

# Structural and Morphological Properties of Titanium Aluminum Nitride Coatings Produced by Triode Magnetron Sputtering

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## Abstract

$Ti_xAl_{1-x}N$  coatings were grown using the triode magnetron sputtering technique varying the bias voltage between -40 V and -150V. The influence of bias voltage on structural and morphological properties was analyzed by means of energy dispersive spectroscopy, x-ray diffraction and atomic force microscopy techniques. As the bias voltage increased, an increase in the Al atomic percentage was observed competing with Ti and producing structural changes. At low Al concentrations, the film presented a FCC crystalline structure; nevertheless, as Al was increased, the structure presented a mix of FCC and HCP phases. On the other hand, an increase in bias voltage produced a decrease films thickness due to an increase in collisions. Moreover, the grain size and roughness were also strongly influenced by bias voltage.

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**Key words:** TiAlN; bias voltage; sputtering; Atomic percentage; XRD.

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## Propiedades morfológicas y estructurales de recubrimientos nitruro de titanio aluminio producidos por *magnetron sputtering triodo*

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### Resumen

Se crecieron recubrimientos de  $Ti_xAl_{1-x}N$  empleando la técnica de magnetron sputtering triodo, variando el voltaje de polarización entre -40 V y -150V. Por medio de espectroscopía de energía dispersiva, difracción de rayos x y microscopía de fuerza atómica, se analizó la influencia del voltaje de polarización sobre las propiedades morfológicas y estructurales de los recubrimientos. A medida que el voltaje bias se incrementó, se observó un aumento en el porcentaje atómico de Al, compitiendo con la concentración de Ti y produciendo cambios estructurales. A bajas concentraciones de Al, la película exhibió una estructura cristalina FCC; sin embargo, a medida que le porcentaje de Al disminuyó, se pudo detectar una mezcla de fases FCC y HCP. Por otro lado, el incremento en el voltaje de polarización produjo una disminución en el espesor de las películas, debido al aumento en el número de colisiones. Además, el tamaño de grano y la rugosidad se vieron fuertemente afectados por el voltaje bias.

**Palabras clave:** TiAlN; voltaje de polarización; sputtering; porcentaje atómico; XRD.

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## 1 Introduction

Currently, hard coatings for wear reduction of cutting tools, like TiN, TiCN and TiAlN are well established. The consequence of increasing productivity and product quality requirements is the need of improving the performance of coatings using in tools [1]. Regarding to TiAlN, recent improvements in the life of cutting tools have been achieved by the development of titanium aluminum nitride (Ti,Al)N coatings [2]. Films such as TiAlN display a unique combination of properties as high hardness at elevated temperature together with thermal and chemical stability, as well as low thermal conductivity [3],[4],[5]. Moreover, these materials have been considered for bio-implants [6]. Several methods have been used for growing TiAlN not only as monolayer but also as multilayers coatings, such as multi-arc physical vapor deposition [7], pulsed laser deposition [8], ion plating [9], among others.

Magnetron sputtering is a very useful method for producing different type of coatings including TiAlN. Nevertheless, in order to improve the coatings process efficiency, several modifications have been carried out to this technique. One of the sputtering technique improvements is triode magnetron sputtering (TMS). Compared to diode magnetron sputtering, it offers an enhancement in the ionization rate by introducing a polarized grid in front of the target. Fontana et al. [10], reported TiN produced by this technique. They found that higher homogeneity results from greater electron collection by the grid. Besides, denser films at lower substrate temperature and compact film structure at temperatures of around 300°C among other characteristics were observed. As is known, deposition parameters influence the coating characteristics; for instance, the effect of substrate temperature [11], gases flow rate [12], substrate rotation in a PVD system [13], and bias voltage [14], among others on the coatings has been analyzed. The bias voltage during the coatings growth is a strongly influential parameter controlling the energy of the impacting ions [15]. Ahlgren and Blomqvist [16], studied TiAlN coatings deposited by arc evaporation with approximately 3  $\mu\text{m}$ , varying the negative substrate bias, which was changed from -40V to -200 V and producing a strong influence on the crystallographic texture. Petrov et al. [17], reported that the energy of the impinging ions influenced the predominant orientation of TiN and TiAlN coatings. Results showed that increasing ion energy, the texture changes from (111) to (200); moreover, the bombardment causes continuous re-nucleation due to disturbance of the local epitaxial growth.

