INFLUENCE OF DEPOSITION CONDITIONS ON MICROSTRUCTURE AND TEXTURE OF TI$_{1-X}$AL$_X$N PVD COATINGS

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Abstract

This study is focused on how the application of pulsed substrate bias during cathodic arc deposition affects the microstructure, texture, grain size and phase composition of (Ti,Al)N coatings. A series of $Ti_{x-1}Al_xN$, $0.25 \leq x \leq 0.55$ coatings were deposited on WC-Co cemented carbide substrates with -30 V, -60 V and -300 V pulsing bias (duty cycle 10 % and a frequence of 1 kHz) under controlled chamber conditions at 4.5 Pa N_2-gas and a substrate temperature about 400 °C. The pulsing parameters for the bias (voltage, duty cycle and frequency) were deliberately selected to influence structure, microstructure and composition of the deposited coatings. All $Ti_{x-1}Al_xN$ coatings had a consistent columnar cubic B1 structure regardless of their chemical composition. Coatings grown at -30 V and -60 V pulsed bias exhibited a pronounced <111> texture attributed to a kinetically driven mechanism influenced by the relative flux of ion species, affecting the surface migration of adatoms during growth. In contrast, the coatings grown with a pulsed bias of -300 V exhibited a reduced <111> texture and the onset of grains with <100> preferred orientation. The transition to the <100> orientation with increased ion energy agrees with the fact that the <111> directions expose the densest array of atoms to the ion beam during growth while the <100> are the most open channeling directions in a B1 structure. The correlation to the preferred with respect to pulsing conditions during growth, correlated to microstructure, grain size and phase composition be further discussed. Surface roughness was highest ($S_a \approx 0.17\text{-}0.22$ μm) for coating deposited at pulsed bias -30 V.

Keywords: Pulsed bias, $Ti_{x-1}Al_xN$ coatings, structure, texture, roughness.

1. INTRODUCTION

In the last decades cathodic arc deposition, or arc ion plating, has maintained its prominence in the industrial application of TiAlN coatings due to its merits like high deposition rates, strong adhesion, and compatibility with a broad range of partial pressures [1,2]. Nonetheless, the properties of these deposited coatings are notably influenced by factors like microstructure, defect structure, and defect density [2-4]. The process of cathodic arc deposition typically leads to an occurrence of crystallographic defects, vacancies, interstitials, and dislocations. This increased defect density is attributed to the substantial energy imparted by metal ions during the coating's growth [3-5]. This is particularly pronounced in TiN-based coatings created under direct current (DC) mode through Physical Vapor Deposition (PVD), and often resulted in compressive residual stresses. These structural features consequently influence the coatings' overall properties and performance [4,5].

Cathodic arc deposition involves the application of high bombardment energies and ionization ratios [7]. In this context, adjusting the substrate bias voltage has proven to be a robust strategy for governing ion energies. This control subsequently influences factors like composition, growth dynamics, microstructure, morphology, defect formation, and stress generation in the coatings [3,8,9]. Another strategy for regulating coating growth

involves the periodic pulsing of the substrate bias. This technique modifies the extent of metal and gaseous ion implantation. This modification occurs because ions experience acceleration during the pulse-on interval, while the plasma exists also during the pulse-off phase [10]. The advantage of pulsing the substrate bias lies in its capacity to fine-tune additional parameters such as peak voltage, frequency, pulse duty cycle ratio, and arc current. These adjustments enable precise manipulation of the coatings' microstructure and properties.

While prior investigations have explored the impact of pulsed substrate bias in cathodic-arc-deposited TiAlN coatings, a substantial portion of these studies have primarily focused on pulse frequencies, high negative bias voltages (>300 V) [5, 8]. To understand how the coating's microstructure and defects are influenced by variations in duty cycle during pulsed substrate bias cathodic arc deposition, in-depth insights into the microstructural alterations is needed. This study is focused on how the application of pulsed substrate bias during cathodic arc deposition affects the microstructure, texture, grain size and phase composition of (Ti,Al)N coatings. Our investigation involves depositing $Ti_{x-1}Al_xN$, $0.25 \leq x \leq 0.55$ coatings onto polished cemented carbide substrates. The experiments maintain a constant N_2 pressure, uniform frequency, while systematically varying pulsed bias voltage. Subsequently, microstructural changes will be analyzed using X-ray diffraction, electron microscopy, and profilometry.

