THE CORROSION PROPERTIES OF MULTILAYER COATINGS DEPOSITED ON STAINLESS STEEL AND Ti4Al6V SUBSTRATES

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Stainless steel (SS), titanium (Ti) and its alloys are the most widely used for clinical applications. The surface modification of metals with ceramic coatings by means of modern plasma methods is perspective way to reduce corrosion, to achieve better biocompatibility and to improve the performance of medical devices. The comparative analysis of the TiN, ZrO_2, Al_2O_3 and multilayer nitride/oxide coatings adhesion properties, hardness, elastic modulus, thickness, and corrosion resistance parameters at 05 N NaCl and SBF solution was made.
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1. INTRODUCTION

The ceramic coatings play an important role in the surface modification of tools and instruments for various industrial sectors. 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 [1]. Corrosion of implants in the aqueous medium of body fluids takes place via electrochemical reactions [2] and it is necessary to understand the electrochemical principles that are most relevant to the corrosion processes. 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 [3]. 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 [4,5]. Release of metal ions into the tissues adjacent to the implants results in accumulation of harmful products at tissue and internal organs of animals [6]. This may also be detrimental to the bone attachment and further bone growth on the implant surface.

2. MATERIALS AND METHODS

At present study the comparative analysis of parameters for various coating types such as TiN, deposited by means Arc-PVD technology, oxide ZrO_2 coatings deposited by EB-PVD technology and Al_2O_3 films deposited by magnetron sputtering (MS) method and also multilayer TiN/ZrO_2, TiN/Al_2O_3 on the stainless steel (1H18N9) and titanium-based material (Ti4Al6V) has been made. The main parameters of the process of TiN (Arc-PVD) coatings deposition were described in our previous study [6]. The Al_2O_3 (MS) and multilayer coating deposition was performed in high vacuum pumping system with the base pressure about 10^{-5} mBar. The main details of the magnetron and ion source in the sputtering chamber were demonstrated at [7]. The coatings adhesion properties, hardness and elastic modulus, thickness were evaluated by standard methods. 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 0.5 N NaCl and 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) solutions were made by Potentiostat PARSTAT 2263 (AMETEK, USA). The samples were immersed in the electrolyte and the potential was monitored as a function of time until the potential reached a stable value. Corrosion in the form of anodic dissolution occurs at solution like uniform removal process for substrates and corrosive electrolyte pore penetration process for ceramic coatings.

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 in 0.5 N NaCl and SBF solution. Platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively between the frequency ranges 100 kHz…10 MHz at constant 5 mV amplitude and 250 mV initial potential for all measurements. The impedance parameters $|Z|$, polarisation resistance Rp and capacitance C were calculated from Nyquist and Bode plots. The surface topography before and after corrosion test was investigated by SEM (HITACHI, Japan) and AFM (Quesant Instrument Corporation, USA).

3. RESULTS AND DISCUSSION

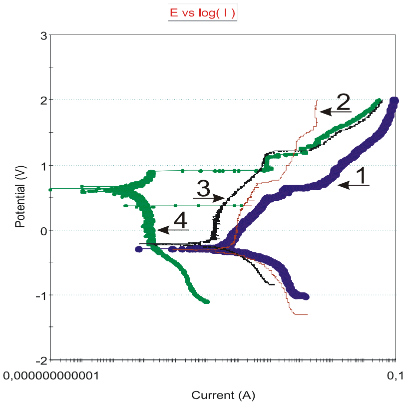
The coatings adhesion properties, hardness and elastic modulus are presented at the Table.