Ljungcrantz et al. [18], reported the influence of the bias voltage on the residual stresses. At low bias voltages from 0V to -100 V, the residual compressive stress increased due to an increase in the density of defects. At bias voltages greater than -150 V, the ion bombardment induced mobility of atoms being this the predominant effect during the growth process. This effect causes a decrease in the residual stress because of an annihilation of defects enhanced. Sato et al. [19], reported that as the bias voltage increased, the Al concentration in TiAlN coatings decreased, whereas the residual compressive stress and hardness increased up to -100 V, and decreased for higher bias voltages. Similar results were also published by other authors [20],[21]. In spite of the quantity of works reported about TiAlN coatings, a depth analysis of the relationship between structure and

morphology with the bias voltage during the production process employing modern systems as triode magnetron sputtering is required.

The aim of the present work was to deposit TiAlN coatings by triode magnetron sputtering in order to investigate the effect of the bias voltage on the Ti-Al-N coating system. We focused here on the relation between structure, chemical composition and morphology at room temperature.

## 2 Experimental setup

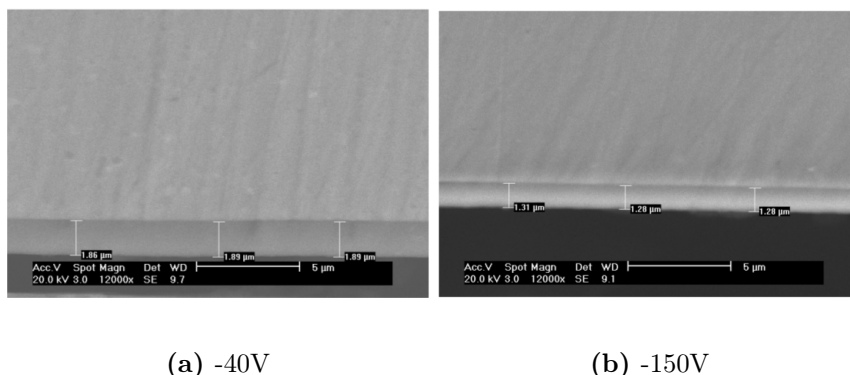
TiAlN coatings were deposited on AISI O1 tool steel substrates using a target of  $\text{Ti}_{0.5}\text{Al}_{0.5}$  by triode magnetron sputtering (TMS) technique in a non-commercial system [22],[23]. A continuous gas flow of argon and nitrogen ( $\text{Ar}+\text{N}_2$ ) were injected into the chamber for the coatings production. The most suitable  $\text{N}_2$  flow (5 sccm) was obtained carrying out an experimental hysteresis curve of pressure (Pa) depending on the flow (sccm) and remaining the argon flow constant at 20 sccm. At this value, the target poisoning (material deposition on the target) was avoided, increasing the sputter yield and then, the films deposition. A vacuum pressure of  $2.67 \times 10^{-4}$  Pa was reached, and then, a working pressure of 0.4 Pa was employed. The films were grown during 60 min, with a current of 2 A, with bias voltages of  $-40\text{V}$ ,  $-70\text{V}$ ,  $-100\text{V}$  and  $-150\text{V}$ . The thickness was measured by scanning electron microscope (SEM) and elemental analysis was carried out employing energy dispersive spectrometry (EDS) with Philips XL 30 FEG equipment. For X-ray diffraction characterization, a D8 Bruker AXS Diffractometer was used. It is composed by an X-ray source of  $\text{Cu K}\alpha$ , with  $\lambda = 15.406$  nm and a secondary monochromator of graphite. The diffraction patterns were taken under parallel beams with a grazing incidence of  $2^\circ$  and a  $2\theta$  scanning range between  $30^\circ$  and  $80^\circ$ . The surface morphology was measured by using a scanning probe microscopy (SPM) in the atomic force microscopy (AFM) mode. Hardness and Young's modulus were determined by nanoindentation in a Triboscope Hysitron nanoindenter coupled with a Shimadzu SPM 9500 J3 AFM.

