COMPOUND FORMATION IN NITROGEN ION IMPLANTED TITANIUM AFTER ANNEALING

VLCAK Petr[1], DRAHOKOUPIL Jan[1], NEHASIL Vaclav[2]

[1]*Department of Physics, Faculty of Mechanical Engineering, Czech Technical University in Prague, Czech Republic, EU*

[2]*Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic, EU*

Abstract

Titanium materials are widely used in aerospace industry, in chemical industry and in total joint replacements because of their low density, high strength, good corrosion resistance, high toughness, and good biocompatibility. However, titanium materials have poor wear resistance and high friction. Implantation of nitrogen into titanium and its alloys significantly improves their surface properties such as hardness, friction, wear and corrosion resistance. Titanium nitride nanolayer was prepared by nitrogen ion implantation on titanium. The evolution of phase composition after annealing was investigated. The samples were analysed by X-ray diffraction, X-ray photoelectron spectroscopy and nanoindentation. The aim of this work is to examine the effect of the nitrogen concentration on phase representation in the modified surface area and the structural mechanisms of hardening after annealing.

Keywords: Ion implantation, annealing, structure, phase composition

1. INTRODUCTION

Titanium materials are widely used in aviation, in the automotive industry, and in total joint replacements because of their low specific weight, good corrosion resistance, high yield strength, and biocompatibility [1,2]. However, titanium and its alloys have poor wear resistance, high friction, low hardness [3,4]. The risk of allergic reactions and also possible ways to prevent allergic reactions to titanium have come under discussion [5]. The surface properties of titanium materials therefore often need to be modified. Ion implantation, i.e. kinetic doping of atoms into the surface area, has been shown to provide improved mechanical characteristics, wear resistance, and corrosion resistance in a range of engineering materials including titanium alloys [6]. This advanced technique has several merits in comparison with other surface modification methods. For example, (1) there is high adhesion of a thin layer integrated into the surface area, (2) it is a low-temperature process, and (3) the process parameters (ion energy, fluence, and depth distribution) can be precisely controlled. Species implanted into the titanium matrix can produce a surface layer composed of metastable, amorphous, and crystalline phases, solid solutions, and crystal lattice defects [7]. Liu et al. [8] and Schmidt et al. [9] showed that nitrogen ion implantation in titanium alloys stabilizes the α-Ti phase and forms compounds of varying composition and stoichiometry. Firouzi-Arani et al. [10] studied the nature of TiN_x substoichiometric nitride formation in titanium thin foil during nitrogen ion implantation, as a function of the substrate temperature. The results showed the development of titanium nitride with different compositions in the implanted samples, the presence of titanium oxides was also observed. Berberich et al. [11] studied the mechanism of degradation of surface hardening at elevated temperature. The XRD experiments showed that the TiN phase is stable up to temperature of 650 °C.

In this work, we present the evolution of a phase representation in implantation zone after post-implantation annealing in the temperature stability range of δ-TiN. A phase analysis by X-ray diffraction (XRD), chemical states by X-ray photoelectron spectroscopy (XPS) and nanoindentation investigations have been performed, with particular emphasis on phase characterisation of the implantation zone.

2. EXPERIMENTAL PART

The substrates were made of commercially pure titanium grade II in the form of a cylinder 14 mm in diameter and 3 mm in height. The samples were cut from a titanium bar and were then ground with a series of waterproof abrasive papers. Final polishing was performed with an colloidal solution to a mirror-like surface finish. The samples were ultrasonically cleaned in isopropyl alcohol. The titanium samples were irradiated by nitrogen ions. The accelerating voltage was 90 kV and the maximum ion current density was approximately 1.5 $\mu A \cdot cm^{-2}$. The sample temperature did not exceed 90 °C during implantation. The fluence of implanted nitrogen atoms was about $1 \cdot 10^{18}$ cm^{-2}. The ion current was measured by the Faraday cup and the sample temperature was measured by a thermocouple located in the sample holder. After ion implantation, the samples were vacuum annealed at temperatures of 300, 400, 500 and 600°C. The time of annealing was 6 hours. An experimental arrangement of the ion implantation process is illustrated in **Figure 1**.

