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Synthesis and characterization of TiN / Ti / AISI 410 coatings

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Resumen

La síntesis y caracterización de películas delgadas de Ti y TiN de diferentes espesores se llevó a cabo sobre un sustrato de acero inoxidable martensítico AISI 410 utilizado para la fabricación de herramientas. Se midió los parámetros mecánicos entre las superficies interactuantes tales como espesor, adherencia y dureza. Mediante el microscopio electrónico de barrido (SEM) se observó la morfología superficial de la interfase Ti/TiN, encontrando que el crecimiento fue de granos columnares y mediante EDAX se comprobó la existencia de titanio. Utilizando difracción de rayos X (XRD) se pudo observar la presencia de tensiones residuales (~ -3.1 GPa) debido a las diferentes fases cristalinas en el recubrimiento. Bajo espectroscopía de foto emisión de rayos X (XPS) se consiguió observar la composición química molecular de la superficie del recubrimiento, siendo compuestos de Ti-N, Ti-N-O y Ti-O los predominantes.

Palabras clave: TiN, Plasma, SEM, XRD, XPS

Abstract

The synthesis and characterization of Ti and TiN thin films of different thicknesses was carried out on a martensitic stainless steel AISI 410 substrate used for tool manufacturing. The mechanical parameters between the interacting surfaces such as thickness, adhesion and hardness were measured. By means of the scanning electron microscope (SEM) the superficial morphology of the Ti/TiN interface was observed, finding that the growth was of columnar grains and by means of EDAX the existence of titanium was verified. Using X-ray diffraction (XRD) it was possible to observe the presence of residual stresses (~ -3.1 GPa) due to the different crystalline phases in the coating. Under X-ray photoemission spectroscopy (XPS) it was possible to observe the molecular chemical composition of the coating surface, being Ti-N, Ti-N-O and Ti-O the predominant ones.

Keywords: TiN, Plasma, SEM, XRD, XPS.

1. Introduction

In the metal-mechanical industry there is a constant need to improve the performance of some tools, therefore some heat treatments are applied to metals. However, these treatments are not enough to improve the performance of the tools. It is well known that some thermo-chemical surface treatments improve the fatigue resistance of mechanical parts. These processes produce increased surface hardness and wear resistance of the material, resulting in the formation of high residual compressive stresses on or near the surface of the tools, as well as residual tensile stresses at the core of the material. Residual stresses affect the full distribution of resistance under cyclic loads, resulting in a consequent decrease in tensile stresses which is effective on the surface of steel used in the chemical, pharmaceutical and food industries, etc. However, a

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better performance of the steam phase deposition process using plasma is required and the research in this area focuses on the study of plasma parameters in order to improve the process [1,2,3].

2. Materials and Methods

The coating was created by the PVD method with cathodic arc evaporator, by means of a bright direct current discharge the surface coating treatment was carried out on the AISI 410 steel. The experimental conditions of deposition were: base pressure 2 x 10^{-5} Torr, cleaning pressure 1.5 x 10^{-4} Torr, this was done for 10 minutes with a discharge current of 80 A and -800 V, using argon gas, then an interface coating was made of titanium, this was done at a pressure of 1 x 10^{-3} Torr for 5 minutes, with a discharge current of 80 A and -400 V. Finally, the TiN coating was carried out at a pressure of 2 x 10^{-2} Torr for 20 minutes, with an arc discharge current of 80 A and polarization of -100 in the substrate. The characteristics of a bright-discharge plasma were determined by means of a Langmuir unit probe, in order to determine the plasma density values, the electron temperature and the plasma potential. Optical emission spectroscopy was used to determine the excited chemical species present at the discharge.

In the experiments present the 2 cm x 1 cm and 0.5 cm thick AISI 410 steel samples were exposed to the plasma. The composition of the steel is shown in table 1.

