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Temperature behaviour on deposition of the titanium nitride thin films on H13 steel by the electric arc discharge in vacuum

Comportamiento de la temperatura en la deposición de películas delgadas de nitruro de titanio sobre acero H13 mediante la descarga de arco eléctrico en vacío

Comportamento da temperatura na deposição dos filmes delgados de nitreto de titânio sobre el acero H13 mediante la descarga de arco elétrico no vácuo

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Abstract

Objective: This research studies the behaviour of temperature of the substrate manufactured in AISI H13 steel, in the range of and , during of surface deposition of titanium nitride (TiN) thin films by the technique of cathodic arc in vacuum. **Results:** The physical properties of the TiN films were obtained and analysed by the techniques of micro-indentation, Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD). **Conclusion:** It was determined that the increase in the temperature of the substrate during the deposition of TiN films improves the mechanical properties of the surface of the steel of type AISI H13, where the highest hardness was present in the coating deposited at a temperature of , which has a preferential orientation in the plane determined by the XRD patterns.

Keyword: Coatings, Metal substrates, Substrate temperature

Resumen

Objetivo: En el presente trabajo de investigación se estudia el comportamiento de la temperatura del sustrato, fabricado en acero de tipo AISI H13, en el rango de y , durante la deposición superficial de películas delgadas de nitruro de titanio (TiN) por la técnica de arco catódico en vacío. **Resultados**: Las propiedades físicas de las películas de TiN fueron obtenidas y analizadas mediante las técnicas la micro-indentación, microscopía de fuerza atómica (AFM) y la difracción de rayos x (DRX). **Conclusión:** Se determinó que el incremento en la temperatura del sustrato durante la deposición de las películas de TiN, mejora las propiedades mecánicas de la superficie del acero de tipo AISI H13, donde la mayor dureza se presentó en el recubrimiento depositado a una temperatura de , el cual tiene una orientación preferencial en el plano determinada por los patrones de DRX.

Palabra Clave: Revestimientos, Sustratos metálicos, Temperatura del sustrato

Resumo

Objetivo: No presente pesquisa é estudado o comportamento da temperatura do substrato, feito de aço de tipo AISI H13, no intervalo de e , durante a deposição superfície das películas finas de nitreto de titânio (TiN) por meio da técnica de arco catico em vácuo. **Resultados:** As propriedades físicas dos filmes de TiN foram obtidos e analisados pelas

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técnicas de micro-indentação, microscopia de força atómica (AFM) e difracção de raios-X (DRX). **Conclusão:** determinou-se que o aumento de temperatura do substrato durante a deposição do filme de TiN, melhora as propriedades mecânicas da superfície do aço de tipo AISI H13, onde a maior dureza foi apresentada no revestimento depositado a uma temperatura de , que tem uma orientação preferida no plano determinados pelos padrões de DRX.

Palavras-chave: Revestimentos, Substratos metálicos, Temperatura do sustrato

1. Introduction

The properties of thin films necessarily depend on the physical variables that govern the process and on the characteristics of the materials involved [1], [2]. For example, in the case of a thin film, adhesion thereof to the substrate simultaneously depends on the conditions of prior surface cleaning of the substrate, its surface roughness, the mechanical properties, the physicochemical compatibility of the substrate materials and of the coating, of the reference potential, further to the temperature of the substrate during the film forming process and of conditions such as the rate of coating formation, impurities present in the plasma, among other factors [3].

A process of physical vapour deposition (PVD) consists of the evaporation under vacuum of a material called target, that is subsequently transported, deposited and condensed on the surface of a piece (substrate); Taking into account that the transport of species is carried out by physical means, it is essential to have a high vacuum (approximately 10^{-6} *torr*) so that the mean free path of the atoms and molecules surpass the target-substrate distance [4]. The cathodic arc technique consists of a self-sustained high current electric discharge and low potential drop with current density in the range of 102-108 A/cm^2 [4].

