Nanoscale characterization of anodic oxide films on Ti-6Al-4V alloy

M. Lewandowska [a,*], M. Pisarek [a,b], K. Rożniatowski [a], M. Grądzka-Dahlke [c],
M. Janik-Czachor [b], K.J. Kurzydłowski [a]

[a] *Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[c] *Faculty of Mechanical Engineering, Białystok Technical University, Wiejska 45c, 15-351 Białystok, Poland*

Abstract

The paper analyses, at nanoscale levels, the chemical composition and mechanical properties of the anodic oxide films formed on Ti-6Al-4V alloy by galvanostatic polarization at maximum final voltages of 12–100 V. For the investigations Auger Electron Spectroscopy, Photoelectron Spectroscopy and nanoindentation measurements have been used. The results have shown that anodizing the Ti-6Al-4V alloy produces an oxide film whose thickness depends on the final voltage. The chemical composition is not significantly dependent on the thickness, the film consists of TiO_2 and Al_2O_3. However, the best insulating properties of the films, determined from the growth parameter nm/V, are achieved with a final voltage between 30 and 65 V. Nanohardness and Young's modulus measurements have shown that the anodic films formed by different voltages exhibit similar mechanical properties which is consistent with the results of the surface analysis.
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1. Introduction

Titanium and titanium alloys have many applications, notably as aerospace, cryogenic or biomedical materials. For biomedical applications, it shows such attractive properties as high strength, low Young's modulus and good biocompatibility.

None of the bioactive ceramics possess a fracture toughness as high as human cortical bone and thereby are unable to be used as a substitute for highly loaded bones. Materials currently available for this purpose are the biocompatible metals which have a high fracture toughness, typically Ti and its alloys [1,2]. Ti-6Al-4V is widely used for biomedical applications, as the introduction of alloying elements enhances the mechanical properties. This is in spite of the fact that Ti-6Al-4V seems to exhibit a poor wear resistance [3–5], which can cause significant release of Al and V. The release of Al and V from the implant into body is most undesirable due to the element's toxic effects [6].

Anodic oxidation of the alloy in an acidic electrolyte may be considered as a method of producing an effective barrier between the alloy and the surrounding environment without affecting the biocompatibility of the material. There is also a chance that selective dissolution of the alloying elements, due to their amphoteric character, may occur during the pretreatment to eliminate them from the surface of the material, as suggested by literature [7].

Stability of the passive films formed on Ti-6Al-4V in acidic solutions is markedly superior to the natural air-formed passive films [8]. Its composition, however, is still a subject of investigation and discussion—see [8] and the references therein. In particular, there is no clear knowledge of the composition of the thin passivating film formed on this alloy [8]. While the titanium in the film is presented as TiO_2 and aluminum as Al_2O_3, because of the small amount of vanadium in the alloy, its chemical state in the film is not known unambiguously. The lateral and depth distributions of the elements in the film are still a subject of controversy [8], some authors, e.g., suggest a "general" enrichment of Al within the film [9–11], but another claims an Al_2O_3 enrichment in the uppermost part of the film [12].

Thick anodic films may be more homogenous laterally than the air-formed films which would tend to reproduce the chemical heterogeneity of the multiphase underlying alloy [8,13,14]. It follows that surface analytical measurements of the anodic

* Corresponding author. Tel.: +48 22 234 84 41; fax: +48 22 234 85 14.
E-mail address: malew@inmat.pw.edu.pl (M. Lewandowska).

oxide films formed on this alloy may provide an insight into the true situation.

The aim of this work was to undertake a detailed investigation of the composition of the anodic films formed on Ti-6Al-4V alloy in 0.5 M H_2SO_4 at constant current density up to final voltages ranging from 12 to 100 V and to determine their influence on the mechanical properties of the film.

2. Experimental

2.1. Materials

The samples of Ti-6Al-4V alloy were cut from a rod of 20-mm diameter into the 8-mm-long samples. All specimens were carefully polished mechanically before electrochemical pretreatment. The samples were then anodically treated in 7% H_2SO_4 at 19 °C at a constant current density up to various maximum voltages of 12, 30, 47, 65, 82 and 100 V.

