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Structural and tribo-mechanical characterization of nitrogen plasma treated titanium for bone implants

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ABSTRACT

Bioactive layers produced on titanium to induce osseointegration may not be mechanically stable and/or attend to the requirement for the bone-matching elastic modulus. The previous surface modification by ion nitriding can eventually improve adhesion and mechanical properties of such bioactive coatings. Titanium samples were DC plasma nitrided in low conditions of temperature (673 K and 873 K) and time (1 h and 3 h). The surfaces were studied by grazing-incidence X-ray diffraction, micro-Raman spectroscopy, atomic force microscopy, scanning electron microscopy, instrumented indentation and nanoscratch tests. The treatments at 873 K produced a stratified surface containing δ-TiN, ε-Ti$_2$N and N-solid solution Ti(N), whereas the 673 K samples presented Ti(N) and evidence of nitride precipitates at a very shallow depth, as suggested by micro-Raman (depth of analysis $\leq$25 nm). The asperity degree and distribution increased with the treatment temperature and time, whose effects on hardness and elastic modulus were corrected by the contact stiffness analysis. The most significant changes in the near surface hardness (5 to 15 GPa) and elastic modulus (170 to 200 GPa) profiles in respect to the pristine Ti were observed for 873 K treatments. However, the 673 K – 3 h sample presented scratch hardness twice as high as the substrate value, even if the ductile-like tribological response was preserved. Afterwards, Ca–P containing titania coatings were produced by anodic oxidation on selected samples. The layers presented reduced brittleness under normal loading if grown on the previously nitrided surfaces, whereas elastic modulus profiles (75–90 GPa) were kept lower than bulk Ti. We conclude that Ti surfaces can be tailored by plasma nitriding to improve their load bearing capacity for deposition of bioactive layers.

1. Introduction

Synthetic replacements for bone and teeth are expected to match mechanical features (notably elastic modulus) with the surrounding bone, thus allowing a better transfer of functional loads. The large differences in stiffness between implant and surrounding bone may lead to the undesirable stress shielding phenomenon and consequently the bone resorption [1–3]. Ti and Ti alloys present several physicochemical requirements for use in prosthesis [1–4], and they are customarily modified by surface treatments in order to induce osseointegration. Recent studies have drawn attention to several bioactivity inducing methods such the Ca–P based layers [5], alkali treatment [6], oxidation by heat treatment [7], shot blasting [8], deposition of organic components of natural bone [9], ion implantation [10], and anodic oxidation or micro-arc oxidation [11,12]. However, results in the literature have shown that such bioactive layers or films may not be mechanically stable and/or attend the elastic modulus matching [13–15]. Noticeable case is the anodic oxidation process, in which the modified titanium surfaces can present morphology, microstructure and chemical conditions that favor osseointegration [11,12,16]. Although the layer's elastic modulus was found to approach the bone values (30–70 GPa), they are brittle under normal and tangential loads lower than 1 N [14,15].

A possible answer to the film integrity can be the control of the growth parameters. However, in the case of anodic oxidation, bone response is significantly influenced by the oxide features such as crystalline structure, porosity and elemental composition [11,12], so that improvement in adhesion may lead to deterioration in the intended bioactivity. Alternatively, the modification of the pristine surface can increase the tribological and mechanical resistance of deposited films as well. As it has been demonstrated in different situations, film properties can be changed by the previous ion nitriding of the substrate, due to the induced changes in the chemical conditions, wettability and load bearing capacity [17–20].

Regarding the latter option, the surface tailoring by ion nitriding can eventually improve adhesion and integrity of bioactive layers grown or

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deposited on Ti without affecting the favorable features for osseointegration. It is well known that, aiming high performance workpieces, the Ti and Ti alloys nitriding by plasma-based methods can promote increase in the surface hardness, elastic modulus and wear resistance, as shown by several studies from the last decades [21–27]. The efficiency of the Ti and its alloys nitriding is temperature-dependent, increasing as the $\alpha \rightarrow \beta$ phase transition is approached at 1155 K [21,25], whereas the surface mechanical properties increase accordingly [26]. However, concerning biomedical implants, the treatment on titanium by nitriding with subsequent deposition of a bioactive layer must take into consideration the aforementioned requirement for the bone-matching elastic modulus, that is, keeping values as close as possible to the bone ones [3]. The surface elastic modulus is a combination of the film and the substrate beneath (nitrided or not), even for small deformations confined inside the coating [28]. Hence, addressing mechanically compatible coatings on implants, the nitriding of Ti is expected not to change excessively its elastic modulus, which can be achieved by employing low temperature and time conditions in the plasma processes.

The present study aims to contribute to the understanding of tribo-mechanical changes occurring on Ti surfaces nitrided by the plasma DC method, performed in relatively low conditions of temperature (673 K and 873 K) and time (1 h and 3 h). The ion processing effects on the mechanical properties and scratch resistance were studied in nanoscale and correlated with the morphological, chemical and structural changes. Finally, bioactive layers grown by anodic oxidation on selected nitrided Ti samples were analyzed.