TiN is a chemically stable and inert compound and because of its interstitial structure has a combination of ionic, covalent and metallic bonds, which allows it to combine the physical properties of ceramic and electrical metals [5]. For this reason, the TiN it is one of the coatings most industrially used to prevent problems of abrasive wear or adhesive in machining tools, punches and dies [6], [7].

Given the diversity of existing processes and the possible thin films that can is deposited according to their functional goal or physical-chemistry properties to enhanced, in this work a study is performed on the substrate temperature behaviour, of the AISI H13 steel, during deposition of titanium nitride thin films [8] by means of electric discharges of cathodic arc in vacuum implemented in the JUPITER device [9]-[11]. Previous studies about thin films have shown the need to identify the variables that contribute to optimizing both the formation process of these films and the improvement in their mechanical and tribological properties [11]-[15].

2. Materials and methods

Substrates of a square flat geometry of 10*mm* in length, 10*mm* in width and 5*mm* in thickness, were designed and manufactured in AISI H13 steel [8], where one of their faces was prepared superficially with silicon carbide (SiC) abrasive paper up to grade

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1500 Subsequently, the removal of greases and impurities of the substrates were carried out a cleaned by an ultrasonic bath in ethanol and acetone solution during 15 minutes each. Thin films of TiN were deposited by cathodic arc in vacuum using a Ti target, with a purity of the , and installed in the discharge chamber of the JUPITER reactor (see Figure 1), where in the normal mode of operation, the cathodes dots move through the cathode surface of the electric arc evaporator in vacuum in the spontaneous regime [9]-[11].

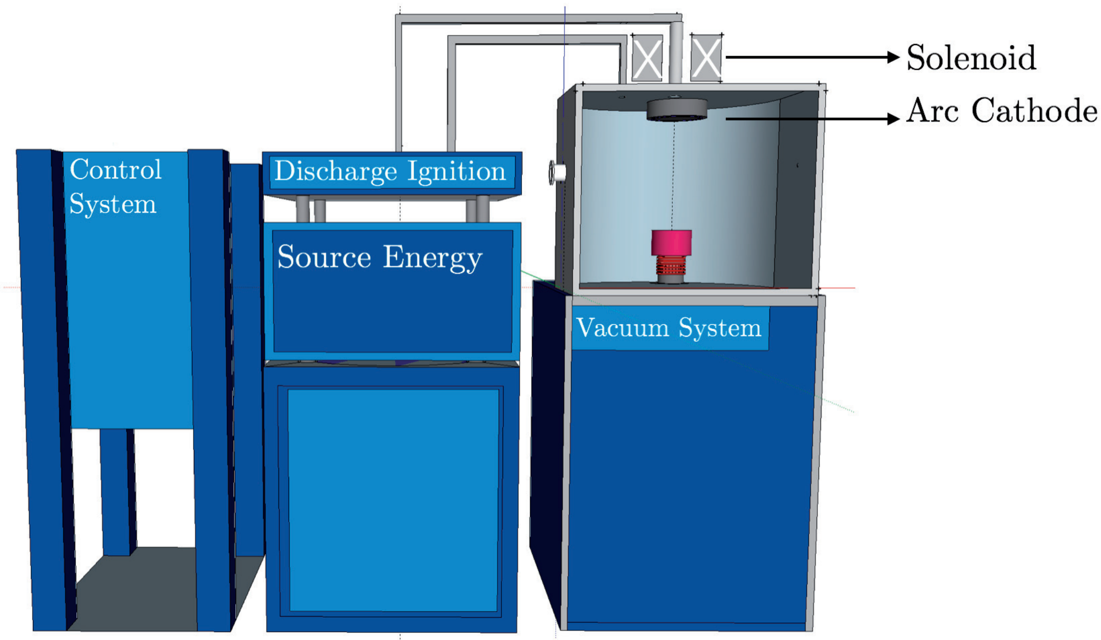

Figure 1. Scheme of JUPITER reactor.

