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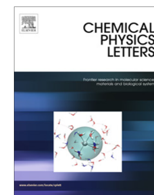

Research paper

Evolution of the nitrogen depth distribution in an implanted titanium alloy with a surface carbon nanolayer

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ABSTRACT

The impact of the thickness of the carbon nanolayer on the depth distribution of the implanted nitrogen was examined. Ti6Al4V samples with a carbon nanolayer (20 and 40 nm) were implanted with nitrogen with fluence of $1.2 \cdot 10^{17}$ cm^{-2} and an accelerating voltage of 90 kV. GD-OES measurements showed an almost Gaussian-like nitrogen depth profile. The nitrogen peak moves deeper into the sample with increasing thickness of the nanolayer. The experimental depth profiles are in good agreement with the calculated results from the analytical model and from the SRIM2013 code.

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1. Introduction

Nitrogen doping of titanium materials significantly improves their surface properties, e.g. hardness, friction coefficient, wettability, corrosion resistance and wear resistance [1–3]. Ion implantation is a very promising technology in titanium alloy metallurgy for surface modifications by nitrogen implantation. When nitrogen is implanted into a titanium matrix, radiation defects and TiN compounds are formed and accumulated, leading to modified surface properties [4]. Detailed knowledge of the nitrogen depth distribution helps to clarify the mechanisms for improving surface properties, and also indicates the most promising implantation conditions. The course of the monitored property can often be controlled by changing the nitrogen concentration in the implanted zone [5,6]. The depth profile reflects the course of the nitrogen concentration in the direction of the surface normal, and also the thickness of the modified surface area. One of the big advantages of ion implantation for industrial use is the real-time control of the process. The fluence and the depth profile of implanted atoms can be directly inferred from the ion energy and the ion current of the accelerated atoms [7]. Because of the high reactivity of titanium materials, surface adsorption of neutral and excited species causes the formation of a thin surface nanolayer. Sputtering of the exposed sample holder can contaminate the implanted surface due to the re-introduction of metallic species to the surface [8]. In addition, there can be a residual atmosphere (e.g. O_2 and C) and oil vapours from the diffusion pump in the vacuum chamber. If the contaminants adsorb to or are co-implanted into the surface in large quantities, oxidation and carburization causes structural and chemical changes of the implanted surface [9]. High affinity of titanium to oxygen spontaneously causes the formation of a passivation nanolayer between 2 and 20 nm in thickness [10]. The oxidation kinetics of titanium involves rapid oxygen adsorption followed by slowing down of the oxidation until surface saturation is reached [11]. Titanium oxides with various stoichiometries were found, e.g. TiO, TiO_2 and Ti_2O_3 formed in the first stages of oxidation [12]. The passivation titanium oxides can modify the range of implanted ions if the thickness exceeds a few nanometers [13]. The thickness of the titanium oxide film is influenced by the sputtering process before and/or during ion implantation, which can cause oxygen to be removed from the surface [14]. Surface oxidation can be reduced by a low sample temperature, by short time of implantation with a larger ion current, and also by low pressure of the residual gas in the vacuum chamber [15]. Vaquila et al. [16] showed that the oxidation kinetics is independent on the oxygen pressure below $6.7 \cdot 10^{-6}$ Pa; no adsorption stage was detected. The chemical composition and the thickness of the surface nanolayer alter the depth profile of the implanted atoms due to changes in the ion energy distribution. A comparison between the experimental depth profiles and the calculated depth profiles by Lacoste et al. [17] showed that they are consistent if no

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impurities are present. Skewing and translation of the nitrogen depth profile in implanted stainless steel due to a surface contaminant layer has been observed by Tian et al. [18]. Bunzynki et al. [19] studied the effect of a carbon thin film on the surface properties of nitrogen implanted Ti6Al4V alloy. The author concluded that the observed differences between the experimental depth profiles and the calculated depth profiles in the titanium alloy can be affected by radiation enhanced diffusion (RED), but the effect of the thickness of the carbon thin film has not been explained.

The role of a thin surface nanolayer on the implanted titanium alloy needs to be examined in greater detail in order to understand the deformations of the depth profile. We have investigated the effect of carbon nanolayers of various thicknesses on the nitrogen depth distribution. A simple near-Gaussian mathematical model has been developed of the nitrogen depth profile, including the ion energy distribution.

