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Influence of bias voltage on properties of AlCrN coatings prepared by cathodic arc deposition

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ABSTRACT

AlCrN coatings were prepared by vacuum cathodic arc deposition. This low-temperature technique has been chosen due to its versatility, allowing the industrial up-scaling.

In this study, the attention was focused on the correlation of the bias voltage with the resulting mechanical–tribological properties. For this purpose, the bias voltage was varied from 0 to −150 V. Indeed, the variation of grain sizes from 24 to 16 nm as well as the residual stresses from −0.68 to −8.94 GPa lead to obtain different mechanical–tribological properties. In this context, the sample deposited at −100 V exhibited an enhanced hardness (50 ± 2 GPa) and an acceptable wear resistance.

1. Introduction

The vacuum cathodic arc deposition (CAD) processes have been extensively employed in industrial scale manufacture of protective coatings for cutting tools, metal forging and casting dies [1,2].

In recent years, the application of AlCrN-type coatings in the industrial metal forming has increased since a major productivity is expected. In this context, the reason for the success of this type of coating is mainly due to its high hardness, good thermal stability, low thermal conductivity as well as its oxidation resistance, if compared with aluminum-free coatings such as TiN or CrN [3–6].

The cutting edge of coated tools may exceed 1000 °C, therefore the oxidation resistance is a very important matter [7]. The oxidation resistance, high temperature mechanical properties and wear resistance of AlCrN are improved compared with other ternary nitrides such as AlTiN [8–10]. Willmann et al. [11] showed that AlCrN coatings exhibit good thermal stability at 900 °C in inert atmospheres (N, Ar), as well as in air over 900 °C imputed to the formation of complex oxides $(Cr,Al)_2O_3$. These oxides reduce the thermo-chemical phenomena involved in machining, such as the oxygen diffusion into the bulk. This phenomenon allows to increase the tools lifetime [12].

In addition, the AlCrN coatings present good tribological properties up to 500 °C, as low friction coefficient which is generally found at high temperatures [13].

In the present work, AlCrN coatings produced by CAD at different bias voltage values were submitted to a physico-chemical analysis, as well as room-temperature mechanical and tribological characterizations. The principal aim of this paper is to contribute to the actual knowledge about AlCrN coatings, especially in terms of the bias voltage influence on mechanical properties.

2. Experimental details

For the production of the different coatings, a reactor IMD 700 Plassys system equipped with four random arc BMI sources (100 mm in diameter) and with a threefold rotating substrate holder was used [14,15]. Target composition was Al/Cr (60:40 at.%). The schematic illustration of the device is represented in Fig. 1.

Coatings were deposited on AISI M2 HSS (63 HRc- $\Phi = 30$ mm.). Substrates were degreased in alcohol prior deposition.

Argon ion etching was performed at 0.3 Pa in pure argon (bias ≈ − 800 V) during 30 min prior to a metal etching (chromium) performed in pure Ar at 1 Pa (bias ≈ − 600 V) for 10 min. Finally, the coatings were deposited in pure nitrogen atmosphere, keeping the chamber pressure ≈ 3.5 Pa, varying the bias voltage (step 50 V- MDX 10 KW, Advance Energy) from 0 (without bias – labeled as "floating" in this study) to - 150 V. The experimental conditions are summarized in Table 1.

The surface morphology was observed by means of scanning electron microscopy (SEM) (JEOL 5800 V) on coated-M2 HSS substrates. Samples were submitted to X-ray diffraction (XRD, Bruker D8 Focus in a θ-2θ mode) using the $CoK_{\alpha 1}$ radiation ($\lambda = 1.788970$ Å). Furthermore, the

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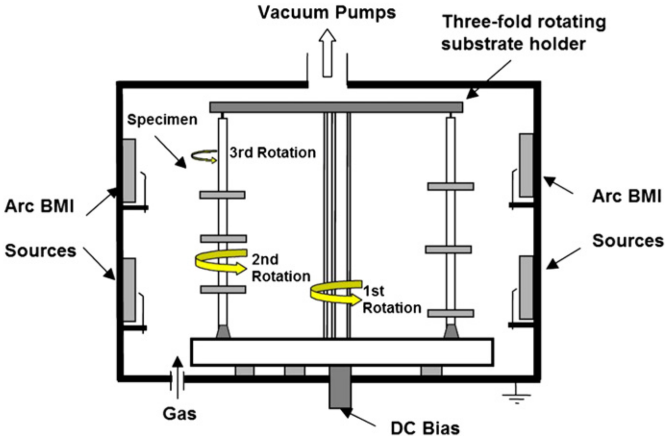

Fig. 1. Schematic illustration of the vacuum cathodic arc evaporation system [2].

composition of coatings was measured by means of SEM in the energy-dispersive X-ray spectroscopy (EDS) mode.