### 3 Results and analysis

The elemental concentration of TiAlN coatings as a function of the bias voltage ( $V_S$ ) is shown in Table 1. According to the reports, the elemental concentration in TiAlN coatings has a strong influence on several properties as the oxidation resistance, hardness and wear resistance [24]. Nitrogen percentage did not present significant changes as  $V_S$  was increased, while aluminum increased from 24.2% to 40.9%, contrary to the titanium percentage that decreased from 71,9% to 52,5%. These concentrations are similar to those reported by Wuhrer and Yeung [25]. They showed that Ti percentage decreases as  $V_S$  increases, presenting a competition between Ti and Al. As  $V_S$  increases, the Al concentration also increases because of its lower molar weight than titanium (26.98 g/mol for Al and 47.9 g/mol for Ti) facilitating the mobility of Al atoms and incorporating a greater quantity of atoms on the surface. The high mobility of adatoms could promote the formation of Ti-Al bonds. It entails to the solubility limit of Al atoms in the lattice of the salt-NaCl type structure [15]. Results presented by Mayrhofer [26], indicate that the FCC phase stability is determined by the number of Ti-Al bonds that depends on the ionization induced by the increase in  $V_S$ .

According to the analyses carried out by Paldey and Deevi, [27], the ionization degree of Ti and Al are 80% and 50%, respectively. Therefore, the increase of  $V_S$  produces an increase in the collisions between ions and/or molecules, causing energy and linear momentum changes, dissociating and decelerating the particles because of the collisions between them. The number of collisions depends on the mean free path, that increases as a function of  $V_S$  producing a greater charge exchange between ions and/or molecules; these ions and/or molecules of Ti and Al become neutral. Due to the energy lost in the collisions, and because the neutral particles are not affected by the magnetic field, they can no longer reach the substrate surface; therefore, the element concentrations in the TiAlN compound change. On the other hand a low nitrogen concentration was observed in all the films. The N concentration is also an indication of the stoichiometry of the film considered as  $N/(Ti+Al)$ . This low N concentration is due to the low pressure of work and the low nitrogen flow (5 sccm). For instance Saoula et al [28], produced titanium nitride coatings by RF reactive magnetron sputtering

varying the bias voltage between  $-25\text{V}$  and  $50\text{V}$ . the used as a pressure of work  $0.5\text{Pa}$  and a  $\text{N}_2$  flow of varying between  $0$  to  $12$  sccm. They observed an increase in the nitrogen concentration as the nitrogen flow was increased. The coatings thickness was obtained by means of SEM according to the experimental description. Figure 1 shows micrographics of TiAlN coatings produced at  $V_S$  of  $-40\text{V}$  and  $-150\text{V}$  that allow measuring the film thickness.



**Figure 1:** SEM images used for measuring the TiAlN coatings produced at several bias voltage (a)  $-40\text{ V}$  and (b)  $-150\text{ V}$

Table 1 shows that the films thickness decrease from  $1.875$  to  $1.295\ \mu\text{m}$  as a function of  $V_S$ .

**Table 1:** Elemental concentration of N, Al and Ti as a function of the bias voltage. Thickness dependence on the bias voltage.

