STRUCTURAL STABILITY UPON ANNEALING OF PULSED ARC DEPOSITED (Ti,Zr)N FILMS

O.A. Trujillo 1, L.C. Agudelo 1, C.D. Salazar 1, P.J. Arango1, A. Devia 1*

- ✓ Este artículo forma parte del "Volumen Suplemento" **S1** de *la Revista Latinoamericana de Metalurgia y Materiales* (*RLMM*). Los suplementos de la RLMM son números especiales de la revista dedicados a publicar memorias de congresos.
- ✓ Este suplemento constituye las memorias del congreso "*X Iberoamericano de Metalurgia y Materiales (X IBEROMET)*" celebrado en Cartagena, Colombia, del 13 al 17 de Octubre de 2008.
- ✓ La selección y arbitraje de los trabajos que aparecen en este suplemento fue responsabilidad del Comité Organizador del *X IBEROMET*, quien nombró una comisión *ad-hoc* para este fin (véase editorial de este suplemento).
- ✓ La *RLMM* no sometió estos artículos al proceso regular de arbitraje que utiliza la revista para los números regulares de la misma.
- ✓ Se recomendó el uso de las "Instrucciones para Autores" establecidas por la *RLMM* para la elaboración de los artículos. No obstante, la revisión principal del formato de los artículos que aparecen en este suplemento fue responsabilidad del Comité Organizador del *X IBEROMET*.

Suplemento de la Revista Latinoamericana de Metalurgia y Materiales 2009; **S1** (3): 1089-1093

STRUCTURAL STABILITY UPON ANNEALING OF PULSED ARC DEPOSITED (Ti,Zr)N FILMS

O.A. Trujillo 1, L.C. Agudelo 1, C.D. Salazar 1, P.J. Arango1, A. Devia 1*

1: Laboratorio de Física del Plasma, Universidad Nacional de Colombia sede Manizales. Manizales, Colombia

** E-mail:oatrujillomo@unal.edu.co*

Trabajos presentados en el X CONGRESO IBEROAMERICANO DE METALURGIA Y MATERIALES IBEROMET
Cartagena de Indias (Colombia), 13 al 17 de Octubre de 2008

Selección de trabajos a cargo de los organizadores del evento

Publicado On-Line el 29-Jul-2009
Disponible en: *www.polimeros.labb.usb.ve/RLMM/home.html*

Abstract

Single-phase [NaCl]-structure Titanium Zirconium nitride (Ti,Zr)N thin films have been deposited using plasma assisted physical vapor deposition (PAPVD) with a target segmented (Ti70%-Zr30%). For the production of films, two faced electrodes (target and substrate of stainless steel AISI 304) were placed into the reaction chamber which was filled up with nitrogen gas until reaching the different working pressures between 3.5 mbar and 4.5 mbar with increments each 0.5 mbar. The discharges were performed using a non-commercial switched DC arc power supply which allows making variations of inter-electrode voltage (V) from 0 up to 280 volts rms (root mean square), with a maximum current of 300 amperes. The active arc time (t_a) and inactive arc time (t_i) values can be controlled. The working conditions were V = 230 volts, t_a = 2 seconds and t_i = 6 seconds in all cases. With GIXRD (Grazing Incidence X ray Diffraction) the texture coefficient, crystallite size, micro-strain and lattice parameter were evaluated. We used the Scherrer equation in order to determinate the crystallite size and micro-strain taking in account the instrumental broadening of XRD equipment. Cagliotti functions were used for determinate that constant. Rietveld refinement was employed with a pseudo voigt function. GIXRD analysis shows the formation of ternary (Ti,Zr)N nitride phase with (200) preferred orientation in all cases, lattice parameter was between 0.434 nm and 0.436 nm and the crystallite size in the (Ti,Zr)N thin films was found to be 17,90 nm and 66,19 nm at different working pressures, besides, We found that micro-strain decreases when working pressure increases. By means EDS (Energy Dispersive X-ray Spectroscopy) elemental composition of coatings was obtained. These analyses show uniform distribution of elements on the sample surface.

