

Niobium and titanium surface modification via anodic oxidation in Ca/P containing solutions for osteogenesis

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Summary. — Transition metals are the materials of choice for the development of orthopaedic implants due to their biocompatibility. We focused on the surface modification of niobium and titanium through anodic oxidation to promote their osteogenic properties. Anodizing in solutions containing Ca and P allowed us to tailor the oxide morphology and chemical composition. By tuning the anodizing potential, mesoporous oxide layers with a surface chemical composition mimicking hydroxyapatite are obtained. By combining AFM, SEM and XPS we evaluated the increase in porous size and layer thickness as a function of the applied potential and correlated it to the oxide chemical composition.

1. – Introduction

Biocompatibility properties of transition metals derive from the thin oxide layer that spontaneously forms on their surface and prevents metal ion release from the bulk when in contact with biological environment. In the last years, niobium (pure and in some of its alloys) has gained importance for biomedical applications in parallel to the traditional titanium and its alloys (mainly Ti-6Al-4V). To improve the surface characteristics, the target is to imitate the morphology and the chemical composition of the bone. This means a porous surface to simulate the trabecular structure and the presence of calcium and phosphorous in a 1.67 ratio to mimic the hydroxyapatite chemical composition. Among the many methods to modify the morphology and chemical composition of a metal surface, anodizing is a simple, fast and easy way to grow an oxide layer with the possibility to include ions in the oxide matrix. This result is obtained when the anodizing is conducted above the breakdown potential, in the so-called Anodic Spark Deposition (ASD). This means that properly tuning the electrolyte composition, the limiting voltage and current, the anodizing occurs with presence of sparks on the sample surface that locally melt the surface creating pores and helping in ion inclusion.

In this work the anodizing of pure titanium and pure niobium has been explored using an electrolyte containing Ca and P in a 1.67 ratio. This electrolyte has already been used on titanium in an interesting work from Frauchiger *et al.* [1]. Here we used the same electrolyte on niobium under proper condition to obtain anodizing in ASD regime, paralleling the work with anodizing of titanium in the same conditions. AFM was used to

study morphology, while SEM cross-sectional analysis was used to evaluate the thickness of the oxide layer. The surface chemical composition was studied with the very surface sensitivity of XPS using an electron neutralizer to avoid sample charging.

2. – Material and methods

2.1. Sample preparation. – Substrates are 1 cm × 1 cm squares of c.p. niobium (kindly provided by Dr. Musenich, INFN Genova) and 1 cm × 1 cm squares of c.p. titanium (Advent Research Materials Ltd.). All samples were polished using SiC papers till P2500 grain size and ultrasonically rinsed in Milli-Q water, ethanol and acetone. A two-electrode cell was used for anodizing with a Pt grid as counter-electrode. Anodizing was carried out using a solution (hereafter named Ca/P solution) composed as follows: monocalcium orthophosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 0.025 M, calcium acetate $\text{Ca}(\text{OOCCH}_3)_2$ 0.075 M and di-sodium ethylenediamine tetraacetate $\text{Na}_2(\text{EDTA})$ 0.12 M [1]. NaOH was added to adjust pH at a value of 13. A 2 A current was used to maintain a galvanostatic regime with limiting potentials of 150 V, 200 V and 250 V. Exhaustive information on sample preparation can be found in [2].

2.2. Characterization methods. – Sample morphology was analyzed with Atomic Force Microscopy (AFM) using a Multimode/Nanoscope V system (Bruker) in tapping mode (OMCL-AC160TS Si cantilevers). Cross-section imaging was carried out using a High-Resolution Field Emission Scanning Electron Microscope (Crossbeam 1540 XB, Carl Zeiss) using the In-Lens detector with an electron energy of 20 kV. The chemical analysis of the sample surfaces was carried out by XPS measurements using a PHI 5600 multi-technique apparatus with Al-monochromatized source ($h\nu = 1486.6$ eV). High-resolution spectra were acquired with a pass energy of 23.5 eV. A neutralizer (low energy electron flood gun) was used during measurements to avoid sample charging. The binding energy scale was calibrated by setting the C1s component of adventitious carbon at a binding energy of 284.8 eV. Deconvolutions were performed with CasaXPS using voigt functions (30% Gaussian). Exhaustive information on characterization methods can be found in [2].

3. – Results and discussion

Titanium and niobium foils anodized in the Ca/P solution produced sparking formation on samples surface in all the considered conditions. The presence of sparks means an anodization above the breakdown potential and formation of pores, as can be inferred from fig. 1.

Figure 1 reports the AFM images of titanium (left column) and niobium (right column) samples after anodizing with limiting potential of 150 V (upper row), 200 V (middle row) and 250 V (lower row). Both the materials show, for any limiting potential, a distribution of pores with the maximum reached diameter enlarging with growing potential. For titanium, pores diameter spam up to 1500 nm at the maximum potential explored, while for niobium this value is larger and some pores reach 6000 nm in diameter. Thanks to the AFM capability of acquiring the z -dimension, the pores depth can also be measured. For samples anodized with a limiting potential of 250 V, pores depths of 1200 nm are observed in titanium samples and a bigger value of 3000 nm can be found in niobium anodized surfaces. The differences in pore dimensions can be also appreciated considering the roughness values (R_a) of the surfaces. Considering a $10 \mu\text{m} \times 10 \mu\text{m}$ scan size, R_a values up to about 400 nm and about 600 nm are observed for titanium and niobium,