XRD investigations were performed using a PANalytical X'Pert PRO horizontal powder diffractometer equipped with a Co anode (k = 0.1789 nm). Parallel beam geometry was used to enhance the contribution of the surface layer - a Gobel mirror in the primary beam, a parallel plate collimator with divergence 0.09 in the diffracted beam. The angle of incidence was fixed to 0.3°, 0.5°, 0.75°, 1°, 2°, 5° and 10°, resulting in calculated 90%-penetration depths of 90, 149, 222, 294, 571, 1310, and 2301 nm, respectively. The measurements were evaluated by the Rietveld-like TOPAS 3 program. The X-ray photoelectron spectroscopy XPS experiments were performed using an Omicron EA 125 multichannel hemispherical analyzer with the Al Kα line (1486.6 eV) as a primary photon source.The nanoindentation technique in continuous measurement mode (CMX) was used to obtain depth profiles of the surface hardness. The CMX indentation function was prescribed by a quasistatic force (P_{qstat}) in the range from 2 to 10000 μN. The dynamic actuation force (P_{dyn}) was prescribed in the range from 3 to 202.9 μN at a frequency of 200 Hz. For each sample, average values were obtained from 16 indents in a 4 x 4 matrix with a separation step of 5 μm. The nanoindentation testing was carried out at a temperature of 22.9°C.

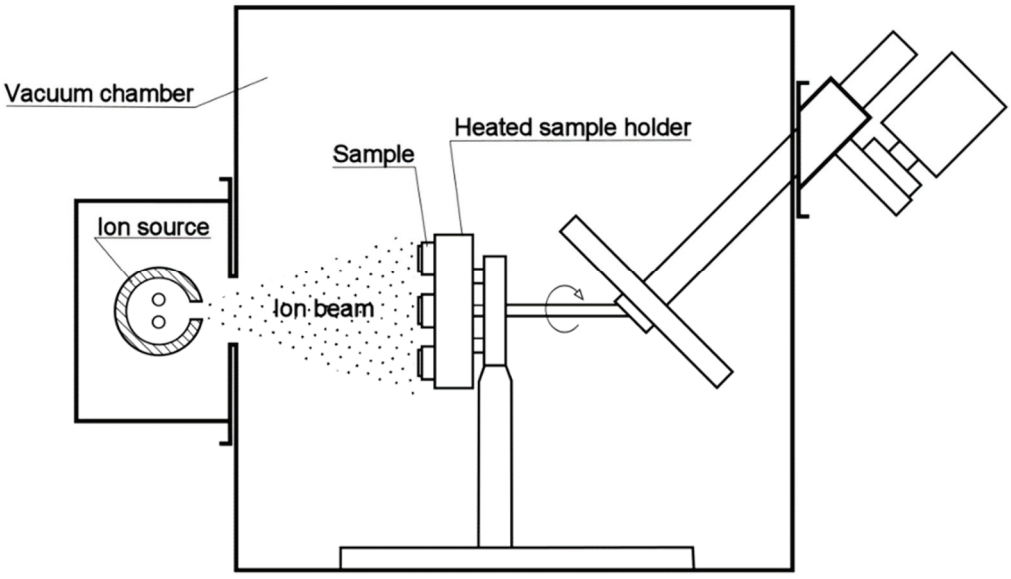

Figure 1 An experimental arrangement of the ion implantation process

3. RESULTS AND DISCUSSION

Phase representation in the nitrogen ion implanted samples was investigated by XRD. An exact diffraction study of the microstructure as a function of depth is complicated, due to the exponential character of the X-ray

absorption in the material. However, an interesting view into the depth dependence is given by changing the angle of incidence. A comparison of the diffraction patterns for various angles of incidence (0.3°, 0.75°, 1° and 10°) is presented in **Figure 2**. It is evident that the XRD information of each phase is provided by the integrated concentration from the material volume characterized by the penetration depth (angle of incidence).