Table 1. Steel composition AISI410 (%wt)

C	Si	Mn	P	S	Cr	Ni
≤ 0.15	≤ 1.0	≤ 1.0	≤ 0.004	≤ 0.030	11.50 13.50	≤ 0.75

In order to determine the optimal conditions of the experiment, the coating process was carried out and some mechanical and chemical-structural tests were performed, for which microhardness, adhesion and coating thickness were measured. The surface hardness was measured, which was done with a Vickers microindenter, the equipment used was a Vickers microhardness meter, Akashi Mod. MVK-H200. Measurements were made with loads of 25, 50 and 100 gf, adhesion tests were carried out in a CSEM REVETEST scratching equipment with a Rockwell C diamond tip indenter of 0.2 mm radius, to determine the thickness the spherical abrasion system was used (Calo Test). The chemical-structural details of the coating were studied by X-ray diffraction, working with Cu-Kα copper lines, and Cr-Kα chrome with wavelengths of 0.15406 nm for copper and 0.22896 nm for chrome to ensure the presence of the crystalline phases formed in the coating, in addition to the crystalline orientations (crystallographic texture), residual stresses and microdeformations. The equipment used was a Philips PW 1810 diffractometer.

To determine the microstructure and molecular chemical composition of the TiN coating, a VG ESCA3 Mark electron spectrometer was used. Through the XPS technique and the XPSPEAK41 software it was possible to identify and solve the different compounds. A PHILIPS FEI QUANTA 200 scanning electron microscope was used to characterize the morphology and microstructure of the TiN coating.

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3. Results

Hardness measurements were carried out with different loads and the results are shown in Figure 1 below. In the three specimens, the hardness increases as the load decreases, which is a result of the elastic recovery of the indentation at low loads (ISE effect).

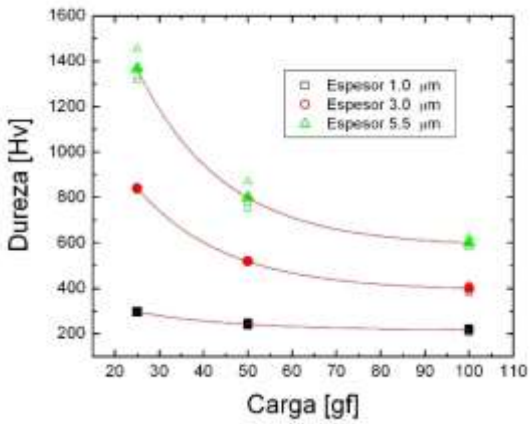

Figure 1. Microhardness measurements of Ti-N/Ti/AISI 410 coated samples.

Figure 2 shows that the adhesion increases with the thickness of the film. This is also an indicator of the greater resistance to deformation of the coating, as its thickness increases, since a greater load is required for the deformation to reach a sufficient level to reduce the cohesive failure of the coating due to fracture.

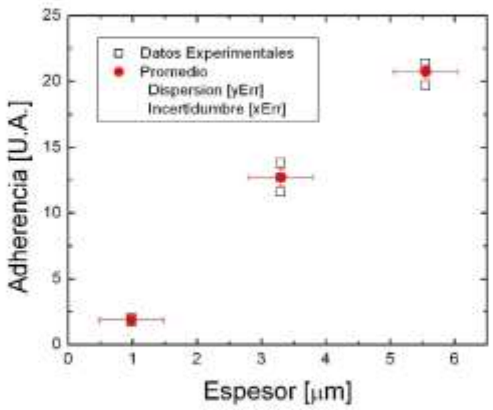

Figure 2. Adherence measurements of Ti-N/Ti/AISI 410 coated samples.

Chemical-structural properties

The diffractograms in Figures 3 and 4 show the peaks corresponding to the Fe base material and the peaks corresponding to the TiN coating. The influence of the potential on the texture is evident in the latter: for a potential of -300V the 111 planes of the coating are predominantly oriented parallel to the surface of the sample. Other relevant information arising from the diffractogram analysis relates to the density of the coating. Considering that the thickness of the layer measured by optical methods is thin, the intensity of the diffraction peaks in the sample is indicating the existence of a uniform coating i.e. not very porous.