Hardness and the effective Young's modulus $E^* = E/(1\text{-}\nu^2)$ — where E and ν are the Young's modulus and Poisson ratio — of coatings were measured by means of a nanohardness tester (NHT CSM Instruments) using a *Berkovich* diamond tip from loading/unloading curves. Values were calculated using the Oliver and Pharr method [16] and correspond to an average of 40 indentations with imposed penetration depths shallower than 10% of the coatings' thickness according to the Bückle's rule [17]. Young's modulus values thus obtained could be overestimated because of the substrate influence on thin film elastic response for relative indentation depth above 1–2% of coating thickness [18].

Residual stress was determined using a bending method. Curvature of steel foils was measured by optical profilometry (ALTISURF 500) and the stress level was deduced from the Stoney Equation [19].

Ball-on-disc tests were performed by using a CSM tribometer. WC/Co balls of 6 mm in diameter were employed. All the tribological tests were made under the following conditions in air: a constant load of 10 N, a wear track nominal diameter of 10 mm, a sliding velocity of 100 mm s^{-1}, a sliding distance of 600 m, a relative humidity between 33 and 39 %RH and a temperature range of 19–22 °C.

The same profilometer was employed in order to quantify the wear after ball-on-disc tests at four different areas. The resolution is 10 nm on the height measurements (z-height), while its spatial resolution is 0.5 μm (x direction). In the present study, the scanning speed was fixed at 15 μm s^{-1}.

3. Results

3.1. Structure and composition analysis

The composition of the different coatings — determined by means of EDS — and the deposition rates are given in Table 2.

Table 1
Deposition parameters.

Targets composition	$Al_{60}Cr_{40}$
Targets current	≈100 A
Targets voltage	≈20 V
Nitrogen pressure	3.5 Pa
Substrates	M2 HSS
Bias voltage range	Floating → −150 V
Holder rotation	4 rpm
Deposition time	90 min
Deposition temperature	≈220 °C

Table 2
Stoichiometry, deposition rate and residual stress of the coatings at different bias voltage values.

Bias [V]	Stoichiometry	Deposition rate [μm/h]	Residual stress [GPa]
Floating	$Al_{0.44}Cr_{0.56}N$	3.12	−0.68
−50	$Al_{0.45}Cr_{0.55}N$	2.58	−5.06
−100	$Al_{0.46}Cr_{0.54}N$	2.24	−8.94
−150	$Al_{0.47}Cr_{0.53}N$	1.92	−8.14

No significant differences in terms of stoichiometry were observed. The obtained stoichiometric ratios are close to the commercially-available products [5]. The nitrogen content was not reported, since it is well known that EDS presents some limitations when light elements are measured. On the contrary, the deposition rate decreased as a function of the bias voltage from 3.12 to 1.92 μm/h from the floating condition up to −150 V.

This phenomenon is ascribed to the re-sputtering due to the higher collision ions' energy thus producing denser coatings [20].

In Fig. 2, the XRD diffraction patterns are presented. As expected, the crystalline microstructure matches with the NaCl-B1 type structure (FCC) of aluminum nitride and chromium nitride (JCPDS card # 00-046-1200 and # 01-070-2942). Initially, the preferential orientation corresponds to (2 0 0) and the ratio between (2 0 0) and (1 1 1) varies as a function of the bias voltage. This phenomenon could be related to the increase of the intrinsic residual stresses — when the bias voltage is increased — which may directly affect the texture. This fact was observed by Ahlgren et al. for TiAlN systems when bias voltage is increased [21].

From the different XRD patterns, the grain size was calculated by applying the *Scherrer's method* [22]. This method is based on a rough estimation of the crystallite size, since the fitting method used to determine the full width at half maximum of the diffraction peaks cannot take correctly into account the shape resulting of crystallite size distribution.

This estimation also considers the absence of strain broadening in the diffraction peaks, which could lead to underestimate the crystallite size. Furthermore, lattice parameters were calculated from the average peak positions of (1 1 1) for B1-type structure according to the Bragg's law.

The comparison between the lattice parameter-grain size at different bias voltage is presented in Fig. 3.

Grain size decreases rapidly from about 24 to 16 nm when bias voltage varies between floating potential and −100 V. Then, it remains stable up to −150 V. The same phenomenon was noted by Gautier et al. [23] for CrN coatings prepared by means of vacuum CAD.

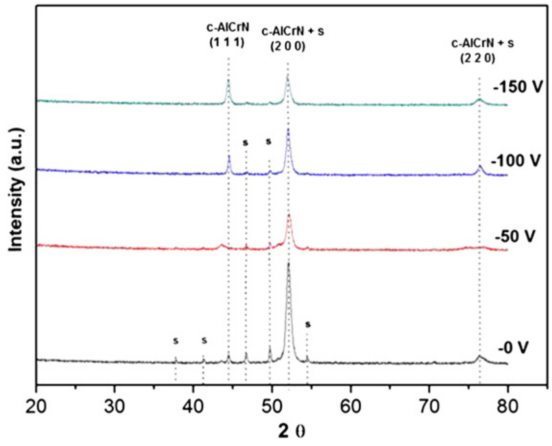

Fig. 2. XRD patterns of the different samples ("s" index substrate peaks).