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Surface elastic properties of Ti alloys modified for medical implants: A force spectroscopy study

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Abstract

We report here the first nanoscale surface elasticity measurements on surface-modified titanium alloys using the force spectroscopy mode in scanning force microscopy. Samples of three vanadium-free titanium alloys, Ti–7Nb–6Al, Ti–13Nb–13Zr and Ti–15Zr–4Nb, were investigated. Surface modification of the three alloys was produced by thermal oxidation in air at 750 °C for different times, which resulted in the formation of protective oxide layers with different surface composition and morphology. The elastic properties of the surface layers were studied comparatively in the as-received Ti alloys and after the oxidation process using cantilevers with different stiffness to evaluate the influence of the indentation depth. In all cases, Young's modulus of the sample surfaces was found to be lower than 65 GPa, and as low as 20 GPa for some of the oxidized samples. Variations observed for the three oxidized Ti alloys can be related to the different chemical composition of the outer layers generated for the different oxidation times.

Keywords: Nanoindentation; SFM (scanning force microscopy); Biomaterials; Metal alloy; Elastic behavior

1. Introduction

Their high strength-to-weight ratio and low elastic modulus combined with a satisfactory corrosion behavior make titanium and titanium-based alloys outstanding biomaterials and promising candidates for the replacement of hard tissues such as those present in artificial hip joints or dental implants. The spontaneous development of a stable and protective passive layer with a thickness of a few nanometers when exposed to an oxygen-containing atmosphere provides these materials with a high biocompatibility associated with a high corrosion resistance in aggressive biological environments. During the past 50 years the standard alloy for these purposes has been Ti–6Al–4V, but it has been recently reported that the release of vanadium ions from the alloy might cause health problems due to their toxicity [1]. For this reason, there is growing research activity aimed at developing vanadium-free titanium alloys for biomedical applications presenting a good combination of biocompatibility, corrosion resistance and mechanical properties similar to those of Ti–6Al–4V. Within this approach, three α–β Ti alloys of composition (in wt.%) Ti–7Nb–6Al, Ti–13Nb–13Zr and Ti–15Zr–4Nb, proposed as potential biomaterials, have been previously characterized [2,3]. In those works, the in vitro corrosion behavior of the alloys, immersed in Hanks' solution, as well as the microstructure and chemical composition of the passive layer spontaneously formed in air, were studied. The electrochemical investigations pointed to a similar corrosion

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resistance for the three alloys, with values lower than those obtained for Ti–6Al–4V. The microstructural study revealed the existence of two different phases, α and β, with the α/β ratio being dependent on the alloy composition. Thus, the Ti–13Nb–13Zr alloy surface is rich in the β-phase due to a high content of Nb, a β-stabilizer element. Meanwhile, as Al is an α-stabilizer, and Zr is neutral, both Ti–7Nb–6Al and Ti–15Zr–4Nb surfaces are richer in α-phase.

One way to improve corrosion prevention and wear resistance in titanium alloys would be to increase the thickness of the passive layer. In order to do that, we have used a simple thermal treatment in air at 750 °C to generate a highly protective, bioinert oxide layer on the alloys' surface. Previously to the present study, complementary techniques had already been used to investigate some properties of these layers. In particular, characterization by soft X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) showed differences in composition of the oxide layer grown on the three alloys [4,5]. The passive Ti_2O_3 oxide layer formed on the as-received Ti–7Nb–6Al surface evolves, after an oxidation time of 1.5 h, into an Al_2TiO_5 layer on top of which an Al_2O_3 layer grows and thickens with further oxidation time. However, for the two TiNbZr alloys a TiO_2 rutile layer is formed on the alloy surface independently of the oxidation time. Cross-sectional scanning electron microscopy (SEM) and electrochemical measurements were also performed to follow the development of the layer as a function of the oxidation time and to investigate the protective character of the oxidized layers against corrosion [6]. More recently, we have conducted a scanning force microscopy (SFM) study that reveals a correlation between roughness, oxidation time and surface composition of these oxide layers [7]. In the present study we attempt a further characterization of these layers by determining their nanoscale elastic properties.

Despite the great progress that has been achieved in producing orthopedic biomaterials, one of the major reasons for implant loosening following stress shielding in bones is the mismatch between the Young's moduli of the biomaterials employed (between 110 GPa for Ti and 230 GPa for Co–Cr alloys) and the surrounding bone (10–30 GPa). Therefore, the elastic characterization of the outermost layers, which may present different elastic properties than the bulk and are those in direct contact with the bone, is crucial when suggesting alternative alloys.

We report here the results obtained using SFM in the force spectroscopy mode to investigate the elastic modulus in the very outermost layers of the aforementioned surface-modified Ti alloys. In recent years SFM has become a powerful technique for the study of the nanoscale surface structure of materials. In addition to the topographic analysis, the sensitivity of SFM to sub-nano-Newton forces has led to its use in the characterization of surface properties such as friction, adhesion and elastic modulus. In the latter case, force vs. distance curves measured with the SFM tips lead to indentation curves and, by analogy with classical indentation techniques, the respective surface moduli can be obtained [8–12].

Validation of the elastic moduli obtained in the present work is discussed by comparing data obtained with cantilevers of different stiffness and by assessing the non-invasive character of the technique in the force regime employed, where neither wear nor plastic deformation occurred as confirmed by SFM imaging verification. Furthermore, by taking advantage of the imaging capability of the SFM, we have analyzed the correlation between nanoscale elasticity and surface characteristics.

2. Experimental

2.1. Materials and sample preparation

The Ti-based alloys of composition (in wt.%) Ti–7Nb–6Al (T1), Ti–13Nb–13Zr (T2) and Ti–15Zr–4Nb (T3) were prepared as explained elsewhere [2]. The sample surface was abraded and polished using diamond pastes with successively finer particle size. In the final stage, colloidal silica was used to ensure a surface free of mechanical deformation. The material in this state is the as-received sample. For each composition, four different samples were investigated: the as-received one, exhibiting a thin native oxide layer, and three samples after oxidation treatments at 750 °C in air for 1.5, 6 and 24 h. At the final stage, the oxide layers were 2, 10 and 25 μm in thickness for T1, T2 and T3, respectively, as determined by SEM cross-sectional observations [6].

2.2. Scanning force microscopy and force spectroscopy

SFM measurements were performed using a commercial scanning force microscope (TMX 2100 Explorer, TopomeMetrix, now Veeco Metrology, Santa Barbara, CA).[1] Two types of Ultralever, V-shaped, Si_3N_4 probes (Park Scientific Instruments, now also Veeco Metrology) with nominal spring constants (k) of 0.4 and 2.1 N/m, respectively, were used. Since actual spring constants can differ from their nominal values, the cantilevers were calibrated using the "reference-spring method" [13], which revealed an accuracy of 0.08 N/m. Furthermore, particular attention was given to the estimation of the tip radius, which is an essential parameter in our elasticity analysis. The probe was characterized by field emission scanning electron microscopy (FESEM) and a half opening angle of approximately 12.5° and a radius of about 15 nm were obtained [14]. This holds for all Ultralever tips used in the experiments.

In order to ensure grease-free and dust-free surfaces, the samples were cleaned in an acetone ultrasonic bath for 10

[1] For details of the experimental set-up (photographs and schematics), see http://electron.mit.edu/~gsteele/mirrors/elchem.kaist.ac.kr/jhkwak/TopometrixWeb/TopoHome.htm.

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