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Nanomechanical Characterization of Titanium Alloy Modified by Nitrogen Ion Implantation

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Abstract**—**An ion implantation technique was used for designing the surface area of a titanium alloy and for irradiation-enhanced hardening of the surface. The Ti6Al4V alloy was treated by nitrogen ion implantation at fluences of $2 \cdot 10^{17}$ and $4 \cdot 10^{17}$ cm^{-2} and at ion energy 90 keV. The depth distribution of the nitrogen was investigated by Rutherford Backscattering Spectroscopy. The gradient of mechanical properties was investigated by nanoindentation. The continuous measurement mode was used to obtain depth profiles of the indentation hardness and the reduced storage modulus of the modified surface area. The reduced storage modulus and the hardness increase with increasing fluence. Increased fluence shifts the peak of the mechanical properties as well as the peak of nitrogen concentration towards to the surface. This effect suggests a direct relationship between mechanical properties and nitrogen distribution.

Keywords**—**Nitrogen ion implantation, titanium-based nanolayer, storage modulus, hardness, microstructure.

I. Introduction

TI6ALV4 titanium alloy is widely used in the aerospace industry, in the automotive industry, in the chemical industry, and in biomedical engineering for its low density, high tensile strength, efficient biocompatibility, and resistance to corrosion in some common environments [1]-[4]. However, a serious disadvantage of titanium alloys is their poor performance in sliding, hardness, and wear [5], [6]. The surface properties of titanium alloys therefore often need to be modified. Several methods can be applied for modifying the surface properties, e.g. plasma assisted chemical vapor deposition (PACVD), ion implantation (II), and ion beam assisted deposition (IBAD) [7]-[9]. Yilbas and Shuja [10] investigated the properties of laser and physical vapour deposited (PVD) TiN coatings on Ti6Al4V alloy. They concluded that laser treatment enhanced the adhesion between the TiN coating and the titanium alloy substrate. The TiN coating increased the hardness and led to less severe wear of Ti6Al4V alloy. Conventional nitridation was applied by Hong and Zhilhua [11]. This technique also improved the hardness, the wear resistance and the corrosion resistance, but the surface properties were significantly affected by the process parameters; e.g., temperature, time and pressure. In addition, conventional nitridation is carried out at high temperature for a long period of time, which causes the microstructure of the bulk alloy to degenerate.

Ion implantation may be a useful advanced technique for modifying the unsatisfactory surface properties of titanium alloys. Reactive elements implanted into a titanium matrix can produce a functionalized surface layer composed of metastable, amorphous and crystalline phases, solid solutions and crystal lattice defects [12]. It has been reported that ion implantation may provide improved mechanical and tribological properties. Schmidt et al. [13] found that ion implantation of nitrogen into Ti-6Al-4V alloy led to reduced wear during a sliding test against UHMWPE. High wear resistance was achieved by a combination of the high hardness of the implanted area and the low friction oxide on the surface.

This paper reports on an investigation of the effect of nitrogen concentration on the shape of the profiles of mechanical properties. We present the relationships between the chemical composition and the mechanical properties of titanium alloy modified by nitrogen ion implantation.

II. Materials and Methods

A. Sample Preparation and Modification

Ti6Al4V alloy was used as substrate material in this investigation. The fundamental chemical composition is presented in Table I. Samples 6 mm in thickness were cut from a rod 20 mm in diameter and were then polished with 150–2500 grid paper. Final polishing was carried out with two steps of diamond paste 5 µm and 0.5 µm. The samples were degreased with acetone, followed by ultrasonic cleaning in isopropyl alcohol.

TABLE I
FUNDAMENTAL CHEMICAL COMPOSITION OF TI6AL4V

Element	Range (wt.%)
C	0.1
O	0.2
N	0.05
H	0.0125
Fe	0.3
Al	5.50-6.75
V	3.50-4.50
Ti	balance

The polished samples were placed on a sample holder, and the base pressure in the vacuum chamber was $1.0 \cdot 10^{-4}$ Pa. Nitrogen ion implantation was carried out at an accelerating voltage of 90 kV at fluences of $2 \cdot 10^{17}$ and $4 \cdot 10^{17}$ cm^{-2}. The

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work pressure was ~$5\cdot10^{-3}$ Pa, the ion beam current was ~2 μA, and the temperature of the sample was below 80 °C during the implantation process [14].

B. Concentration Profile

The concentration profiles of the implanted nitrogen were measured by Rutherford backscattering spectroscopy (RBS), using a 2.1 MeV He beam scattered at an angle of 170° [14].