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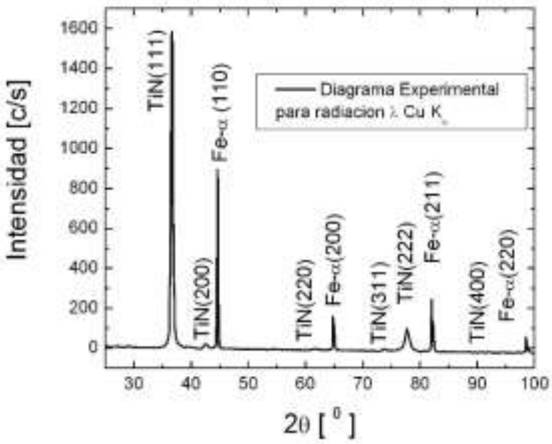

Figure 3. X-ray diffraction patterns for a Ti-N/Ti/AISI 410 coated simple

The residual stresses σ were determined using that the variation of angle 2θ is directly proportional to sen^2 Ψ in linear form, the constant that relates it is 1.83 with which the residual stresses have a value of -3,11 GPa, which indicates that there are compressive stresses in the coating. Since we are in a range of less than 10 GPa, it favours the non-detachment of the coating.

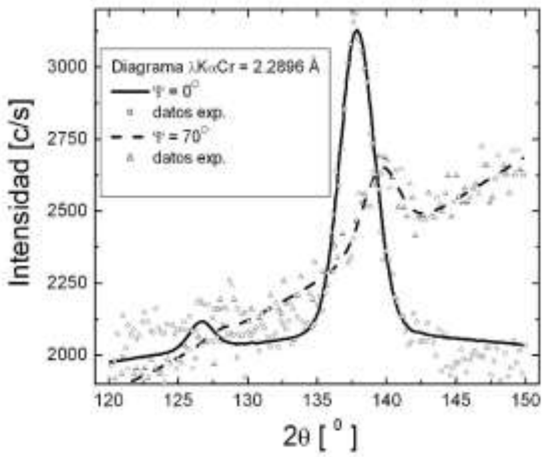

Figure 4. Current diagram in function of 2 for two angles of Ψ is determined for 2θ = 126° the phase of TiN(113) and for 2θ = 138° the phase TiN(222).

The SEM image of the morphology of the cross-section of the coated sample, and a measure of the TiN film thickness can be seen in figure 5. Given the difference in atomic weight between Ti and Fe the coating thickness (~4.72μm) can be precisely determined when the microscope is operated in reflective mode.

There is also a great uniformity in the coating, which has a fine and clear columnar grain structure. The existence of a thin Ti film is expected to be responsible for greater adhesion between the coating and the substrate, and an improvement in anti-corrosive properties.

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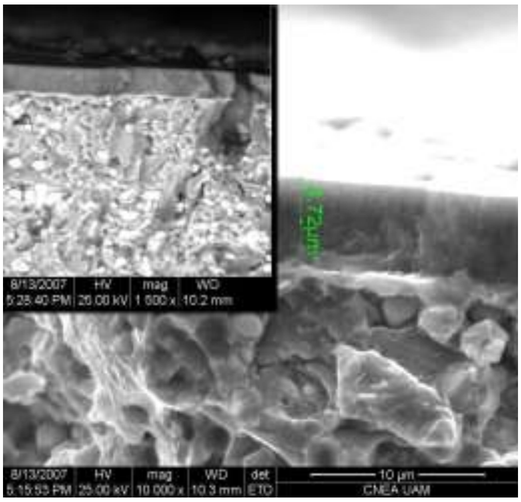
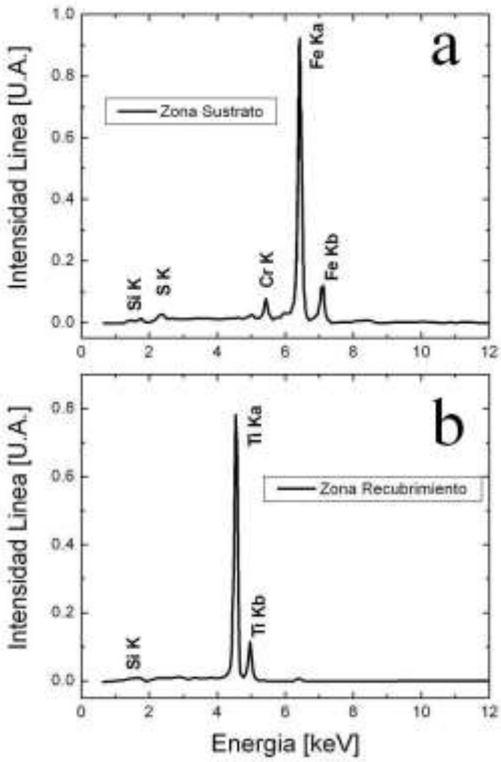