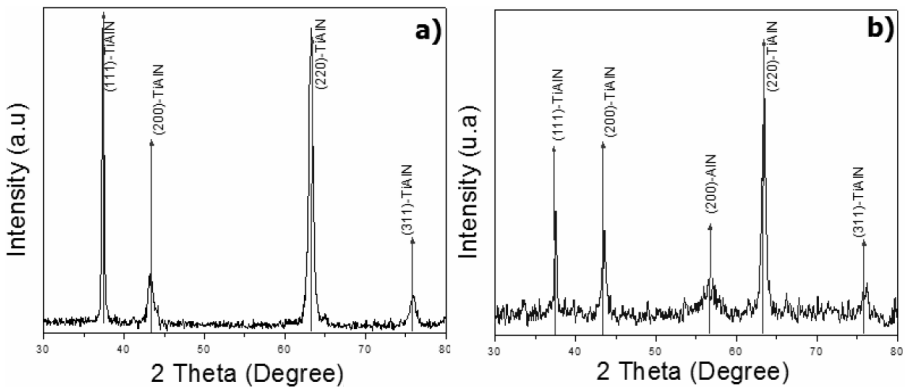
$V_S$	Elemental concentration			Thickness
	Nitrogen	Aluminum	Titanium	
-40	2.8	25.28	71.92	$1.875 \pm 0.015$
-70	3.92	31.31	64.27	$1.425 \pm 0.032$
-100	4.37	55.65	40.11	$1.33 \pm 0.026$
-150	6.49	65.95	27.57	$1.295 \pm 0.016$

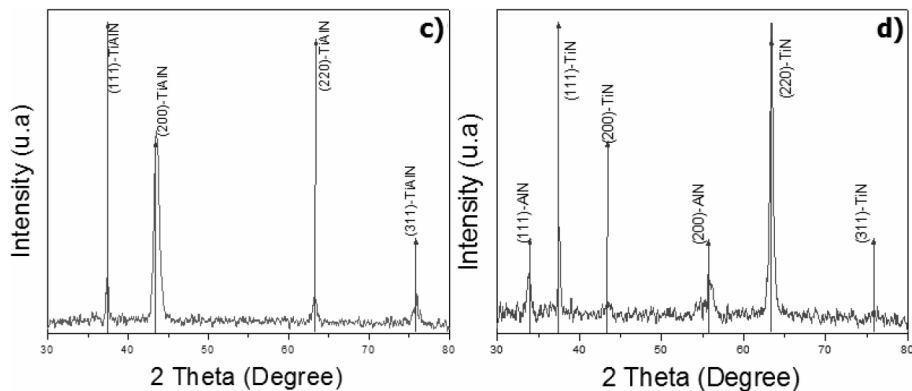
Although the sputtering technique tends to produce denser films than other techniques used in surface treatments according to Recco et al [22],

the triode sputtering Magnetron produces an increase in the ionization rate that combined with the high ionic energy and the substrate reference potential causes a thickness decrease because of the energy saturation as was described by Yate et al for AlCN coatings [29].

The thickness decrease can also be attributed to two factors: the first factor is the inverse sputtering process, which usually occurs when the high ionic bombardment forces the active species (ions or excited atoms) to interact with other ions. If the energy level of the ions bombarding the surface is increased, it can generate surface atom desorption. This phenomenon produces surface porosities and defects [23]. The second factor is the increase in the collisions that, depending on to the elemental ionization degree, can cause energy loss allowing the production of neutral particles, making the magnetic field does not affect their movement. Because of that, the particles do not possess the energy necessary to reach the surface or to be adsorbed.

The crystalline structure was studied as a function of  $V_S$ . This result is shown in Figure 2. This analysis showed the crystallographic orientations are in the planes (111), (200), (220) and (311) at Bragg angles of  $37.5^\circ$ ,  $44^\circ$ ,  $64^\circ$  and  $72^\circ$  that corresponds to the TiAlN compound as is reported by Jiménez [30]. No peaks corresponding to the material of the third electrode (stainless steel 304 net) were observed, indicating no visible contamination in the coatings.





**Figure 2:** Diffraction patterns of the TiAlN coatings produced at different Bias voltage: a) -40V, b) -70V c)-100V and d)-150V.