2.   MATERIAL AND METHODS

Cemented carbide (WC-Co) $12.7 \times 12.7 \times 4.5$ mm³ plates platelets [Seco Tools "HX", chemical composition (wt. %) WC 93.5-Co 6-(Ta,Nb) C 0.5] with a hardness of 1635 HV10 were used as substrates. The average WC grain size was ≈1 μm. The substrates were ground on diamond disks and polished using diamond slurry. As final pretreatment, the substrates were degreased in an ultrasonic cleaning line. All substrates were deposited in a customized Oerlikon Balzers Metaplas MZR323 industrial reactive cathodic arc evaporation system. The system was equipped with two 100 mm diameter $Ti_{0.75}Al_{0.25}$ (Evaporator A) and $Ti_{0.45}Al_{0.55}$ (Evaporator B) cathodes. Two series of the sample were located in the center of evaporators (Line 1 and Line 3) and the third series - in the middle between previous two lines (Line 2), in order to vary the Ti/Al ratio of the coatings. During deposition, the residual base pressure was below 10^{-4} Pa. Prior to nitride deposition, the substrates were Ar-etched for about 30 min. The nitride layers were then grown in pure N_2 gas at a pressure of 4,5 Pa and a substrate temperature of about 400 °C. The pulsed substrate bias voltage was varied as follows: -30 V, -60 V and -300 V, while the duty cycle was kept 10%, frequency of 1 kHz. The films were grown to a thickness of about 3-4 μm.

Phase-structural x-ray diffraction studies were carried out on a Bruker D8 Discover instrument using Cu Kα radiation and symmetric θ-2θ set-up (Bragg-Brentano). The measurements were carried out in the range of angles 2θ = (30 - 66)°. Scanning step was 0.05°. The average coherent domain size of TiAlN was evaluated by Scherrer's formula. Scanning electron microscope (SEM) Jeol JSM-7900F equipped with Oxford Instruments X-MaxN EDX detector operated between 2 and 20 kV was used to study morphology and microstructure of deposited coatings and chemical analysis. Cross-sectional sample preparation for SEM consisted of mechanical cutting, and as a final pre-treatment, the coatings were cleaned before analysis. The surface morphologies and roughness of surfaces were characterized using 3D surface imaging which were quantified using parameter S_a values through optical profilometry (Contour GT-K, Bruker).

3.   RESULTS AND DISCUSSION

According to EDX results (**Table 1**), as expected, the aluminium content increases with its increase in the cathodes. The average atomic compositions of the as-deposited $Ti_{1-x}Al_xN$ coatings at different heights in the chamber were determined to be $Ti_{0.75}Al_{0.25}N$, $Ti_{0.5}Al_{0.5}N$, and $Ti_{0.45}Al_{0.55}N$ for the Line 1, Line 2 and Line 3, respectively. The presence of oxygen (~2-3 at. %) in the coatings obtained under the action of the pulsed potential may be the result of the occurrence of pores and defects. The increasing of pulsed bias does not change the Al/(Ti+Al) ratio.

Table 1 Characteristics of $Ti_{x-1}Al_xN$ coatings

Pulsed bias (V)	Position of sample	Al/(Al+Ti)	S_a, µm	Grain size (nm)	$I_{(111)}/(I_{(111)}+I_{(200)})$	$2\theta_{(111)}$ (deg)
-30	Line 1	0.25	0.165	25.4	0.58	37.24
	Line 2	0.50	0.194	25.4	0.73	37.54
	Line3	0.55	0.22	22.7	0.73	37.64
-60	Line 1	0.25	0.158	22.7	0.45	37.19
	Line 2	0.48	0.142	24.7	0.52	37.54
	Line3	0.53	0.144	32.3	0.60	37.65
-300	Line 1	0.26	0.148	20.4	0.41	37.04
	Line 2	0.49	0.132	24.0	0.37	37.40
	Line3	0.56	0.168	24.7	0.41	37.50
Table value $I_{(111)}/(I_{(111)}+I_{(200)})$ (PDF 00-038-1420)					0.41	36.66

Analysis of SEM images (**Figure 1 a, b, c**) shows the presence of droplets and defects related to the droplets (voids, overcoated particles, pin-holes, cone-like defects). With an increase in pulsed bias, a change in the shape of grains from acicular to globular was observed (**Figure 1 a, b**). At the same time a rough surface and a columnar structure of the coating $Ti_{1-x}Al_xN$ can be seen in **Figure 1 c**. The surface had a high roughness (due to the fact that the columnar grains themselves reach the surface of the coating, creating such a relief) (**Table 1**).In most cases the columns observed consisted of one single grain. The rough surfaces is caused by facetted column tops, and open column boundaries [10]. The open and porous structure (**Figure 1 c**) with narrow columns also forms when ad-atoms to the growing film have low energy which limits diffusion [10].