Keywords: *(Ti,Zr)N, GIXRD, EDS, Annealing, Structural Stability*

Resumen

Películas delgadas de Nitruro de Titanio Zirconio (Ti,Zr)N en una sola fase de estructura [NaCl] fueron crecidas usando deposición física de vapor asistida por plasma (DFVAP) con un blanco segmentado (Ti70%-Zr30%). Para la producción de las películas, dentro de la cámara de reacción se ubicaron dos electrodos enfrentados (Blanco y Sustrato) la cámara de reacción fue llenada con gas nitrógeno hasta alcanzar las diferentes presiones de trabajo entre 3.5 y 4.5 mbar con incrementos cada 0.5 mbar. Las descargas se hicieron con una fuente de potencia DC no-comercial la cual permite hacer variaciones de voltaje inter electrodico (V) de 0 a 280 voltios rms, con una corriente máxima de 300 amperios. Los valores del tiempo activo del arco (t_a) y el tiempo muerto (t_i) pueden ser controlados. Las condiciones de trabajo fueron V=230 Voltios, t_a= 2 segundos, t_i= 6 segundos, en todos los casos. Con GIXRD (Difracción de Rayos X a Incidencia Rasante) se evaluaron el coeficiente de textura, el tamaño del cristalito, la micro deformación y el parámetro de red de las películas. Usamos la ecuación de Scherrer para determinar el tamaño del cristalito y la micro deformación teniendo en cuanta el ensanchamiento instrumental del equipo de DRX. Las funciones de Cagliotti se usaron para determinar esta constante, además para el refinamiento Rietveld se empleo una función pseudo voigt. El análisis de GIXRD muéstrala formación de la fase del nitruro ternario (Ti,Zr)N con orientación preferencial en el plano (200) en todos los casos, el parámetro de red encontrado estuvo entre 0,434 y 0,436 nm, Para el tamaño del cristalito de las películas de (Ti,Zr)N encontramos valores entre 17,90 y 66,19 nm para las diferentes presiones de trabajo, además, encontramos que la micro deformación disminuye cuando la presión de trabajo incrementa. Por medio del análisis EDS la composición elemental y mapas de rayos - x de los recubrimientos fueron obtenidos, este análisis muestra una distribución uniforme de los elementos en la superficie de los recubrimientos.

Palabras Claves: *(Ti,Zr)N, GIXRD, EDS, Tratamiento Térmico, Estabilidad Structural*

1. INTRODUCTION

Ternary transition metal ceramics are becoming the subject of a rapidly number of studies. Research in this area is driven by the prospects of finding functional properties for cutting tools and electronics applications from a range of relatively unexplored materials. Nitride-based ceramics are widely used to protect materials against wear, abrasion and corrosion [1-3]. Due remarkable properties such as high hardness and wear resistance these coatings are employed in various machining applications to improve the performance of tools and mechanical components. But in the process of work the temperature of the tool and of the coatings can reach 800°C or more. This poses strong requirements on the quality of the coatings, such as a high hardness combined with a high temperature stability and oxidation resistance. Ternary transition metals nitride coatings provide a wide range of structures that enable to control composition, hardness and thermal stability of these films [4-5].

Ternary nitride coatings offer several advantages over binary ones. They showed significantly higher hardness values, [6] wear resistance [7] and oxidation resistance [8] compared with binary nitrides.

In the present paper we studied the elemental and phase composition of multicomponent (Ti,Zr)N films grown by Pulsed Arc Deposition with variation of the working pressure. And the best sample was annealed for studying the structural stability of the (Ti,Zr)N coating.

2. EXPERIMENTAL SETUP

The deposition of the films was made through plasma assisted physical vapor deposition by the pulsed arc technique, in a non-commercial monovaporizer system described elsewhere [9]. This system counts with two faced electrodes, one of them was the cathode with a segmented target (Ti70% –Zr30%) and the other one was the anode with stainless-steel AISI 304 as substrates. The substrates were polished previously and then cleaned with an ultrasonic cube.

