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Effects of Hot Isostatic Pressure on Titanium Nitride Films Deposited by Physical Vapor Deposition

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Films of titanium nitride deposited by physical vapor deposition on 304 L stainless steel substrates were hot isostatic pressed (HIP) under 150 MPa at 550 °C. To study the effects of this treatment on the microstructure of those films, X-ray diffraction analyses, Rutherford Backscattering spectroscopy, scanning electron microscopy, and atomic force microscopy were performed. Surface hardness, and roughness were also evaluated to characterize the TiN properties. The hot isostatic pressure leads to an increase of hardness for depths up to 0.1 µm and a crystallographic texture change from (111) to (200). The original TiN golden color turned to red after the treatment. An increase of the grain size has been observed for hot isostatic pressed samples, but the stoichiometry of the TiN film was determined to be 1:1 by RBS. The microstructure observed by atomic force microscopy indicated that the TiN film surface is smoother after the HIP treatment.

Keywords: *Titanium nitride, PVD, HIP*

1. Introduction

Hard films deposited by chemical vapor deposition (CVD) on metals have been used industrially since the 60's. Physical vapor deposition (PVD) uses lower processing temperatures compared to the ones needed for CVD[1]. The first industrial use of titanium nitride films deposited by PVD on tools designed for cold forming processes was reported in 1977[2]. Films deposited by CVD and PVD usually improves the tribological properties of mechanical components, cutting tools, and they can also be used for decorative purposes. In the PVD process, a metallic reactive component, for instance, solid titanium, replaces the gas media usually used in the CVD process[1]. The first stage in the PVD process involves the transport of ions, atoms, or molecules, to the top of the substrate. The second stage is the adsorption of these species by the substrate, or by the growing film, and diffusion over the surface, and finally, the incorporation of those species in the film. The last stage is the atomic diffusion into the bulk. The film deposition depends on the process chamber geometry, target size, and gas pressure. The diffusion stage depends mainly on the substrate temperature. Since the incident species come from a limited number of directions, the film grain structure tends to be columnar[3].

There are some unique differences in the microstructure and residual stresses of films deposited by PVD and CVD. High residual compression stress and fine grains originated by the PVD process usually improve the hardness and toughness.

Titanium nitride films usually have low friction coefficient, high hardness, are high temperature resistant, and adhere well to several substrates[4]. Besides that, cutting tools deposited with those films show improved machining performance, and wear and corrosion resistance[5]. Titanium nitride films also show an attractive aesthetic appearance due to their golden color.

2. Structural Zone Model

The growth of TiN films happens in well defined regions depending on the electrical potential applied to the substrate and the deposition temperature.

Mochvan e Demchishin[6] were the first ones to classify the microstructure and to identify three structural regions depending on the deposition temperature. In the region named zone 1 (low temperatures), the microstructure consists of round-topped conic columns, and it is due to the relatively low atomic mobility. As the temperature is raised, diffusion becomes important in the film growth, and the microstructure becomes columnar with parallel sides and smooth topography. This region is named zone 2. If the

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temperature is further raised, the microstructure gets the appearance of equiaxial grains and this region is named zone 3. Latter on, Thornton[7] suggested that the presence of a gas phase during the deposition process could alter the model proposed by Mochvan and Demchishin, and a new microstructure region was identified (named zone T) which consists of fibrous grains.

3. Phase Transformation

Below 882 °C titanium has a hexagonal close packed crystalline structure (HCP) known as α-Ti. According to the Ti-N phase diagram, by increasing the nitrogen concentration, the titanium lattice expands in order to accommodate dissolved nitrogen atoms. The maximum concentration of nitrogen that can be dissolved in the titanium lattice is 23 atomic % at 1050 °C, corresponding to a ratio N/Ti = 0.3. For nitrogen concentrations around 33 atomic %, and temperatures lower than 1050 °C, the Ti_2N phase with a body center tetragonal structure can be observed. For nitrogen concentrations around 37.5%, and temperatures lower than 800 °C, the existence of $Ti_2N(\alpha)$ or δ'-Ti_2N phases is thermodynamically possible[3,8-9].

The TiN phase, which has a face centered cubic structure (FCC), also known as δ-TiN, can be found with non-stoichiometric compositions, TiN_x, in the wide nitrogen compositional range of 40-55 at%[8-9].

