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The Electrochemical Impedance Spectroscopy and Wettability Analysis of Ti6Al4V Alloy Modified by Atomic Layer Deposition ALD Method

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The purpose of the article was to evaluate the physicochemical properties of the Ti6Al4V titanium alloy with a zinc oxide layer deposited by the atomic layer deposition method. The surface modification promotes changes in the chemical character of the surface according to two basis wettability states, namely the Wenzel state and the Cassie–Baxter state. To evaluate the mechanisms of wettability changes, the contact angle measurements and the surface free energy calculations (according to the Owens–Wendt methods) were performed. It was found, based on X-ray photoelectron spectroscopy, that the hydrophobic properties of the oxide layer are related to the presence of metal cations, oxygen anions, and hydroxyl groups on the surface. Additionally, the method of electrochemical impedance spectroscopy was used to define the morphological peculiarities of the coating on the basis of the registered impedance spectra.

topics: atomic layer deposition (ALD), zinc oxide, wetting angle, electrochemical impedance spectroscopy (EIS)

1. Introduction

The atomic layer deposition (ALD) method is a variation of the chemical vapor deposition (CVD) method [1]. ALD method is characterized by sequencing of the process and the self-limitation of layer growth. This means that the precursors are supplied alternately, between which the working chamber is flushed with inert gas, i.e., argon or nitrogen [2]. This solution allows for the successive deposition of single thin layers with a thickness of several nanometers — one atomic layer in each cycle. Each cycle increases the layer thickness by a specific value (0.01–0.3 nm), and the number of cycles depends on the expected layer thickness.

The ALD process offers high quality and chemical homogeneity of layers and enables the entire element to be covered, even if it is of a complex shape [3, 4]. Currently, silver (Ag), gold (Au), tin dioxide (SnO_2), and zinc oxide (ZnO) are commonly used in medicine, e.g., as a material for antibacterial coatings. However, based on literature data, the issue of the biomaterial modification by applying zinc oxide layer is still not fully resolved. Therefore, the aim of the study was to deposit the ALD ZnO layer on the Ti6Al4V alloy surface and investigate the influence of the surface modification on the physicochemical and electrochemical properties of proposed biomaterial.

2. Research methodology

The substrate material was Ti6Al4V titanium alloy. The samples were prepared using the standard metallographic technique of grinding with SiC abrasive paper and polishing with diamond paste, followed by final polishing with OP-U colloidal Al_2O_3 suspension. The ZnO layer has been deposited by an atomic layer deposition method, using a Beneq P400 ALD reactor. The diethylzinc $Zn(C_2H_5)_2$ (DEZn) was used as the zinc precursor, which reacted with deionized water. The pulse time of 0.01 s for each precursor was applied. Nitrogen (Ni) was used as an inert gas to transport precursors and clean the chamber between dosing cycles. The flow of Ni was equal to 200 sccm, and the purging time was 4 s for DEZn and 5 s for deionized water. The chemical reaction in the ALD process was thermally supported, and the temperature in the chamber was 200°C. The number of the cycles was 1500.

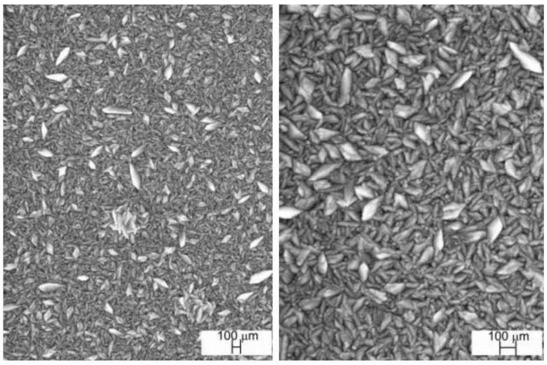

Fig. 1. SEM image of ZnO layer on the Ti6Al4V substrate material.

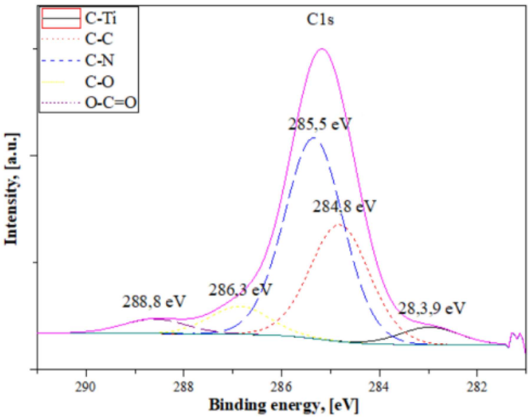

Fig. 2. XPS spectrum of C 1*s* for S1_ZnO sample.

TABLE I

Results of wettability test.