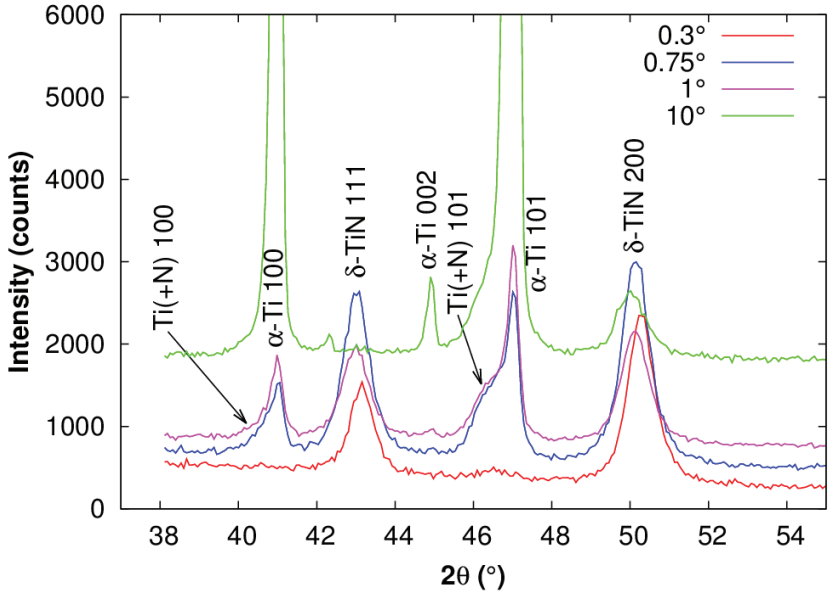

Figure 2 A comparison of the diffraction patterns measured at various angles of incidence on a implanted titanium sample without subsequent annealing

The peaks in the XRD patterns in **Figure 2** were described with a hexagonal structure of the α-Ti matrix, a mixed Ti(+N) solid solution and cubic δ-TiN titanium nitride. The Ti(+N) marks the hexagonal structure derived from the α-Ti phase, but with enlarged lattice parameters due to the presence of nitrogen ions in interstitial positions in the titanium substrate [25].

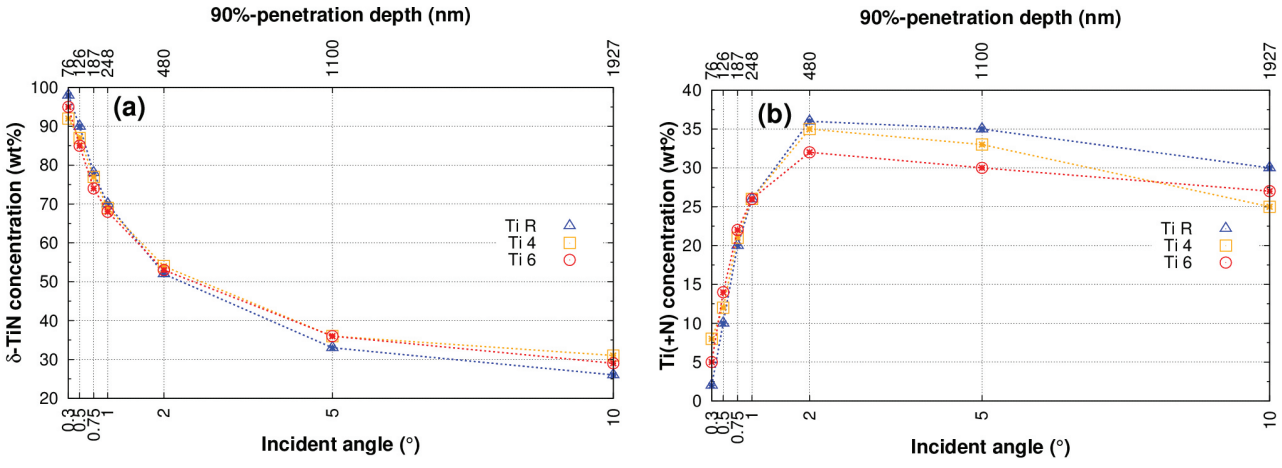

Figure 3 (a) A comparison of the δ-TiN distribution and (b) the Ti(+N) distribution measured on the implanted sample without annealing (Ti R), and on the annealed sample at 400°C (Ti 4) and at 600°C (Ti 6). Each point is generated at a different incident angle with a characteristic 90%-penetration depth