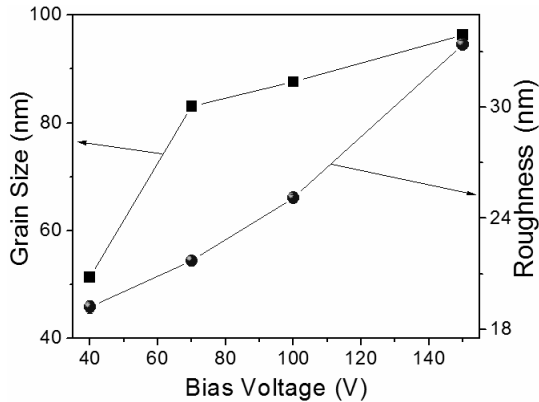
According to the literature, the compact plane (111) originates sliding when stress is present, producing a low (cutting) strain. Another crystallographic referent is the plane (200) that theoretically contains the lowest energy in the case of materials with NaCl type structure [31]. As the bombardment energy increases, the Al atoms in the crystallographic lattice increase and also the plane (111) peak's intensity decreases rapidly. Also an increase in the Al concentration in the crystallographic lattice was observed, according to the semi-quantitative EDS analysis. The transformation from the preferential orientation of the plane (111) toward (200) as  $V_S$  is increased is caused by the reduction in the average energy of the ions arriving to the surface, inducing desorption in the active species. These results are in agreement with those reported by Cheng [32], who stated that an increase in  $V_S$  produces increment in the adatoms mobility and in the mass transfer in the orientation of the plane (111), changing to (200) where less compact structures can be found.

For  $V_S$  of -40V, -70V and -100V, only the FCC structure of TiAlN was observed. On the other hand, in the case of  $V_S = -150V$ , a peak placed at  $33^\circ$  corresponding to AlN was found. Then, a coexistence of HCP and FCC phases can be found, caused by the excess of Al. In this case, the salt-NaCl type structure is shifted toward the HCP structure. In the chemical composition analysis, an increase in the Al concentration as a function of  $V_S$  was observed. Therefore the increase in the Al percentage in the TiAlN



compound determines the type of crystalline structure. Paldey and Deevi [27] found similar results for Al concentrations greater than 65%, where FCC-HCP type lattices were observed. At an Al percentage lower than 65%, the crystalline structure was FCC type.

Because of the final coatings application in manufacturing processes, the surface properties are an important topic to study, specially the roughness and grain size. Roughness values and grain size as a function of  $V_S$  are presented in Figure 3.



**Figure 3:** Grain size and roughness of TiAlN coatings dependence on the bias voltage.

In this figure, an increase in the roughness from  $51.3 \pm 0.4$  to  $96.3 \pm 0.8$  was observed. The surface roughness mainly depends on the films growth process and the grain size [33].

During the growth process, the atoms arrive perpendicularly to the surface improving the adatoms mobility. This phenomenon originates a pyramidal growth which produces a decrease in defects as microdroplets or inclusions in the coating surface according to the T zone described by the Thornton model [33]. Figure 3 shows an increase of the grain size as a function of the bias voltage. Normally, as the bias voltage is increased, more defects could be created resulting from the enhanced ion bombardment. It is well known that the defects in the sputtered film will prohibit the migration of grain boundaries and small grains will be formed [34],[35]:

Nevertheless, by using a grounded or positively biased grid in front of the substrate strike the substrate surface, resulting in the target, it is possible to add the effect of a uniform electric field in the grid sheath to the conventional magnetic trapping, resulting in a higher ionization rate than that of a diode system, maintaining a high deposition rate with very good stability of the discharge, and a better film morphology. It also can provide an enhanced low energy ion bombardment, taking advantage of a high rate of ion bombardment per deposited atom, which produces a rather dense film and reduces the formation of undesirable defects in the films created by the high energy ion bombardment and allowing the adatoms mobility, which then promotes the migration of particles to the grain boundaries and hence the grain sizes increase [10].

## 4 Conclusions

$Ti_xAl_{1-x}N$  coatings were produced by means of the triode magnetron sputtering technique, observing the influence of bias voltage on structural and morphological properties. A structural transformation from FCC to FCC-HCP phases was observed as bias voltage was increased. It is attributed to the higher Al concentration present in the coating, because of its lower molar weight. Moreover, a decrease in the thickness and increase in the roughness and grain size was observed as a function of  $V_S$ . These variations were caused by changes in the deposition process resputtering process, increased collisions and atoms arrival direction among others.

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