

Supplementary material

Electrochemical properties of the surface layers were investigated using VersaSTAT MC system (Princeton Applied Research, USA) with the computer interface. Measurements were carried out in a three-electrode cell K0235 with Ringer solution used as an electrolyte at the temperature of 37°C. A platinum coated niobium mesh was used as a counter electrode. The K0265 Ag/AgCl Reference Electrode was used as a reference electrode. The exposed sample surface area was 1 cm². Prior to the electrochemical measurements, the samples were kept in the solution for 60 min in order to reach the steady state. The values of polarization resistance R_p were determined in separate experiments from the linear potential-current density plot in range of $E_c \pm 20$ mV as the $R_p = \Delta E \Delta j^{-1}$ at a scan rate of 0.167 mV s⁻¹, as recommended in [32,33]. Potentiodynamic polarization curves were recorded in the range from -250 to 1250 mV vs open circuit potential. The Levenberg-Marquardt (LEV) method was used to fit the experimental polarization curve (i.e., potential, E , versus current density, j) by the following equation:

$$j = j_c (10^{(E-E_c)\beta_a} + 10^{-(E-E_c)\beta_c}) \quad (1)$$

which gives best fit values of the Tafel constants, β_a and β_c , corrosion potential, E_c , and corrosion current density, j_c [34,35]. This procedure gives the possibility to derive the Tafel slopes and corrosion current values using limited polarization range.

For the electrochemical impedance spectroscopy (EIS) measurements, a sinusoidal perturbation signal with 10 mV-r.m.s. amplitude was used. Impedance spectra were acquired in the frequency range from 0.1 MHz to 0.01 Hz with logarithmic sweep (10 points per decade). The experiments were controlled and analyzed with an aid of VersaSTUDIO (PAR), ZView and CorrView software (Scribner Associates, USA). During EIS measurements, the open circuit potential was held potentiostatically (Fig. S1). The value of the open-circuit potential of the coating with AO nanoparticles throughout the experiment was higher than that of the unmodified coating, which indicates its higher corrosion resistance.

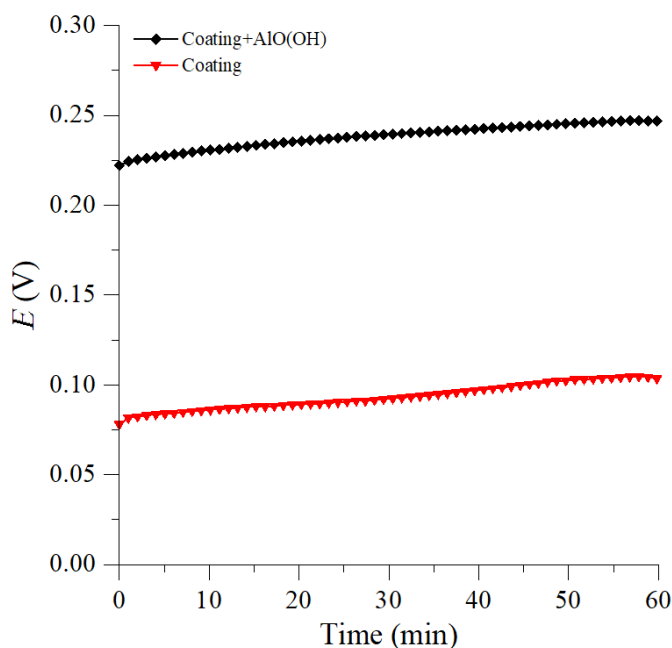


Fig. S1. (Color online) The evolution of the open circuit potential.

The coating/electrolyte interface for the coated titanium samples was studied by electrochemical impedance spectroscopy (Fig. S2). The Equivalent electric circuit (EEC) with a serial-parallel connection of two R-CPE-circuits was used for fitting the impedance spectra. The first R_1 -CPE₁ chain characterizes the geometric capacitance of the whole coating including outer porous part and R_2 -CPE₂ chain is a consequence of the presence of a non-porous sublayer of the coatings. In this study, a constant phase element CPE was used in equivalent electric circuits instead of the ideal capacitance. The necessity for such replacement results from the heterogeneity of the objects under the study. The CPE impedance was calculated according to the Equation:

$$Z_{CPE} = 1/Q(j\omega)^n \quad (2)$$

where ω is the angular frequency ($\omega = 2\pi f$), j — is an imaginary unit, n — is the exponential coefficient, and Q is the frequency independent constant.

Nyquist plots confirm the relevance of the proposed EEC showing two capacitive semicircles and no apparent diffusion limitations (Fig. S2).

