Effect of nitrogen ion implantation on the surface morphology of implanted titanium alloy

Relevant for: thin layer, surface morphology, titanium alloy, AFM, SEM

AFM and SEM methods were used to characterize the morphology of nitrogen ion implanted surfaces of titanium parts suitable for biocompatible medical implants and high-strength, wear-resistant mechanical components.

1 Introduction

Titanium and its alloys—including e.g., the well-proven TiAl6V4 alloy or multi-element beta titanium (β-Ti) alloys such as β-TiNb35Zr7Ta5 (1), are lightweight, strong and stable materials used in many industries as well as in biomedical applications. However, they suffer from inferior friction and wear resistance, and this is why a variety of surface modification techniques such as thermal and anodic oxidation, gas nitriding and ion implantation have been subject to numerous studies in connection with surface treatments of titanium materials. In particular, nitriding is seen as a promising (and already proven) method applied to improve the surface (mainly, tribological) properties and corrosion resistance of these materials. An advanced technique adopted to introduce nitrogen into the titanium surface is ion implantation; it can be performed even at low temperatures and is effective when fluences higher than ca. 5·10^{16} \text{ cm}^{-2} are employed. A mixed surface layer containing nitride is formed which extends as deep as tens to hundreds of nanometers into the alloy. There is an improvement in hardness by a factor of 7-9 even after annealing, in comparison with the non-implanted sample (1).

This has been confirmed by numerous studies which have also revealed that at nitrogen fluences of up to ca. 8·10^{17} \text{ cm}^{-2}, the free corrosion potential and the passive range tend to shift to nobler potential values as the fluence is raised, resulting in an improvement in corrosion resistance up to about a fluence of 4·10^{17} \text{ cm}^{-2}, whereas at even higher fluences the corrosion behavior is impaired by surface roughening. It has also been found (2) (3) that specific surface defects and pores form at titanium surfaces implanted at excessive fluence levels.

For instance, the TiNbZrTa alloy exhibits a nitrogen saturation limit of approx. 60 at.% N beyond which the implanted alloy is prone to blistering and its corrosion resistance is impaired. However, the susceptibility to localized corrosion attack remains unaffected (2). On the whole, a nitried (TiN-based) surface layer provides mechanical properties that are greatly superior to those of a ‘naturally’ oxidized, i.e. passive layer (mainly consisting of TiO_2).

This technical report presents the evolution of surface morphology after nitrogen ion implantation of TiNb35Zr7Ta5 titanium alloy. Morphology measurement was performed by AFM and SEM techniques whose results are compared.

2 Experimental

The substrate used was commercial purity TiNb35Zr7Ta5 alloy, ground to 2500 grit and polished to mirror finish using 1 μm diamond paste. Ultrasonically cleaned samples were implanted with nitrogen ions at an incident ion beam angle of 90° and an accelerating voltage of 90 kV, in a Tecvac 221 Ion Implanter apparatus, at fluence levels graduated from 1·10^{17} to 1·10^{18} \text{ cm}^{-2}. The ionic current was measured using a Faraday cup, and the ion current density was kept below 2 μA cm^{-2} to avoid overheating.
The morphology of the implanted samples was analyzed by the scanning electron microscope (SEM), optimized for imaging nanostructured surface modifications and atomic force microscope (AFM). The corresponding AFM measurements, i.e., surface analysis, were carried out with atomic force microscope Tosca 400 by Anton Paar. It employs a color, 5 megapixel overview camera equipped with a CMOS sensor which has a spatial resolution of 50 µm for macro navigation, a side view camera which has a spatial resolution of 70 µm for a quick and safe tip engagement and another color, 5 megapixel video microscope with a spatial resolution of 5 µm for micro navigation. The state-of-the-art sample navigation with three cameras allows users to easily and safely navigate to the desired measurement positions within a short period of time and to start the AFM measurement. All AFM images were acquired using tapping mode. Surface roughness was calculated and the geometries of various features were measured.

3 Results and Discussion

Fig. 1 depicts the surface morphology measured by SEM and AFM techniques for titanium alloy samples modified by nitrogen ion implantation with fluences in the range \((1 – 9) \cdot 10^{17} \text{ cm}^{-2}\). The results demonstrate that both techniques provide a unique surface view and complement each other. The nature of surface morphology is maintained by using both techniques. Top view micrographs in Fig. 1 show that the sputtering of the surface becomes more visible with increasing fluence of the implanted ions. Defects are formed on the surface of the sample implanted with fluence \(4 \cdot 10^{17} \text{ cm}^{-2}\) or higher. Observed defects appear to be typical for lattice oversaturation of the nitrogen in the implanted material (2). The nitrogen oversaturation of implanted TiNb35Zr7Ta5 alloy is accompanied by bubbles on the surface, as shown AFM and SEM top view micrographs for sample implanted with fluence \(4 \cdot 10^{17} \text{ cm}^{-2}\). The bubbles (blisters), with cracks and open cavities, are observed on samples implanted at fluences of \(6 \cdot 10^{17}\) and \(9 \cdot 10^{17} \text{ cm}^{-2}\). Observed craters are a sign of the significant blister spherical cap sputtering. The high applied fluence (6 and \(9 \cdot 10^{17} \text{ cm}^{-2}\)) led also to the formation of surface cracks. Comparable magnification allows the comparison of observed morphologies by both methods. Surface defects display is very good. Imaging capability at given magnification is comparable. No significant differences in surface imaging were found. The advantage of the AFM method is the 3D image and the possibility of evaluating height changes and roughness. The calculated RMS roughness \(S_q\) values according to the ISO standard ISO25178 are shown on the AFM images. The two methods appear to be substitutable for investigation of the studied morphologies at the considered magnifications.

<table>
<thead>
<tr>
<th>Fluence</th>
<th>SEM morphology</th>
<th>AFM topography</th>
<th>AFM 3D display</th>
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<td>Reference sample</td>
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<td><img src="image2" alt="AFM topography" /></td>
<td><img src="image3" alt="AFM 3D display" /></td>
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\(S_q = 2.85 \text{ nm}\)
<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>SEM Image</th>
<th>AFM Image</th>
<th>Square Roughness (Sq)</th>
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<tbody>
<tr>
<td>$2 \cdot 10^{17}$</td>
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<td><img src="image8.png" alt="AFM Image" /></td>
<td>$3.39$ nm</td>
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</table>

Figure 1. Surface morphology measured by SEM and AFM techniques for titanium alloy samples modified by nitrogen ion implantation with fluences.
4 Summary

Specimens of TiNb35Zr7Ta5 titanium alloy were implanted with nitrogen ions at graduated fluence levels ranging from $1 \cdot 10^{17}$ to $9 \cdot 10^{17}$ cm$^{-2}$, at 90 kV accelerating voltage in an experimental implantation chamber. Fluence had a profound effect on morphology examined by SEM and AFM methods. Both techniques allow the surface display at a level sufficient for the evaluation of surface defects. The presented results show that the methods used here are complementary and can be considered substitutable for investigation of the studied morphologies at the considered magnifications.

5 References


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