C. Nanomechanical Testing Condition

Nanomechanical analysis was performed by the Hysitron TI950 TriboIndenter™ (Hysitron, Inc., Minneapolis, MN, USA) using a diamond Berkovich tip as an indenter probe. Continuous measurement mode (CMX) was used to obtain depth profiles of the mechanical properties of the modified titanium alloy. CMX is carried out by applying a small dynamic force oscillation which is continuously superimposed and scaled to a quasistatic force during loading. The harmonic force and the corresponding displacement signal are analyzed according to nanometric dynamic mechanical analysis (nanoDMA), which gives variety of mechanical parameters such as storage modulus and hardness [15], [16]. The CMX indentation function was prescribed by quasistatic force (P_{qstat}) in the range from 10 to 10000 μN. The dynamic actuation force (P_{dyn}) was prescribed in the range from 9.4 to 286.6 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 experiment was carried out at a temperature of 22.7 °C.

D. Theory of NanoDMA

The dynamic driving force $P_0\sin(\omega t)$ with amplitude P_0 and frequency $f=\omega/2\pi$ is superimposed on the quasistatic loading P_{max} and stands for a particular term in an equation of motion of the indenter relative to the indenter head:

$$P_0 e^{i\omega t} = m\ddot{x} + C\dot{x} + Kx. \tag{1}$$

The solution to the above equation, where the compliance $C=C_i+C_s$ and the stiffness $K=K_i+K_s$ of the system in Fig. 1 are defined, is a steady-state displacement oscillation at the same frequency as the harmonic loading:

$$x = X_0 e^{i(\omega t-\phi)}, \tag{2}$$

where X_0 is the amplitude of the displacement oscillation and Φ is the phase shift of the displacement with respect to the driving force. Both terms in (2) are recorded by the nanoindentation system.

The standard analytical solution for the model on Fig. 1, which assumes that the machine frame stiffness K_i is infinite, follows.

The amplitude of the displacement signal, X_0, and the phase shift between force and displacement, Φ, are given by

$$X_0 = \frac{P_0}{\sqrt{(K_s + K_i - m\omega^2)^2 + \left[(C_i + C_s)\omega\right]^2}} \tag{3}$$

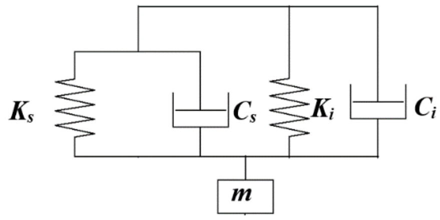

Fig. 1 Dynamic model of the indenter system in contact with the specimen, where m is the indenter mass, C_i is the damping coefficient of the air gap in the capacitive displacement sensor, C_s is the damping coefficient of the specimen, K_s is the contact stiffness, and K_i is the spring constant of the leaf springs that hold the indenter shaft

$$\phi = \tan^{-1}\frac{(C_i + C_s)\omega}{K_s + K_i - m\omega^2} \tag{4}$$

where m is the indenter mass, ω is the frequency in rad/s, C_i is the damping coefficient of the air gap in the capacitive displacement sensor, C_s is the damping coefficient of the specimen, K_i is the spring constant of the leaf springs that hold the indenter shaft, and K_s is the contact stiffness [16].

The reduced storage moduli (E') and the hardness (H) were computed as:

$$E_r' = \frac{K_s\sqrt{\pi}}{2\sqrt{A_c}} \tag{5}$$

and

$$H = \frac{P_{qstat} + P_{dyn}}{A_c}, \tag{6}$$

where K_s is the storage stiffness, and A_c is the projected contact area [16]. The contact area function $A_c(h)$ was calibrated on fused quartz [15].

III. Results and Discussion

The RBS depth profiles of the nitrogen of the modified surface area are shown in Fig. 2. The high applied fluences lead to an increased concentration of nitrogen in the modified samples. The nitrogen enrichment ranged up to a depth of approximately 176 nm (for fluence of $4\cdot10^{17}$ cm^{-2}). The nitrogen distribution starts at the surface, and the shape of the nitrogen concentration profile reflects the secondary effects of ion implantation. The first factor is sputtering of the surface during the ion implantation process, together with the nitrogen ions that are adsorbed there. The second factor is diffusion of the implanted nitrogen. A large amount of energy is delivered by nuclear collisions of ions in the surface area. This leads to the formation of point defects and a higher concentration of these defects in the near-surface region. The increased concentration of these defects and their migration deform the concentration profiles in this area through radiation enhanced diffusion (RED). The RED effect on the shape of the concentration profile can be enhanced by elevated temperature during ion implantation [12].