According to Wittmer[10], phase transformations can be explained considering that at low nitrogen pressures, nitrogen atoms firstly occupy hexagonal interstitial sites of the titanium hexagonal close packed structure (two sites per unit cell). Nitrogen atoms, being larger than the interstitial sites, give rise to expansion of the titanium lattice, raising the internal stresses of the crystalline lattice. When approximately half of the interstitial sites are occupied, the lattice distortion leads to the transformation of HCP to FCC. This is possible considering that the ratio Ti:N is 2:1. Since the FCC unit cell has four atoms of titanium and eight tetragonal interstitial sites, the ratio 2:1 corresponds to the filling of half of the FCC interstitial sites by nitrogen atoms. By increasing the nitrogen gas pressure, all interstitial sites tend to be filled out and titanium nitride is formed. If the nitrogen amount is further increased, nitrogen atoms will be concentrated in the grain boundaries[3].

The deposition of ceramic films has been intensively investigated in the last two decades. Hot isostatic pressure (HIP) can improve the consolidation of films deposited by PVD[11]. HIP is performed by using high pressures and temperatures simultaneously. Pressure is applied by loading an inert gas or nitrogen. The commercial use of HIP is relatively recent. New machines have been improved to raise the reliability of this technique, and a large volume of materials have been already processed by this technique[11].

In the present work the effects of HIP in the microstructure of titanium nitride films deposited by PVD are studied[12].

4. Experimental

Titanium nitride films were deposited on 304 L stainless steel substrates by the PVD process. The substrates were cylindrical pellets 15 mm in diameter and 10 mm thick. The substrates were cut, and polished to a finish of 600 mesh using SiC paper. Thirty-five specimen were prepared for this work. The substrate was chosen on the basis that deposition of TiN on stainless steel could be used in orthopedic implants.

HIP was performed by using a Asea Brown Boveri Autoclave model QIH-3. Nitrogen was used as the load gas since the aim of this work was to increase the nitrogen concentration in the titanium nitride film.

The HIP was performed by keeping the samples under 150 MPa at 500 °C for 100 min. This specific thermal cycle was chosen to avoid structural changes of the substrate. No other cycles were tried on.

The surface roughness (Ra and RMS) was determined by using a Atomic Force Microscope (AFM) Topometrix model Explorer. Measurements were performed on different areas of the film.

The film hardness was measured (Micro Hardness Fisher), and a software known as Hart was used to fit the depth profile curves. These measurements were performed by keeping the indenter perpendicularly to the film surface.

Rutherford Backscattering (RBS) was performed by using a Van der Graff tandem accelerator (NEC - National Electrostatics Corp. model 5SDH) with He^+ 2 MeV beam. Samples 5 mm^2 were cut and placed in a sample-holder. This technique allows the determination of the Ti:N ratio through the scattering of energetic particles with energies that depend on the atomic weight and position of the elements.

X-ray diffraction was performed (Bruker AXS modelo D 8 Advance) by using Cu Kα radiation in the 2θ range of 10° to 80° at 2° per minute to determine changes of the texture caused by the heat treatment.

Scanning electron microscopy (SEM) was performed by using a SEM Philips model XL 30. Samples were previously prepared by mounting them with epoxy resin, grinding with 220, 300, 400, 600 e 1000 SiC paper, and polishing with 6, 3 e 1 µm diamond pastes.

5. Results and Discussion

Titanium nitride films deposited by PVD are typically golden. After HIP, films turned red, what can be an indication that changes in the crystalline plane orientation occurred. Possible oxygen contamination during the HIP process were checked by RBS and EDS, which could cause oxidation, but no evidences were found.

Figures 1 and 2 show the depth profile of the indenter penetration as a function of the load applied to measure the hardness in samples with and without HIP treatment, for different limits of maximum penetration (1 µm and 0.1 µm respectively). Hardness values shown on the top of the figures are related to the maximum depth reached by the indenter. Figure 1 shows that, for depths up to 1 µm, the loads to reach a certain depth are similar for both type of samples (with and without heat treatment). On the other hand, Fig. 2 shows that in the region closest to the surface (maximum depth of 0.1 µm), the indenter loads to reach a certain depth depend on the heat treatment and the values are very apart. A large difference of hardness can also be noticed for depths up to 0.1 µm (Fig. 2). For deeper regions hardness values are close, as shown in Fig. 1. Therefore, a large variation of hardness was only found in the region closest to the surface (up to 0.1 µm) which could be caused by the nitrogen diffusion in the TiN film.

