Physical and chemical effects of the hydrogen irradiation on nitrided titanium surfaces

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ARTICLE INFO

ABSTRACT

Many applications aiming the use of titanium and titanium-based materials involve the surface interaction with protons or hydrogen isotopes, such as in chemical and nuclear power plants, marine and aerospace environments. Because of the high affinity of titanium for hydrogen and the consequent deleterious effects, the study of surface interactions contributes to the understanding of the protection mechanisms, such as the H-diffusion barrier provided by nitriding, as well as the fine surface tailoring achieved by hydrogenation. Nitrided titanium surfaces were produced via plasma nitriding (PN), carried out at 400 °C and 600 °C. Afterwards, titanium and nitrided titanium were submitted to the hydrogen plasma immersion ion implantation (H-PIII), using ion energies from 1.2 to 5.0 keV. The hydrogen modifications imposed were restricted to the nanometer depth range, causing no significant variations in hardness and elastic modulus (measured in depths larger than 70 nm) or in the crystalline structure, as inferred from nanoindentantion and grazing incidence X-ray diffraction, respectively. From the X-ray photoelectron and micro-Raman spectroscopies, the hydrogen irradiation was found to cause denitriding on the nitrided titanium, changing the TiN stoichiometry as a consequence of conjoined physical and chemical effects on the surface atoms. The atomic N/Ti ratio changed from 0.9 (not hydrogenated) to 0.6 (5 keV) up to ~2 nm depth. The Ti/N decrement and the resulting TiO_2 surface layer growth followed approximately linear correlations with the implantation energies. Additional investigations with Fourier-transform infrared spectroscopy disclosed vibrational bands featured by a strong line at 668 cm^{-1} (possibly $OTi(OH)_2$) in samples submitted independently to PN and H-PIII, suggesting that different mechanisms of hydroxyl absorption on titanium took place on those surfaces.

1. Introduction

Varied technological areas have drawn attention to titanium, titanium-based compounds and titanium-based alloys, substantiated by the superior properties of these materials or even due to their unique responses to physical and chemical conditions. For instance, photocatalytic properties of titanium oxides and oxinitrides can be used in super hydrophilic windows, air purification devices, and for degradation of organic molecules on their surfaces [1]. In a different approach, titanium-graphene composites were investigated to be used as hydrogen storage means in fuel cells, due to the large H-affinity of these materials [2]. It was reported that the surface bioactivity (i.e., induction of the bone healing and growth) can be attained in titanium prosthesis directly through high energy hydrogen implantation [3,4]. In the situations above, titanium interacts with hydrogen in varied degrees of severity. Those circumstances where the hydrogen influx is significant demand

special attention, due to the well-known embrittlement of the bulk material, mediated by the precipitation of titanium hydrides [5–7]. Thus, the use of titanium-based materials in hydrogen-rich environments, which might be found in chemical plants and marine and aerospace applications, faces restrictions.

Another strategic area of research demanding special materials is the fusion energy production. Titanium alloys are candidates to be used as raw materials in the reactor first wall and other structures in the power plant, because of their suitable mechanical properties, low expansion coefficient, resistance to high heating fluxes and fast induction of radioactive decay [8,9]. In these situations, strong interaction of highly energetic particles from the plasma with the reactor walls occurs, notably proton, deuterium and tritium. Moreover, a product from the last two isotopes reaction is 14.1 MeV neutrons [10], which eventually decays into a proton, an electron and an antineutrino. Fast neutrons are also obtained in vacuum neutron tubes and gas filled neutron tubes, in which tritium is stored in titanium targets [11].

The bulk mechanical properties of hydrogen-containing titanium have been extensively studied [5–7], motivated by the technological

challenge to extend this material applicability to many environments. Regarding titanium surfaces, the hydrogen diffusion, trapping and barrier effect were investigated using H-ion implantation in surfaces containing different dopants such as C, N and O [12,13]. In a previous work [14], the surface ductile to brittle transition induced by the hydride precipitation was investigated at nanoscale level by tribological and mechanical tests, in titanium surfaces submitted to the glow discharge hydrogenation. The same hydrogen processing carried out on nitrided titanium revealed some singular phenomena. The hydrogen penetration at shallow depths into the nitride barrier caused escalation of the surface brittleness due to imposed competitive tensile stresses. Moreover, XPS chemical analysis strongly suggested the *denitriding* of the surface, i.e., suppression of Ti—N bonds, as well as changes in the surface oxidation states.

The work reported here investigated further the surface effects of the hydrogen irradiation, focusing on the structural and chemical changes produced at near surfaces. Titanium and nitrided titanium samples were subjected to controlled and energetic H irradiation, attained trough the plasma immersion ion implantation (PIII) technique. The findings are presented in three sections. The crystalline structure and mechanical properties are discussed in Section 3.1, which allowed the inference of depth range of the H-induced modifications. The next two sections analyze the denitriding effect (Section 3.2) and the surface hydroxylation (Section 3.3), disclosed through different spectroscopic methods.

2. Materials and methods

2.1. Surface preparation

Commercially pure titanium samples (grade 2) were ground with sandpaper and polished with diamond paste and colloidal silica to the mirror-like surface finishing. Subsequently, samples were cleaned with successive ultrasound baths of acetone, isopropyl alcohol and distilled water. The surfaces were initially treated through the conventional plasma nitriding (PN) method, and then submitted to hydrogenation.

