Microstructure changes induced by low-energy high-temperature nitrogen ion implantation on vanadium-titanium alloys.

M. Varela*, J.A. García**, R. Rodríguez**, D. Cáceres* and C. Ballesteros*

* Universidad Carlos III de Madrid, Depto. Física, Avda. Universidad 30, 28911 Leganés, Madrid. Spain, balleste@fis.uc3m.es
** AIN-Centro de Ingeniería Avanzada de Superficies, Cordovilla, 31191 Pamplona, Spain,

ABSTRACT

A detailed structural and tribological characterization of unimplanted and low-energy, nitrogen implanted V5at. %Ti alloy is presented. Samples were nitrogen-implanted at 1,2 kV and 1 mA/cm2, up to a dose of 1E19 ions/cm2, at a temperature of 673 K. Alloys were analyzed in cross-section by transmission electron microscopy and electron dispersive x-ray. Depending on the deep from the surface, the ion beam treatment dramatically changes the microstructure of the material. Partial amorphization of the implanted alloy in a region of 250-800 nm in deep is observed, following by a fully crystalline region at 800-1000 nm in deep, where TiN precipitates and dislocations are imaged. A clear correlation between the microstructure of the implanted layer and the reported improvement in the tribological and mechanical properties has been demonstrated.

Keywords: Ion implantation; TEM; nanoindentation; vanadium alloys; tribological properties.

1 INTRODUCTION

Vanadium-based alloys are promising candidates as high-performance structural materials for fusion power devices. The addition of Ti solute results in the improvement of the mechanical properties, increasing their creep resistance and suppressing irradiation swelling[1-4]. The improvement in the mechanical properties has been associated with the microstructure of defects induced by the Ti atoms and in particular with the formation of Ti-rich precipitates with matrix-impurities[5,6]. However these alloys show a poor tribological performance. After low-energy nitrogen-implantations the improvement in their tribological properties, hardness, friction coefficient and wear resistance, is obtained[5]. In this paper the structural modifications induced by low-energy nitrogen implantation on V5at%Ti alloys were analyzed in cross-section by transmission electron microscopy (TEM) and electron dispersive x-ray (EDX), the obtained results are discussed in correlation with the measured tribological and mechanical properties.

2 EXPERIMENTAL

V5at%Ti alloys were produced by repeated arc melting in a high-purity He atmosphere. Samples were nitrogen-implanted at 1,2 kV and 1 mA/cm2, up to a dose of 1E19 ions/cm2, at a temperature of 673 K. Cross-sectional specimens suitable for transmission electron microscopy (TEM) were prepared by standard procedures: mechanical grinding, dimpling and argon ion milling in a liquid-nitrogen-cooled holder with an acceleration voltage of 5 kV and an incidence angle of 8°. The electron diffraction, energy-dispersive x-ray analysis and TEM images were carry out using a Philips Tecnai 20F FEG analytical microscope operating at 200 kV. Tribological properties: hardness, wear resistance and friction coefficient have been measured as is described in ref. 5

3 RESULTS

3.1 Tribological and mechanical properties

The measured tribological properties on ref.5 are summarized in table 1.. A wear decrease of more than a factor 2 was obtained for a load of 1 N. Three different periods in the friction coefficient were observed: At the first stage the implanted samples showed a low friction coefficient, μ=0,2-0.42, after a "rising" period or transition period is observed. At 800 cycles, the friction coefficient rises to the value of μ=0.9. The last regimen behaviour is the same for implanted and unimplanted samples, μ=0.9 and is associated to a severe wear regimen. The observed wear decrease is expected after the hardness increase measured in micro and nano-indentation tests, see figure 1.
Mechanical properties of both, implanted and unimplanted, samples were measured by means of the nanoindentation technique.
Hardness evolution of the implanted sample as a function of the contact depth of the indenter tip, figure 1a, shows an important increase in the region close to the surface as compared to the unimplanted sample. This important increase in hardness must be associated to the structural

changes induced by the nitrogen ion implantation process. The hardness values slowly tends to the value of the unimplanted sample as the indentation depth is increased.
The evolution of the Young's modulus in the implanted sample, figure 1b, shows a similar behaviour as that found in the hardness.

We have the higher Young´s Modulus value in the region close to the surface sample followed by an important decrease in its value. The Young´s Modulus remains below than the corresponding for the unimplanted sample with a tendency to reach the values of he unimplanted sample at the higher depths. This behaviour is related to the structural changes induced by ion implantation.

