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# Nanomechanical properties of surface-modified titanium alloys for biomedical applications

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**Abstract**

The mechanical properties of the oxide layers developed at elevated temperature on three vanadium-free titanium alloys of interest for biomedical applications were investigated by means of the nanoindentation technique. The as-received alloys (Ti–13Nb–13Zr, Ti–15Zr–4Nb and Ti–7Nb–6Al) and their oxide scales formed by reaction with air at 750 °C for several oxidation times were analysed comparatively. In particular, the hardness and the Young's modulus exhibit larger values for the thermally oxidized alloys than for the untreated specimens. However, the Ti–7Nb–6Al alloy shows a different tendency to that of the TiNbZr alloys, which seems to be related to a different oxide layer growth as a function of the oxidation time.


*Keywords:* Titanium alloys; Nanoindentation; Biomaterials; Oxidation; Hardness

## 1. Introduction

In the past few years, new Ti alloys have been intensively investigated and developed for biomedical applications as possible substitutes of the well-established Ti–6Al–4V alloy [1–4]. Though this alloy presents excellent mechanical and corrosion properties, it contains vanadium, which is known to be cytotoxic [5,6]. Thus, avoiding metal ion release and obtaining vanadium-free alloys with similar properties has been the focus of interest of recent investigations [7–10]. One important factor, which controls some of the notable properties of pure titanium and its related alloys, is the passive layer, i.e. the native oxide thin film spontaneously formed on the material surface when in contact with air. This protective film is responsible for the excellent corrosion resistance of these materials, which involves low metal ion release even in aggressive environments [11–14]. In order to enhance the corrosion resistance and biocompatibility of Ti alloys, different surface modification techniques have been investigated. Among them, an easy and economic method to generate an oxide film on the surface alloy has been recently proposed. Depending on the alloying elements, this oxide would satisfy the desired surface properties [15,16]. In previous works, some of the properties of three V-free Ti alloys, of composition (in wt.%) Ti–13Nb–13Zr, Ti–15Zr–4Nb and Ti–7Nb–6Al, selected as potential materials for biomedical applications, were investigated before and after oxidation treatments in air at 750 °C [17,18]. The achieved materials were expected to show higher biocompatibility in orthopaedic implants than the most widely used Ti–6Al–4V alloy for two different reasons: the composition of these alloys is free of vanadium, thereby avoiding toxicity problems, and, as expected, the oxidation treatment provides a thicker protective oxide

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film than the native oxide. Previous characterization of the surface composition and morphology of these surface-modified alloys has produced very promising results [19–21]. Moreover, highly surface-sensitive scanning force spectroscopy (SFS) measurements have provided some insights into the elasticity properties of their very topmost layer (tens of nanometres) [22]. In Ref. [22], although attempts were made to interpret the elasticity data in terms of alloy composition, their evaluation as a function of indentation depth produced a large dispersion of results. That was an indication of the importance of the specific roughness or composition of the surface. These parameters can differ from those of the bulk material and, consequently, can provide unexpected mechanical properties. Moreover, the gap existing between practical needs and the extremely local information (lateral and vertical) obtained from those scanning force microscopy (SFM) experiments points to the necessity of studying these protective layers on a larger scale (hundreds of nanometres), the region directly in contact with the bone. Important properties that need to be determined include, among others, hardness and Young's modulus. In particular, for a material to be a successful orthopaedic implant it needs a Young's modulus similar to that of bone (10–30 GPa) [23].

Nanoindentation is a non-destructive, versatile and unique technique for determining the mechanical properties of surfaces. When an indentation system is used, loads as small as one nanonewton and displacements of about 0.1 nm can be accurately measured continuously throughout a test. Different mechanical properties can then be determined from the load–displacement data without imaging the indentations [24]. For these reasons, this technique has been used to measure the hardness and Young's modulus of the oxidized films generated as described above. For comparison, this study has also been carried out on untreated alloys.