Figs. 3 and 4 show the reduced storage modulus E' and the indentation hardness H of the samples after nitrogen implantation, in comparison with the Ti6Al4V reference sample before nitrogen implantation. Constant trends of the mechanical properties of the reference sample throughout the indentation depth are shown in Figs. 3 and 4. It is evident that mechanical properties increase with increasing fluence of the implanted nitrogen atoms. The highest reduced storage moduli and indentation hardness were obtained after applying fluence of $4{\cdot}10^{17}$ cm^{-2} (Table II). The values of the mechanical properties decrease and converge to the values of the mechanical properties of reference sample as the indentation depth increases. The peak of the mechanical properties moved to the surface with increasing fluence as in the case of the concentration profiles (Figs. 2-4). Analogous trends of the depth profiles of the indentation hardness and the concentration profiles suggest a direct effect of the nitrogen concentration on the mechanical properties of the nanolayers. If the 1/10 rule [17] is applied to the maximum nanoindentation hardness values, we can say that the maximum portion of nitrogen was implanted to a depth of 155 nm for fluence of $2{\cdot}10^{17}$ cm^{-2}, and to a depth of 126 nm for fluence of $4{\cdot}10^{17}$ cm^{-2}. This should to be in agreement with the depth of the maximum concentration of nitrogen in Fig. 2.

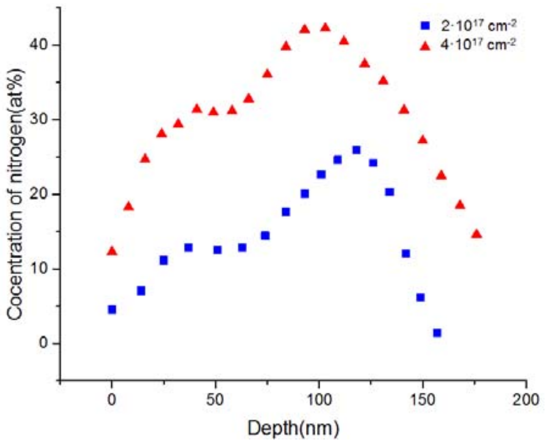

Fig. 2 Concentration profiles of nitrogen implanted in the surface of the Ti6Al4V sample

TABLE II
MAXIMUM MECHANICAL PROPERTIES OF A TITANIUM NITRIDE-BASED NANOLAYER

Fluence of implanted nitrogen (cm^{-2})	Ref. sample	$2{\cdot}10^{17}$	$4{\cdot}10^{17}$
Maximum reduced storage modulus (GPa)	130.1±15.0	176.0±20.0	211.5±23.6
Contact depth (nm)	3.1	3.96	3.57
Maximum indentation hardness (GPa)	5.0±0.6	15.1±1.8	18.6±1.9
Contact depth (nm)	15.9	15.5	12.6

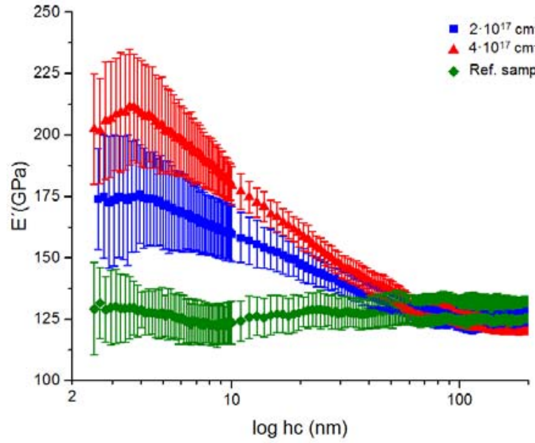

Fig. 3 Depth profiles of reduced storage moduli

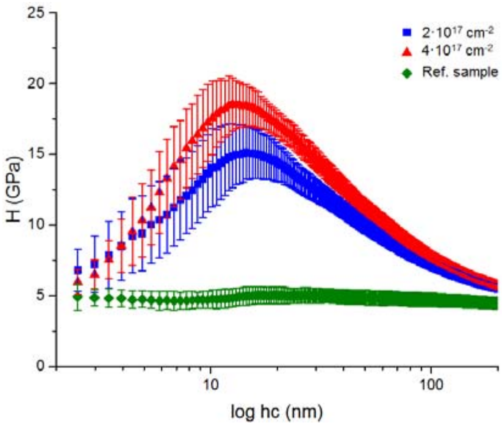

Fig. 4 Depth profiles of indentation hardness

IV. CONCLUSION

Nanomechanical characterization of the titanium alloy modified by nitrogen ion implantation was performed successfully. The CMX method provides a large number of points and low variance values. This is advantageous for measurements of structures with a variable gradient of mechanical characteristics. Depth profiles of indentation hardness and concentration profiles suggest a direct effect of the nitrogen concentration on the mechanical properties of the nanolayers modified surface area.

