitrogen-to-metal atomic ratio of $\text{N}/(\text{Cr} + \text{Al})$ maintained an average value of 0.79 (from 0.78 to 0.80).

Fig. 2a illustrates the GIXRD patterns at 2° incidence angle for $\text{Cr}_{1-x}\text{Al}_x\text{N}$ ($0.51 \leq x \leq 0.69$) films. For films with Al content under 69 at.%, the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films exhibit a B1 cubic fcc structure, which is similar to the pure CrN, with (1 1 1) preferential orientation. For an AlN-rich composition ($x = 0.69$), we can observe the B4 Wurtzite-type crystal structure, which coexists with the B1-type crystal structure. As reported by Lin et al. [11], the coexistence of cubic and hexagonal phases in $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films is observed when the Al concentration in the film is at or beyond $x = 0.64$. When the Al at.% increases, the Al atoms are incorporated into the cubic CrN lattice, and then substitute the Cr lattice sites to form $\text{Cr}_{1-x}\text{Al}_x\text{N}$ ternary phase. If the Al content in the film is beyond the maximum solid solution concentration, the phase transformation to hexagonal structure will occur. In addition, it is clearly seen that at all Al contents, the (1 1 1) peak has a shoulder on the right side of the peak, as it can also be seen near the (2 0 0) peak at $x = 0.51$ and 0.54 (Fig. 2a), which indicates that phase segregation occurred [16].

The lattice parameters of the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ were calculated from the peak positions of (1 1 1) and (2 0 0) for B1-type structure coatings according to X-ray diffraction profiles by whole pattern

Table 1

Relative ratios of $x = \text{Al}/(\text{Al} + \text{Cr})$ and $\text{N}/(\text{Al} + \text{Cr})$ atomic percent in the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films as functions of the discharge power applied to the Al target.

Discharge power of Al target (W)	Chemical composition (at.%)	$x = \text{Al}/(\text{Al} + \text{Cr})$	$\text{N}/(\text{Al} + \text{Cr})$
300	27Cr–27Al–43N	0.51	0.80
350	25Cr–29Al–44N	0.54	0.80
400	20Cr–35Al–43N	0.63	0.78
450	17Cr–38Al–43N	0.69	0.79

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