## 2. Materials and methods

The three Ti-based alloys were prepared by arc melting and then casting in a copper coquille under high vacuum, using high-purity (better than 99.9%) constituent elements. Therefore, interstitial impurities, such as oxygen, nitrogen, carbon or substitutional transition metals, have just residual values. At this level, the effect of impurities upon the oxidation process of Ti alloys is not significant. The nominal composition of these alloys was (in wt.%) Ti–13Nb–13Zr, Ti–15Zr–4Nb and Ti–7Nb–6Al, which in at.% correspond to $Ti_{84.5}Nb_{7.7}Zr_{7.8}$, $Ti_{89.1}Zr_{8.6}Nb_{2.3}$ and $Ti_{85.9}Al_{10.5}Nb_{3.6}$, respectively. The actual chemical compositions of the alloys in at.% are $Ti_{85.36}Nb_{7.32}Zr_{7.32}$, $Ti_{89.23}Zr_{8.49}Nb_{2.28}$ and $Ti_{84.8}Al_{11.8}Nb_{3.4}$, respectively, as was determined in a previous work [25] by Rutherford backscattering spectroscopy.

The oxidation treatment was performed on samples cut from as-cast ingots by electrospark erosion. Previous to the thermal treatment, the sample surfaces were abraded and polished using diamond paste with successively smaller particle sizes. Colloidal silica was used to ensure a surface free of mechanical deformation. Before performing the oxidation treatment it is important to remove foreign particles and organic contaminant from mechanical polishing. To clean the samples, it is essential to put some gel on the rotating polishing cloth and then to flush with water for approximately 10–15 s before the machine stops. The samples are then cleaned again ultrasonically with acetone and dried with a strong stream of air. After these cleaning steps, optical microscope examination was employed to make sure that there were no residues of silica on the sample surface. Finally, the specimens were cleaned ultrasonically with acetone. The material in this state was named "as-received". The surface cleanness after this procedure was check by X-ray photoemission spectroscopy [26]. At this stage, some samples were isothermally oxidized in air in a tube furnace at 750 °C for exposure times of 1.5 h, 6 h and 24 h.

A microstructural study revealed the existence of two different phases, α and β, whose ratio depended on the alloy composition [17]. The root mean square (rms) roughness values for the three as-received alloys are relatively low (3, 4 and 12 nm for Ti–13Nb–13Zr, Ti–15Zr–4Nb and Ti–7Nb–6Al, respectively) and their surface morphology exhibited two regions with different contrast [21]. This effect might be ascribed to the coexistence of α and β phases since colloidal silica performs selective polishing of each phase due to their different hardnesses.

The cross-sections of the oxidized samples were examined by scanning electron microscopy (SEM) equipped for energy-dispersive X-ray microanalysis. For this analysis, specimens of the three oxidized alloys were submitted to a metallographic preparation, which included mounting the samples in bakelite and polishing by the conventional method. To prevent scale loss during metallographic preparation, the surface of these oxidized samples were coated with a thin gold layer by sputtering. A thicker layer of copper was then deposited electrolytically.

In the present work, nanoindentation tests were made with a Nanoindenter II (Nanoinstruments-MTS Systems, Oak Ridge, TN) using a Berkovich diamond tip. Diamond is the most frequently used indenter material because its high hardness and elastic modulus minimize the contribution of the indenter itself to the measured displacement. For probing properties such as hardness and elastic modulus at the smallest possible scales, the Berkovich triangular pyramidal indenter is preferred over the four-sided Vickers or Knoop indenter because a three-sided pyramid is more easily ground to a sharp point.

Each specimen was tested at room temperature using the continuous stiffness measurement (CSM) technique developed by Oliver and Pethica [27,28]. The CSM is accomplished by imposing a small, sinusoidally varying signal on top of a DC signal that drives the motion of the indenter. The data are obtained by analysing the response of the system by means of a frequency-specific amplifier. This