Figure 3(a), (b) shows the distribution of δ-TiN and Ti(+N) phases of in the modified surface area in dependence on post-implantation temperature, using incident angles from 0.3° to 10°. It is shown, that the very low representation of Ti(+N) slightly increases with rising temperature in the near surface region (marked by

incident angle 0.3°- 0.7°). The high concentration of δ-TiN in this region prevents the formation of Ti(+N) to a greater extent, although there the Ti(+N) increases. The comparison of the phase distribution in **Figure 3** indicates, that part of the interstitially located nitrogen migrates to the surface and strained part of δ-TiN crystallites are transformed back to the solid solution of Ti(+N).

XPS spectra of C1s, N1s, $Ti2p_{3/2}$ and O1s predominantly show the atmospheric contamination on the implanted surface. O1s binding energy of 529.5 eV corresponds to the TiO_2 and C1s binding energy of 284.5 eV indicates graphitic carbon on the surface. After annealing the C1s energy increases to 286.5-287 eV (defect sp2 bonds). The N1s peak is located at 395.6-395.8 eV, corresponding to nitride. The presence of δ-TiN compound confirms the $Ti2p_{3/2}$ peak located at 457.8 - 458.1 eV.

The hardness profiles in **Figure 4** show that the peak of indentation hardness of the implanted samples decreases with temperature of post-implantation annealing. The peak indentation hardness of the implanted sample without annealing and of the annealed samples ranges between approx. 30 and 20 GPa. This is an hardness improvement by a factor of 9 - 7 in comparison with the reference titanium sample. The surface hardness after post-implantation annealing at 600 °C is comparable with the surface hardness of nitrogen-implanted titanium at an elevated temperature of 800°C, as reported by Fouquet et al. [27]. Other researchers [12, 28] have reported on the indentation hardness of implanted titanium at elevated temperatures in a wide range between 6 and 25 GPa, based on implantation condition and on temperature.

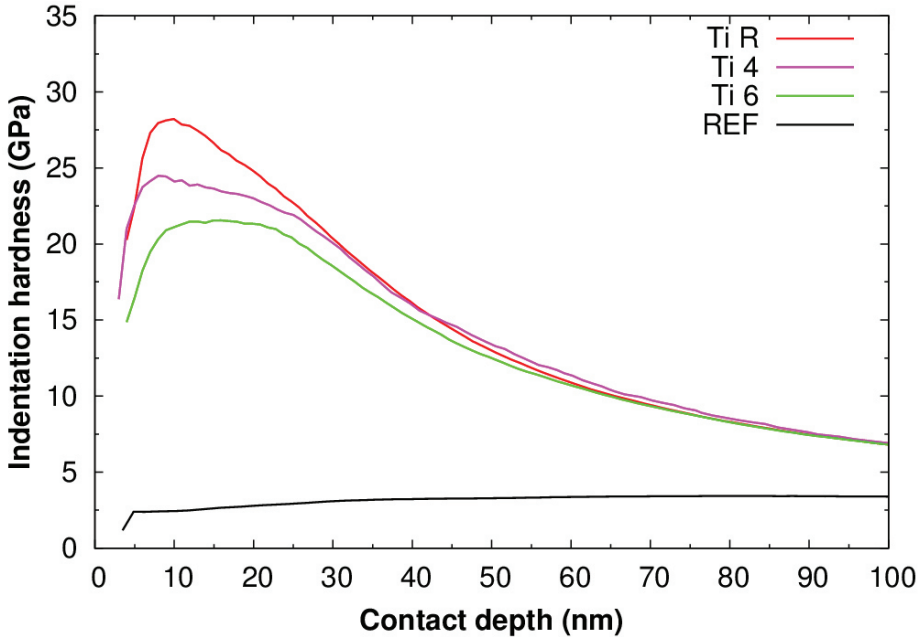

Figure 4 Indentation hardness versus contact depth for the titanium sample modified by ion implantation without subsequent annealing (Ti R) and subsequent annealed at 400 and 600 °C (Ti 4, Ti 6) and for the reference sample (REF)