Table I:

	Nanoindentation (GPa)	Friction Coefficient at contact pressure of				Wear Coefficient (m^2/N) at load of				Roughness	
Sample		0.4 GPa	0.5 GPa	0.6 GPa	0.65 GPa	0.25 N	0.5 N	0.75 N	1 N	Ra nm	Rq nm
Unimplanted	1.8±0.3	-	0.9	0.9	0.9	-	1,4 E-13	2,7 E-13	3,0 E-13	25±5	70±30
Implanted	5.7±1.1		0.25 →0.9	0.25 →0.9	0.42 →0.9	-	-	2,6 E-13	1,4 E-13	60±20	90±40

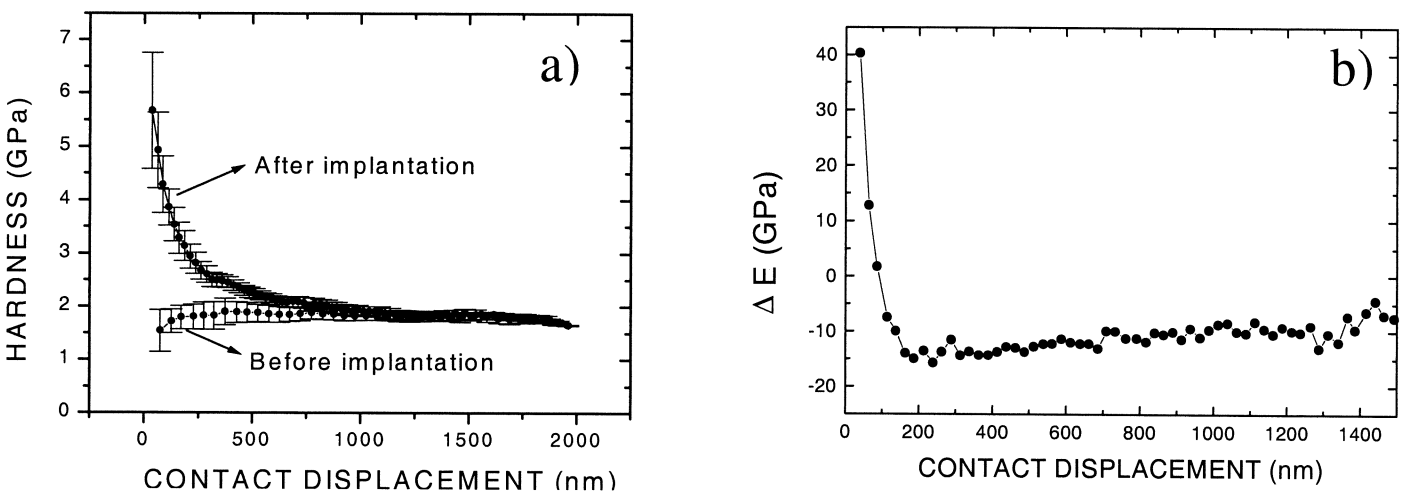

Figure 1. a) Nanoindentation hardness profile for the implanted and unimplanted sample. b) Incremental increase in Young Modulus after implantation.

3.2 TEM

3.2.1 Unimplanted samples

Unimplanted alloys appear clean and free of defects, indicating that the sample preparation process for TEM does not introduce appreciable modifications on the defects distribution. Only very isolated needle-shape precipitates are observed (figure 2). X-ray microanalysis was performed on the precipitates to analyse their compositional profile, see fig 3, the precipitates are rich in Ti and C.

Carbon is a common impurity in TEM and so differences between EDX spectra from precipitate and matrix in the same conditions are needed in order to estimate the C-content of the precipitates, close to 30% . Using the alloy matrix as an internal calibration in the microdiffraction pattern, see inset on fig. 2, the precipitate reflections correspond to an fcc crystal structure with a lattice parameter a_0=0.42 nm. As can be seen in the high-resolution image of figure 2 the precipitates are coherent with the matrix

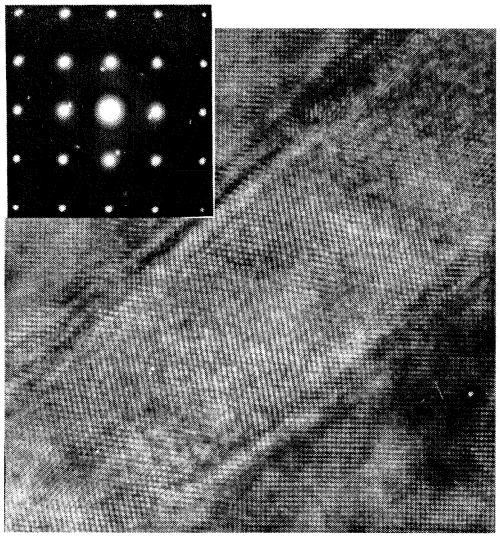

Figure 2. HREM image showing the orientation relationship between the matrix and a TiC non-stoichiometric precipitate. The inset shows the microdifraction pattern.