The reaction chamber was filled up with nitrogen gas until reaching the different working pressures between 3.5 mbar and 4.5 mbar with increments each 0.5 mbar. The discharges were performed using a non-commercial switched DC arc power supply which allows making variations of inter-electrode voltage (V) from 0 up to 280 volts rms (root mean square), with a maximum current of 300 amperes [10]. The active arc time (t_a) and inactive arc time (t_i) values can be controlled. The working conditions were V = 230 volts, t_a = 2 seconds and t_i = 6 seconds in all cases.

The phase composition and preferred orientation in (Ti,Zr)N films were investigated by GIXRD (Grazing Incidence X ray Diffraction) using a Bruker-AXS D8 Advance X-Ray Difractometer parallel beams theta/theta geometry, CuKα radiation (λ= 1.5406 Å). The scanning was made at 2 seg/step speed and a 0.02º increase. Operated at 40 kV, 30mA.

Annealing

After deposition, Annealing treatment was performed in a HTK2000 high-temperature chamber fits to a BRUKER AXS D8 ADVANCE diffractometer. Films were annealed in air at the temperatures between room temperature (RT) and 800°C with increments each 100°C.

3. RESULTS AND DISCUSSION

3.1 GIXRD Analyses

Figure 1. Shows GIXRD patterns obtained from the as-deposited (Ti,Zr)N films. The sigle-phase [NaCl]-structure is evidenced by the (111), (200), (220) and (311) peaks. [5] The films exhibits (200) preferred orientation. The intensity of the peaks of the film is higher for the sample grown at 4,0 mbar working pressure.

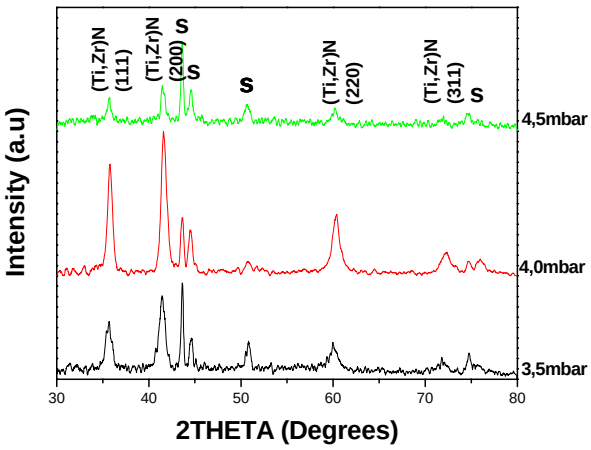


Figure 1. GIXRD patterns of the as deposited (Ti,Zr)N films at different Working Pressures. (S: Substrate)

The texture coefficients of the (Ti,Zr)N films as a function of working pressure are calculated from their respective GIXRD peaks using the following formula [11]; the results are shown in figure 2.

$$\text{Texture Coefficeint(TC)} = I(hkl)/\sum I(hkl) \quad (1)$$

Where (hkl) represents the (111), (200), (220), and (311) orientations. The TCs of (200) and (111) orientations are high compared to other orientations in the (Ti,Zr)N films. In all cases the TC of (200) orientation is the highest, although the sample grown at 4,0 mbar shows increase in the TC of (111) orientation, however it does not exhibit a change in the preferential orientation. The competition between surface energy and strain energy during film growth might contribute to changes in preferred orientation [12]. We can say for the film grown at 4,0 mbar that the strain energy increases because it helps the film grown on the (111) orientation, which is observated with the TC increase.

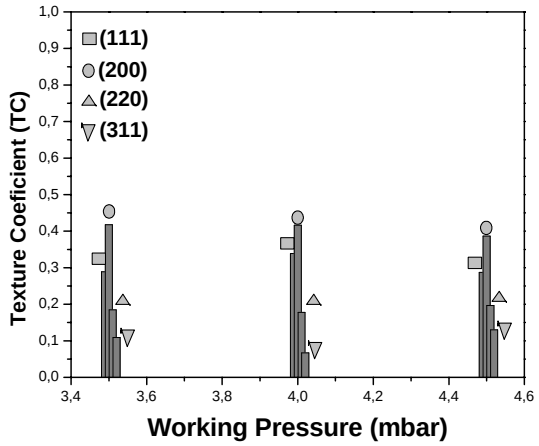


Figure 2. Texture Coefficients of (Ti.ZrN) films at different Working Pressures.