The mechanical properties of coatings deposited on SS(1H18N9) and Ti alloy (Ti4Al6V)

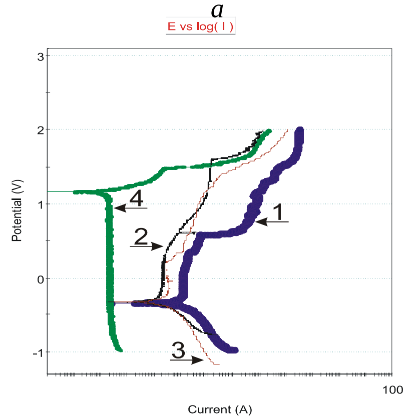
Coatings type	Mechanical properties (average results 10 tests)			
	Hardness, Hv	Hardness, H[Mpa]	Young Modul. [Gpa]	Adhesion, [N]
SS/TiN	2051.6	22138.8	411.6	80.4
SS/ZrO_2	429.5	4634.5	96.7	38.3
SS/ Al_2O_3	752.0	8115.2	209.4	40.1
SS/TiN/Al_2O_3	797.36	8604.4	216.5	86.7
Ti/TiN	1935.2	20893.2	340.8	29.3
Ti/ZrO_2	136.5	1472.4	49.3	13.4
Ti/ Al_2O_3	953.6	8289.9	172.0	27 .1
Ti/TiN/Al_2O_3	970.1	8523.2	177.7	39,9

The best mechanical parameters were obtained in the case of nitride coatings both at SS and Ti substrates and also for multilayer nitride/oxide coatings.

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.1 for SS, SS/TiN,SS/ZrO_2, SS/ Al_2O_3 (at NaCl, Fig.1a, and SBF, Fig.1b, solutions) and Fig. 2 for Ti, Ti/TiN, Ti/ZrO_2, Ti/Al_2O_3 (at NaCl – Fig.2a and SBF– Fig. 2b solutions) coatings by Tafel -0.050V…+0.050V and Stern – -0.020V…+0.020V range curves.

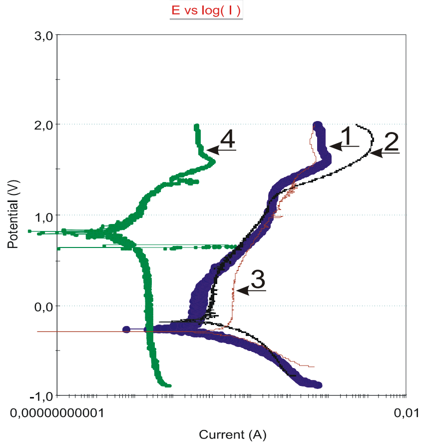


a

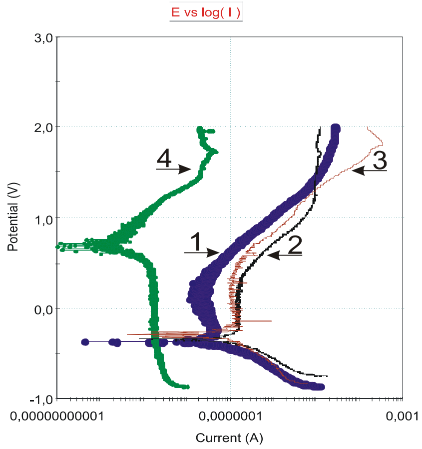


b

Fig.1. The anodic polarization curves for coatings at: a) 0.5 N NaCl and b) SBF solutions; SS-1, SS/TiN-2, SS/ZrO_2-3 and SS/Al_2O_3-4



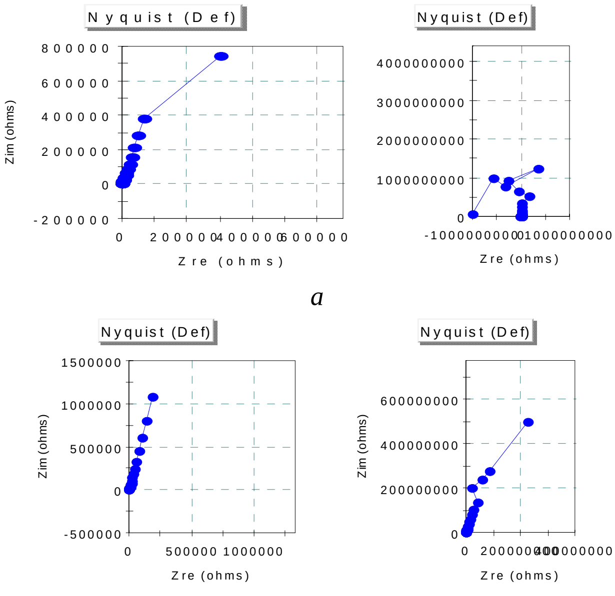
a



b

Fig.2. The anodic polarization curves for coatings at a) 0.5 N NaCl and b) SBF solutions; Ti-1, Ti/TiN-2, Ti/ZrO2-3 and Ti/Al2O3-4

