

H-IMPLANTATION CHANGES STOICHIOMETRY AND HYDROXYLATION STATES OF NITRIDED TITANIUM SURFACES

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1. Introduction

As versatile materials, titanium and titanium-based devices are often exposed to challenging situations, which can compromise their mechanical integrity. In super-hydrophilic films, fuel cells, fusion reactor walls or tritium storage targets, the surface interacts with hydrogen in varied degrees of severity, which can eventually lead the material to undergo embrittlement mediated by the precipitation of hydrides [1]. A nitride layer produced, e.g., by plasma-based methods, operate as a barrier for the H-diffusion into the bulk [2]. On one hand, the hydrogen interaction with nitrides at near surface is not yet completely understood; on the other hand, the controlled irradiation of TiN and the native surface oxides can lead to interesting modifications due to the charge balance in the surface. These issues were investigated in the work reported here.

2. Experimental

Titanium samples were plasma nitrided in a conventional glow discharge chamber at 600 °C, and subsequently hydrogen-implanted through plasma immersion ion implantation, using ion energies from 1.2 keV to 5.0 keV. The surfaces were analyzed by scanning electron microscopy, instrumented indentation, X-ray diffraction, micro-Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR).

3. Results and Discussions

The plasma nitrided surfaces consisted in hardened (40% higher hardness than substrate) and stiffer (200% higher elastic modulus) layers constituted of Ti₂N and TiN. Differently from the intense plasma-based hydrogenation, described elsewhere [3], the H-implantation were restricted to very shallow depths on the nitrided surfaces, producing no assessable changes in the crystalline structure, mechanical properties or morphology. Such features corroborated with the *H-barrier effect* provided by the nitrides layer.

The Ti2p doublet, N1s and O1s XPS analyses disclosed that the TiN amount reduced with the rising H-implantation, as the TiO₂ contribution to the spectra increased. From the photoelectron detection theory [4], and assuming a stratified TiO₂ + TiN_xO_y + TiN layer on the top surface, it was demonstrated that

$$\ln \frac{I_{ox}}{I_{lay}} = \ln \frac{I_{0,ox}}{I_{0,lay}} + \ln \left[1 - \exp \left(-\frac{d}{\lambda \sin \theta} \right) \right] \quad (1)$$

is directly proportional to the increase of the oxide layer and decrease of the TiN one, which correlated in a linear-like fashion with the H-implantation energy, as shown in Fig. 1. In the equation above, *I* are integrated intensities of Ti2p XPS peaks ascribed to the layer (*lay*) and the oxide (*ox*), where the index *0* denotes values calculated for photoelectron beams emerging from “infinitely thick” materials. θ is the take-off angle from the surface, *d* the layer thickness, and λ the inelastic mean free path.

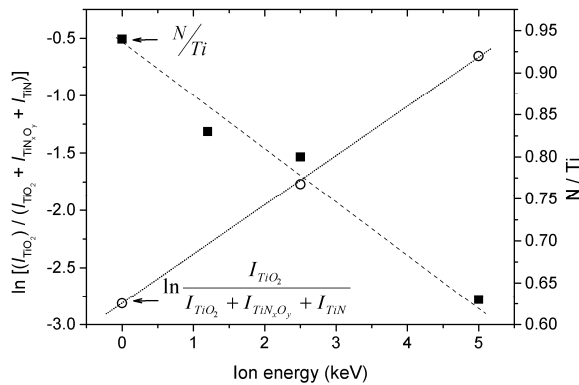


Fig. 1. Correlations of the H-implanted ion energies with features of the nitrided surfaces. Open symbols are ascribed to Equation 1 and addressed to the left side axis. The close symbols address to the right side axis, which were calculated through Equation 2. Lines are only guides for the eyes.

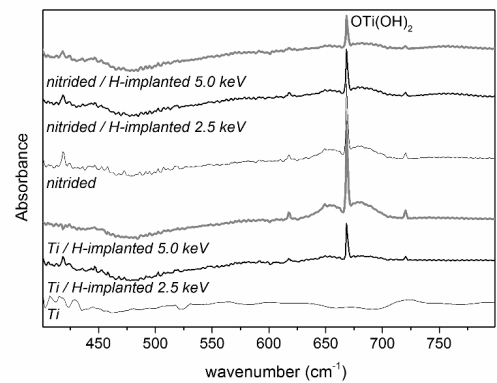


Fig. 2. FTIR spectra of titanium and nitrided titanium surfaces, prior and after the H-implantation with ion energies 2.5 keV and 5.0 keV.

Also linear with the H-implantation energies were the N/Ti atomic ratio, inferred for the TiN compound from Raman spectra by [5]

$$\frac{N}{Ti} \propto \frac{I_{TO}+I_{LO}}{I_{TA}+I_{LA}} \quad (2)$$

In this relation, the integrated peak intensities I stands for first-order transversal and longitudinal optic (TO, LO) and acoustical (TA, LA) scattering modes. Differently from equation (1), the N/Ti ratio was nearly inversely proportional to the H-implantation energy, as also shown in Fig. 1. The evolutions of equations (1) and (2) with respect to the H-implantation energy were indicative of the *surface denitriding*. This phenomenon is probably a conjunction of physical and chemical effects, promoted by momentum transfer from the energetic ions and the environmental chemical conditions.

Fig. 2 presents FTIR spectra of titanium and nitrided titanium, prior and after the H-implantation. A strong and narrow line at 668 cm^{-1} was produced on the H-implanted titanium. It was also observed in the plasma nitrided samples, which persisted after hydrogenation, although with lower absorbance intensities. These peaks are ascribed to Ti-OH stretching in the OTi(OH)_2 molecule bonded in the surface [6]. It was produced on titanium through changes in the *hydroxylation states* of native oxides by the energetic H-bombardment. On nitrided titanium surfaces, the formation mechanism possibly involved photocatalysis in air atmosphere, enhanced by the presence of oxinitrides. The subsequent H-implantation changed the oxinitrides stoichiometry, as seen in Fig. 1, with consequences to the hydroxylation states of the nitrided surface. Perhaps, some photocatalysis controlling can be attained by the H-irradiation on titanium and nitrided titanium.

4. References

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