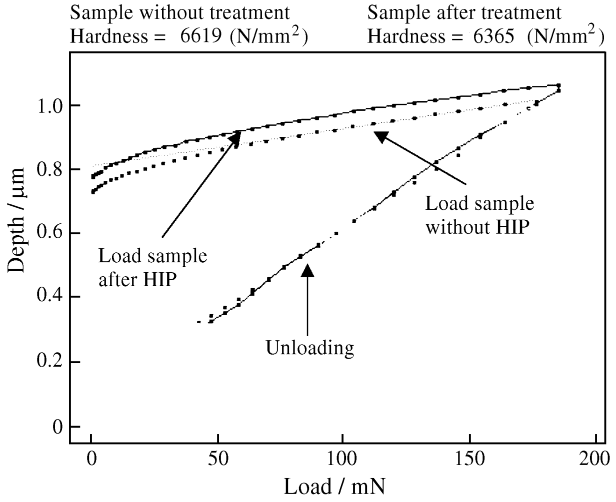

Figure 1. Depth reached by the indenter versus applied load for hardness measurement - maximum depth 1 µm.

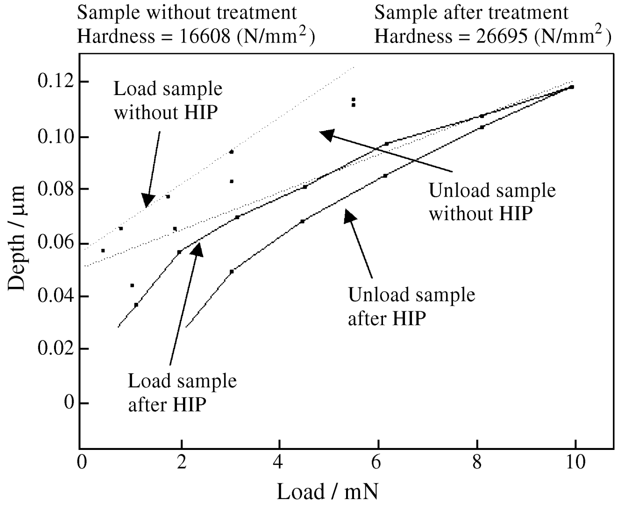

Figure 2. Depth reached by the indenter versus applied load for hardness measurement - maximum depth 0.1 µm.

Table 1 shows the average values and the standard deviation of Ra and RMS related to the surface roughness determined by AFM. These values are relatively smaller for hot isostatic pressed samples.

Figures 3 and 4 show the X-ray diffraction pattern of samples previous and after the HIP treatment, respectively. It is noticed that there was a texture change due to the HIP treatment. The intensity of the peak located at $2\theta = 42°$ is higher after the HIP treatment compared with the one without treatment. This peak is related to (2 0 0) crystalline plane of TiN[13]. The peak located at $2\theta = 36°$ is due to the (1 1 1) crystalline plane of TiN[13], and because its intensity is higher than the other ones, we conclude that there is a preference for this orientation. Table 2 show the grain size calculated by the Scherrer's equation to $2\theta = 36°$ and $2\theta = 42°$. It is concluded that the HIP treatment causes the increase of the grain size. This fact can be explained considering that the sample was heated to 550 °C, which is favorable for grain growth; it could be also considered that the amount of nitrogen in the TiN increased. These two factors could explain the change of crystalline plane orientation. The increase of nitrogen in TiN films has been previously observed and related to the texture changes, although no changes in Ti:N ratio was detected by RBS in the present work.

The lattice parameter determined after the HIP (4.224 Å) is smaller than the original one (4.271 Å). This fact indicates that nitrogen atoms in the grain boundaries are compressing the crystalline lattice in "hipped" samples.

It is also important to mention that from the X-ray pattern, there is no evidence of any amorphous phase originated by the inclusion of nitrogen atoms in the TiN layer.

