NITROGEN DOPED TITANIUM BY ION IMPLANTATION

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Abstract

Titanium and its alloys attract much attention due to their low specific weight, good corrosion resistance, high toughness, high yield strength and efficient biocompatibility. However, these materials have poor wear resistance, high friction and low hardness. Therefore, the surface properties often need to be modified. In the present work, nitrogen ion implantation was used to modify the titanium surface. Nitrogen doped layer integrated into the surface of titanium were investigated by several methods aimed primarily at determination of chemical composition, surface microstructure, surface mechanical properties and coefficient of friction. The present study includes results of Secondary Ion Mass Spectrometry, X-ray diffraction and nanoindentation.

Keywords: Nitrogen doping, Ion implantation, Titanium, Microstructure, Properties

1. INTRODUCTION

This paper deals with characterization, mechanical properties and sliding behavior of nitrogen doped titanium. Titanium and its alloys are widely used in aviation, in automotive and in biomedical applications [1-3]. However, a serious disadvantage of titanium materials is their poor performance in sliding and hardness. Nitrogen doping may be a useful technique for modifying the surface of titanium. Reactive nitrogen atoms introduced into a titanium matrix can produce metastable, amorphous and crystalline phases, solid solutions and crystal lattice defects in the surface area [4]. Conventional nitridation improves the hardness, the wear resistance and the corrosion resistance, but the material properties are significantly affected by the 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 material to degenerate. Nitrogen ion implantation has several merits in comparison with conventional nitridation, e.g., (1) it is a low-temperature process, and (2) the process parameters can be precisely controlled. It has been reported that ion implantation of nitrogen into titanium materials led to reduced wear during a sliding test against UHMWPE [5]. High wear resistance was achieved by a combination of the high hardness of the implanted area and the low friction oxide on the surface. Budzynski [6] and others [7 - 9] have investigated the influence of nitrogen ion implantation at energies up to 200 keV and at fluences from $1 \cdot 10^{16}$ cm^{-2} up to $1 \cdot 10^{18}$ cm^{-2} on the surface properties of titanium alloy. They concluded that implanted nitrogen increased the hardness and the wear resistance at higher fluences, resulting in the formation of a surface layer composed of hard TiN_x phases. Liu et al. [10] have showed that nitrogen ion implantation in Ti-6Al-4V stabilizes the a-Ti phase and forms compounds of varying composition and stoichiometry. Firouzi-Arani et al. [11] investigated the TiN_x substoichiometric nitride formation in titanium during nitrogen implantation, as a function of the substrate temperature. The results showed the development of TiN with different compositions in the modified samples.

In this work we present the improvement of tribo-mechanical properties of titanium modified by nitrogen ion implantation. The friction coefficient was measured by pin-on-disc tribometer. Hardness was investigated by naniondentation, phase composition by X-ray diffraction (XRD) and chemical composition by Secondary Ion Mass Spectrometry (SIMS).

2. EXPERIMENTAL PART

The substrates were made of commercially pure titanium in the form of a cylinder 14 mm in diameter and 3 mm in height. The cylinders were ground on one side with a series of waterproof abrasive papers and polished with diamond paste. The samples were ultrasonically cleaned in isopropyl alcohol before the implantation process.

Nitrogen ion implantation was carried out at a room temperature. The ion beam had a normal incidence angle. The samples were implanted with nitrogen ions at fluences of $4{\cdot}10^{17}$ and $6{\cdot}10^{17}$ cm^{-2} and energy of 90 keV. The ion current density was about 1µA cm^{-2} and the work pressure was about $5{\cdot}10^{-5}$ mbar.

The chemical composition was measured by means of secondary ion mass spectrometry (SIMS). A quadrupole SIMS Atomik 3000 was used. O_2 primary ion beam at energy of 12 keV and ion current of 500 µA had 100 nm in diameter. 500 x 500 µm area was analyzed (**Figure 1**).

Phase composition was investigated by means of Xray diffraction method (XRD). Cobalt radiation with wavelength 0.1789 nm and Geometry with the parallel beam with an incident angle of 0.5° were used.