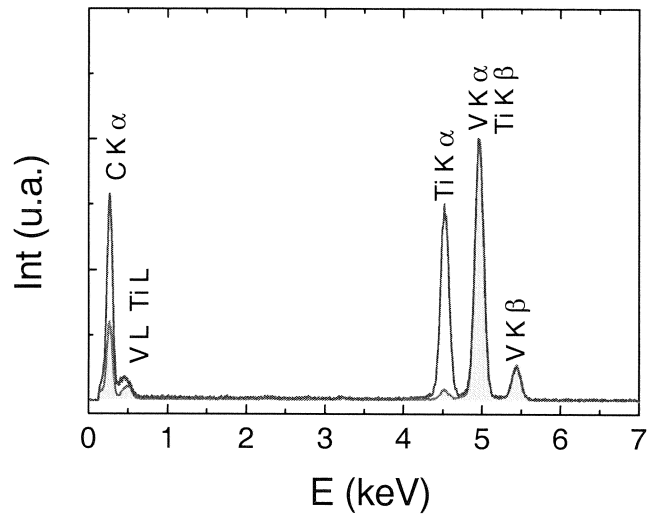

Figure 3. Energy dispersive x-ray spectra from a Ti rich precipitate and a region of a unimplanted alloy close to the precipitate (solid curve).

3.2.1. Implanted samples

The ion beam treatment dramatically changes the microstructure of the material, as a is analyzed by TEM. Three regions can be differentiated: a region close to the sample surface, up to 250nm deep, heavily contaminated with carbon and other impurities. Deeper in the sample, from 250 nm to 800 nm, and free of contamination, the crystal structure is mainly amorphous, TEM images show a distribution of nanocrystals embedded in the amorphous matrix fig.4a. The size of the nanocrystals increases as a function of deep from the surface. From 800 nm to 1000 nm, a fully crystalline area is observed, where precipitates and dislocations are imaged, see fig 4b. The nanocrystals and precipitates were analyzed by EDX, microdiffraction and selected area diffraction. The corresponding X-ray spectrum indicates that some of the nanocrystals are rich in Ti. Unfortunately no X-ray signal can be associated to N due to the overlapping of the K_α line of N with the L lines of Ti and V, and the relatively low intensity expected for the N K_α line. In several spectra the K_α C line was observed but in all cases no noticeable differences between the carbon K_α line intensity from the precipitates or the nanocrystals and the surrounding matrix was measured. The size and concentration of the nanocrystals and precipitates makes possible to analyse their crystal structure by selected area diffraction. Using the diffraction spots from the unimplanted region as an internal calibration the patterns were identified as a cubic fcc structure with a lattice parameter of 0.42 nm, essentially the same that the corresponding to TiN. However the differences in lattice parameter do not allow distinguishing between non-stoichiometric titanium carbide and titanium nitride, both with fcc structure. The low number of precipitates observed in the unimplanted alloys, no more than two or three per imaged sample, the clear differences in shape and size and in matrix-precipitate coherence and the fact that in fresh analysed samples no carbon contamination was observed out of the 250nm surface layer, strongly support that the precipitates are TiN.

A nanocomposite layer is formed "in situ" by N-implantation; the reinforcement particles are titanium nitride precipitates. The increase in hardness measured by nanoindentation tests and the thickness of the implanted layer active for this hardness increase, close to 1000 nm, can be directly correlated with the thickness of the layer where structural modifications are observed by TEM. The decrease in Young Modulus is associated with the amorphous layer and no modifications can be observed in the nanocomposite layer.

