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Microstructure, residual stress and hardness study of nanocrystalline titanium–zirconium nitride thin films

D. Escobar[a,b,c], R. Ospina[a], A.G. Gómez[d], E. Restrepo-Parra[a,b,*]

[a]Laboratorio de Física del Plasma, Universidad Nacional de Colombia Sede Manizales, Km. 9 vía al Magdalena, Manizales, Colombia
[b]PCM Computacional Applications, Universidad Nacional de Colombia Sede Manizales, Km. 9 vía al Magdalena, Manizales, Colombia
[c]Grupo de Magnetismo y Simulación, Instituto de Física, Universidad de Antioquia, Antioquia, 1226 Medellín, Colombia
[d]Pontificia Universidad Javeriana Seccional Cali, Facultad de Ingeniería, Departamento de Ciencias de la Ingeniería y la Producción, Cali, Colombia

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Abstract

The pulsed cathodic arc deposition technique was used to synthesize titanium–zirconium nitride (TiZrN) thin films at different substrate temperatures. A microstructural analysis extracted from the X-ray powder diffraction pattern was performed to identify the dependence of crystallite size and microstrain on T_S. The residual stress state was also determined with the X-ray powder diffraction pattern assuming that the material behaved isotropically based on Young's modulus and the Poisson coefficient. The morphological analysis used atomic force microscopy to determine the grain size evolution with substrate temperature during deposition. The nanohardness values were obtained using nanoindentation measurements. Finally, the synthesis–property relationships were obtained with the microstructural information.
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1. Introduction

Titanium–zirconium nitride (TiZrN) is used by a growing number of researchers for the preparation of an extensive variety of new materials, in the form of bulks, membranes, fibers and especially for the preparation of thin films [1,2]; however, ternary systems can present a better behavior. Among these, the ternary nitride films are important because their interstitial nature can be applied to many processes [3–6]. Furthermore, titanium–zirconium nitride (TiZrN), one of these films, has properties such as oxidation and corrosion resistance, low wear and high hardness [7–9] and is the subject of this work.

To advance technological development in the field of materials science and engineering, it is critical to find better techniques and to clearly establish the relationship between synthesis of materials with specific characteristics and mechanical properties. Microstructures can vary greatly depending on their synthesis process. Thus, the microstructure is the connecting factor between properties and synthesis conditions [10,11].

The residual stress state is another important factor that depends on synthesis and affects material properties. This parameter describes macrostrains in the crystal lattice that are evident in the variation of the lattice parameter [11,12]. The distance between atoms is important to the final properties of the material and therefore residual stresses are important for synthesis–property relationships. They cannot be considered independently of microstructure to completely characterize the material.

There are several ways to characterize the microstructure and residual stress of materials. One of the most common is X-ray diffraction. This technique has some advantages over others. For example, it permits high penetration depths in the sample, allows for high dislocation density values and is a non-destructive

*Corresponding author at: Laboratorio de Física del Plasma, Universidad Nacional de Colombia Sede Manizales, Km. 9 vía al Magdalena, Manizales, Colombia. Tel./fax: +57 6 8879495.
E-mail address: erestrepopa@unal.edu.co (E. Restrepo-Parra).

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technique [13,14]. Therefore, it is a useful method to characterize materials in terms of their microstructure. In a previous work [15] we presented a detailed microstructural characterization of nanocrystalline TiZrN thin films grown at different substrate temperatures carried out by X-ray diffraction (XRD). We developed a total diffraction pattern modeling based on more meaningful microstructural parameters, such as crystallite size distribution and dislocation density. This model was used to describe the microstructure of the thin films more precisely. The first paper included a detailed microstructural analysis supported on the morphology and texture. On the other hand, the present paper includes results different to the first one regarding residual stress and microstructure correlated with the hardness, observing the influence of the deposition parameters (substrate temperature). Furthermore, the first paper was based on the application of the microstructural model (whole powder pattern modeling) while the present paper discusses the relationship between the synthesis residual stress and microstructure without considering them independently.