Figure 5 show the SEM of sample after the HIP treatment. No large differences are noticed compared to the sample without HIP treatment; however, the TiN film seems to be dense. It is also noticed that a thin layer (approximately 1 µm) in the interface between the substrate

Table 1. Ra and RMS values determined by atomic force microscopy.

Ra (nm)	Average	Standard deviation
After deposition of TiN	23.00	5.66
After deposition of TiN and HIP	18.30	4.45
RMS (nm)		
After deposition of TiN	34.30	6.94
After deposition of TiN and HIP	23.70	7.41

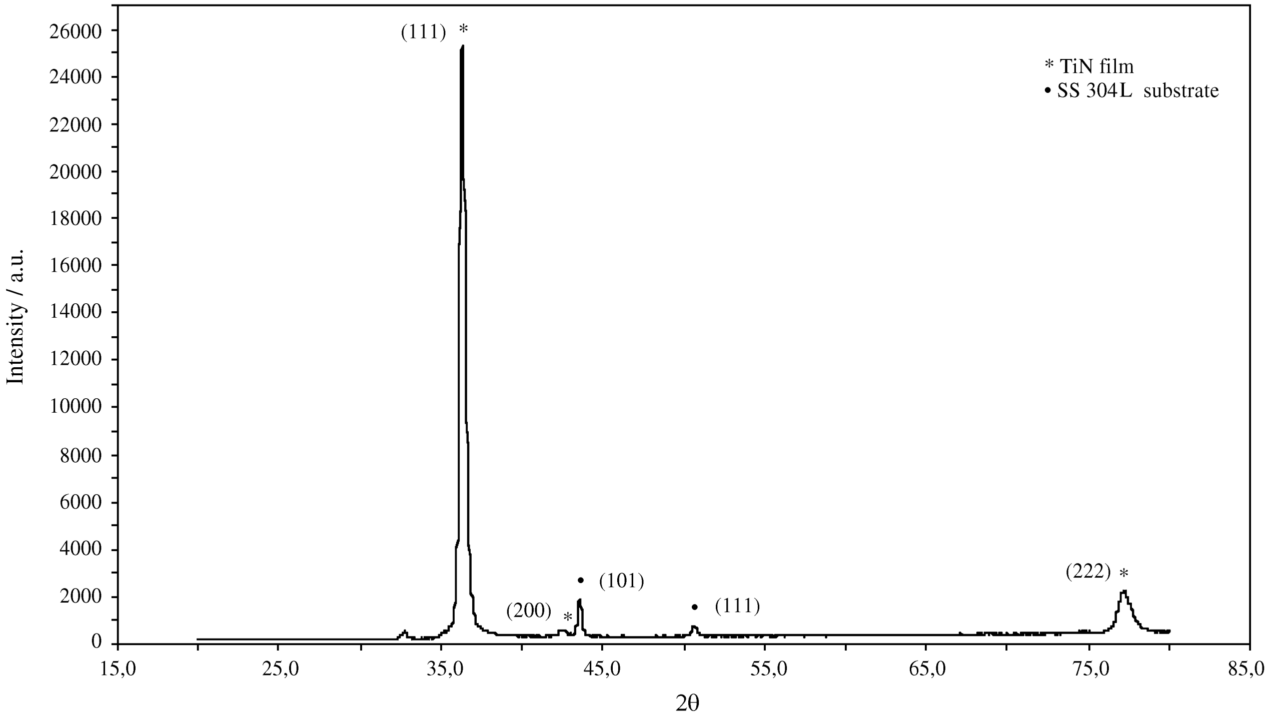

Figure 3. X-ray diffraction pattern for a TiN film without HIP treatment.

