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XPS characterization of surface modified titanium alloys for use as biomaterials

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ABSTRACT

Three different Ti alloys of biomedical interest have been studied by means of X-ray photoelectron spectroscopy (XPS) to determine their surface chemical composition in both as-received condition and after oxidation at 750 °C in air for different times. Compositions of the investigated alloys were, in wt.%, Ti–7Nb–6Al, Ti–13Nb–13Zr and Ti–15Zr–4Nb. XPS analyses showed a behaviour of the Ti–7Nb–6Al alloy different from that of the two TiNbZr alloys, evidencing the role of the chemical composition of the alloys on the oxidation mechanisms. The oxidation process generates an aluminium-oxide rich surface on the Ti–7Nb–6Al, while in the case of the TiNbZr alloys a titanium-oxide rich layer is formed. The effect of the heat treatment on the contribution of the minority elements at the surface is also discussed.

1. Introduction

Ti and Ti alloys are nowadays highly advantageous materials for biomedical use due to the combination of good biocompatibility, excellent mechanical properties and optimal corrosion behaviour [1,2]. Indeed, these materials exhibit a tendency to form a stable surface oxide film. This layer is the result of the strong Ti affinity for oxygen and grows spontaneously when the alloy is exposed to air [3]. Thus, the native oxide layer confers high corrosion resistance to the material, providing protection against the corrosive action of physiological fluids. As a consequence, this layer reduces the ion release related to metallic corrosion, leading to an optimal biocompatibility and low cytotoxicity. With the aim of improving as much as possible the protecting properties of the outermost oxide layer, numerous surface modification treatments have been investigated. An economic and simple method to generate on a material a thicker barrier against the harmful effects of aggressive environments is to expose it to a thermal treatment in an oxygen rich atmosphere. This procedure, which leads to the formation of thicker surface oxide layers, has been in some cases successfully applied [4], while in other cases the outcome was unfavourable [5]. To consider a material for biomedical applications, several properties should be studied [6]. Amongst them, the corrosion behaviour, the mechanical attributes and the biocompatibility must be underlined. However, the material surface plays also an important role in the success of a biomaterial. On the one hand, corrosion processes take place mainly at the surface and, therefore, are governed by surface properties, as composition or topology. On the other side, the biomaterial surface is the region in direct contact with living tissues, which has an influence on the biocompatibility. For this reason, the determination of the surface chemical composition of an implant is an essential step for its complete characterization. Important tools for evaluation of the surface chemical composition are X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). The first one has been widely used to determine the composition of passive layers of materials used for biomedical applications [7,8]. However, sampling depth of XAS is larger than that of XPS, which gives information of only the last atomic layers of a material. Additionally, this valuable technique allows also the determination of the oxidation state of the detected elements. This makes possible to obtain the chemical species contributing to the most external region. In this work, three different Ti alloys of biomedical interest have been studied by means of XPS to determine their surface chemical composition. Compositions of the investigated alloys were, in wt.%, Ti–7Nb–6Al, Ti–13Nb–13Zr and Ti–15Zr–4Nb. The surface of these alloys was modified by thermal oxidation at 750 °C in air for different times to improve the material properties. The effects of the heat treatment on the surface chemical contribution are discussed from the XPS data.

2. Experimental details

Three Ti-base alloys, with compositions (in wt.%) Ti–6Al–7Nb, Ti–13Nb–13Zr and Ti15Zr.4Nb, were prepared by arc melting high purity Ti (99.9%) with the corresponding amount of each alloying

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element, also of high purity. The melt was casted in a copper coquille under high vacuum. The corresponding atomic percent composition was Ti85.9Al10.5Nb3.6, Ti84.5Nb7.7Zr7.8 and Ti89.1Zr8.6Nb2.3. The samples were cut from as-casts ingots by electro-spark-erosion, then the sample surfaces were abraded and mechanically polished and, lastly, the specimens were ultrasonically cleaned in acetone. The specimens in these conditions were designated as "as-received" samples. On the other hand, some specimens were isothermally oxidized in air at 750 °C during 1.5 h, 6 h and 24 h, respectively. Surface elastic properties, as well as root mean square roughnesses (rms) of the oxide layers were previously reported [9,10]. By using scanning force microscopy in contact mode, rms values up to 25 nm were found for as-received samples, and around 125–225 nm for 24 h oxidized samples. X-Ray Photoelectron Spectroscopy (XPS) spectra were recorded with a VG-CLAM hemispherical electron energy analyser using Mg K_α radiation (1253.6 eV) in an ultrahigh vacuum chamber with a base pressure better than 10^{-9} mbar. XPS spectra were least-squares fitted using standard Gaussian–Lorentzian lines.