Surface hardness was investigated by nanoindentation. The partial unload function was used for the measurement of the depth profile of the surface hardness. Maximum indentation load was 5000 μN. 12 indents in a matrix 3×4 were performed. Coefficient of friction, was investigated on pin on disc tribometer with 100Cr6 steel ball with diameter 6 mm. The normal load was 2 N, the radius of rotation was 4 mm, and the velocity was 6 $cm{\cdot}s^{-1}$.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical SIMS spectra of the nitrogen and carbon in the modified area of the titanium sample implanted with nitrogen ions wit fluence of $4{\cdot}10^{17}$ cm^{-2}. The thickness of the modified surface area corresponds to the maximum ion range (approximately 200 nm). Increased concentration of carbon at the surface is observed. This may be due to surface contamination by the atmosphere in vacuum chamber. The nitrogen ion implantation causes penetration of nitrogen into the titanium substrate. The TiN phase was formed during ion implantation in the enriched surface region, as show the results of XRD analysis.

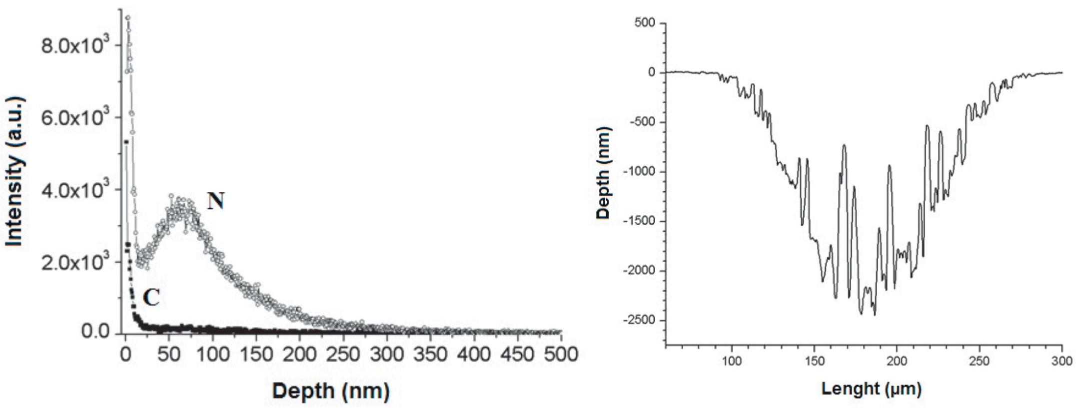

Figure 1 SIMS spectra for implanted titanium sample with fluence of $4{\cdot}10^{17}$ cm^{-2} (left) and depth profile of the crater after the SIMS measurement (right)

Phase composition was investigated by means of Xray diffraction (XRD). TiN phase was identified in the implanted surface area. Chemical composition analysis and phase analysis show that in the modified surface area is created thin nitrogen enriched nanolayer, with phase of titanium nitride.

The dependence of indentation hardness on contact depth (hardness profile) obtained for samples implanted with nitrogen ions is represented in **Figure 2**. Maximum measured indentation hardness of modified samples was higher than 21 GPa. It was four times bigger value than that measured for unmodified substrate. The hardness values at depths below 14 nm were excluded from graphs at the **Figure 2**. The results at this region are influenced by the error originating from standard calibration of tip area function on fused quartz [4].

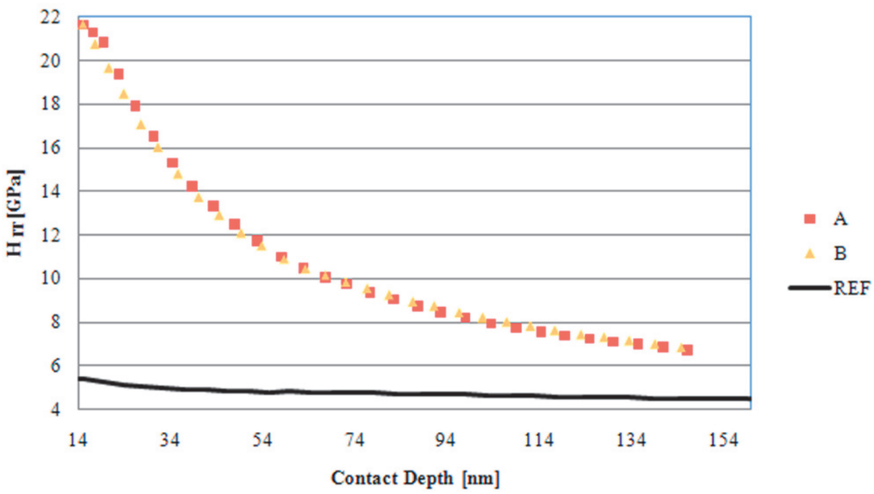

Figure 2 Indentation Hardness H_{IT} vs. Contact Depth obtained for implanted samples and reference sample. Ion energy: 90 keV; fluences of nitrogen atoms: A - $4x10^{17}$ cm^{-2}, B - $6x10^{17}$ cm^{-2}, REF - referential sample (without implantation)

