MICROSTRUCTURE, SURFACE TOPOGRAPHY AND ADHESION OF ZEIN COATINGS ELECTROPHORETICALLY DEPOSITED ON TITANIUM SUBSTRATES

FILIP MACIĄG[1]*, TOMASZ MOSKALEWICZ[1], ZOYA HADZHIEVA[2], ALDO R. BOCCACCINI[2]

[1] FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, CZARNOWIEJSKA 66, 30-054 KRAKÓW, POLAND
[2] INSTITUTE OF BIOMATERIALS, UNIVERSITY OF ERLANGEN-NUREMBERG, CAUERSTR. 6, 91058 ERLANGEN, GERMANY
*E-MAIL: MACIAG@AGH.EDU.PL

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Introduction

Titanium and its alloys are characterized by relatively good biocompatibility, high corrosion resistance, favourable fatigue strength and high strength to weight ratio [1]. They are commonly used as metallic biomaterials. However, this material is inert to our body and has poor osteoinductive properties [2]. Another significant problem is biofilm formation on implants [3]. |To solve these problems, polymer and composite polymer-based coatings are deposited on their surfaces. One promising polymer is zein. Zein is a natural protein polymer obtained from corn. Due to its biocompatibility, biodegradability and antibacterial ability, this material is growing in interest for biomedical applications [4]. A convenient method for the deposition of zein coatings on titanium substrates is electrophoretic deposition (EPD). The aim of this work was to investigate the influence of the chemical composition of the suspension and EPD parameters on the coating morphology and surface topography, as well as adhesion to the titanium substrates.

Materials and Methods

A commercially pure titanium (CP-Ti) Grade 1 was used as the substrate material for the EPD of zein coatings. The samples in the as-received condition were washed with distilled water and degreased with technically pure ethanol prior to deposition. In addition, some samples were chemically treated in the following way: washing in acetone, soaking in a 0.06 M $Na_3PO_4 \cdot 12H_2O$ solution at 80 °C, washing in hot water, soaking in an acid solution (5 ml HF 40 vol. % + 35 ml HNO_3 70 vol. % in 60 ml H_2O) for 5 min., washing in water and drying.

To prepare a suspension for the EPD process, zein powder in various concentrations (100, 150 or 200 g/l) was gently added to the solutions of anhydrous ethanol (75 or 80 or 90 vol. %), glycerol (20 wt. %) and distilled water (25, 20 or 10 vol. %, respectively).

An austenitic stainless steel plate (X2CrNiMo17-12-2) was used as a counter electrode in the EPD cell. The distance between the electrodes was 10 mm. The deposition time was 5 minutes. The applied voltage was in the range of 3-10 V.

The as-deposited coatings were subjected to initial macroscopic observation and then the morphology of selected samples was examined by scanning electron microscopy (SEM). Phase identification was performed by grazing incidence X-ray diffractometry (GIXRD). The coating microstructure was investigated by transmission electron microscopy (TEM) on lamellae prepared by FIB from a cross-section. The surface topography of coatings was examined using atomic force microscopy (AFM) and optical profilometry. The adhesion of coatings to the substrate was investigated using the cross-cut tape-test, in accordance with ASTM D3359-17.

Results and Discussion

The coatings deposited on titanium substrates from suspensions containing 90 vol. % of ethanol, 10 vol. % distilled water, 20wt.% of glycerol, 150 g/l or 200 g/l of zein were macroscopically uniform. They were very similar macroscopically to each other and the value of voltage during EPD did not noticeably affect the quality of the coatings. Meanwhile, the coatings deposited from suspensions of different compositions were morphologically inhomogeneous with the presence of microcracks.

It was found during the tape-tests that, among all the coatings, the coating deposited from the suspension containing 200 g/l of zein, 90 vol. % of ethanol, 10 vol. % distilled water and 20wt.% of glycerol exhibited the highest adhesion (class 4B) to the as-received substrates. Moreover, the adhesion of this coating to the chemically treated substrates was much lower (class 0B). Thus, this coating was selected for further investigation.

The coating deposited at a voltage of 5 V during 300 s was dense and relatively homogeneous. However, open pores with a diameter in the range of 1-25 μm sporadically occurred. The microstructure of the coating observed with the use of TEM was dense. The thickness of the coating was 4.4 μm. It could be observed that, between the coating and the titanium substrate, a passive oxide layer with the thickness of ~10 nm was present. The GIXRD pattern revealed the presence of an amorphous zein phase in the coating.

The coating was relatively smooth. Its surface topography was different from the surface topography of the substrate. Typical surface topography parameters of the coating had the values: R_a (average roughness) = 234 ± 64 nm, R_q (mean square roughness) = 285 ± 75 nm and R_{max} (total roughness) = 1272 ± 266 nm, while those of the substrate material were as follows: R_a = 419.8 nm, R_q = 572.9 nm and R_{max} = 22.8 nm.

Conclusions

EPD conditions for the deposition of pure zein coatings on titanium substrates were elaborated. The coatings were dense and relatively homogeneous with few open pores. The coatings deposited from the suspension containing 200 g/l of zein in a dispersion phase composed of 90 vol. % of ethanol, 10 vol. % distilled water and 20 wt. % of glycerol, at 5 V during 300 s had the highest adhesion to the titanium substrate in the as-received condition. It was found that the coating exhibited poorly developed surface topography.

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