3. Results and discussion

Fig. 1 exhibits the 2p spectra of the dominant alloying element, Ti, for as-received and heat-treated Ti–7Nb–6Al alloys. The solid line through the data points represents the result of the least-squares fit and the dashed-dotted curve shows the integral background. Similar spectral shapes can be observed for all oxidized samples with two main narrow peaks, contrasting with that of the as-received alloy, with a wider feature extending from 453 to 470 eV. To fit properly the spectrum corresponding to the native oxide layer in the as-received sample, four doublets were needed, which correspond to Ti^0, Ti^{2+}, Ti^{3+} and Ti^{4+}. Thus, each oxidation state exhibits two peaks, i.e. a doublet, formed by the Ti-2p3/2 and 2p1/2 signals, which are separated by the Ti-2p spin-orbit splitting, 5.6 eV. Although the more intense signal corresponds to Ti^{4+}, lower oxidation states have also a significant contribution. Indeed, the Ti^0 emission, corresponding to metallic Ti, is also present. This signal rises from non-oxidized Ti atoms underneath the native oxide layer due to a sampling depth for XPS rather similar to the thickness of this outer film. In contrast to the as-received sample, the three oxidized Ti–7Nb–6Al samples show only the presence of the doublet ascribed to Ti^{4+} states. This indicates that the heat-treated alloys are totally oxidized. For the two TiZrNb alloys, the behaviour of the Ti-2p emission is identical to that of Ti–7Nb–6Al (not shown). In all cases, the as-received samples exhibit the presence of several oxidation states, including the metallic emission coming from the base material. All heat-treated alloys show only the fully oxidized Ti contribution.

As an example of the minority alloying elements, Fig. 2 exhibits XPS Nb-3d spectra of Ti–13Nb–13Zr in as-received and heat-treated conditions. Similarly to the case of Ti-2p, the as-received spectrum shows a rather different shape as compared to the spectra of the heat-treated alloys. A double peak is observed for oxidized Ti–13Nb–13Zr samples while a wider structure appear for the as-received specimen. In the niobium case, a doublet corresponding to the Nb-3d5/2 and 3d3/2 emissions were used to consider each oxidation state. For the as-received sample spectrum, Nb^0, Nb^{2+}, Nb^{4+} and Nb^{5+} contributions were needed to reproduce the broad spectral shape. The Nb^0 metallic emissions, at 202.8 and 205.5 eV, are assigned to electrons arising from the base material beneath the native oxide layer. For heat-treated alloys, only two sub-spectra are needed to perform an optimal analysis of the experimental curves. The corresponding peaks are located at a binding energy of ≈207.5 and ≈210.2 eV, respectively, corresponding to the 3d5/2 (dashed curve) and 3d3/2 (dotted curve) core levels of Nb^{5+}. This result is evidence that, for the three heat-treated Ti–13Nb–13Zr samples, the outer layer is fully oxidized. The Nb-3d spectra XPS of Ti–7Nb–6Al and Ti–15Zr–4Nb alloys (not shown) present the same tendency as that observed for the Ti–13Zr–13Nb sample. For the rest of alloying elements that can contribute to the surface composition of the Ti alloys, the same

