Corrosion properties of nitride, oxide and multilayer coatings on stainless steel and titanium-based substrates

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Abstract. A comparative analysis is made of the parameters of oxide, nitride and multilayer coatings, such as TiN, deposited by means of Arc-PVD, oxide Al₂O₃ films deposited by magnetron sputtering (MS), and of multilayer TiN/Al₂O₃ on stainless steel (1H18N9) and a titanium-based material (Ti4Al6V). The corrosion examinations of anodic polarization by potentiodynamic method, Tafel and Stern curves and also impedance method at NaCl and SBF solutions were presented. The best corrosion resistance characteristics are exhibited by TiN/Al₂O₃ multilayer coatings on both stainless steel and titanium substrates.

1. Introduction
Various modern techniques are widely used for multilayer (including nano-structured) coatings deposition: electrochemical oxidation, plasma spray, modified Arc-physical vapor deposition (PVD) with separation, magnetron sputtering (MS) and ion-beam assisted deposition (IBAD). Novel multilayer coatings are applied in different industrial areas thanks to their high hardness and wear resistance properties [1]. However, many such applications require high stability in an aggressive and corrosive environment. Acquiring detailed information on the mechanical and corrosion properties of multilayer coatings depending on the deposition method and the specific technological conditions is very important for future successful application in real processes and devices.

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], so that 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, which have been 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].

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Release of metal ions into the tissues adjacent to the implants results in accumulation of harmful products in the tissues and internal organs of animals [7]. This may also be detrimental to the bone attachment and further bone growth on the implant surface.

2. Materials and methods

The substrates for deposited coatings were stainless steel (1H18N9) and a titanium-based material (Ti4Al6V) samples. The substrates were ultrasonically cleaned consecutively in acetone, ethanol and deionized water and then dried.

The TiN coatings were deposited by means of Arc- PVD. The main parameters of the process were described in our previous study [7, 8]: reactive atmosphere N₂, deposition pressure 8 × 10⁻² Pa, arc current 100 A, substrate bias – 150 V, deposition temperature 593 K, thickness of deposited coatings 2 - 5 μm. TiN (MS), Al₂O₃ (MS) and multilayer coating deposition were performed in a high-vacuum pumping system with base pressure about 10⁻⁸ mBar. Details on the magnetron and the ion source in the sputtering chamber were given in [9]. The coatings thickness, adhesion properties, hardness and elastic modulus were evaluated by standard techniques [9].

A comparative analysis was made of the corrosion parameters of multilayer coatings types such as TiN (Arc)/Al₂O₃ and TiN (MS)/Al₂O₃. This was performed using Potentiostat PARSTAT 2263 (AMETEK, USA) equipment and included anodic polarization by applying the potentiodynamic method in the potential range 1.0 V - +2.0 V at a scanning rate of 1 mV/s, Tafel 0.050 V – +0.050 V and Stern 0.020 V – +0.020 V range curves and the impedance method in the frequency range 100 kHz – 10 MHz in 0.5 N NaCl and SBF (NaCl - 8,035, NaHCO₃ - 0,355, KCl - 0,225, K₂HPO₄ 3H₂O - 0,231, MgCl₂ 6H₂O - 0,311, CaCl₂ - 0,292, Na₂SO₄ - 0,072 at pH = 7.4 and temperature of 37°C) solutions. The samples were immersed in the electrolyte and the potential was monitored as a function of the time until the potential reached a steady value. In the solutions corrosion occurs in the form of anodic dissolution, namely, uniform removal process for the substrates and corrosive electrolyte pore penetration for the ceramic coatings.

Electrochemical impedance spectroscopy (EIS) is a powerful analytical technique, which can provide a large amount 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 behavior, oxidation-reduction reactions and mass migration which are determined by the electrical and chemical properties of the corrosion medium and the electrode materials. Over the frequency bandwidth of interest, the impedance are presented in various ways by both the Nyquist and Bode plots. The EIS spectra describe the electrical charge transfer kinetics and details on the physical and electrochemical corrosion characteristics of the substrate/coating interface. EIS measurements were performed in 0.5 N NaCl and SBF solutions. Platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively, in 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 the corrosion test was investigated by SEM (HITACHI, Japan) and AFM (Quesant Instrument Corporation, USA).

3. Results and discussion

The best mechanical parameters were obtained in the case of nitride coatings on both SS and Ti substrates and for multilayer nitride/oxide coatings [9]. The anodic polarization corrosion tests using the potentiodynamic technique in the potential range 1.0 V - +2.0 V at a scanning rate of 1 mV/s are presented in figure 1 a) for SS, SS/TiN, SS/Al₂O₃, SS/TiN(Arc)/Al₂O₃, SS/TiN(MS)/Al₂O₃ and in figure 1 b) for Ti, Ti/TiN, Ti/Al₂O₃, Ti/TiN(Arc)/Al₂O₃, Ti/TiN(MS)/Al₂O₃ coatings in 0.5 N NaCl solutions and by means of Tafel 0.050 V - +0.050 V and Stern 0.020 V - +0.020 V range curves. The impedance spectra of all samples were recorded before and after polarization to evaluate the performance of the coatings under equilibrium conditions and after the onset of the corrosion process, respectively.
The Nyquist impedance plot was obtained from the real \( (Z_{re} = \frac{R_s + R_p}{1 + \omega^2 R_p^2 C_d^2}) \) and the imaginary \( (Z_{im} = \omega R_p^2 C_d / (1 + \omega^2 R_p^2 C_d^2)) \) impedance at different frequencies to determine the charge-transfer kinetics (\( R_s \) is the electrolyte solution resistance, \( R_p \) is the polarization resistance and \( C_d \) is the capacitance at the interface).

**Figure 1.** Anodic polarization curves for a) SS, SS/TiN, SS/Al2O3, SS//TiN(Arc)/Al2O3, SS/TiN(MS)/Al2O3 and b) Ti, Ti/TiN, Ti/Al2O3, Ti//TiN(Arc)/Al2O3, Ti/TiN(MS)/Al2O3 coatings in 0.5 N NaCl solutions.

Figure 2, a) and b) show the Nyquist plots for SS, SS/Al2O3 and for Ti, Ti/Al2O3 coatings in SBF solution. The data show that coating deposition improves charge-transfer kinetic at 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. The data for the coatings in Figure 3 further confirms the main results inferred from the polarization curves and EIS measurements.

**Figure 2.** Nyquist plots for a) SS, SS/Al2O3 and b) Ti alloy, Ti/Al2O3 in SBF solution.
Figure 3. Surface topography and failure after corrosion tests (0.5 N NaCl) by AFM: a) Ti/TiN (Arc)/Al₂O₃ and Ti/TiN (MS)/Al₂O₃ and b) SS/TiN (Arc)/Al₂O₃ and SS/TiN (MS)/Al₂O₃ coatings.

4. Conclusion
The results show that the best corrosion resistance characteristics in NaCl and SBF solutions were exhibited by the multilayer coatings TiN/Al₂O₃ both on stainless steel and titanium substrates. However, the nitride corrosion resistance is lower on 1H18N9 than on Ti4Al6V and lower than that obtained for oxide coatings. The formation of TiN interlayers results in improvement of the mechanical parameters and corrosion resistance characteristics of multilayer coatings TiN/Al₂O₃ deposited by Arc – PVD and magnetron sputtering.

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