The corrosion properties of zirconium and titanium load-bearing implant materials with protective oxide coatings

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Abstract. At present study the comparative analysis of parameters for oxide Al_2O_3 and ZrO_2 films deposited by reactive magnetron sputtering (RMS) method on the load-bearing implant materials such as titanium-based (Ti4Al6V) and Zr has been made. The corrosion examinations of anodic polarization by potentiodynamic method, Tafel and Stern curves and also impedance method at SBF solution were presented.

Keywords: Corrosion protection; Magnetron sputtering; Biocompatibility.
PASC: *81.65.Kn; 87.85.jj.*

1. Introduction

Good mechanical properties, coupled with excellent biocompatibility and corrosion resistance properties have made titanium and alloys the most popular materials for various biomedical applications. But more demanding expectations for orthopedic and trauma defects reconstruction are driving the development of alternative bearing materials. Zirconium and alloys are presented as alternative to other load-bearing materials in order to increase the biocompatibility for needs of metal sensitive (Ti, V, Al) patients.

Novel functional coatings are widely applied in different industrial areas due to the high hardness and wear resistance properties [1]. However, many of such applications require the high stability in an aggressive and corrosive environment.

Corrosion is one of the major processes that cause problems when metals and alloys are used as implants in the body [2]. Corrosion of implants in the aqueous medium of body fluids takes place via electrochemical reactions [3]. The body fluid environment may well decrease the fatigue strength of the metal implant and enhance the release of iron, chromium, nickel, titanium ions and these ions are found to be powerful allergens and carcinogens [4]. The presence of titanium in the surrounding tissues of these implants in the form of titanium compounds and subsequent failure of implants due to fatigue, stress corrosion cracking and poor wear resistance have been reported [5,6]. Release of metal ions into the tissues adjacent to the implants results in accumulation of harmful products at tissue and internal organs of animals [7]. The comparative analysis of corrosion properties of zirconium and titanium materials with novel oxide coatings deposited by reactive magnetron sputtering method (RMS) is of great interest for next biomedical applications

2. Materials and Methods

The substrates for deposited coatings were the popular load-bearing implant materials such as titanium-based alloy (Ti4Al6V) and Zr samples. The substrates were ultrasonically cleaned in acetone, ethanol and deionised water in sequence and next were dried in dryer.

The oxide Al_2O_3 and ZrO_2 (RMS) coating deposition was performed in high vacuum pumping system with the base pressure about 10^{-5} mBar. The main details of the magnetron

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and ion source in the sputtering chamber were demonstrated at [8]. The magnetron discharge power was 1-4 kW, power of activated oxygen source up to 1 kW, coating deposition rate 8 μm/hour. There was the problem of target oxidation during deposition process. At the excessive oxygen flow conditions the process shifts to the target passivation regime (lower part of. volt-ampere characteristics (VAC) curves Fig.1) The sputtering process should be made in the regimes far from the target passivation areas both for aluminum and for zirconium target materials for next oxide coatings deposition with highly stoichiometric composition. Also, such deposition conditions allow to avoid micro-arcs and micro-drops formation increasing the corrosion resistance properties. The optimum conditions were realized for the upper part of VAC curves of magnetron discharge in argon with oxygen both for aluminum and zirconium target materials (Fig. 1 a, b).

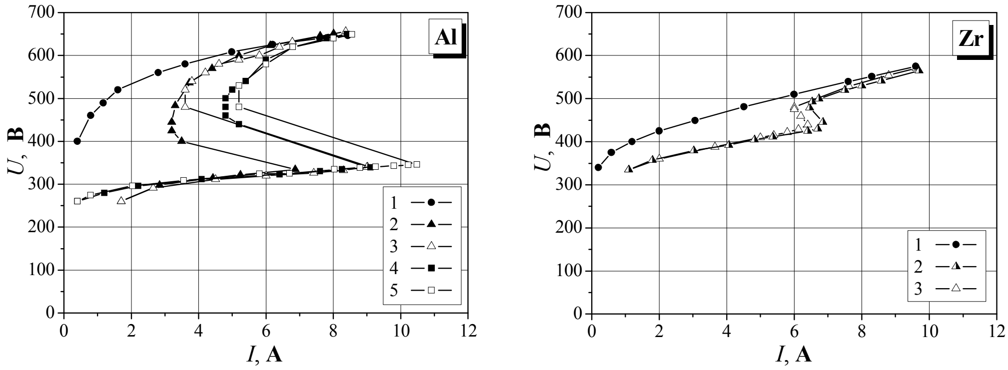


Fig.1. Volt-ampere characteristics of magnetron discharge in argon with oxygen a) aluminum target, b) zirconium target. The pressure Ar was 6 10^{-2} Pa, oxygen flow 1-q=0 sm^3/min, 2,3 –q=17 sm^3/min, 4,5-q=26 sm^3/min for aluminum target material and 1-q=0 sm^3/min, 2,3 –q=35 sm^3/min for zirconium target material.