Figure 5. SEM image of two characteristic areas, the upper left corner, shows the definition of the coating through difference in atomic weights, the background image shows the growth of columnar grains.

EDS profiles are obtained for two characteristic regions of the sample, where the atomic composition of the substrate (Fig 6-a) and coating (Fig 6-b) is observed.



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Figue 6. Spectra obtained by EDS, through an EDAX detector, and for substrate zone (a) and for coating zone (b).

To study the chemical composition of the coating spectra were obtained through XPS. A complete spectrum of the composition can be seen in figure 7. There appears the spectrum of oxygen, titanium and nitrogen.

The chemical structure of the surface can be determined through the associated energies, as can be seen in figure 7. By making a finer spectrum it is possible to break down the information into multiple peaks, which indicate the presence of more complex compounds.

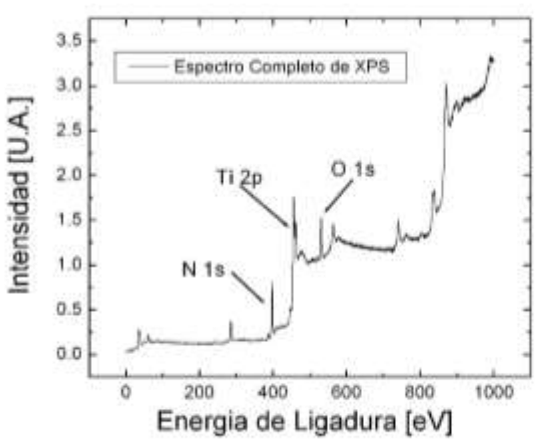

Figure 7. Wide spectrum of XPS, the characteristic bands of a Ti-N coating are recognized, corresponding to N 1s, Ti 2p and O 1s.

Figure 8 shows narrow spectra and an adjustment for different areas of interest, Nitrogen (1s), Titanium (2p), Oxygen (1s), and Carbon (1s) respectively in descending order. The fine spectrum for the different characteristic bands for the TiN coating can be seen in Fig 8, where the Intensity (U.A) is related to the Binding Energy (eV).