The TiN coating was manufactured by maintaining a pressure in the discharge chamber of the JUPITER reactor of 0.6Pa in a nitrogen atmosphere, which reacts with the titanium plasma generated by an arc current of $175A$ and with a polarization potential in the substrate of $20V$ [11]-[13]. In order to improve the adhesion at the substrate-coating interface, the deposition of a titanium layer, of approximately thick, was performed. The temperature of the substrate was varied from $350°C$ to (see Table I), allowing to obtain a TiN film between $1\mu m$ and $2\mu m$ thick, which was measured by AFM in non-contact mode.

Table I. Parameters established in the deposition process of the TiN coatings.

SUBSTRATE	SUBSTRATE TEMPERATURE (°C)	TIME (MIN)	PRESSURE (PA)	BIAS VOLTAGE (V)	CURRENT (A)
M 1	350	10	0,6	20	175
M 2	425				
M 3	450				
M 4	475				

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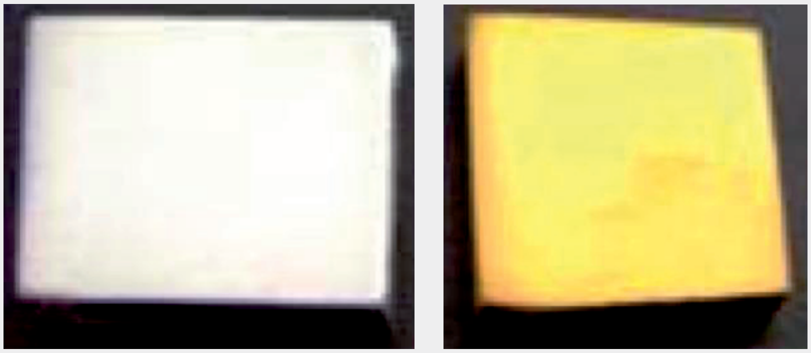
In figure 2, shows the surface of the substrates of AISI H13 steel uncoated and coated with TiN.



(a) **(b)**
Figure 2. Substrate of AISI H13 steel, (a) uncoated and (b) coated with TiN to.

The surface hardness of the AISI H13 steel substrates with and without coated of TiN was evaluated by micro-indentation tests. The micro-hardness test was the Vickers type, which consists of doing a trace, on the order of micrometres, on the surface of the material; with an indenter that has the shape of the square base straight pyramid. The Vickers hardness is obtained by measuring the diagonal of the recorded footprint and using the equation (1) [16], [17].

$$H_v = \frac{2P\sin\left(\frac{\alpha}{2}\right)}{d^2} = \frac{0.18909P}{d^2} \qquad (1)$$

Where, P is the applied load in Newton *(N)*, d is the mean diagonal of the footprint in *mm*, and α is the angle formed by faces of the diamond penetrator.

The morphological characterization of the surfaces of AISI H13 steel uncoated and with coated was carried out in of Atomic Force microscope CP-II of Veeco mark, performing a sweep in non-contact mode at a frequency of 0.3*Hz*.

The structural characterization, diffraction patterns and crystalline orientations of TiN coatings deposited on the surface of AISI H13 steel at temperatures of 350°*C*, 425°*C*, 450°*C* and 475°*C* were performed by the X-Ray Diffraction technique using the diffractometer SIEMENS model D500. The qualitative analysis of the present phases was carried out by comparing the obtained or observed profile with the one reported in the database of the PDF-2 diffraction profiles of International Centre for Diffraction Data (ICDD).

3. Results and analysis

The micro-indentation tests were performed using a Vickers indenter with loads of 500*g*, 1000*g*, 1300*g* and 1500*g* for 15 seconds. The Vickers hardness values obtained from equation (1) are reported in Table II.

Table II. Average values of Vickers hardness of substrates surface uncoated and coated to different temperatures.