2. Experimental details and theory

2.1. Experimental details

Ti6Al4V alloy samples 14 mm in diameter and 3 mm in thickness were ground, polished and ultrasonically cleaned in isopropylalcohol. The carbon nanolayer was deposited by a controlled coating process. The samples were sputtered with 700 eV argon ions to etch and activate the surface, and were then coated with a thin carbon nanolayer 20 or 40 nm in thickness before nitrogen ion implantation. A nanolayer was deposited at room temperature by electron beam evaporation of a high purity carbon target without ion bombardment. A quartz crystal monitor was used for measuring the deposition rate and the thickness of the nanolayer. The deposition rate was about $0.2\ \mathrm{nm\cdot s^{-1}}$, and the work pressure was about $4 \cdot 10^{-4}$ Pa. The deposited nanolayer had an amorphous character with sp^2 rich bonds [20]. Nitrogen ions were implanted at a normal incidence angle, at an accelerating voltage of 90 kV and at a fluence of $1.2 \cdot 10^{17}\ \mathrm{cm^{-2}}$. The ion beam current was ~2 μA, and the temperature of the sample was below 90 °C. The ion distribution in the nitrogen ion beam, as measured by mass spectrometry by Tecvac Ltd. company [21], was 15% for N^+ ions and 85% for N_2^+ ions. It is assumed that the energy of 90 keV of N_2^+ ions is distributed between these two atoms due to a collision with the surface atoms of the substrate. This assumption corresponds to experimental and theoretical results [17,22]. The average energy of the dissociated atoms is 45 keV. N^+ and N_2^+ ions, accelerated onto the substrate under the same voltage, are also implanted in the substrate at two distinct projection depths, see Fig. 2b. The nitrogen enrichment of the implanted samples was depth profiled using glow discharge optical emission spectroscopy (GD-OES). The elemental chemical composition of the surface area was verified by Auger electron spectroscopy (AES).

2.2. Theory

The simplest Gaussian distribution was used for calculating the depth distribution of the implanted atoms. The Gaussian formula can be written as follows:

$$N(x) = \frac{\Phi}{\sigma_p\sqrt{2\pi}} \exp\left[-\frac{(x-R_p)^2}{2\sigma_p^2}\right], \qquad (1)$$

where σ_p is straggling, R_p is projected range and Φ is fluence (i.e. the number of atoms implanted during the implantation period per unit of area) [23]. The surface nanolayer causes energetic losses of accelerated ions. The ions penetrate into the substrate with modified ion energy from E_{min} to E_{max}, where E_{min} = 0 keV and E_{max} is nominal ion energy. The straggling and the projected range are then a function of the ion energy

$$\sigma_p = \sigma_p(E), \qquad (2)$$

$$R_p = R_p(E). \qquad (3)$$

The modified Gaussian formula for the case of continuous ion energy distribution from 0 to E_{max} can therefore be rewritten as

$$N(x) = \int_0^{E_{\max}} \frac{\frac{\partial\Phi(E)}{\partial E}dE}{\sigma_p(E)\sqrt{2\pi}} \exp\left[-\frac{(x-R_p(E))^2}{2\sigma_p^2(E)}\right]. \qquad (4)$$

In Eq. (4), $\frac{\partial\Phi(E)}{\partial E}$ expresses the energetic density of the fluence of the implanted atoms (i.e. the number of atoms at energy E implanted during the implantation period per unit of area) that were implanted at energy $E \in \langle 0; E_{\max}\rangle$ into the titanium substrate after passing the surface nanolayer. The ion energy distribution was deduced using the SRIM2013 code [24]. Fig. 1a shows the ion energy distribution of 45 keV ions behind a thin carbon nanolayer 10, 20, 30, 40, 50 and 60 nm in thickness. The peak of the fluence of the implanted nitrogen shifts to lower energies with greater thickness of the carbon nanolayer. For the narrow interval of ion energy used in the experiment, we used the approximate linear relations,

$$\sigma_{\mathrm{p}}(E_S) = k_{\sigma_p} E_S, \qquad (5)$$

$$\mathrm{R_p}(E_S) = k_{R_p}\mathrm{E}_S, \qquad (6)$$

where E_s is the mean ion energy of the implanted ions behind the carbon nanolayer, and σ_p and R_p are deduced from the SRIM2013 code. The nitrogen depth distribution *N(x)* was obtained by integrating Eq. (4). Table 1 compares the projected range and the longitudinal straggling of the nitrogen ions for carbon, Ti and Ti6Al4V. The projected range decreases with increasing atomic mass and with greater atomic density of the target atoms. Fig. 1b shows the evolution of the calculated concentration profiles in dependence on the thickness of the nanolayer in relation to the C/Ti interface and the surface of the sample.

3. Results and discussion

Fig. 2a presents a comparison of nitrogen depth profiles obtained by GD-OES after implantation in a Ti6Al4V alloy sample without a carbon nanolayer (sample C0) and with a carbon nanolayer 20 nm in thickness and 40 nm in thickness (sample C20 and sample C40). The nitrogen depth profile of unmodified sample is also plotted in Fig. 2a. The nitrogen distribution shows a roughly Gaussian profile, with distortion on top of the surface, due to nitrogen adsorption. The nitrogen peak moves deeper into the sample with increasing thickness of the nanolayer. The peak position is approx. 80 nm for sample C0, approx. 88 nm for sample C20, and approx. 92 nm for sample C40. The values of these peaks are approx. 15.8 at.% for sample C0, approx. 17.4 at.% for sample C20, and approx. 18.9 at.% for sample C40 sample. The observed trend for nitrogen peak movement is in agreement with the SRIM simulation, see Fig. 2b. The resulting SRIM nitrogen profile is composed from two profiles corresponding to the ion populations in an ion beam, i.e. N^+ and N_2^+. The observed peak shoulder on the substrate side is caused by the minority 90 keV fraction of the ion beam. According to the SRIM simulation, the projected range of nitrogen ions is 80 nm for sample C0, 85 nm for sample C20, and 90 nm for sample C40. This is in good agreement with the experimental findings.

The changes in the nitrogen concentration profiles observed in Fig. 2 are due to the physical properties of carbon and the ion energy distribution behind the carbon nanolayer. Collisions

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