The coatings adhesion properties, hardness and elastic modulus, were evaluated by standard methods with the use of Revetest (CSEM) and the Rockwell indenter with the tip radius 200 μm, within the load range 200N [9].

The comparative analysis of corrosion parameters for oxide Al_2O_3 and ZrO_2(MS) coatings has been made. The corrosion examinations of anodic polarization by potentiodynamic method at the potential range -1.0V-+2.0V with scanning rate 1mv/s, Tafel -0.050V - +0.050V and Stern - -0.020V-+0.020V range curves and also impedance method for frequency range 100 kHz – 10 MHz at SBF(NaCl-8,035, $NaHCO_3$-0,355, KCl-0,225, K_2HPO_4 $3H_2O$-0,231, $MgCl_2$ $6H_2O$-0,311, $CaCl_2$-0,292, Na_2SO_4-0,072 at pH=7.4 and temperature 37°C) solution were made by Potentiostat PARSTAT 2263 (AMETEK, USA).

Electrochemical Impedance Spectroscopy (EIS) is a powerful analysis technique, which can provide a lot of information on the corrosion reactions, the mass transport and electrical charge transfer characteristics of coated materials in various solutions. The impedance spectrum reflects dielectric behaviour, oxidation-reduction reactions and mass migration, which are determined by the electrical and chemical properties of the corrosion medium and the electrode materials. Over a frequency bandwidth of interest the impedance was presented in various ways by both the Nyquist and Bode plots. EIS spectra describe the electrical charge transfer kinetics and details of physical and electrochemical corrosion characteristics of substrate/coating interface. EIS measurements were obtained at SBF solution. Platinum and Ag/AgCl wires were used as counter and reference electrodes, respectively between the frequency ranges 100 kHz-10 MHz at constant 5mV amplitude and 250mV initial potential for all measurements. The impedance parameters $|Z|$, polarization resistance R_p and capacitance C_d were calculated from Nyquist and Bode plots. The surface topography and corrosion failure after corrosion test was investigated by means of Interferometric Microscope Talysurf CCI (Taylor Hobson) and AFM (Quesant Instrument Corporation, USA).methods.

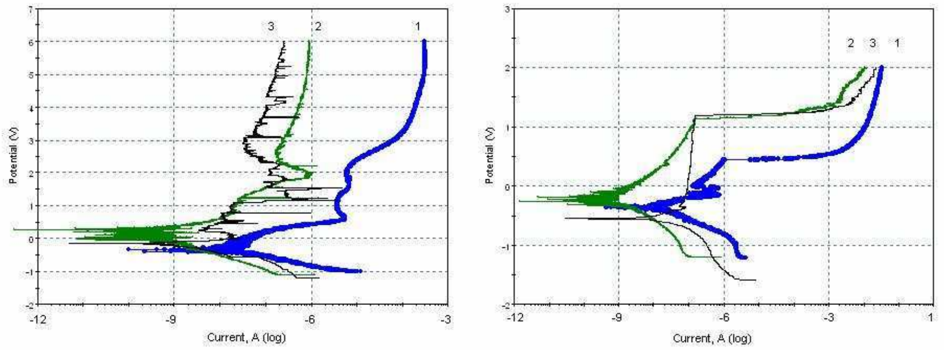
3. Results and Discussion

The mechanical parameters of the oxide Al_2O_3 and ZrO_2(RMS) coatings deposited on the Ti and Zr substrates were presented in the Table 1.

Table 1.
Mechanical and tribological characteristics of oxide coatings Al_2O_3 and ZrO_2

Material/	Mechanical parameters (average results 10 tests)			
Coating type	Hardness Hv	Hardness H [Mpa]	Young Modulus [Gpa]	Adhesion [N]
Zr/ZrO_2	755.5	7831.5	167.7	28.5
Zr/ Al_2O_3	782.0	8115.2	184.4	27.1
Ti/ZrO_2	767.5	8072.4	172.3	38.4
Ti/ Al_2O_3	953.6	8289.9	197.0	40.3

The corrosion tests of anodic polarization by potentiodynamic method at the potential range -1.0V-+2.0V with scanning rate 1mv/s were presented in Fig.2a for Ti, Ti/Al_2O_3, Ti//ZrO_2 and Fig. 2b for Zr, Zr/Al_2O_3, Zr/ZrO_2 coatings at SBF solution and by Tafel -0.050V - +0.050V and Stern - -0.020V-+0.020V range curves, The impedance spectra of all samples were recorded before and after polarization conditions, to evaluate the performance of the coatings under equilibrium conditions and after the onset of the corrosion process respectively.