4. CONCLUSION

The evolution of phase composition in nitrogen implanted commercially pure titanium grade II after annealing was investigated. The distribution of the phases identified as δ-TiN, Ti(+N) has been shown to be influenced by the temperature of post-implantation annealing. The comparison of the phase distribution of δ-TiN and Ti(+N) indicates, that part of the interstitially located nitrogen migrates to the surface and strained part of δ-TiN crystallites are transformed back to the solid solution of Ti(+N). The observed decrease in indentation hardness reflects the observed microstructural evolution.

ACKNOWLEDGEMENT

This research has been supported by research project No. GA16-22276S of the Czech Science Foundation.

REFERENCES

[1] SCHAUERTE O., Titanium in Automotive Production, Advanced Engineering Materials, Vol. 5, 2003, pp. 411-418.

[2] PODZIMEK S., TOMKA M., NEMETH T., HIMMLOVA L., MATUCHA P., PROCHAZKOVA J. Influence of metals on cytokines production in connection with successful implantation therapy in dentistry, Neuroendocrinology Letters, Vol. 31, No. 5, 2010, pp. 657-662.

[3] M. GEETHA M., SINGH A. K., ASOKAMANI R., GOGIA A. K., Ti based biomaterials, the ultimate choice for orthopaedic implants-a review, Progress in Materials. Science, Vol. 54, No. 3, 2009, pp. 397-425.

[4] CHEN D., SUN M., BAI G., MA X., TANG G. Tribological properties of Ti6Al4V alloy co-Implanted with N and F ions, Journal of Vacuum Science and Technology, Vol. 36, 2016, pp. 1279-1285.

[5] BELOHLAVEK J., BELOHLAVKOVA S., HLUBOCKY J., et al., Severe allergic dermatitis after closure of foramen ovale with amplatzer occluder, Annals of Thoracic Surgery, Vol. 96, 2013, pp. E57-E59.

[6] VLCAK P. The effect of ion irradiation and elevated temperature on the microstructure and the properties of C/W/C/B multilayer coating, Applied Surface Science, Vol. 365, 2016, pp. 306-313.

[7] VLCAK P., HORAZDOVSKY T., VALENTA R., KOVAC J. Evolution of the nitrogen depth distribution in an implanted titanium alloy with a surface carbon nanolayer, Chemical Physics Letters, Vol. 679, 2017, pp.25-30.

[8] LIU Y.Z., ZU X.T., QIU S.Y., CAO J., LI C.X., HUANG X.Q., WEI C.F., Phase formation and modification of corrosion property of nitrogen implanted TiAlV alloy, Vacuum, Vol. 81, 2006, pp. 71-76.

[9] SCHMIDT H., SCHMINKE A., SCHMIEDGEN M., BARETZKY B., Compound formation and abrasion resistance of ion-implanted Ti6Al4V, Acta Materialia, Vol. 49, 2001, pp. 487-495.

[10] FIROUZI-ARANI M., SAVALONI H., GHORANNEVISS M., Dependence of surface nanostructural modifications of Ti implanted by N + ions on temperature, Applied Surface Science, Vol. 256, 2010, pp. 4502-4511.

[11] BERBERICH F., MATZ W., KREISIG U., SCHELL N., MUCKLICH A., Mechanism of degradation of surface hardening at elevated temperature in TiAlV-alloys by in situ synchrotron radiation diffraction, Nuclear Instruments and Methods in Physics Research, Vol. 199, 2003, pp. 54-58.