SUBSTRATE	VICKERS HARDNESS HV
AISI H13 steel	352.62 ± 10.00
M 1 (TiN to 350°C)	741.15 ± 46.65
M 3 (TiN to 450°C)	1151.82 ± 403.50
M 4 (TiN to 475°C)	755.11 ± 45.68

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The obtained results of the micro-indentation show a significant increase of the surface hardness of the substrates of steel of type AISI H13 coated with TiN, influenced by the temperature of the substrate. In the coating deposited at a lower temperature, 350°*C*, an approximate 100% increase in hardness was obtained in relation to the reference substrate (uncoated), while the film deposited at 450°*C* showed the highest value of hardness Vickers (1151.82*Hv*) with an approximate increase of 226% with respect to the uncoated surface.

Figure 3 shows the morphology, in an area of 20 x 20μm^2 and sweep speed of 0.3*Hz* in non-contact mode, acquired by AFM on the surface of the AISI H13 steel substrates uncoated and coated with a TiN monolayer, deposited at different temperatures of the substrate.

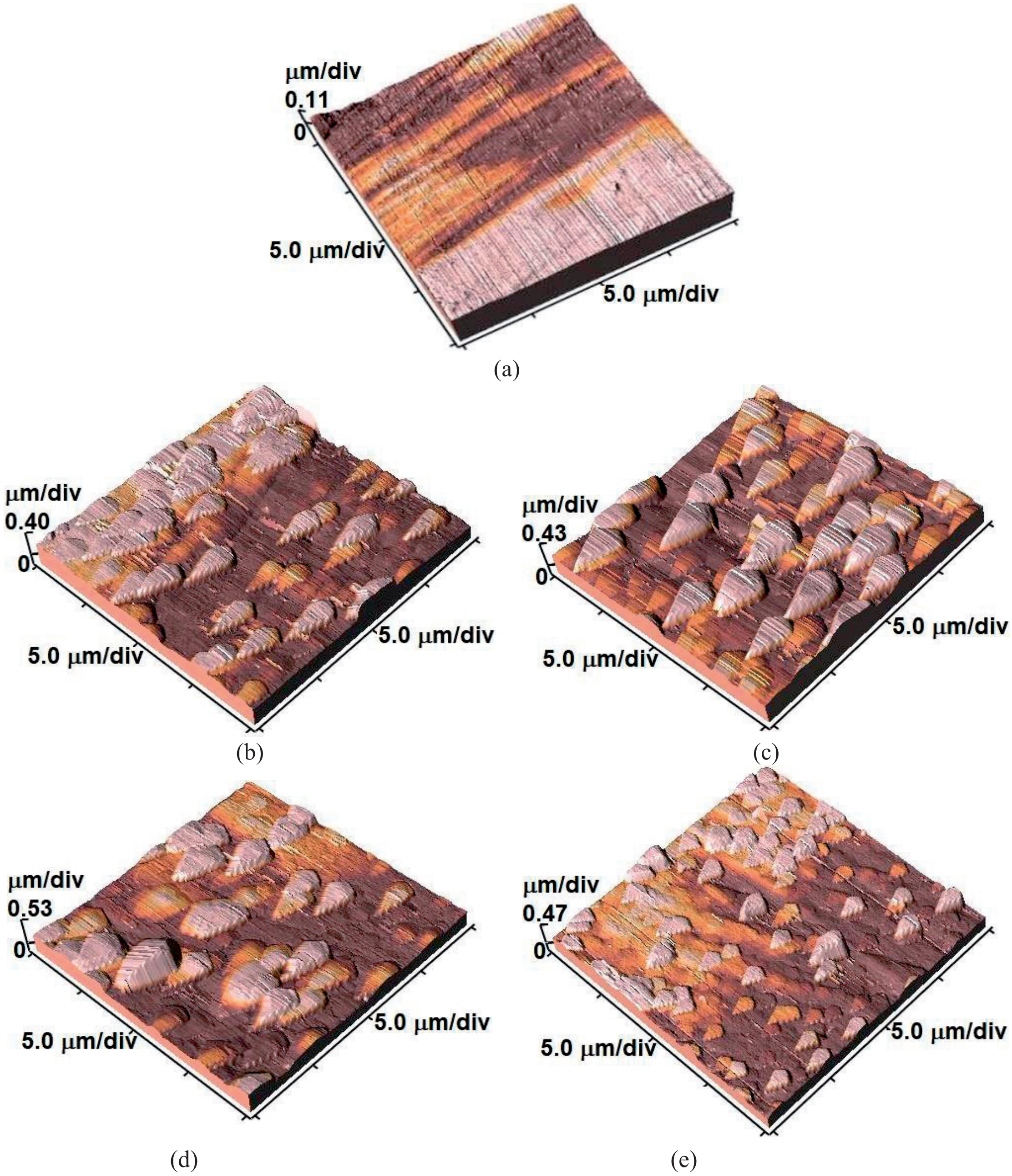

Figure 3. Superficial morphology of AISI H13 steel uncoated (a) and coated with TiN to a temperature of the substrate of: (b) 350°*C*, (c) 425°*C*, (d) 450°*C* y (e) 475°*C*