The X-ray diffractograms of $Ti_{0.75}Al_{0.25}N$, $Ti_{0.5}Al_{0.5}N$, and $Ti_{0.45}Al_{0.55}N$ coatings manufactured with -30 V, -60 V and -300 V pulsing are presented in **Figure 2 a-c**. The analysis showed that all coatings had the typical cubic B1 structure (NaCl-structure). The XRD peaks at ~37°, ~43° and ~62° correspond to the c-(Ti,Al)N (111), (200) and (220) diffraction peaks, respectively. The rest of the peaks matched the WC-Co substrate. The observed shift in diffraction peaks towards higher angles (**Table 1**) with increasing aluminum content aligns with studies, where this shift was attributed to a reduction in lattice parameter due to the substitution of Ti atoms with Al in the cubic solid solution [11]. Al has a smaller atomic size than Ti, which decrease the lattice parameter of the $Ti_{x-1}Al_xN$ crystal, and the interplanar spacing (d). It means that such shifting of reflects related to residual stresses in the coatings, difference in atomic radius and defects, which are produced during deposition in the pulsing mode. Additionally, variations in pulsing mode values led to changes in peak heights. From Scherrer's formula, the average crystal size is ~20…25 nm (**Table 1**).
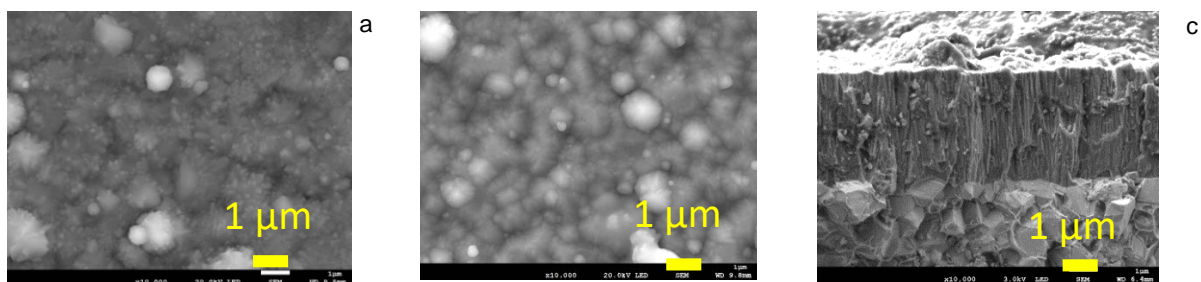
Figure 1 SEM images of $Ti_{0.75}Al_{0.25}N$ coating (pulsing -30 V, Line 1) surface (a) and (pulsing -300 V, Line 1) surface (b), cross sectional (c)

According to XRD results pulsed bias does not influence the phase composition of the $Ti_{1-x}Al_xN$ coatings for any composition, but it does influence the structural state and change the preferred orientation of crystallites

in the coatings. Increasing the pulse bias to -300 V the intensity of peaks became lower compare with coatings deposited at -30 V and - 60 V (**Table 1**). There is also a change in texture in these coatings.
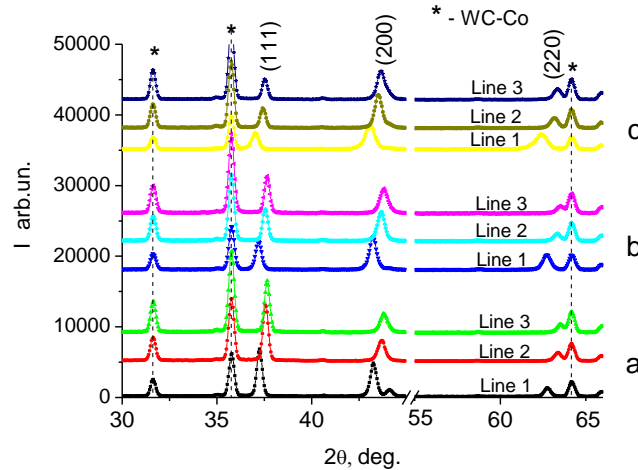

Figure 2 X-ray diffractograms of the $Ti_{0.75}Al_{0.25}N$ (a), $Ti_{0.5}Al_{0.5}N$ (b), and $Ti_{0.45}Al_{0.55}N$(c) coatings deposited at -30 V, -60 V and -300 V (duty cycle 10%, frequency of 1 kHz)

The importance of texture development in transition metal nitrides (TM nitrides) is great. The evolution of texture in TiN thin films has been explained in terms of thermodynamics and kinetics. Several authors [12-14] have proposed that the transition from (001) to (111) orientation arises from a drive to minimize the overall free energy per surface film area (U_{tot}). In this thermodynamic approach, total energy can be expressed as the sum of surface energy ($U_{s,hkl}$), elastic strain energy density ($U_{el,hkl}$), and stopping energy (E_{hkl}) of the film (**Equation 1**). $U_{tot} = U_{s,hkl} + U_{el,hkl} * h + E_{hkl}$, where h - the film thickness.