Rietveld refinement was employed with a pseudo voigt function to calculated lattice parameter; the results are shown in table 1. We found that the lattice parameter of (Ti,Zr)N film is higher than lattice parameter of TiN which is 0,424 nm. This increment in the lattice parameter of TiN clearly evidences the substitution of Ti with Zr in the lattice of TiN [13].

The relationship between working pressure and crystallite size and micro-strain estimated by the full width at half maximum (FWHM) intensity of GIXRD peaks using Scherrer's equation is in the table 1. We found that micro-strain decrease and the crystallite size increase when working pressure increase.

Table 1. GIXRD results

Pressure (mbar)	*Lattice parameter (nm)*	*Cristallite size (nm)*	*Micro strain*
3,5	0,435	17,90	0,014
4,0	0,434	46,91	0,011
4,5	0,436	66,19	$8{,}66 \times 10^{-3}$

3.2 SEM-EDS Analyses

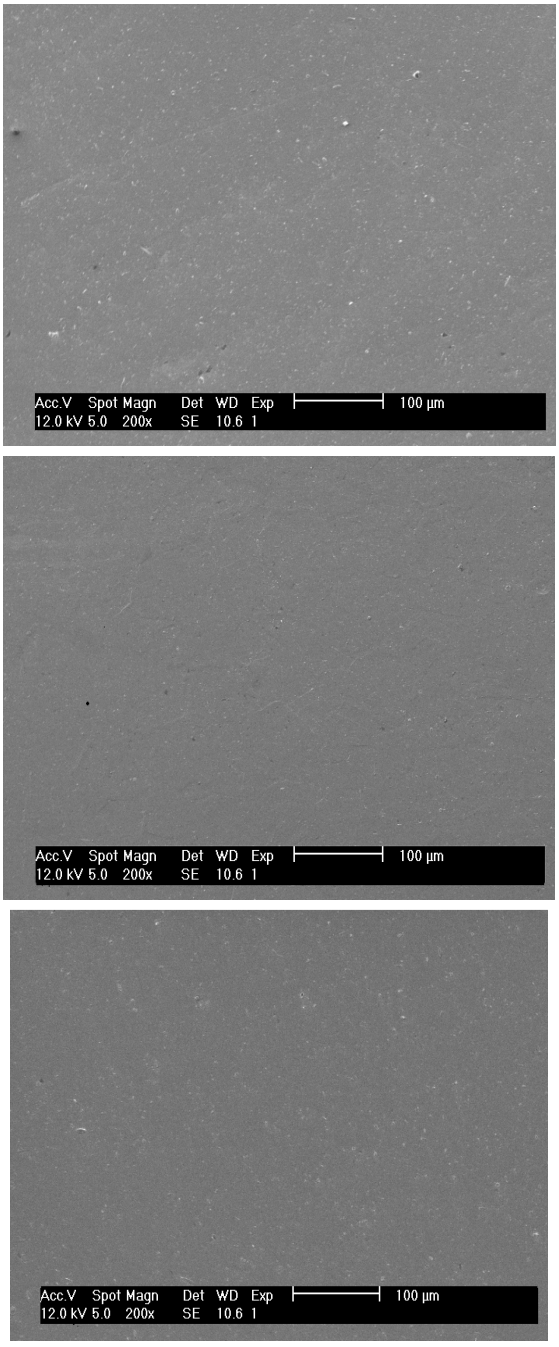


Figure 3. SEM micrographs of (Ti,Zr)N Films: top (3,5 mbar), middle (4 mbar), bottom (4,5 mbar).

The SEM micrograph, as shown in figure 3. depicts a smooth and clean surface morphology without loose y attached macroparticles. This fine surface finish of as-deposited (Ti,Zr)N. Similar results were obtained by Wang DY et al in (Ti,Zr)N hard coatings synthesized by unbalanced magnetron sputtering[14].