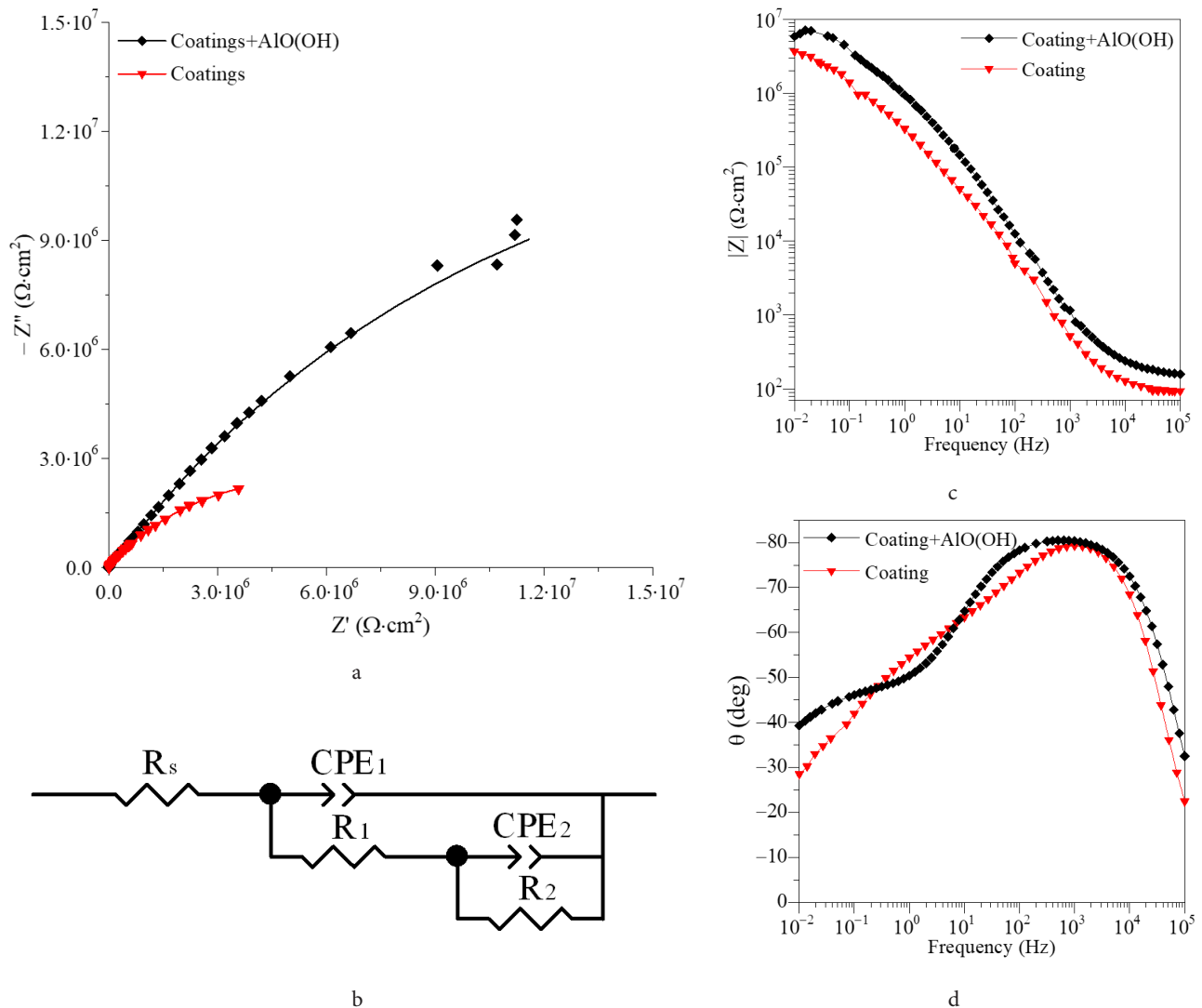


Fig. S2. (Color online) The Nyquist plot (a), equivalent electrical circuit used to calculate the impedance data (b) and Bode plots (c, d).

The results of the EEC elements calculation using experimental impedance spectra fitting are presented in Table S1. The analysis of the calculated parameters of the EEC elements allows us to conclude that the protective properties of the coating are largely due to the high resistance values of the porous sublayer R_2 , which is 4 times greater for coatings with AO nanoparticles than for unmodified coatings. In addition, the resistance of the nonporous sublayer R_1 of the coating with AO nanoparticles is an order of magnitude higher compared to the unmodified coating.

Table S1. Calculated parameters of the elements of the equivalent electrical circuit.

Samples	R_s	CPE ₁		R_1 ($\Omega \cdot \text{cm}^2$)	CPE ₂		R_2 ($\Omega \cdot \text{cm}^2$)	$ Z _{f=0.01 \text{ Hz}}$ ($\Omega \cdot \text{cm}^2$)
		Q_1 ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n		Q_2 ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n		
CP coatings with AlO(OH)	142.5	$4.3 \cdot 10^{-8}$	0.92	$3.8 \cdot 10^5$	$2.5 \cdot 10^{-7}$	0.58	$4.4 \cdot 10^7$	$1.4 \cdot 10^7$
CP coatings without AlO(OH)	84.5	$1.5 \cdot 10^{-7}$	0.90	$9.0 \cdot 10^4$	$6.7 \cdot 10^{-7}$	0.51	$1.1 \cdot 10^7$	$4.6 \cdot 10^6$

References

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33. A. G5-94, Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, ASTM International, West Conshohocken, PA (2004).
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