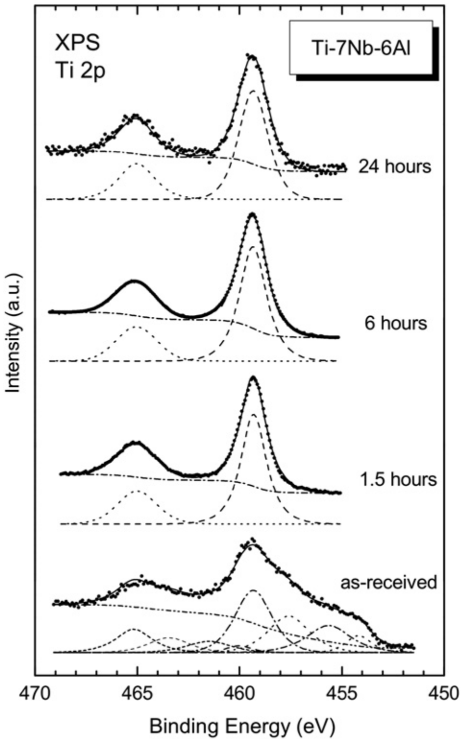

Fig. 1. Ti-2p spectra of as-received Ti–7Nb–6Al and oxidized at 750 °C for 1.5, 6 and 24 h.

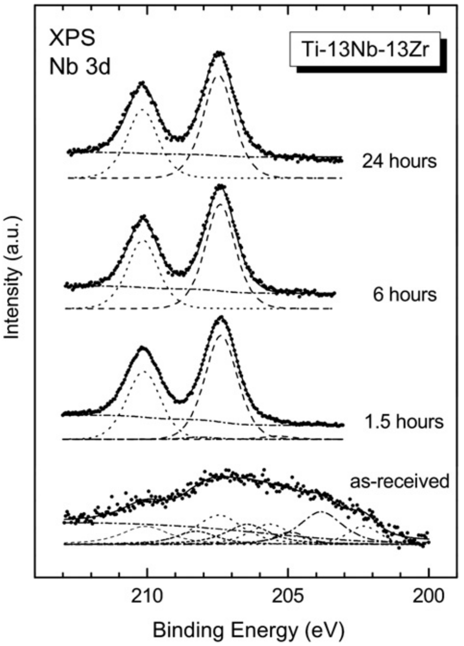

Fig. 2. Nb-3d spectra of as-received Ti–13Nb–13Zr and oxidized at 750 °C for 1.5, 6 and 24 h.

fitting procedure was followed. Accordingly, Zr-3d XPS spectra, in the case of the two TiNbZr alloys, and Al-2p XPS spectra for Ti–7Nb–6Al, were measured and analyzed. In all cases as-received alloys have shown the confluence of different oxidation states and the metallic contribution. For Ti–7Nb–6Al, Al^{3+} and Al^0 emissions were observed whereas for the two TiNbZr alloys, Zr^{4+}, $Zr^{3+}$and Zr^0 signals were detected. Again, these results are an indication of the formation of a native oxide layer not fully oxidized with a thickness smaller to the XPS sampling depth. For the heat-treated alloys, fully oxidized contributions of the corresponding elements were found at the surface of the alloys. Consequently, the XPS data establish a fundamental difference between oxide layer generated by heat treatment and native oxide layer grown spontaneously on the Ti alloy at room temperature. Fig. 3 shows surface atomic percentages for as-received and heat-treated Ti alloys. To calculate these values, the XPS areas, extracted from the least-squares fits, were normalized by using atomic sensitivity factors for the corresponding element. The nominal bulk atomic percentage is also represented. In all three alloys, the contribution of the three minority elements (Al, Nb and Zr) to the native oxide layer for as-received samples exhibits an enhancement with respect to the bulk nominal values. Consequently, the Ti percentage at the surface decreases with respect to the bulk values, although it remains the main contribution. The effect of the heat treatments on Ti–7Nb–6Al is different to that observed on the two TiNbZr alloys. For Ti–7Nb–6Al, the oxidation process favours Al diffusion towards the surface. This phenomenon, which is already observed at the native oxide layer, continuously increases during the heat treatment, due to thermal activation. On the other hand, the TiNbZr alloys show at the initial stages of the oxidation process an important Ti diffusion towards the surface with a pronounced decrease of Zr as compared to the native oxide layer. As the oxidation time increases, the surface Ti contribution slowly decreases due to the diffusion of Nb, and Zr in less proportion, from the bulk material. The different behaviour between Al and Zr containing alloys leads to the formation of oxidized layers with different properties. For the oxidized Ti–7Nb–6Al alloys the outer layer is composed mainly of Al oxide with some contribution of Ti oxide. Contrasting with this result, for the oxidized TiNbZr alloys the outer layer is formed mainly of Ti oxide with non-negligible amounts of both Nb and Zr oxides. The chemical composition of the surface of these alloys has an important effect on their properties. Indeed, the mixture of oxides at the surface of heat-treated TiNbZr alloys has a detrimental effect on the protecting properties of the outer oxide scale, as it was observed in previous experiments [11,12]. Electrochemical studies of the three alloys revealed a worse corrosion behaviour for the oxidized TiNbZr alloys as compared to that of Ti–7Nb–6Al. Heat-treated TiNbZr alloys exhibited a porous oxide layer with some fissures, while the Ti–7Nb6Al oxide scale was uniform, compact and thin. Additionally, both Ti and Al oxides, which are the components of the oxidized layer of heat-treated Ti–7Nb–6Al, are known to exhibit excellent biocompatibility. In summary, considering the three Ti alloys, oxidized Ti–7Nb–6Al presents optimal surface characteristics for biomedical applications thanks to the properties of its outer oxide layer.