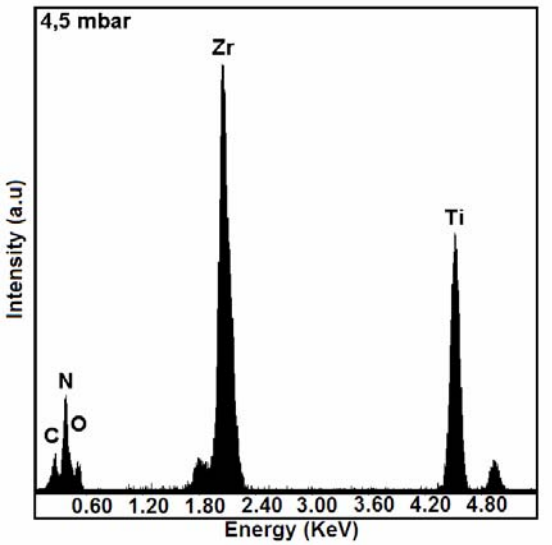


Figure 4. EDS spectrum of (Ti,Zr)N Films.

Through EDS analyses, the presence of main elements Ti, Zr and N fundamentally is confirmed, as C and O in less proportion, due to contamination into the deposition chamber and to the environment exposition of the film. Figure 4. shows EDS spectrum, identifying these elements.

Annealing

Figure 5 shows the results of the annealing experiment performed on the sample grown at working pressure of 4.0 mbar which showed the best structural properties. We found structural stability until 500°C due the diffraction patterns do not show noticeable changes on the position and the intensity of the peaks, however the lattice parameter was around 0.434 nm from raw temperature until 600°C. Similar results were obtained by Hoerling A, et al [5], At 600°C the peaks intensity decrease but at 700°C the formation of Ti_2ZrO phase is observed according to the data base ICSD: 020119 [14], and at 800°C the (Ti,Zr)N coating is totally oxidized founding the Ti_2ZrO [15] and the Ti_2ZrO_6 phases according to the data base JCPDF: 000461265 [16].

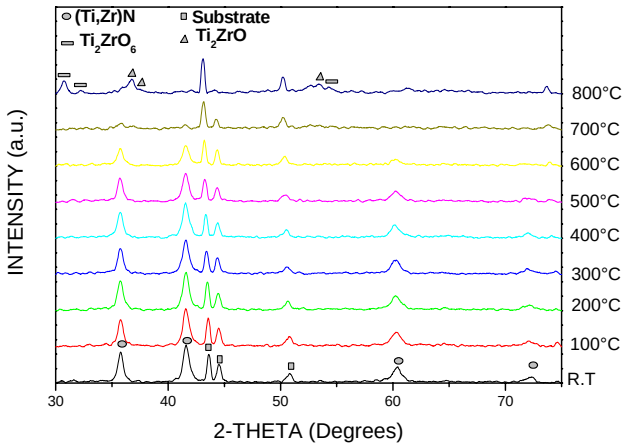


Figure 5. GIXRD patterns of the annealing (Ti,Zr)N film at working pressures of 4,0 mbar.

We found that the texture coefficient of (200) orientation stays almost constant as function of temperature between RT and 600°C. (figure 6). While the TC of (111) orientation increase lightly. These results indicate that the (Ti,Zr)N film is structurally stable.

Figure 7 shows EDS spectra of the post-annealing (Ti,Zr)N film at working pressure of 4,0 mbar. In this spectra is evident the increase of oxygen peak and disappear of nitrogen peak which is agree with the GIXRD after annealing at 800° C results, where we found only the presence of two oxide phases. (figure 5).

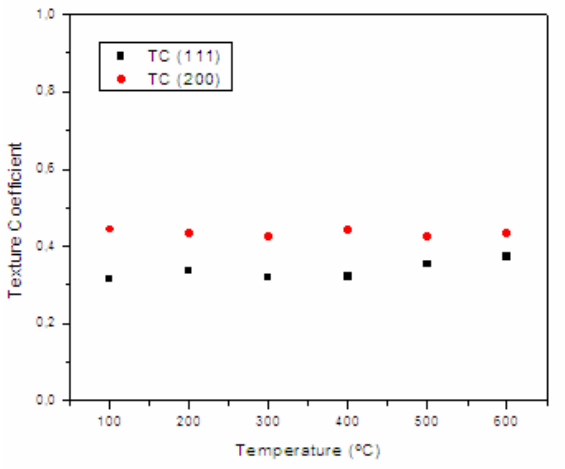


Figure 6. Texture Coefficients of (200) and (111) orientations of (Ti.ZrN) film as function of temperature.