The plasma nitriding (PN) was carried out in a DC regime with 60% N_2 40% H_2 atmosphere using 99.9995% purity gases for 3 h. The treatment temperatures were 400 °C and 600 °C. The chamber's base pressure was 3×10^{-2} Pa. After the working gas mixture inlet, the pressures were 470 Pa (400 °C) and 570 Pa (600 °C). Voltage and current were adjusted in order to set the treatment temperatures. The choice of parameters followed results reported in a previous paper [15].

The surface hydrogenation of nitrided titanium samples was attained by means of the hydrogen plasma immersion ion implantation (H-PIII), using pure H_2 gas. Titanium samples, not nitrided, were also submitted to H-PIII for comparison purposes. The system consisted of a DC plasma source, a heated filament producing electron shower at the vicinity of the sample holder, a vacuum system and a high voltage

pulse generator, as detailed in reference [16]. The base pressure was in the order of 10^{-3} Pa, whereas the treatment pressure was 3×10^{-1} Pa. Pulse width, frequency and current density were 30 μs, 300 Hz and 2 mA/cm^2, respectively. Samples were hydrogenated for 15 min under maximum pulse voltages 2.5 kV and 5 kV. An additional hydrogen implantation at 1.2 kV was prepared to support the Raman analysis, as discussed in Section 3.2.2. The treatment temperatures were inferred with an optical pyrometer. Because of the device lower end of the scale, it was possible to assert that treatment temperatures were lower than 250 °C.

Table 1 shows the sample nomenclature and treatment parameters for all the employed combinations of PN and H-PIII. It is worth mentioning that approximate ion energies could be ascribed to each of the PIII high voltages employed, as summarized in Table 1. This is appropriate since a fair approximation for energies of the incoming ions on the top surfaces can be the potential energy transferred to them through the plasma sheath. By considering a collisionless situation, the energy conservation gives [17]

$$\frac{1}{2}mv^2(x) - E_s = -e\Phi(x) \tag{1}$$

where $v(x)$ is the ion velocity in the sheath, E_s is the ion energy when penetrating the plasma and sheath interface, and m and e are the ion mass and charge, respectively. $\Phi(x)$ is the sheath voltage, which drops to the maximum negative value in the sample holder ($\Phi_{cathode}$). Assuming that the ion kinetic and potential energies when it is in the bulk plasma (in the order of eV) are much smaller than the cathode potential (keV), the equation above can be reduced to

$$\frac{1}{2}mv_{max}^2 = -e\Phi_{cathode} \tag{2}$$

where the left hand side is the maximum ion energy.

Of course, in a realistic situation where momentum transfer events to the neutral or ionic species take place during the ion time of flight through the sheath, the above assumption can be taken just as a rough estimate for the implantation energy. It is worth considering that H^+ is the dominant species in the hydrogen plasma at the employed PIII working pressures, followed by smaller fractions of H_2^+ and H_3^+ [18,19]. Thus, for referencing purposes, Table 1 also presents the projected ranges into TiN (density 5.4 g/cm^3, angle of ion incidence 0°) for the H^+ implantation ion energies, as calculated by the SRIM simulation method [20]. The computations simulated the implantation time employed in the study, sampling 10^5 ions. The input data were as follows: displacement energies of 25 eV and 28 eV for Ti and N, respectively [21]; cohesive energies of 3.1 eV for both elements [22]. Individual binding energies were employed: 4.89 eV for Ti and 2.00 eV for N, in accordance with [23,24].

Table 1

Sample nomenclature and variable treatment parameters of titanium samples submitted to plasma nitriding (PN) and hydrogen plasma immersion ion implantation (H-PIII). Estimated ion energies, projected ranges and sputtering yields ratios are presented for each of the H-PIII treatments. The last two columns correspond to experimental values from the XPS (Fig. 4 and Eq. (10)) and micro-Raman (Fig. 8 and Eq. (11)) spectroscopies, respectively.

Nomenclature	Temperature in PN (°C)	Ion energy in the H-PIII (keV)[a]	Projected ion range (nm)[b]	Sputtering yields ratio[b] Y_N/Y_{Ti}	$\ln \frac{I_{ox}}{I_{lay}} =$, $\ln \frac{I_{TiO_2}}{I_{TiO_2}+I_{TiN_xO_y}+I_{TiN}}$	Atomic N/Ti
ref	–	–	–	–	–	–
ref/2.5	–	2.5	21	–	–	–
ref/5.0	–	5.0	40	–	–	–
nit400	400	–	–	–	–	–
nit400/2.5	400	2.5	21	–	–	–
nit400/5.0	400	5.0	40	–	–	–
nit600	600	–	–	–	−2.8	0.94
nit600/1.2	600	1.2	11	2.0	–	0.83
nit600/2.5	600	2.5	21	2.3	−1.8	0.80
nit600/5.0	600	5.0	40	1.9	−0.7	0.63

[a] Representative values, numerically equal to the PIII pulse maximum voltage. See text in Section 2.1 for details.
[b] Projected ranges and sputtering yields were calculated by the SRIM simulation method [20], considering the H^+ implantation on TiN.