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Figure 3 is appreciated the change in the topography of TiN coatings due to the increase in substrate temperature. Figure 3(a) shows the typical characteristics of the AISI H3 steel prepared superficially with mechanical polishing and in the figures 3(b)-(e) it is perceived that the TiN films deposited on the surface form structures with a trapezoidal symmetry of different dimensions, which vary with the temperature of the substrate. This type of columnar growth indicates that the structure is located in the T zone proposed by Thornton [4], [18], [19].

From the qualitative analysis of the phases present, it was found that the TiN coating grew up with a cubic crystalline structure centred in the faces FCC, in a space group fm-3m. The crystalline structure of the TiN films deposited at different substrate temperatures was determined with the patterns obtained by X-ray diffraction, where the preferred orientation corresponds to the plane (111) and is also present in $2\theta \approx 36°$, likewise, in $2\theta \approx 42°$, $2\theta \approx 61$ and $2\theta \approx 73°$, secondary orientations of the crystallographic planes were identified in the directions (200), (220) and (311), respectively. Additionally, the peaks identified as "S", located in $2\theta \approx 44.05°$ and $2\theta \approx 64.30°$, correspond to the structure of the substrate (see Figure 4).

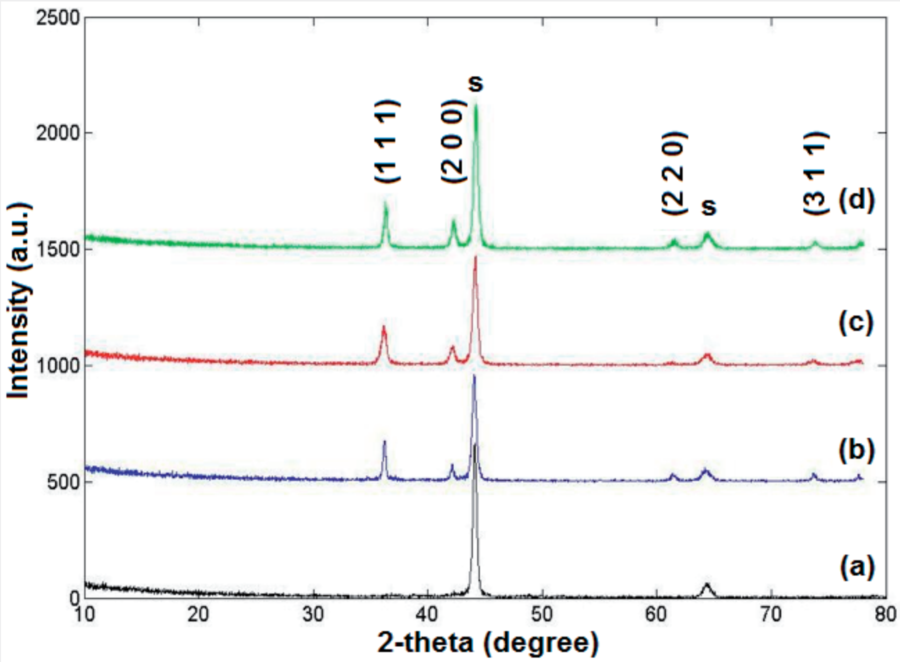

Figure 4. Diffraction patterns obtained on the surface of the AISI H13 steel uncoated and coated with TiN in function of substrate temperature. (a) Substrate, (b) 425ºC, (c) 450 ºC and (d) 475 ºC.