Indeed, both terms ($U_{,hkl}$ and $U_{el,hkl}$) demonstrate directional properties that vary with orientation. The E_{hkl}, quantifies the energy deposited per unit surface area of ions along a specific crystalline direction, and it arises from ion channeling effects [15]. In face-centered cubic (fcc) metals, the <110> direction is the most favorable for channeling [16]. However, in the case of TiN, the <001> direction is the most accessible, while the <111> direction appears to be the orientation that is controlled by the growth process [17]. The <001> direction allows impinging ions to distribute their energy over larger volumes, resulting in less distortion of lattice planes. This increases the likelihood of their survival. Consequently, under high energy influence, a (002) or (220) texture would be anticipated, depending on the angle of incidence of the incoming ions. The surface energy of TiN is lowest for a (001) surface [12], implying that a (001) growth texture should initially form. Pelleg et al. [12] and later Oh and Je [13] argued that as film thickness increases, the texture will transition from (001) to (111) to minimize the strain energy term, attributing the change to the lower elastic modulus along the [111] direction Y_{111} compared to Y_{002}. However, if thermodynamics was the primary driving force, then a (111) texture should prevail in all thick films, which is not observed.

It appears that kinetics-driven forces are the likely explanation for the microstructure and texture development in TiN thin films. In instances of low and low ion irradiation (i.e. temperature) during deposition at low pulsing bias (-30 V), a competitive columnar growth pattern is observed in the present investigation and has been reported in [18]. At lower film thicknesses (≤1 μm), both (002) and (111) grains are present. As thickness increases, the (111) columns, which have the fastest growing direction, begin to overlap the (002) ones. This phenomenon is sometimes referred to as the "evolutionary selection rule" [19].

However, this is not always true for TiAlN as its elastic properties are significantly dependent on the Al content [1]. Recent studies have shown the role of kinetic mechanisms during growth, involving anisotropies in ad-

atom mobility, surface diffusivities, and effects from collisional cascades, in texture development [10, 20]. These mechanisms are directly impacted by deposition parameters like ion flux and ion energies, exerting crucial influence over the final coating microstructure [10, 12, 21]. Given the variation in duty cycle, both kinetic and thermodynamic aspects must be considered in formation of the texture. The pronounced (111) texture exhibited by coatings deposited at -30 V (duty cycle 10%) and the broader (111) texture at -60 V (duty cycle 10%) can be attributed to a kinetically driven process influenced by the relative flux of ion species, which in turn affects the surface migration of ad-atoms during growth [22]. This combination of low duty cycle and low substrate bias results in a growth condition characterized by low average ion energy. These conditions restrict ad-atom mobility, favoring the growth of close-packed surfaces, in the (111) orientation [22].

Raising the pulse bias to -300 V (duty cycle 10 %) led to a mixture of (111) and (200) textures. This could be attributed to a mixed surface and strain energy effects. With higher pulse bias values, increased ion bombardment and localized atomic-scale heating enhance the mobility of ad-atoms during growth [12]. Consequently, at higher pulse bias, the high-energy flux provides sufficient energy to reduce the deposition rate (via resputtering) and facilitates surface diffusion. This leads to a decrease in the average roughness of coatings obtained at -300 V (**Figure 1 c**). In the deposition process of PVD coatings with pulse bias, distinct stages arise: layers are deposited during pulse absence, with low-energy ion bombardment, and during pulse application, high-energy ions cause thermal peaks, partially relieving implantation stresses. In coatings subjected to a pulse bias of up to -300 V, the [200] line intensity increases, while the persistence of the [111] line suggests its formation independent of pulses [23].

4.   CONCLUSION

- In the studied conditions (pulsing bias -30 V, -60 V, -300 V, duty cycle 10 % and a frequency of 1 kHz) the deposited $Ti_{x-1}Al_xN$ (0.25≤x≤0.55) coatings have a FCC crystal lattice (type B1 NaCl). Using of pulsed bias do not affect chemical composition of the coating on different positions in the chamber.

- In all coatings, the dense columnar structure was observed. The columns nucleated at the substrate extended to the surface. There are evidence of pores in the coatings, especially in the coatings manufactured at -30 V pulsing. Increasing the pulse voltage up to -300 V creates a positive effect on the densification of column boundaries.

- An increase in pulse voltage resulted in a change from [111] to [100] texture, which can be a result due to kinetic factors (at higher values of pulsed bias, enhanced ion bombardment and localized heating at the atomic level increase the mobility of ad atoms during growth).

- Applying of high pulse bias (-300 V) leads to decrease of surface roughness to S_a~0.12…0.17 µm. This fact could improve tribology and mechanical characteristics of PVD $Ti_{x-1}Al_xN$ coatings.

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