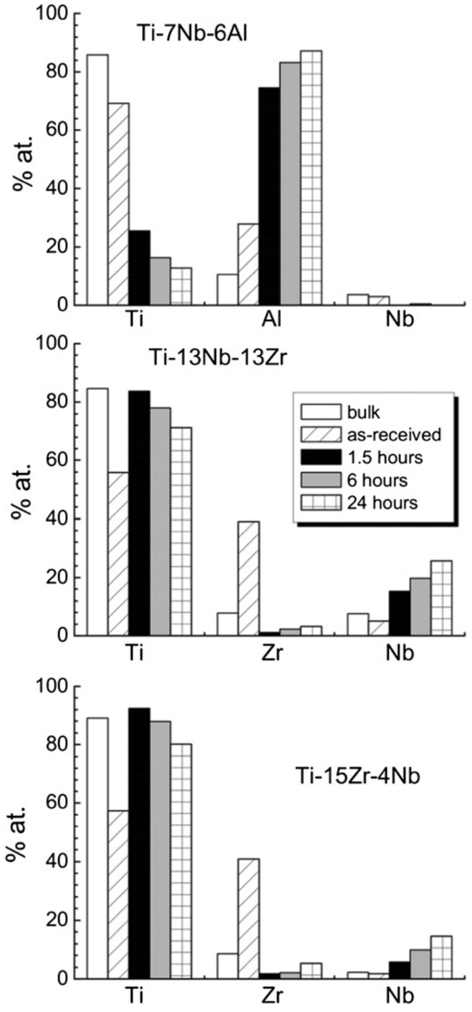

Fig. 3. Surface atomic percentages of the different alloying elements obtained from the XPS data for Ti–7Nb–6Al, Ti–13Nb–13Zr and Ti–15Zr–4Nb both in as-received condition and oxidized at 750 °C for 1.5, 6 and 24 h. The bulk composition of the alloys is also shown for comparative purposes.

4. Conclusions

The surface composition of three different Ti alloys in their as-received state and after heat treatment at 750 °C in air has been studied by XPS. The purpose of the oxidation process on Ti–7Nb–6Al, Ti–13Nb–13Zr and Ti–15Zr–4Nb was the formation of a thick outer oxide layer with improved surface properties. For the three alloys, the XPS results on the surface of the as-received samples indicate the presence of several oxidation states in the native oxide layer. Considering the alloys after heat treatment, the XPS data reveal different surface composition for oxidized Ti–7Nb–6Al and for the two TiNbZr oxidized alloys. The different alloying composition induces different thermal activated mechanisms. On Ti–7Nb–6Al the thermal process leads to the diffusion of Al towards the surface. The oxidized layer is composed mainly of Al oxide with some amounts of Ti oxide. On the other hand, both TiNbZr alloys upon thermal oxidation generate oxide films constituted by Ti oxide with a significant contribution of Nb and Zr oxides.

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