The influence of increasing fluence on the nanomechanical properties and on the nitrogen concentration depending on depth will be investigated in the next step of our investigation.

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REFERENCES

[1] M. Peters, J. Kumpfert, C. H. Ward, C. Leyens, "Titanium Alloys for Aerospace Applications," *Adv. Eng. Mater.*, vol. 5, pp. 419-427, 2003.

[2] O. Schauerte, "Titanium in Automotive Production," *Adv. Eng. Mater.*, vol. 5 pp. 411-418, 2003.

[3] M.A. Khan, R.L. Williams, D.F. Williams, “The corrosion behaviour of Ti–6Al–4V, Ti–6Al–7Nb and Ti–13Nb–13Zr in protein solutions,” *Biomaterials*, vol. 20, pp. 631-637, 1999.

[4] S. Podzimek, M. Tomka, T. Nemeth, L. Himmlova, P. Matucha, J. Prochazkova, “Influence of metals on cytokines production in connection with successful implantation therapy in dentistry,” *Neuroendocrinology Letters*, vol. 31, pp. 657-662, 2010.

[5] Y. Luo, S. Ge, “Fretting wear behavior of nitrogen ion implanted titanium alloys in bovine serum lubrication,” *Tribol. Int.*, vol. 42, pp. 1373-1379, 2009.

[6] Y. Itoh, A. Itoh, H. Azuma, T. Hioki, “Improving the tribological properties of Ti-6Al-4V alloy by nitrogen-ion implantation,” *Surf. Coat. Technol.*, vol. 111, pp. 172-176, 1999.

[7] S. A. Ahmad Kamal, R. Ritikos, S. Abdul Rahman, “Wetting behaviour of carbon nitride nanostructures grown by plasma enhanced chemical vapour deposition technique,” *Appl. Surf. Sci*., vol. 328, pp. 146-153, 2015.

[8] P. Vlcak, F. Cerny, Z. Weiss, S. Danis, J. Sepitka, Y. Tolde, V. Jech, “The effect of nitrogen ion implantation on the surface properties of Ti6Al4V alloy coated by a carbon nanolayer,” *Journal of Nanomaterials*., vol. 2013, art. no. 475758, 2013.

[9] P. Vlcak, I. Jirka, “Protective sliding carbon-based nanolayers prepared by argon or nitrogen ion-beam assisted deposition on Ti6Al4V alloy,” *Journal of Nanomaterials*, vol. 2016, art. no. 1697090, 2016

[10] B. S. Yilbas, S.Z. Shuja, “Laser treatment and PVD TiN coating of Ti–6Al–4V alloy,” *Surf. Coat. Technol*., vol. 130, pp. 152–157, 2000.

[11] J. Hong, X. Zhilhua, “Study on Processing of Titanium Surface Nitrogenization,” *Chinese J. Rare Metals*., vol. 22, pp. 295–299, 1998.

[12] P. Vlcak, F. Cerny, J. Drahokoupil, J. Sepitka, Z. Tolde, “The microstructure and surface hardness of Ti6Al4V alloy implanted with nitrogen ions at an elevated temperature,” *J. Alloys Compounds*., vol. 620, pp. 45-54, 2015.

[13] H. Schmidt, A. Schminke, M. Schmiedgen, B. Baretzky, “Compound formation and abrasion resistance of ion-implanted Ti6Al4V,” *Acta Mater*., vol. 49, pp. 487– 495, 2001.

[14] P. Vlcak, J. Sepitka, J. Drahokoupil, T. Horazdovsky, Z. Tolde, “Structural characterization and mechanical properties of a functionalized titanium nitride-based nanolayer prepared by ion implantation on a titanium alloy“, Journal of Nanomaterials, submitted for publication.

[15] W. C. Oliver, G. M. Pharr, “An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments,” *J. Mater. Res.*, vol. 7, pp. 1564-1583, 1992.

[16] S. A. S. Asif, K. J. Wahl, R. J. Colton, “Nanoindentation and contact stiffness measurement using force modulation with a capacitive load-displacement transducer,” *Review of Scientific Instruments*, vol. 70, pp. 2408-2413, 1999.

[17] ISO 14577-1, “Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 1: Test method,”2002.