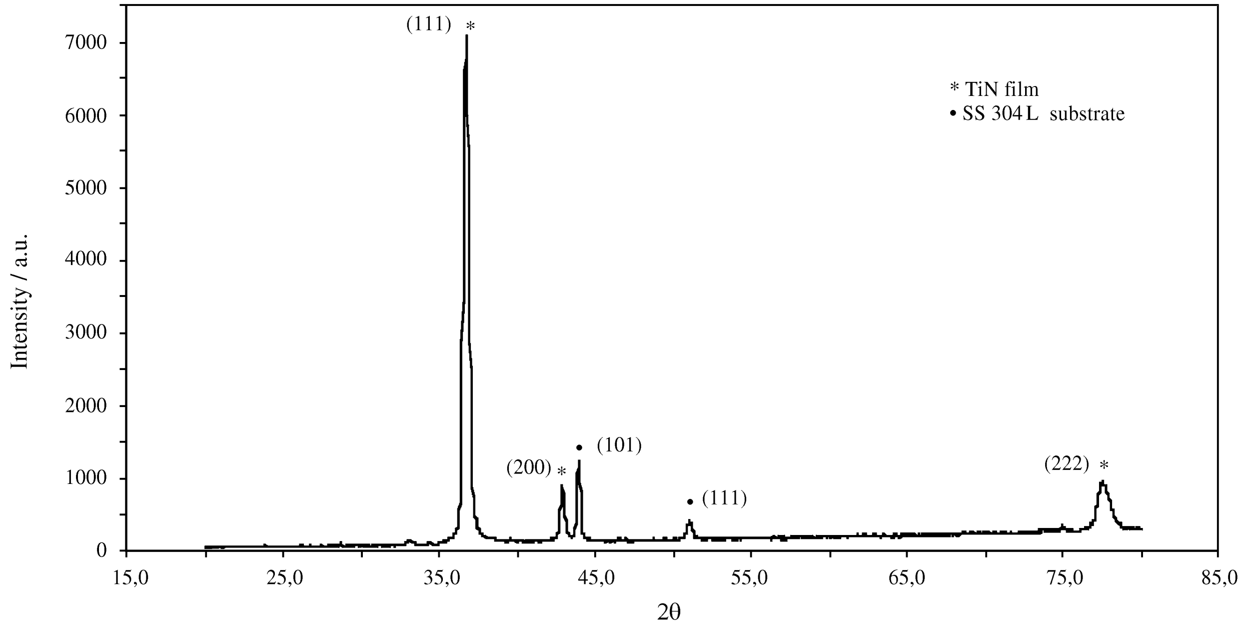

Figure 4. X-ray diffraction pattern for a TiN film after HIP treatment.

and the TiN film was modified by the deposition procedure. Further investigation is necessary to identify this effect.

The RBS spectra shown in Fig. 6 were fitted by using a software known as HUMP. It is noticed that the experimental data are fitted well by the theoretical curve generated by the software. The difference noticed for scattering energies lower than 0.7 MeV is an artifact of the equipment. The spectra are similar for both samples, and the composition of the film was determined to be TiN with Ti:N ratio equals 1:1. This result is not in agreement with the one observed by the X-ray diffraction where a possible variation of Ti:N ratio is suggested. Therefore the RBS technique might be

Table 2. Values of the grain size calculated by the Scherrer's equation to 2θ = 36° and 2θ = 42°.

2 θ	Sample without treatment (nm)	Sample after treatment (nm)
36°	18.2	22.0
42°	16.7	23.7

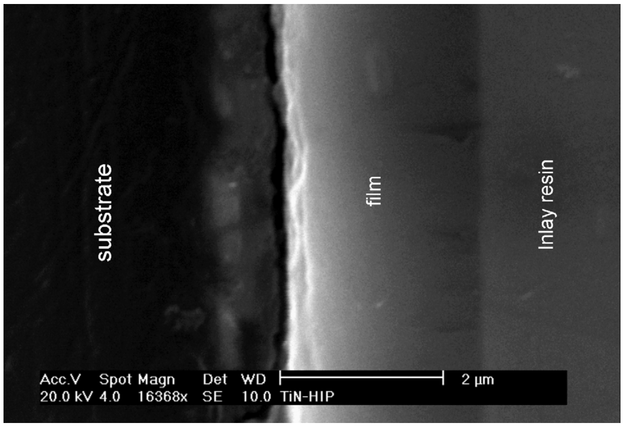

Figure 5. Micrograph of a TiN film after the HIP treatment. Backscattered electron image.