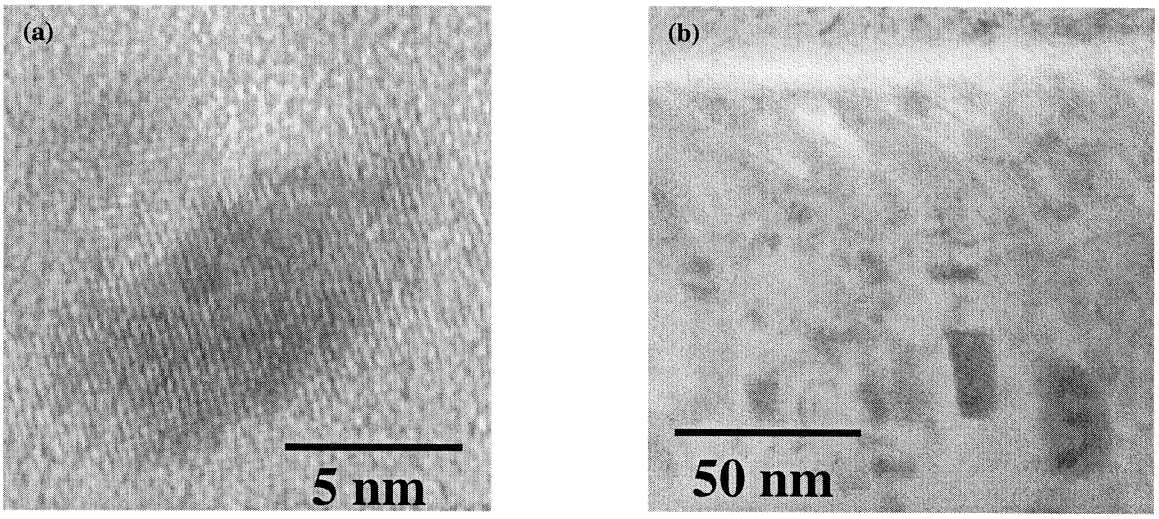

Figure 5: Cross-sectional images of an implanted sample: a) Nanocrystal embedded in the amorphous matrix from a region 250-800 nm in deep. b) Nano-composite layer close to undamaged region of the implanted sample 800-1000 nm in deep.

4 SUMMARY AND CONCLUSIONS

Low energy high temperature N implantation in V-Ti alloys results in great modifications in the crystal microstructure. Despite the fact that only a small part of nitrogen atoms form nitrides, both ballistic and diffusion modes are active. The N ions cause displacement of the sample atoms and partial amorphization in a region near the sample surface. Assuming thermal diffusion of the ions to form precipitates, the high implantation temperatures favour the precipitation processes and the "in situ" formation of a nanocomposite layer. A clear correlation between the microstructure of the implanted layer and the modifications in the tribological properties is demonstrated. The maximum decrease in Young Modulus, between the implanted and the unimplated layer is associated with the partially amorphous structure were nanocrystals have been imaged by TEM. No alterations can be observed at the nanocomposite layer formed "in situ" by the N-implantation, suggesting a strong influence of the upper layer on the Young´s Modulus measurement.

A clear influence of the surface contamination layer on the mechanical properties of the implanted samples is presented. However hardness measurements also indicate an important increase along the implanted layer. The thickness of the implanted layer, where a hardness increase is measured by nanoindentation tests, close to 1000 nm, can be directly correlated with the thickness of the layer where structural modifications are observed by TEM..

5 ACKNOLEEGMENTS

Authors would like to thank the support received from CICYT through the projects MAT-99-1012, and ESP2002-04509-C04-0. TEM work has been made at the LAMET of Universidad Carlos III de Madrid supported by the Comunidad Autónoma de Madrid, 07N/0034/2001. The technical help from L. Gómez and M.I. Ortíz is acknowledged.

REFERENCES

[1] R.E. Gold and D.L. Harrod. Int.Metals. Rev. **25**, 232 (1980)

[2] B.A. Loomis, A.B. Hull and D.L. Smith. J. Nucl. Mater., **84**, 179 (1992)

[3] H. Matsui, K. Fukumoto, D.L. Smith, H.M. Chung, W. Van Witzenburg and S.N. Votinov. J. Nucl. Mater., **92**, 233 (1996)

[4] H. Matsui, H. Nakajima and S. Yoshida. J. Nucl. Mater., **205**, 452 (1993)

[5] T. Leguey, R. Pareja. J. Nucl. Mater., **279**, 216 (2000)

[6] M. Varela, B. Fernández, A. Muñoz, T. Leguey, R. Pareja and C. Ballesteros. Phil. Mag. Lett., **81**, 259 (2001)

[7] J. A. García, R. Rodríguez, R. Sánchez, R. Martínez, J.P. Rivière, P. Méheust, M. Varela, D. Cáceres, A. Muñoz, I. Vergara, C. Ballesteros. Vacuum, **67**, 543 (2002).