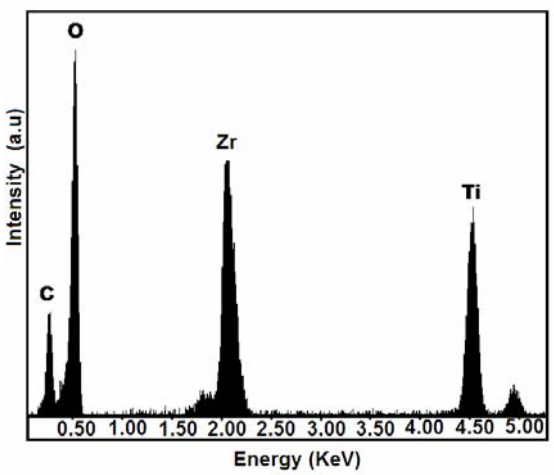


Figure 7. EDS spectra of the post-annealing (Ti,Zr)N film at working pressure of 4,0 mbar.

4. CONCLUSIONS

(Ti,Zr)N films were grown at different working pressures. All films have a NaCl- structure. We found that the best sample was grown at 4,0 mbar.

We found structural stability until 500°C due the diffraction patterns don´t show noticeable changes on the position and the intensity of the peaks.

(Ti,Zr)N films can be used as protective coatings to oxidation of surface of material until 600°C, due it begins to oxide at 700°C.

We found that the texture coefficient of (200) orientation stays almost constant as function of temperature between RT and 600°C. (figure 6). While the TC of (111) orientation increase lightly. These results indicate that the (Ti,Zr)N film is structurally stable.

5. ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Instituto Colombiano para el Desarrollo de la Ciencia y la Tecnnología (COLCIENCIAS) during the course of this research, under Project RC292-2001.

6. REFERENCES

[1] Aouadi SM, Chladek JA, Namayar F, Finnegan N, Rohde SL. *J. Vac. Sci. Technol. B 2002; 20(5): 1967-1973*

[2] Hasegawa H, Kimura A, Suzuki T. *Surf. Coat. Technol. 2000; 132(1): 76-79*

[3] Musil J, *Surf. Coat. Technol. 2000; 125: 322-330*

[4] Uglov VV, Anishchik VM, Khodasevich VV, Prikhodko ZhL, Zlotskit SV, Abadias G, Dub SN, *Surf. Coat. Technol. 2004; 519: 180-181*

[5] Hoerling A, Sjolen J, Willmann H, Larsson T, Oden M, Hulman L. *Thin Solid Films. 2008; 516: 6421-6431*

[6] Han JG, Myung HS, Lee HM, Shaginyan LR. *Surf. Coat. Technol. 2003; 738: 174-175*

[7] Purushotham KP, Ward LP, Brack N, Pigram PJ, Evans P, Noorman H, Manory RR. *Wear 2004; 254: 589-596*

[8] Uglov VV, Anishchik VM, Zlotskit SV, Abadias G, Dub SN, *Surf. Coat. Technol. 2008; 202: 2394-2398*

[9] Marulanda DM, Trujillo O, Devia A. Plasma *Fusion Sci. 2006; 875: 232-235*

[10] Devia A, Arango YC, Devia DM. *Surf. Coat. Technol. 2006; 201(6): 2919-2924*

[11] Chawla V, Jayaganthan R, Chandra R. *Materials Characterization 2008; 59: 1015-1020*

[12] Petrov I, Barna PB, Hultman L, Greene JE. *J Vac Sci Technol A 2003;21(5):S117–28.*

[13] Ramana JV, Kumar S, David Ch, Raju VS. *Materials Letters. 2004; 58: 2553-2558*

[14] Wang DY, Chang ChL, Hsu ChH, Lin HN. *Surf. Coat. Technol. 2000; 130: 64-68*

[15] XRD Database ICSD: 020119.

[16] XRD Database JCPDF: 000461265.