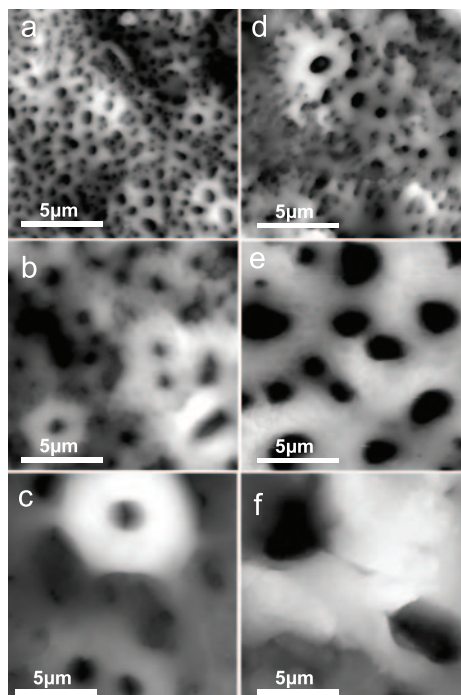


Fig. 1. – AFM images of Ti foil (left column) and Nb foil (right column) anodized at 150 V (a) and (d), 200 V (b) and (e) and 250 V (c) and (f). Z-scale is 700 nm, 1200 nm, 3500 nm, 1000 nm, 2000 nm and 4500 nm for (a), (b), (c), (d), (e) and (f) respectively.

respectively. As already mentioned, the bio-compatibility of a material lays also in the mimicking of the bone trabecular morphology, *i.e.*, micro-meter sized pores. Niobium allows to obtain bigger pores than titanium considering the anodizing in the same conditions (electrolyte, limiting potential and current). Another important aspect related to the biocompatibility is the capability of the surface to prevent metal ion release from the bulk. Corrosion resistance can be improved by the growth of a thick oxide layer. Figure 2(a) shows a typical surface cross-section of a niobium foil anodized at 250 V, with a 10 μm thick oxide layer, well adherent to the metallic bulk.

Surface chemical composition is also very important in view of osteointegration and osteogenesis. A chemical composition mimicking hydroxyapatite can be obtained with the inclusion of calcium and phosphorous in the grown oxide matrix. ASD anodizing regime has been reported in the literature [3-5] as a good method to achieve this

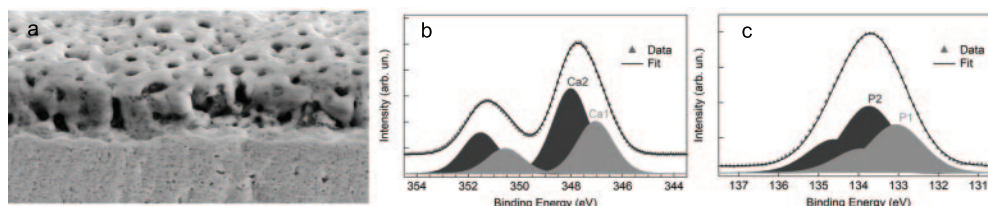


Fig. 2. – (a) SEM cross-section, XPS high-resolution spectra of (b) Ca2p and (c) P2p region, of a typical niobium foil anodized with a 250 V limiting potential.

aim. XPS analysis allowed to investigate the presence, the chemical nature, the amount (with respect to the metal, electrolytes/metal) and the Ca/P ratio (that for HA is 1.67). Figures 2(b) and (c) report high-resolution spectra of Ca2p and P2p regions of a typical niobium sample anodized with a 250 V limiting potential. At this particular limiting potential, differently from all the other anodizing condition explored in this work, both the calcium and the phosphorous signals present two well-distinguishable doublets. The Ca2p is deconvoluted with two doublets with the main $2p_{3/2}$ components at a binding energy of (347.1 ± 0.2) eV (Ca1) and (348.0 ± 0.2) eV (Ca2), respectively. The P2p is deconvoluted with two doublets with the main $2p_{3/2}$ components at a binding energy of (133.1 ± 0.2) eV (P1) and (133.9 ± 0.2) eV (P2), respectively. The lower BE doublets of calcium (Ca1) and phosphorous (P1) can be attributed to compounds like $\text{Ca}_3(\text{PO}_4)_2$, CaHPO_4 or $\text{Ca}(\text{H}_2\text{PO}_4)_2$. The second doublet necessary to properly fit the data for anodization at 250 V, can be assigned to the presence of hydroxyapatite. Other than the composition, it is important to evaluate the amount of ions inclusion and the Ca/P ratio. $(\text{Ca}+\text{P})/\text{Nb}$ and $(\text{Ca}+\text{P})/\text{Ti}$ of about 1 are observed for all the anodizing conditions, with the remarkable exception of the anodizing of niobium at a limiting potential of 250 V that showed a value of 4, indicating a large amount on ions inclusion in the oxide matrix. Moreover, the Ca/P ratio is slightly bigger for niobium samples (values around 1.3) with respect to titanium samples (values in the range 0.6 to 1.2). In particular, an interesting Ca/P of 1.8 was found for the niobium anodized at a limiting potential of 250 V.

4. – Conclusions

The anodizing of titanium and niobium was carried out in an electrolyte containing calcium and phosphorous, obtaining ASD regime in all the explored conditions. Anodizing on niobium with a limiting potential of 250 V produced a porous surface with pores diameter spanning up to $6 \mu\text{m}$, a $(\text{Ca}+\text{P})/\text{Nb}$ of 4 and a relevant Ca/P ration of 1.8. These results suggest niobium as a good candidate for biocompatible application, especially in comparison with results obtained on titanium.

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