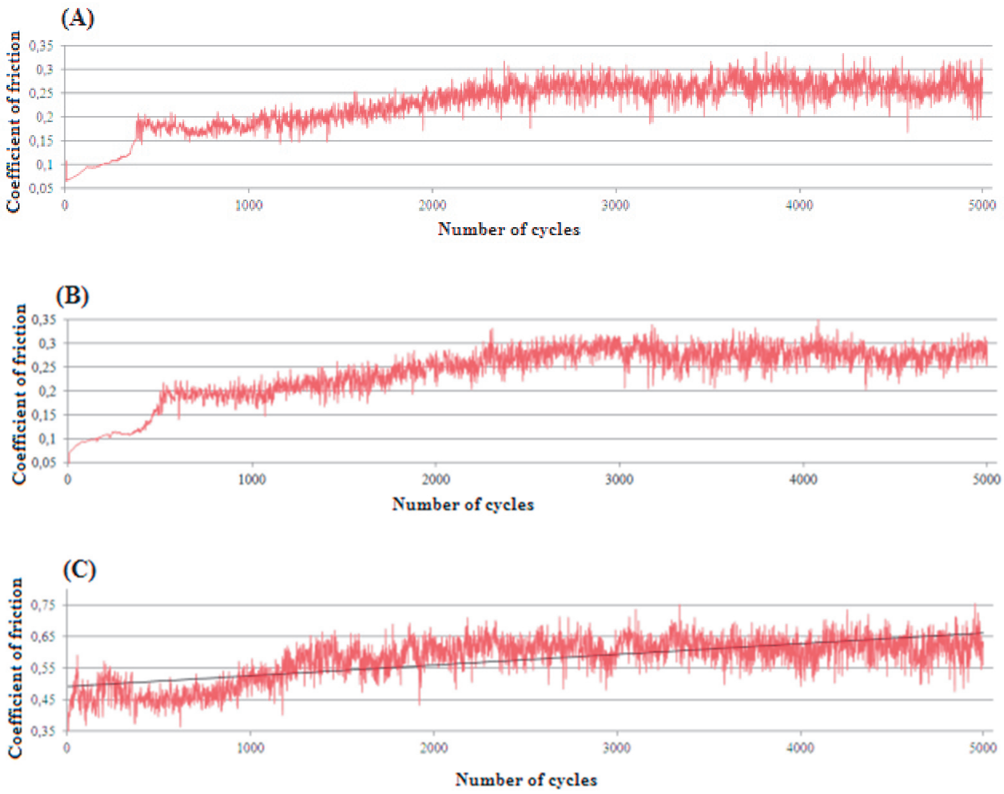

Figure 3 Coefficient of friction versus the number of cycles for implanted samples with fluences of $4 \cdot 10^{17}$ cm^{-2} (A) and $6 \cdot 10^{17}$ cm^{-2} (B) and for the unmodified substrate (C)

Figure 3 shows the course of the coefficient of friction for the implanted samples and for unmodified substrate as a function of the number of cycles. The friction curves can be divided in two parts. The first part represents the low-friction regime, while the second part represents the increased friction regime. The friction coefficient in the low-friction part is very low, having a value of about 0.1 (**Figure 3a, b**). After a certain number of cycles there was observed an increase of the coefficient of friction to value approximately 0.26 in all implanted samples. The part with increased friction explains damage of the surface nanolayer. The unmodified substrate has a coefficient of friction approximately 0.6. This means a two times greater decrease in the friction coefficient of modified samples in comparison with the unmodified substrate.

4. CONCLUSION

Nitrogen doped layer integrated into the surface of titanium was prepared by ion implantation. TiN compound was detected in the nitrogen enriched layer. Maximum measured indentation hardness of modified samples was higher than 21 GPa. The sliding tests showed a twofold reduction in the coefficient of friction of modified samples in comparison with the unmodified substrate.

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