		Samples	
		S0	S1_ZnO
Wetting angle [°]	distilled water	61.7 ± 2.9	114.0 ± 2.0
	diiodomethane	47.0 ± 3.1	53.1 ± 1.0
Surface free energy [mJ/m^2]	γ_s	36.6 ± 0.7	43.4 ± 1.4
	γ_d^s	22.7 ± 1.5	40.2 ± 2.3
	γ_p^s	18.9 ± 1.9	1.3 ± 0.2

To determine the surface wettability, the sessile drop method was used. The contact angle measurements were performed using Surftens Universal goniometer by OEG and PC with Surftens 4.5 software. The distilled water (POCH S.A.) and diiodomethane (Merck) were used as measured liquids, and droplets of each with a volume of 1.5 μl were placed on the tested surface. The duration of a single measurement was 60 s, with a sampling rate of 1 Hz.

The impedance character of the surface was evaluated by electrochemical impedance spectroscopy (EIS), using the test stand comprised of an AutoLab's PGSTAT 302N system, equipped with a frequency response analyzer FRA2 module and three-electrode system (platinum wire PtP-201 — auxiliary electrode, silver/silver chloride Ag/AgCl — reference electrode, and tested samples — anode). EIS frequency ranged from 10^4 to 10^{-3} Hz, and the voltage amplitude of the sinusoidal signal was 10 mV. The recorded impedance spectra (in the form of Nyquist plot and Bode diagram) were adjusted to the equivalent electrical circuits, using the least-squares method. Based on this approach, the values of resistance R and capacity C were determined.

X-ray photoelectron spectroscopy (XPS) was used for the chemical structure of ZnO layer analysis. XPS analyses were carried out in a multi-chamber ultra-high vacuum experimental setup (base pressure 8.8×10^{-9} Pa) equipped with PREVAC EA15 hemispherical electron energy analyzer with the 2D-MCP detector. The tested samples were irradiated with an Al K_α X-ray source (PREVAC dual anode XR40B source, energy 1486.60 eV). For the survey spectra, the pass energy was set to 200 eV, and the scanning step was equal to 0.9 eV. In addition, particular energy regions to 100 eV were scanned with step 0.057 eV. Measurements were carried out with an analyzer's axis perpendicular to the samples' plane. The binding energy BE scale of the analyzer was calibrated to Au 4f7/2 (84.0 eV). Recorded data were fitted utilizing CASA XPS embedded algorithms and relative sensitivity factors. Shirley function was used for background subtraction. The components were fitted with a sum of Gaussian (70%) and Lorentzian (30%) lines. The estimated uncertainty for component energy position determination was 0.09 eV.

3. Results

For the samples with a zinc oxide layer S1_ZnO, examination by a scanning electron microscope (SEM) showed that the grains were characterized by an elongated shape, and were disordered without a dominant direction (Fig. 1). Additionally, it was found that the layers were homogeneous and free from defect.

The results of the wettability test and surface free energy (SFE) calculation are presented in Table I.

The samples in the initial state of S0 were characterized by hydrophilic properties; the value of the water contact angle was lower than 90°. Deposition of the ZnO layer by the ALD method resulted in an increase in the hydrophobic properties of the surface. The obtained values of SFE for both groups of samples were similar. It was also found that the sample groups S0 and S1_ZnO exhibited a greater affinity for the apolar groups of SFE than for the polar groups. However, the SFE value of the polar group for the S1_ZnO samples group was more than 14 times higher compared to the value for the S0 samples group.

Figure 2 shows the XPS spectra of the C 1*s* for the S1_ZnO samples group. The decomposition procedure was performed on the C 1*s* signal located

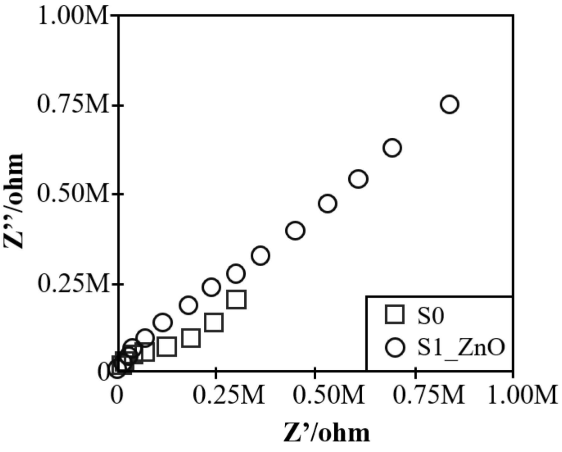

Fig. 3. Exemplary Nyquist diagram.

