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EIS tests of electrochemical behaviour of Ti6Al4V and Ti6Al7Nb alloys

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Materials

ABSTRACT

Purpose: This study has been undertaken in order to establish the influence of parameters of the electrochemical treatment of Ti –alloys on their electrochemical behaviour in Tyrod solution.
Design/methodology/approach: Surface of the Ti-alloys: Ti6Al4V and Ti6Al7Nb in the form of a rod submitted to grounding, electropolishing and anodic passivation. Electrochemical investigations were carried out by means of the electrochemical impedance spectroscopy method. Scope of this paper includes analysis of the impedance spectra based on Bode plot.
Findings: Prolongation time of anodic passivation to 60 minutes caused formation of a two – layer model consisting of an inner layer which is compact and the barrier type, and outer layer which is porous
Research limitations/implications: Obtained results are the basis for the optimization of anodic passivation pareameters of the Ti alloys as a metallic biomaterial. The future research should be focused on selected more suitable parameters of the electrochemical impedance spectroscopy test to better describe process on the solid/ liquid interface.
Practical implications: It has been found that a good resistance to corrosion and homogenous oxide layer on the Ti6Al4V and Ti6Al7Nb alloys surface can be achieved due to the application of electrolytic polishing of these alloys in a special bath and anodic passivation in sulphuric acid (VI), phosphoric acid (V) and inorganic salts.
Originality/value: Results of the experiments presents the influence of various conditions of anodic passivation of the surface of the Ti6Al4V and Ti6Al7Nb alloy. In this cases, when the surface roughness plays important role, this method can be applied in treatment of the material intended for medical applications especially.
Keywords: Metallic alloys; Biomaterials; Anodic passivation; Electrochemical impedance spectroscopy (EIS)

1. Introduction

Titanium and its alloys have been used in medicine since the 40s of the last century. It has been feasible because they showed high corrosion resistance and suitable mechanical properties. This perfect resistance in various environments is caused by a durable passivating oxide film which spontaneously forms in the presence of oxygen and adheres closely to titanium base [1-6]. Surface morphology plays an important role as well; the smoother the surface is, the higher the corrosion resistance it displays. Moreover, electrolytic polishing proves to be very advantageous. It removes the surface layer formed during mechanical processing which is characterized by distorted crystal structure and physico-chemical properties different from those of the material the base is made of.

The corrosive processes can be slowed down by forming a protective passivating film whose quality and properties considerably improve the resistance of an implant to corrosion and thus its biotolerance. The substantial reduction in electrochemical activity of the surface and formation of the passivating film are the reasons why the production of implants from 3126 L steel and titanium alloys (e.g. NiTi, Ti6Al4V, Ti6Al7Nb) involves electrolytic polishing and passivation [7-15].

The study describes research into the corrosion of Ti6Al4V and Ti6Al7Nb alloys intended for implants production. The contemporary literature presents a lot of publications in this field, however, the corrosion research involving electrochemical impedance spectroscopy has not been fully analyzed which made us carry out the research on Ti6Al4V and Ti6Al7Nb alloys using that technique [16-19].

2. Materials and technology

The tests were carried out on Ti alloys: Ti6Al4V and Ti6Al7Nb in the form of a rod (diameter: Ø = 3 mm and length l = 50 mm for Ti6Al4V, and diameter: Ø = 6.6 mm and length l = 40 mm for Ti6Al7Nb alloy. the chemical composition of alloys are shown in reference 13 and 14.

The process of electrolytic polishing of Ti6Al4V and Ti6Al7Nb alloys was carried out in a phosphoric-sulphuric acid solution with an addition of inorganic substances. This special bath have been developed at the Department of Chemistry and Inorganic Technology, Silesian University of Technology [6,7]. Grounded samples had average roughness R_a = 0,31 µm and the electropolished average roughness R_a < 0,16 µm. The process of anodic passivation was run in sulphuric acid(VI), phosphoric acid(V) and inorganic salts [6,7]. The setup of electrolytic polishing of samples were presented in literature [11,12]. The anodic passivation process were carried out on following parameters: time: 60 minutes, and potential value 20V, 40V, 60V and 100V.

The electrochemical behavior of investigated alloy were performed basing on electrochemical impedance spectroscopy technique (EIS). The Eco Chemie B.V PGSTAT30 system with accompanying software FRA for electrochemical tests was applied in thre electrode cell. The electrochemical impedance measurements were made at open circuit potential with the perturbing a.c. signal amplitude of ±0.05 V in the frequency range between 50 kHz and 0.1 Hz. The tests were carried out in Tyrode's physiological solution (pH =6,8 ÷ 7,4), see ref. [8,9].

3. Results and discussion

Several experiments have been made which were essential for choosing reasonable parameter of every measurement. Impedance measurements were performed at an open circuit potential with a constant perturbing a.c. signal amplitude of 0,01 V; 0,05 V and 0,1 V. The optimum parameters for impedance test of Ti6Al4V and Ti6Al7Nb alloys are as follows: the frequency range between 50kHz and 0.1Hz with perturbation amplitude of 0.05 mV (Fig .1).