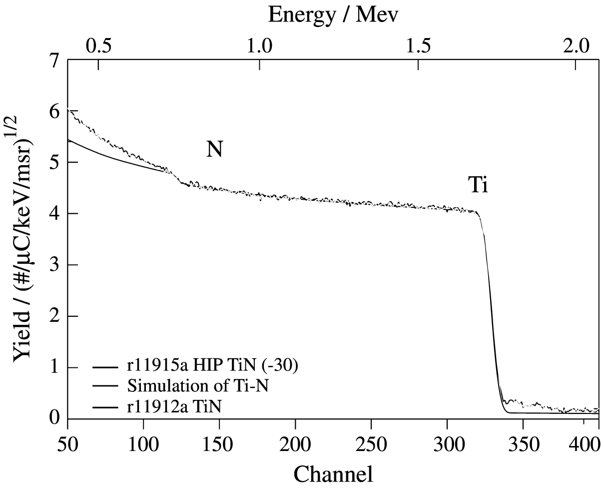

Figure 6. RBS from TiN film. The red line was generated by the software HUMP to fit the experimental data. From this fitness the Ti:N ratio was estimated to be 1:1. A He^+ beam with total accumulated charge of 30 µC was used. The detector was set at the angle -30°.

not enough accurate to indicate this variation, at least, in the order of magnitude observed in the present work.

By using atomic force microscopy it was possible to see the topographic characteristics of the TiN film. Figure 7 shows the AFM micrograph of the TiN film after HIP treatment. By comparing with Fig. 8 (AFM for samples without HIP treatment), it is noticed that the TiN film surface characteristics were affected by the HIP treatment. In the region analyzed, the salient maximum peak is 288.32nm for the "hipped" sample, and 802.92 nm for the as received sample. This is an indication that "hipped samples" have the smoothest surface.

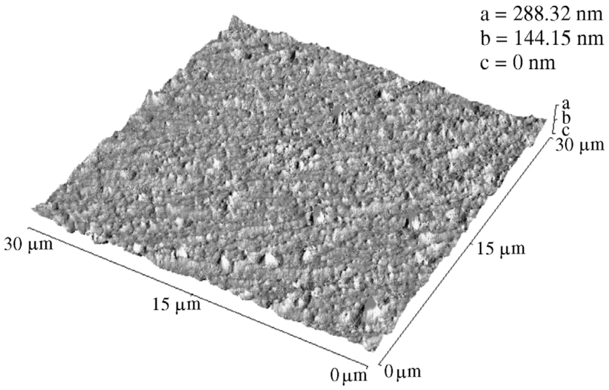

Figure 7. Atomic force micrograph for TiN film after HIP treatment.

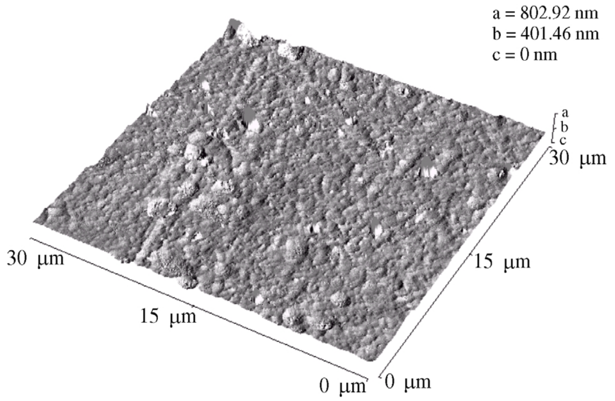

Figure 8. Atomic force micrograph for TiN film without HIP treatment.

6. Conclusions

Hot isostatic pressure of titanium nitride films deposited on stainless steel substrates causes the change of the TiN texture. X-ray diffraction showed that there was an increase of (2 0 0) crystalline planes orientation after "hipping".

The hardness of the TiN film is affected by the heat treatment, but only up to 0.1 µm in depth. That is an indication of the extension of nitrogen diffusion in the adopted experimental conditions.

The microstructure observed by atomic force microscopy indicated that the TiN film surface is smoother after "hipping". These results were possible due to the short depth (20 nm) of the contact tip of the atomic force microscope.

The RBS predicts the TiN film stoichiometric ratio equals to 1:1, but the lattice parameter determined after the HIP (4.224 Å) is smaller than the original one (4.271 Å), what is an indication that nitrogen atoms in the grain boundaries are compressing the crystalline lattice in "hipped" samples.

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