The impedance spectra of all the 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. 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. 3a and 3b show the Nyquist plots for SS, SS/ Al_2O_3 and in for Ti, Ti/Al_2O_3 coatings 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 before and after corrosion tests was investigated by SEM and AFM methods. The Fig. 4 (SS, SS/TiN, SS/TiN/Al_2O_3, at 0.5 N NaCl SEM) data further confirmed the main results of polarization curves and EIS measurements.



b

Fig.3. Nyquist plots for a) SS, SS/ Al_2O_3 and b)Ti, Ti/ Al2O3 coatings at SBF solution

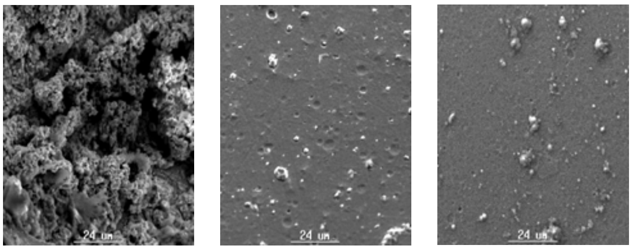


Fig.4. SS, SS/TiN, SS /TiN/Al_2O_3 at 0.5 N NaCl SEM

4. CONCLUSIONS

The results show that the best mechanical parameters were obtained for the nitride coatings both on the stainless steel (1H18N9) and the titanium substrate (Ti4Al6V). However, the nitride corrosion resistances were less on 1H18N9 than on Ti4Al6V and less than those obtained for oxide coatings deposited by both methods. The best corrosion resistance characteristics at NaCl and SBF solutions demonstrate the multilayer coatings TiN/ZrO_2, TiN/Al_2O_3 both on stainless steel and titanium substrates.

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КОРРОЗИОННЫЕ СВОЙСТВА МНОГОСЛОЙНЫХ ПОКРЫТИЙ, НАНОСИМЫХ НА НЕРЖАВЕЮЩУЮ СТАЛЬ И ТИТАНОВЫЕ СПЛАВЫ

А. Зыкова, В. Сафонов, J. Walkowich, R. Rogowska, С. Яковин

Нержавеющая сталь и титановые сплавы широко применяются в современной медицине. Поверхностная модификация металлов путем нанесения керамических покрытий современными плазменными методами является перспективным направлением для уменьшения коррозии, повышения биосовместимости и эффективности применения медицинских изделий. Проведен сравнительный анализ следующих свойств пленок: адгезии, твердости, упругих модулей, коррозионных характеристик различных многослойных нитридных и оксидных покрытий.

КОРОЗІЙНІ ВЛАСТИВОСТІ БАГАТОШАРОВИХ ПОКРИТТІВ, ЩО НАНЕСЕНІ НА НЕРЖАВІЮЧУ СТАЛЬ ТА ТИТАНОВІ СПЛАВИ

Г. Зикова, В. Сафонов, J. Walkowich, R. Rogowska, С. Яковін

Нержавіюча сталь та титанові сплави широко використовуються в сучасній медицині. Поверхнева модифікація металів шляхом нанесення керамічних покриттів сучасними плазмовими методами э перспективним напрямком з метою зменшення корозії та покращення біосумісності та ефективності застосування медичних приладів. Виконано порівняльний аналіз наступних властивостей плівок: адгезії, твердості, пружних модулів, корозійних властивостей різних багатошарових оксидних та нітридних покриттів.