a) b)

Fig. 2. The anodic polarization curves for a) 1-Ti, 2-Ti/ZrO_2, 3-Ti/Al_2O_3, and b) 1-Zr, 2-Zr//ZrO_2, 3-Zr/Al_2O_3 coatings at SBF solution

The Nequist plot of impedance was obtained from real ($Z_{re}= R_s+R_p/(1+\omega^2R_p^2C_d^2)$) and imaginary ($Z_{im}= \omega R_p^2C_d /(1+\omega^2R_p^2C_d^2)$) impedance at different frequencies to determine charge-transfer kinetics (R_s is electrolyte solution resistance, R_p is polarization resistance and C_d is capacitance at interface). Fig. 3. show the Nyquist plots for Zr, Zr/ Al_2O_3 and Zr/ZrO_2 coatings respectively at SBF solution.

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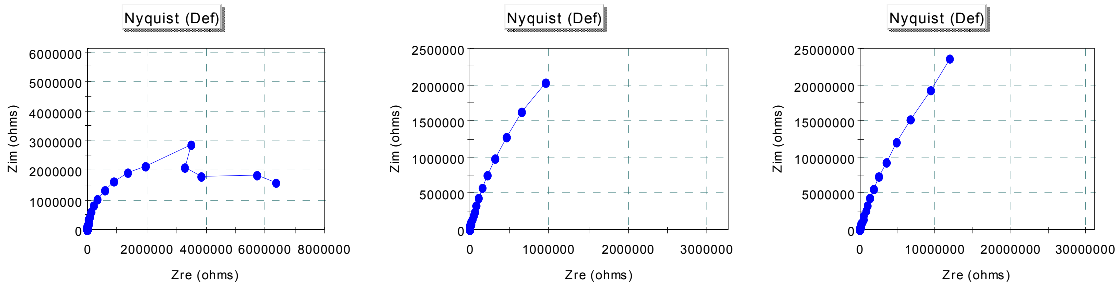

a) b) c)

Fig. 3. Nyquist plots for a.)Zr, b.)Zr/ Al_2O_3, c.)Zr/ZrO_2 materials at SBF solution

The data show that coating deposition had improved charge-transfer kinetic performance in counter electrode-electrolyte interfaces. The surface with ceramic oxide coatings has strong capacitive response due to their electrically inert properties and high dielectric constants. The surface topography and corrosion failure after corrosion tests was investigated by Interferometric Microscope Talysurf CCI and AFM methods

The Figure 4 demonstrate the images of surface failure after corrosion test at SBF solution and the data further confirmed the main results of polarization curves and EIS measurements.

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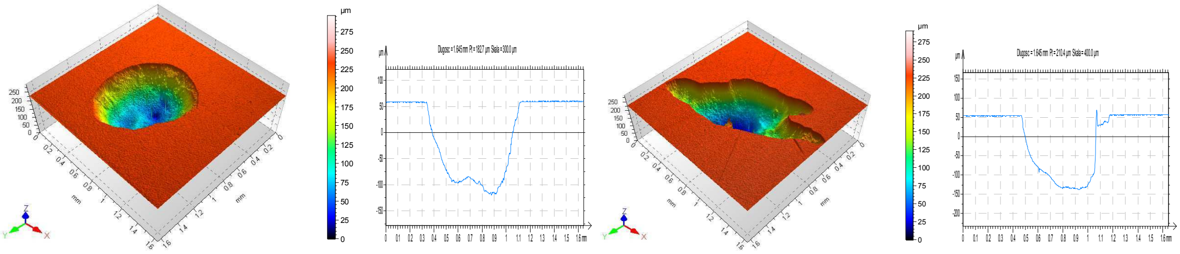

a) b)

Fig. 4. The surface topography and failure after corrosion test at SBF solution by IM:

a) Zr/ Al_2O_3, b) Zr/ZrO_2 coatings

4. Conclusion

The technology is developed allowing to obtain the highly stoichiometric oxide coatings deposited by means of RMS method with hardness parameters up to 9 GPa, adhesion up to 40N and improved corrosion resistance properties both on titanium and zirconium substrate materials. The results show that the best corrosion resistance characteristics at SBF solutions have the oxide coated Ti/ Al_2O_3 and Zr/ZrO_2 ceramic materials. Zirconium with oxide coatings demonstrates the excellent protective properties and presents as alternative load-bearing material for various biomedical applications.

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