2.2. Auger electron spectroscopy (AES)

The anodized samples were examined with AES to determine the composition and to estimate the thickness of the anodically formed film on the surface. A Microlab 350 (Thermo VG Scientific) analytical instrument was used to determine the composition of the anodic surface layer and the chemical state of the components. For this purpose, the high-energy resolution AES function of the Microlab (energy resolution variable from 0.6% down to 0.06%) was used. An Ar^+ ion gun was used to measure the composition profiles of the film. Discontinuous sputtering, at intervals from 90 s up to 270 s depending upon the anodic film thickness, was used to gradually remove the oxide film. The sputtering parameters were 3 keV, $I = 1$ μA, and the crater size was 2×2 mm. The Auger spectra were taken, after each sputtering period, at $E_p = 10$ kV.

2.3. X-ray photoelectron spectroscopy (XPS)

Subtle changes in the chemistry of the surface oxide layer of titanium alloy samples were examined using XPS. The XPS function of the Microlab was used to determine the chemical state of the Ti and Al during the sputtering process. The chemical state of surface species was identified using the high-energy resolution of the analyzer. The energy resolution of the spherical sector analyzer in Microlab 350 instrument is about 0.83 eV for XPS, which is an additional option of the Microlab dedicated scanning Auger microanalyzer. XPS studies gave averaged information from the total surface area of each sample. The Ar^+ ion gun was used in order to measure the chemical state of the components within the film. The sputtering parameters were 3 keV, $I = 1$ μA, and the crater size was 7×7 mm. The appropriate standards for XPS reference spectra were also used. XPS spectra were excited using Al Kα ($h\nu = 1486.6$ eV) radiation as the source. The measured binding energies were corrected referring to the energy of C1s at 285 eV. A data system of Avantage software was used for data acquisition and processing.

2.4. Nanohardness measurements

To estimate the mechanical properties of anodic oxide films produced, nanohardness measurements were performed using the Hysitron Nanoindenter device equipped with a Berkovitz indenter. The indentation parameters were as follows: a loading rate of 0.1 mN/s to a maximum load of 1 mN for period of constant load of 2 s. From the measurements, nanohardness, H, and reduced Young's modulus, E_r, were determined according to the standard procedures [15]. Average values were calculated from 10 measurements for each sample.

3. Results and discussion

3.1. AES investigations

Fig. 1 presents typical examples of the high-resolution Auger spectra for a sample polarized to $V_{max} = 12$ V. It can be seen that even after 180 s of sputtering the Ti LMM spectrum is identical with that of the TiO_x standard spectrum (given below) showing that a typical TiO_x oxide was formed on the surface. After 360 s of sputtering, some distinct changes in the spectrum appear showing that we an intermediate region was being approached
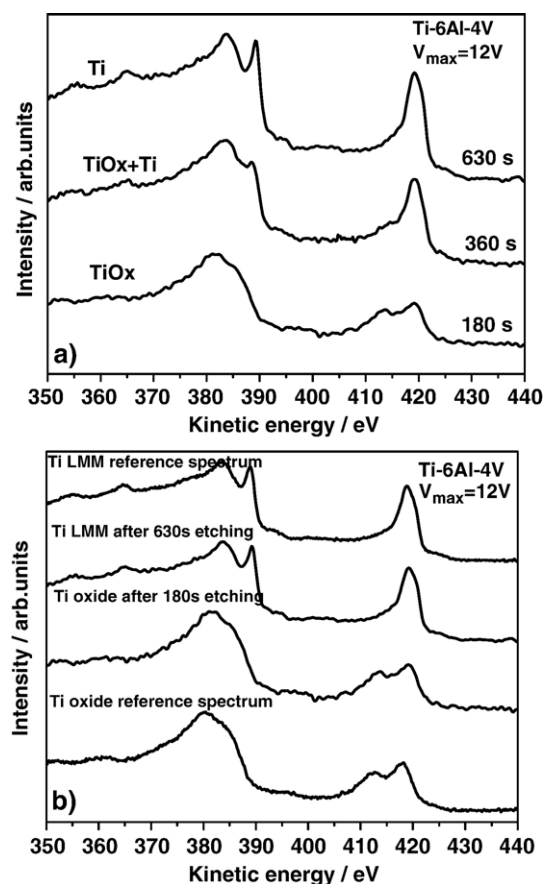
Fig. 1. High-resolution AES spectra presenting change of position and shape of Ti (LMM) Auger signal in the course of sputtering away the anodic oxide film (a) from an oxide state (anodic layer) to a metallic one (substrate Ti-6Al-4V), (b) comparison of the reference Ti^m and TiO_x spectra with those for the sample investigated, $V_{max} = 12$ V. See text for details.