2. Experimental details

Commercially pure titanium samples (grade 2) with 1.0 × 2.0 × 0.2 cm were cut from a plate, sandpapered and polished to the mirror-like surface finishing by diamond paste and silica solution. Successively cleaning in ultrasound bath was performed by using acetone, isopropyl alcohol and distilled water. The plasma nitriding was carried out in a custom designed DC glow discharge system, with a 60% N_2 40% H_2 atmosphere. In order to minimize the oxygen contamination during the nitriding process, the base pressure was 3×10^{-2} Pa attained to a turbo-molecular pump. Previous studies revealed that, among different N_2/H_2 ratios, the 60/40 presented improved nitride formation, surface passivation (reduced oxide amount) and mechanical properties [25,26]. The gas used was a specially prepared 99.9995% purity mixture, following the international standard ISO 6142:2001. The working temperatures were 673 K and 873 K, each one performed during 1 h and 3 h. The atmosphere pressures were 470 Pa and 550 Pa for treatments at 673 K and 873 K, respectively. The voltage and electric current applied during plasma nitriding were 479 ± 9 V and 360 ± 1 mA for treatments at 673 K, and 609 ± 17 V and 391 ± 1 mA for treatments at 873 K, adjusted in order to set the working temperatures.

Untreated and selected plasma nitrided samples were submitted to the anodic oxidation process in order to produce bioactive titania coatings, following the protocol reported elsewhere [14]. In summary, Ca and P based electrolytes were used with current density of 150 mA/cm^2, applied for 100 s.

The structural changes were characterized by grazing incidence X-ray diffraction (GI-XRD) with fixed incidence angle from 1° to 5° in the range 20°–60°, using Cu-Kα radiation (40 kV and 30 mA). The scan velocity was 0.26°/min.

Polarized confocal micro-Raman spectra were obtained from different surface regions by using a spectrometer equipped with a solid state laser with $\lambda = 532$ nm. The laser power was 20 mW with an estimated 2 μm spot size diameter. Each spectrum was collected after 30 s data point acquisition time plus 5 co-additions, with spectral resolution of 5 cm^{-1}.

The morphology of the modified surfaces was analyzed by scanning electron microscopy (SEM). The surface roughness was analyzed by atomic force microscopy (AFM) in non-contact mode with silicon cantilevers.

The surface mechanical properties were obtained by the instrumented indentation technique, using a Berkovich diamond tip. Loads ranged from 2 to 300 mN in 8 loading–unloading cycles. Each sample was tested in 40 different sites. Hardness and elastic modulus profiles were calculated following the Oliver and Pharr method [29].

Scratch tests were performed with the same instrumented indentation facility, following the Berkovich-tip edge direction with ramping load from 50 μN to 400 mN, scratch velocity of 10 μm/s and total length 600 μm. The tip penetration profiles were monitored before, during and after the scratch test. Each surface was tested 5 times in different regions. The grooves were cross-profiled 3 times in the middle scratch length region.

3. Results and discussion

Fig. 1a shows the GI-XRD diffractograms, obtained at 2° incidence angle, for the untreated and the nitrided samples. The expected peak positions for α-Ti and titanium nitrides, according to powder crystallographic data, are also shown. Because of the shallow X-ray incidence, the residual surface stresses (due to polishing), and the presence of a subgrain orientation, the α-Ti peaks for the pristine surface are broad. Another significant point to observe in this figure is that neither titanium oxides nor hydrides were identified on treated samples, corroborating the efficiency of the hydrogen presence in the nitriding atmosphere to remove some residual oxygen contamination during the discharging processes. The differences in the α-Ti peak intensities among untreated and nitrided samples, specially the (002) plane at around 38.4°, can be ascribed to preferential orientations in the bulk microstructures. At a visual inspection, all the nitrided samples were golden colored, a typical optical effect attributed to the Ti ion nitriding, whose intensity increased with the treatment temperature and time. However, the 673 K treated samples presented only the α-Ti peaks, slightly asymmetric to the left (likely due to N-incorporation), whereas nitride crystalline phases could not be identified by GI-XRD. On the other hand, the 873 K treated surfaces presented the ε-Ti_2N phase and smaller contributions of the δ-TiN stoichiometry, with the ε-phase relative intensities increasing from 1 h to 3 h and no significant changes for δ-phase. Results by Manova et al. [30] for plasma nitriding show that the δ-TiN relative contribution in the XRD diffractogram increases with treatment time or increased temperature, ascribed to the transformation of Ti_2N crystallites into TiN. The contributions in 38° and 39.6° can be labeled to α-Ti peaks shifted to smaller diffraction angles by nitrogen solid solution, as discussed below.

Fig. 1b presents the GI-XRD diffractograms for treatments 3 h for different incidence angles (1° to 5°). The asterisk indicates possible average positions for the α-Ti crystalline lattice with nitrogen in solid solution, based on crystallographic data for substoichiometric TiN_x compounds, which shift its diffraction peaks (in this case, ~0.25°) to small diffraction angles. Such Ti(N) "phase" lies beneath the surface region with nitride precipitates, where the nitrogen concentration decreases with depth [25,27,31–33]. The X-ray depth penetration (t) in the material surface can be inferred from the relation [34]

$$t = \frac{3.45\,sen\theta}{\left({}^{\mu}/_{\rho}\right)\rho},$$

where μ is the absorption coefficient and ρ the density. Considering $\mu/\rho = 202.4$ cm^2/g and $\rho = 4.51$ g/cm^3 for titanium, these results correspond to a volume comprised within ~3 μm depth. By decreasing the fixed incidence angle from 5° to 1°, the X-ray penetration reduces in respect to the surface; however, even at the shallowest incidence no