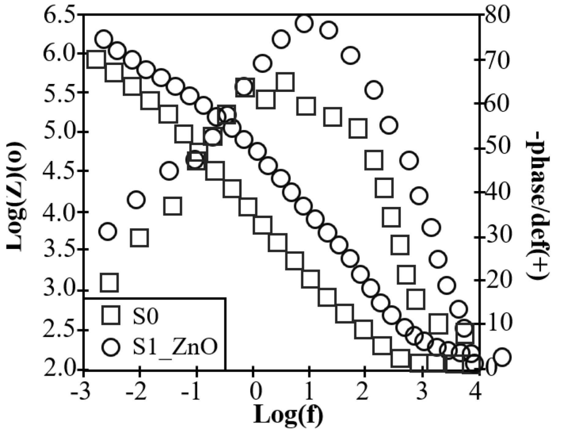

Fig. 4. Exemplary Bode diagram.

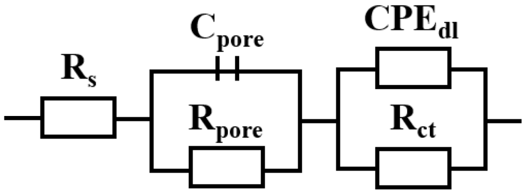

Fig. 5. Electric substitute scheme.

TABLE II

Results of EIS test.

Parameters		Samples	
		S0	S1_ZnO
R_s [Ω cm^2]		62	62
R_{pore} [Ω cm^2]		38	81
C_{pore} [μF]		40	42
R_{ct} [Ω cm^2]		393	1700
CPE_{dl}	Y_0 [Ω^{-1}cm^{-2}s^{-n}]	0.5553×10^{-4}	0.1641×10^{-4}
	n	0.76	0.84

at around 288.8 eV (O–C=O), 286.3 eV (C–O), 285.2 eV (C–N), 284.8 eV (C–C), and 283.9 eV (C–Ti base material).

The impedance spectra of substrate material S0 and samples with zinc oxide layer S1_ZnO in the form of Nyquist plots and Bode diagrams were presented in Figs. 3 and 4, respectively. The Nyquist diagrams (Fig. 3) for both samples group presented fragments of semi-circles, deformed to a different degree. It was found that increasing the angle of inclination of the curves to the ordinate axis for the S1 ZnO samples pointed to increased impedance values and increased corrosion resistance with the ZnO layer deposition. The Bode modulus plot showed that the biggest impedance modulus at full frequency rage was recorded for the samples S1_ZnO. Additionally, the highest value of the phase angle displacement at a broad range of frequency in the Bode phase diagram showed the S1_ZnO samples group — around 80° (Fig. 4).

The impedance spectra of analyzed corrosion systems were studied on alternative electrical circuits shown in Fig. 5. It was found that for both samples group, an equivalent circuit with two-time constants was used to analyze the EIS data, which indicates the occurrence of two sublayers — a cohesive inner one and a porous outer one (evident by two-time constants on the plot). The equivalent circuit consists of R_s — electrolyte resistance, R_{pore} — electrical resistance of the electrolyte in the pores, C_{pore} — capacity of the double layer-porous surface, and R_{ct} and CPE_{dl} — resistance and capacity of the twin substratum, respectively.

It was found that the value of R_{ct} resistance was 4 times bigger for the S1_ZnO samples group compared to the S0 samples group, which confirmed better corrosion resistance properties for surfaces with a zinc oxide layer (Table II).

4. Discussion

The improvement of the biocompatibility of titanium implants is possible by modifying their surface, usually by depositing thin protective layers with controlled chemical, physical and biological properties. Additionally, because the human body's fluids environment is an aggressive corrosion environment, the protective coating cannot be the source of electrochemical corrosion initiation. The performed tests indicate that the modifications of the Ti6Al4V alloy surface may significantly affect its functional properties. It was found that changes in the chemical nature of the modified Ti6Al4V alloy surface by deposited ZnO layer by the ALD method are promoted according to the Cassie–Baxter wettability state. The Cassie–Baxter theory assumes that the hydrophobic properties of the surface of the material are associated with its roughness, where the grooves under the droplet are filled with particles of air [6]. The SEM analysis indicated that the grains in the ZnO layer were characterized by an elongated shape, which may provide the development of surface topography in the nanoscale.

Additionally, the hydrophobic nature of the ZnO layer may be an intrinsic result of the presence of adsorbed hydrocarbons [7], which was confirmed by XPS analysis. Based on the EIS results, it was found that the deposition ZnO layer leads to better corrosion and impedance behaviors of the Ti6Al4V alloy. The impedance response of the oxide layer (ZnO) is related to its thickness and the dielectric constant of individual sublayers.

5. Conclusion

Based on the obtained results, it was found that the surface modification by the deposited zinc oxide layer by the ALD method (S1_ZnO) allows to obtain a hydrophobic surface characterized by higher barrier properties, compared to the uncoated surface S0.

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