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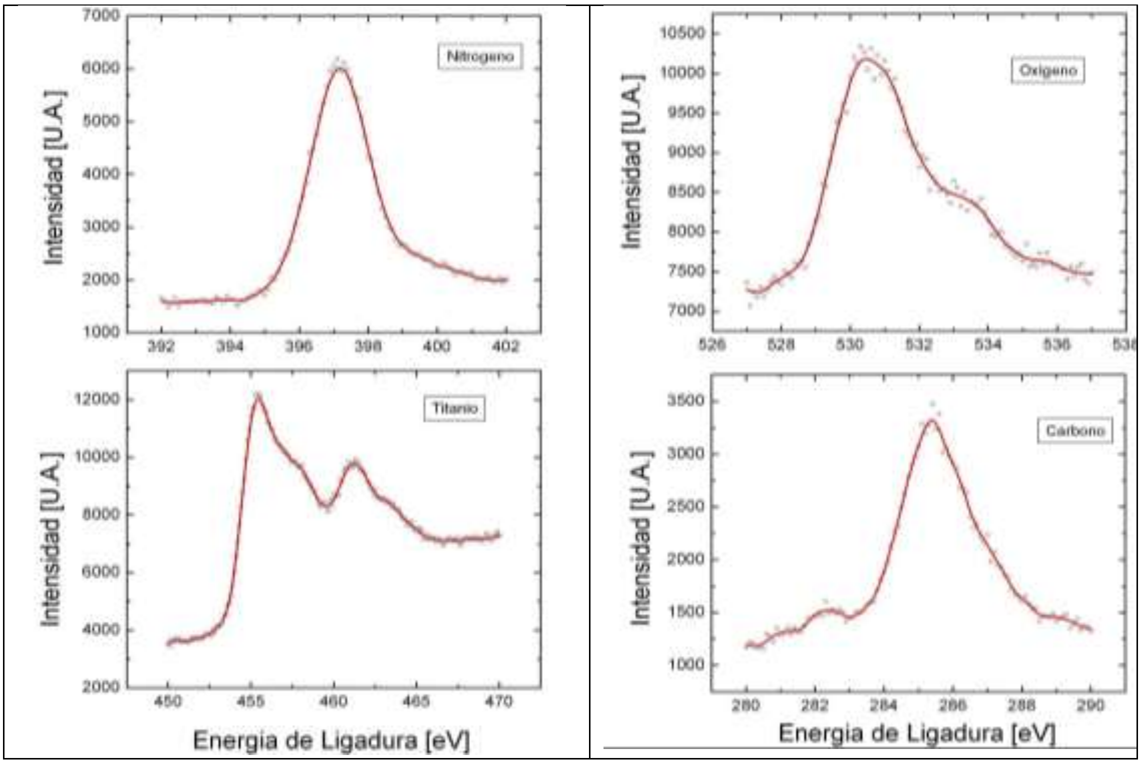

Figure 8. Thin spectrum for the different characteristic bands of a Ti-N coating

In figure 9 of the band 1N s, a central peak of a Ti-N link in the 397 eV is observed, with a small shoulder corresponding to nitrous oxide N-O in the 399.5 eV, which is of little intensity, but appears when deconvolute the spectrum to the linear background adjustment.

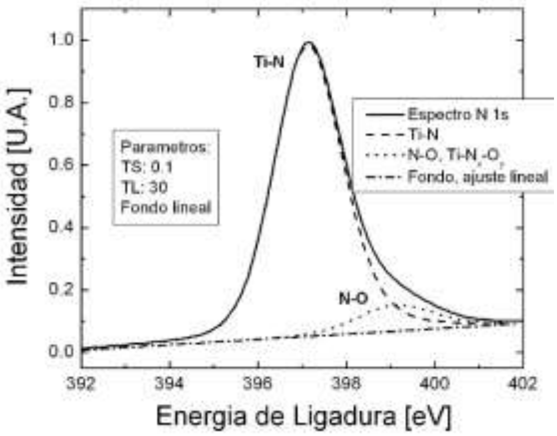

Figure 9. Adjustment curve for band 1N s, and its deconvolution in 2 peaks, corresponding to Ti-N (~397 eV) and N-O (~399 eV) links

In figure 10 of Ti-N p, it is possible to find more complex links, which are 3 groups of doubles that can be assigned to Ti-N 3/2p and 1/2p compounds for 455 and 461 eV, Ti-N-O 3/2p and 1/2p for

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457 and 463 eV and Ti-O for 458 and 464 eV respectively. These results agree very well with what appears in the literature [4].