It can be observed that the modul and phase angle of the impedance are strongly depend on the surface pretreatment. Comparison of impedance spectra recorded on Ti6Al4V and Ti6Al7Nb alloys after grounding, electropolishing and passivating, differences may be observed in their shape, as shown in the plots. In the wide range of the frequencies of the impedance spectra obtained for grounded and electropolished Ti6Al4V alloy, it can be observed that the value of the phase angle is near 80°.

Those impedance responses correspond to the capacitive behavior of the electrode and describe the dielectric properties of the electrical conducting surface film Fig. 2 and Fig. 3 [20-22].

Impedance spectra recorded on passivated Ti6Al4V alloys have not been typical for capacitance response what was mentioned above. At medium frequencies the phase angle reaches value below 80° or in this range it decreased abruptly, see Fig 4 and Fig. 5. It suggests the occurrence of diffusion process in the solid phase and a inferior properties of passive layer. In this case, in the impedance spectra recorded at open circuit potential, two time constants may be observed.

It is common to study the oxide film on a passive metal it is used a two – layer model consisting of an inner layer which is compact and of the barrier type, and an outer layer which is relatively porous [21, 22].

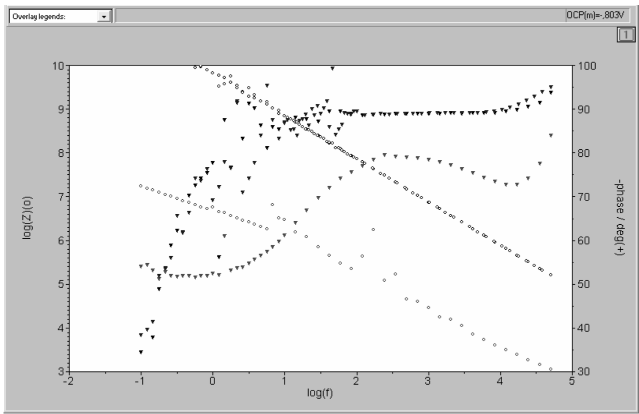

Fig. 1. Bode plots of impedance spectra for Ti6Al4V alloy recorded in Tyrode's solution. Samples electropolished at potential 100V during 10 minutes: amplitude 0.01 (black line), amplitude 0.05 (red line) and amplitude 0.1 (blue line)

The passivation process of Ti6Al7Nb alloy at 40V and 60V caused appearance of compound passive layer, likewise the passivation of Ti6Al4V alloy at higher voltage.

Two and more time constants may be observed in recorded impedance spectra for the Ti6Al7Nb alloy passivated during 60 minutes at 20V, 40V, 60V, 80V and 100V voltage (Examples in Figures from 6 and 7). The oxide film on a passive Ti6Al7Nb it is used a two – layer model consisting of an inner layer which is compact, has got the barrier type, and porous outer layer which. The absence of more than one sloping segments in the Bode plot indicates that the time constants were close together and unresolvable.

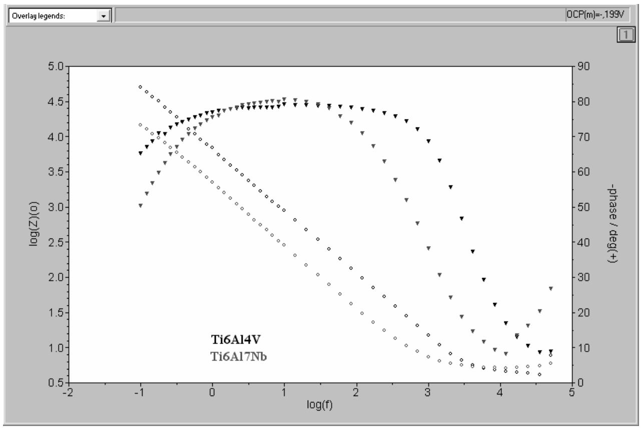

Fig. 2. Bode plots of impedance spectra for grounding Ti6Al4V (black) and Ti6Al7Nb (red) alloys recorded in Tyrode's solution

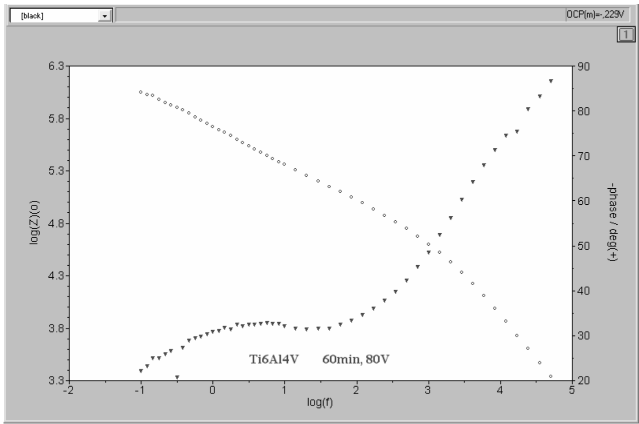

Fig. 5. Bode plots obtained in Tyrod solution corresponding to the Ti6Al4V alloy passivated during 60 minutes by 80V voltage