The TiN coatings deposited on the surface of the AISI H13 steel substrate by the cathodic arc technique in a vacuum, have a structure with a preferred orientation in the crystallographic direction (111) and as it the temperature increases, the orientation is somewhat lighter as in the crystallographic direction (200). In addition, we find that the crystallographic texture coefficient of the planes oriented in the directions (111) and (200) increases as a function of the temperature of the substrate, where the direction (111) has a higher texture coefficient than the direction (200) (see figure 5). On the other hand, it is known that in an FCC structure the main glides of the crystals occur in the plane with direction (111) and that being parallel to the surface the maximum values of hardness are obtained, corroborating the results obtained by micro indentation [20].

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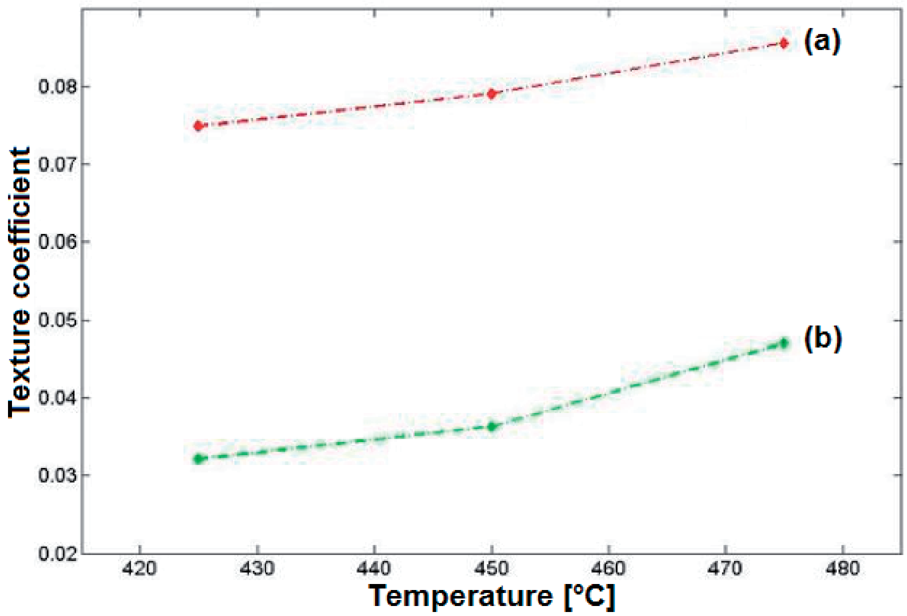

Figure 5. Crystallographic texture coefficient of the TiN films as a function of the temperature of the substrate, in the (a) (111) and (b) (200) directions.

The structural results of the TiN films showed that they have a notable dependence on the ion flow that is impacted on the substrate; however, the hardness of the coating was also influenced by the preferential orientation of the grain, which manifests itself in the presence of stresses residuals [21].

4. Conclusions

The behaviour of the substrate temperature variation on hardness and structure in the TiN coatings deposited by the cathodic arc technique in vacuum, in the temperature range between 350°C and 475°C was evaluated, where it was found the preferred orientation (111) which favors the mechanical properties of the film deposited on the surface of the AISI H13 steel.

Micro-indentation tests demonstrated that TiN films deposited, by vacuum cathodic arc, at different temperatures improved the mechanical properties of the surface of AISI H13 steel substrates with a significant increase of the hardness with respect to the uncoated surface.

The structural analysis of TiN coatings deposited on the surface of the AISI H13 steel substrates, as a function of the temperature, performed to the diffraction patterns and the crystalline orientations, determined the presence of residual stresses in the coating improving the nucleation and the diffusion of activated species in the study material.

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