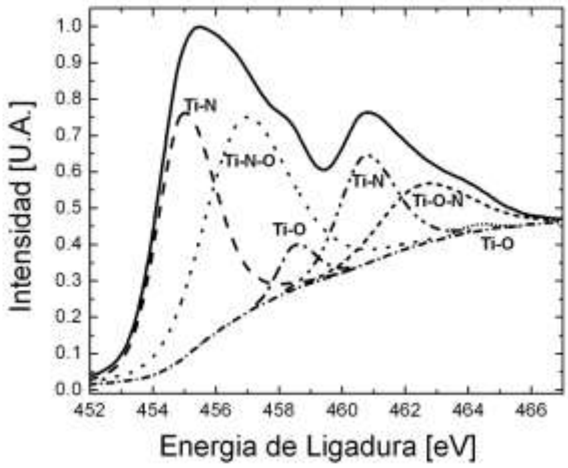

Figure 10. Adjustment curve for band 2Ti p, and its deconvolution in 6 peaks, corresponding to Ti-N (~455,461 eV), Ti-N-O (~457,463 eV) and Ti-O (~458,464 eV) links.

Plasma Current vs Voltage. In a bright DC discharge, the evolution of the current was studied, at the change of the voltage between electrodes, for an air discharge of 5.5 x 10^{-1} mbar. From figure 11, it is observed that after 750 volts, there is an avalanche of electrons, which are responsible for the ignition of the plasma, this then responds proportional to the increase in voltage between electrodes. Then when the voltage drops, the current follows the same path, but since the ignition already exists and a certain temperature (~eV), the minimum voltage for there to be discharge is lower (~500V).

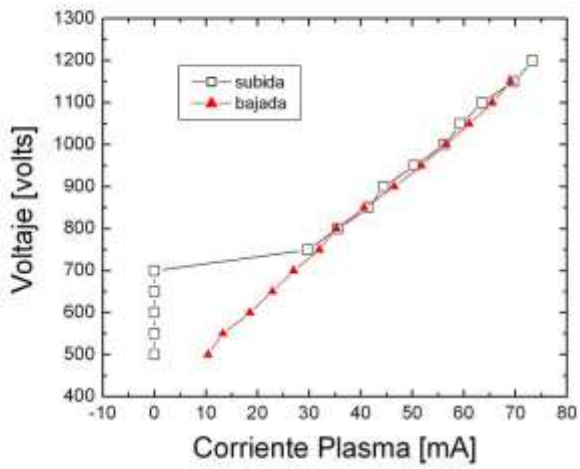

Figure 11. Plasma current characteristic curve as a function of the electrode voltage, for low pressure air discharge.

4. Discussion and Conclusions

The coatings obtained on the AISI 410 steel samples were carried out in a direct current discharge with the PVD cathodic arc process with a bias of -100 V. The coatings obtained on the AISI 410

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steel samples were carried out in a direct current discharge with the PVD cathodic arc process with a bias of -100 V. The coatings obtained on the AISI 410 steel samples were carried out in a direct current discharge with the PVD cathodic arc process with a bias of -100 V. Measurements of the mechanical properties indicate that the greater the thickness of the coating, within the experimental values studied, the greater the hardness and adhesion of the coating. This can be attributed to the higher resistance to deformation of the coating under these conditions. From the diffractograms obtained, the peaks corresponding to the Fe base material and those corresponding to the TiN coating were observed. The influence of the potential on the texture is evident in the latter: for a potential of -100V the $\{111\}$ planes of the coating are predominantly oriented parallel to the surface of the sample. The state of residual compressive stresses generated by the coating process and an increase in the heterogeneity of the microdeformations can be observed. The improvement in fatigue response of the coated material is explained by these two effects: residual compressive stresses of $\sigma = -3.11$ GPa and hardening in the surface layer.

Finally, it was possible to study stoichiometry through XPS, and thus it was possible to determine the predominant bonds in the Ti 2p and N 1s bands, which correspond to Ti-N, Ti-N-O and Ti-O compounds.

In general, it can be concluded that the study of synthesis as the characterization of coatings is indispensable for the development of the industry due to the versatility and variety of applications in it. The advance of characterization methods can go hand in hand with this development, thus achieving a symbiosis helping the development of the countries of the región.

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