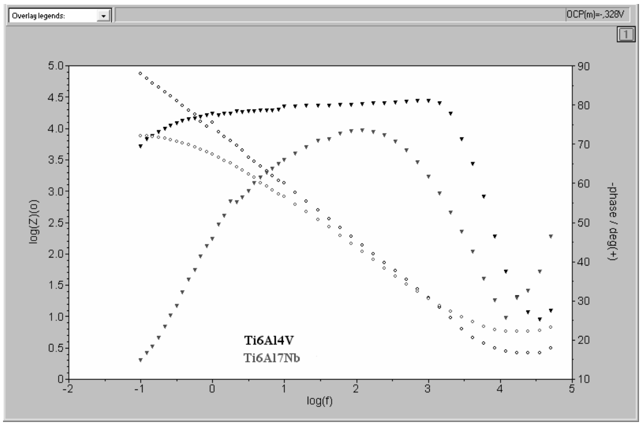

Fig. 3. Bode plots of impedance spectra for electropolishing Ti6Al4V (black) and Ti6Al7Nb (red) alloys recorded in Tyrode's solution

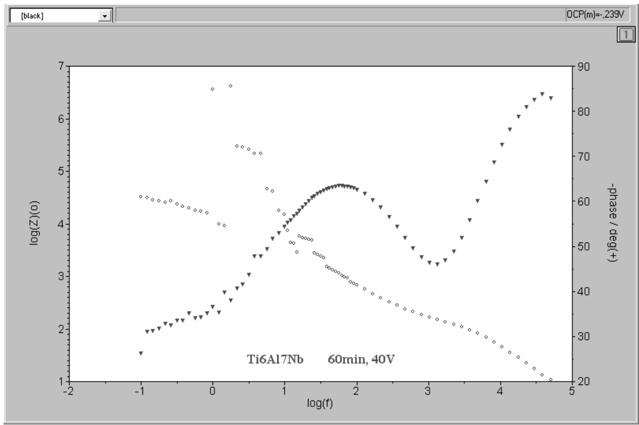

Fig. 6. Bode plots obtained in Tyrod solution corresponding to the Ti6Al7Nb alloy passivated during 60 minutes by 40V voltage

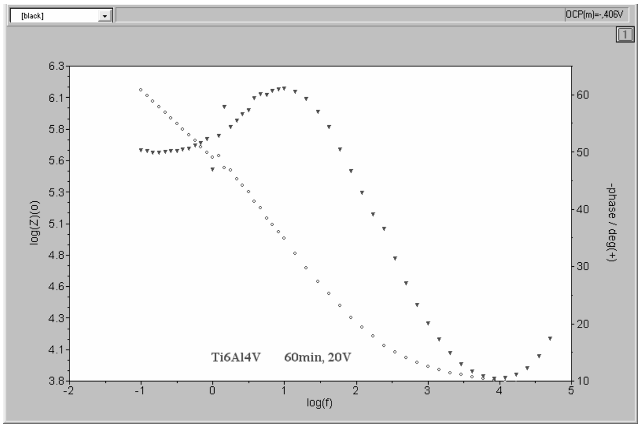

Fig. 4. Bode plots obtained in Tyrod solution corresponding to the Ti6Al4V alloy passivated during 60 minutes by 20V voltage

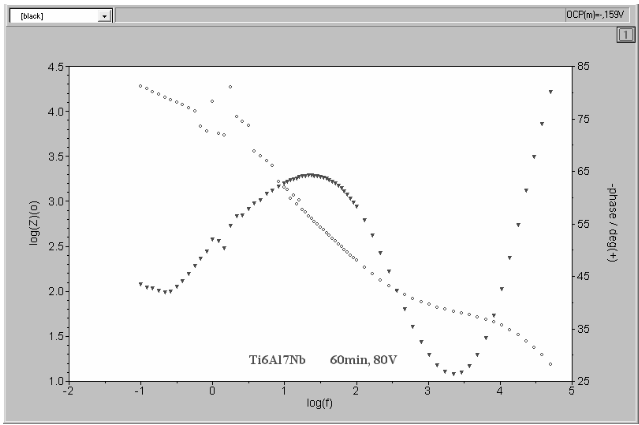

Fig. 7. Bode plots obtained in Tyrod solution corresponding to the Ti6Al7Nb alloy passivated during 60 minutes by 80V voltage

4. Conclusions

The application of electrolytic polishing formed a tight protective film on the surface of Ti6Al4V and Ti6Al7Nb alloys. A further increase in corrosion resistance was obtained by anodic passivation which made the protective oxide film thicker. Its structure depended greatly on the operating parameters of passivation.

The results of impedance tests obtained for Ti6Al4V alloy revealed that the application the whole range of voltages at a time of 60 min produced a complex passivating film. Two time constants were found on the diagrams of impedance spectra. Their shapes pointed to the presence of two oxide films on the surface of the alloy: a porous external film and a homogenous internal one which displayed good protective properties.

The external structure of the protective oxide film formed on the implants made of Ti6Al4V and Ti6Al7Nb alloys depended primarily on the conditions of anodic passivation, while the selection of the operating parameters of anodic passivation depended on the function the implants fulfilled in a body.

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