ADHESION, MICROSTRUCTURE AND SURFACE TOPOGRAPHY OF MESOPOROUS, Cu-DOPED SOL-GEL GLASS/ZEIN COATINGS ELECTROPHORETICALLY DEPOSITED ON Ti-13Nb-13Zr ALLOY SUBSTRATES

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Introduction

Among metallic biomaterials, titanium and its alloys are widely used in biomedical engineering. They are characterized by good biocompatibility, high electrochemical corrosion resistance, favourable fatigue strength and a high strength to weight ratio. However, they are biologically inert to the human body and biofilms are formed on their surface [1]. In order to improve the biological properties, the surface can be modified by the deposition of coatings. For this purpose, polymer-ceramic composite coatings are commonly used. In this work, composite coatings with a zein matrix, containing bioactive, mesoporous sol-gel glass (MSGG) with the addition of CuO (70% SiO_2, 25-x% CaO, 5% P_2O_5 + x CuO (x=1-3), in mol %), were produced on near-β Ti-13Nb-13Zr alloy substrates by electrophoretic deposition (EPD). EPD is an electrochemical surface modification method that allows the co-deposition of polymers and ceramics [2]. Zein is a natural polymer. Due to its biocompatibility, biodegradability and low toxicity, it can be used as a matrix material [3]. MSGG is characterized by high open porosity and a large specific surface area, which are desirable, among others, in the regeneration of bone tissue [4]. CuO has good antimicrobial properties and is widely used in biomedical engineering [5]. The aim of this work was to deposit MSGG/zein composite coatings, to investigate their adhesion to the Ti-13Nb-13Zr alloy substrate and to characterize their microstructure and surface topography.

Materials and Methods

A Ti-13Nb-13Zr titanium alloy was used as the substrate material for coating deposition. The samples were ground with 1200 grit sandpaper and then washed with ethanol and distilled water. To prepare the suspensions for the EPD process, zein powder (200 g/l) was gently added to the solutions of anhydrous ethanol (90 vol. %) and distilled water (10 vol. %), forming a zein solution to which MSGG (10 g/l or 40 g/l or 80 g/l) was gently added. The EPD was held on a two-electrode setup, where the working electrode was a Ti-13Nb-13Zr alloy and the counter electrode was an austenitic stainless steel plate (AISI 316L). The distance between electrodes was 10 mm. The deposition time was 5 minutes. The applied voltage was in the range of 3-10 V. The microstructure of the coatings was investigated by stereoscopic microscopy, scanning (SEM) and transmission (TEM) electron microscopy. The phase composition of coatings was investigated by grazing incidence X-ray diffractometry (GIXRD). The surface roughness of the coatings and the substrate was examined by optical profilometry. The adhesion of coatings to the substrate was investigated using the cross-cut tape-test in accordance with ASTM D3359-D.

Results and Discussion

The quality of coatings deposited on the Ti-13Nb-13Zr alloy substrates from suspensions containing 90 vol. % of ethanol, 10 vol. % distilled water, 20 wt.% of glycerol, 200 g/l of zein and 10 g/l or 40 g/l or 80 g/l of MSGG were varied with the applied voltage and the concentration of MSGG. Together with the increasing concentration of MSGG, the coatings became more porous. Coatings deposited with a voltage of 5 V and a deposition time of 5 minutes from all the prepared suspensions were selected for further research. It was found during the tape-tests that composite coatings had greater adhesion to the substrate than zein coatings. The adhesion class of the zein coatings was 0B (more than 65% area of the coating removed), and the composite coatings were in the range of 4B-5B (less than 5% or 0% area of the coating removed, respectively). Thus, this coating was selected for further microstructure investigation. The selected coatings deposited were dense, contained glass particles and their agglomerates had a diameter in the range of 1-10 μm and numerous pores with a diameter in the range of 5-15 μm. The coating deposited from the suspension with a concentration of 40 g/l of MSGG was selected for the microstructure investigation by TEM. It was dense, with numerous glass particles and their agglomerates homogeneously embedded in the zein matrix. The selected area electron diffraction pattern obtained from the coating exhibited an amorphous nature. The presence of closed pores with a diameter ranging from 0.1–0.3 μm in the central part of the coatings was observed. The thickness of the coating was ~10 μm. Between the coating and the substrate, a passive oxide layer with a thickness of about 50 nm was present. The GIXRD pattern revealed the presence of an amorphous zein and amorphous MSGG phase in the coating. The surface roughness of coatings had a greater roughness compared to the roughness of alloy substrates. The roughness of coatings increased with the increasing MSGG concentration in the suspension used for EPD.

Conclusions

It was shown that EPD allows composite MSGG/zein coatings to be deposited. These coatings are characterized by good adhesion to titanium alloy substrates and well-developed surfaces. The microstructure of the coatings contains separate MSGG particles or their agglomerates in the zein matrix. Further characterization of the coatings is in progress.

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