In this study, TiZrN thin films are synthesized, characterized and evaluated to establish a relationship between the processing parameters, final microstructure and the final residual stress state of the material. The substrate temperature (T_S) was varied during deposition of the thin films, and its influence on nanohardness is ultimately evaluated. Microstructural and residual stresses were characterized based on the theory of thin films growth with an X-ray diffraction technique. Finally, the dependence of nanohardness on microstructure and residual stress as well as a final relationship between all of these quantities was found.

2. Experimental

TiZrN thin films were synthesized with the cathodic arc technique on stainless steel 316L. The substrate temperature was varied from room temperature (RT) to 200 °C. The target material to evaporate was Ti–Zr (50–50%). Pressure in the order of 10 Pa was maintained by the vacuum system to ensure high purity in the reaction. For the coatings synthesis, nitrogen was introduced until the gas pressure reached 300 Pa. Four arc pulses were applied at a 4 mm distance between electrodes while the voltage was 300 V. A detailed description of the system is given elsewhere [16]. Diffraction patterns in grazing incidence mode were obtained to characterize the microstructural and residual stress of the thin films. They were obtained at the synchrotron at the Laboratório Nacional de Luz Síncrotron in Brazil using the X-ray diffraction beamline. The radiation energy was 9 keV (wavelength = 1.377 Å). Residual stress was measured at 1°, 2.5°, 3.5° and 5° angles of incidence to verify the possibility of stress gradients at different information depths. Divergence slits were used in the primary (0.5 mm) and in the diffracted beam (1.0 mm). A graphite analyzer was also used. The diffraction planes scanned were (111), (200), (220), (311) and (222) (Table 1).

Nanoindentation analyses were performed with a Nanovea Microphotonics nanoindenter using a Berkovich type diamond indenter. The applied charge was 2 mN. To improve the statistics, 9 points were taken, and these measurements were made three times per sample to corroborate the results. Atomic force microscopy technique was used to obtain the thickness of the films using a Park Scientific Instruments Autoprobe CP system with step height analysis. These measurements were made under ambient conditions at 24 °C and 70% relative humidity. Grain size values were measured for each sample in five different regions through a morphological surface measurement.

Table 1
Thickness of TiZrN coatings depending on the substrate temperature.

Substrate temperature during deposition (°C)	Thickness (error) nm
RT	279 (9.7)
50	300 (12.3)
100	312 (5)
150	304 (17.1)
200	299 (3.1)

3. Results and discussion

3.1. Residual stress

From the X-ray diffraction analysis, microstrain and residual stress of thin films can be obtained [17]. Residual stress analysis was carried out with the grazing incidence X-ray diffraction technique, which is a variation of the conventional sen$^2\psi$ method. In this technique, the incident beam is kept constant at a fixed low angle (α) because the position of the detector varies along the goniometer circle to register data at several (hkl) reflections. A biaxial state of stress is usually assumed to use this method and this assumption is suitable for thin film systems [18]. The residual stress levels were calculated from the slope of the a_ψ^{hkl} vs. $f(\psi)$ plot [19]. a_ψ^{hkl} is the lattice parameter for each reflection and is calculated by fitting the peak profiles with the Rietveld method using the GSAS + EXPGUI software [20,21]. $f(\psi) = \frac{1}{2}S_2^{hkl} + 2S_1^{hkl}$ sen^2 (ψ). The angle ψ is equal to θ–α.

S_1^{hkl} and S_2^{hkl} are the X-ray elastic constants and were calculated for each scanned plane (hkl) as described elsewhere [22]. The global values of Young's modulus (E^m) and the Poisson coefficient of the material were taken from the literature as 456.6 GPa and 0.201 [23], respectively.

The a_ψ^{hkl} vs. $f(\psi)$ plots obtained at the 1° angle of incidence for the TiZrN thin films are shown in Fig. 1. In addition to showing a good linear fit for all the samples, a compressive stress can be deduced from the negative slopes in the figure.

Planes (111), (220), (311) and (222) were used to make the plots. The plane (200) was discarded from the calculations because it deviated from linearity in all cases. This behavior can be caused by variation in the lattice parameter between the crystallites of the film. In TiN films deposited by the physics vapor deposition technique, deposition occurs by ion impinging at high energies and the [001] direction is open to ion bombardment [24]. These crystallites present more defect

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