ELECTROPHORETIC DEPOSITION AND CHARACTERIZATION OF CuO/GtO/HA/SA COATINGS ON TITANIUM ALLOY

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Introduction

Titanium and its alloys are widely used as implant material due to their interesting properties, such as good electrochemical corrosion resistance, low elasticity modulus, low density and good biocompatibility. They are the most important metallic materials used in biomedical appliances, such as bone implants in orthopedic and dental applications. However, their osseointegration properties are poor [1]. To improve biological properties, bioactive and antibacterial coatings are frequently required. In this study, composite CuO/GtO/HA/SA coatings were fabricated on near-β Ti-13Nb-13Zr alloy by electrophoretic deposition (EPD), which is a useful technique for the co-deposition of inorganic and organic components [2]. Sodium alginate (SA) is one of the most important biopolymers widely used as a matrix of composite coatings [3]. Hydroxyapatite (HA) is a well-known bioactive, osteoconductive and non-toxic ceramic material. Graphite oxide (GtO) consisting of many graphene oxide layers is an antibacterial and biocompatible material [4]. CuO has excellent antibacterial ability against various bacterial strains and is widely used in dental or orthopedic applications [5]. The aim of the present work was to elaborate the EPD conditions for the deposition of CuO/GtO/HA/SA coatings on Ti-13Nb-13Zr alloy substrates and to characterize the coating microstructure and selected properties.

Materials and Methods

A Ti-13Nb-13Zr titanium alloy was used as a substrate material for coating deposition. The substrate was ground with a successively finer grit of sandpaper up to 3000-grit and mechanically polished. The suspension used for EPD consisted of 4 g/l SA, 2 g/l HA, 0.04 g/l GtO and 0.1 g/l, 0.2 g/l or 0.4 g/l of CuO and the dispersion medium contained a volume ratio of distilled water to ethanol equal 60/40. The alloy was the anode and the cathode was made of austenitic stainless steel (AISI 316L). EPD was performed at the constant voltage of 3, 5, 7 and 10 V for a deposition time of 5 minutes. The zeta potential was measured with Laser Doppler Velocimetry in the pH range of 3 to 12. The microstructure of coatings was characterized by light microscopy (LM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The adhesion of the coatings to the substrates was investigated by a cross cut adhesion test in accordance with ASTM D3359-B. The surface topography of the coatings was analyzed by optical profilometry. The contact angle and surface free energy (SFE) were investigated with a goniometer. The antibacterial properties of the coated alloy were evaluated against Gram-positive *S. aureus* and Gram-negative *E. coli* by using Alamar blue assay.

Results and Discussion

The zeta potential of the real suspensions, containing different concentrations of CuO equal 0.1 g/l, 0.2 g/l and 0.4 g/l, exhibited negative values in the entire investigated pH range (3–12). The highest values of zeta potential of suspensions with different concentrations of CuO were -24.5 mV (for pH=7.45, CuO 0.1 g/l), -31.0 mV (for pH=7.70, CuO 0.2 g/l) and -34.1 mV (for pH=7.90, CuO 0.4 g/l), respectively. Macroscopically uniform coatings were obtained from all investigated suspensions at the voltage of 7 V and deposition time of 5 min. If the voltage was higher than 7 V the substrate was oxidizing, but if the voltage was lower than 7 V the coatings were not uniform and only partially coated the alloy. SEM investigations revealed that coatings were smooth, homogeneous and dense with the presence of HA and CuO agglomerates. It was observed that with the increasing concentration of CuO in the suspension (0.1 g/l, 0.2 g/l and 0.4 g/l) the diameter of agglomerates was higher, 7 μm, 10 μm and 13 μm, respectively. The coatings exhibited good adhesion to the alloy substrates (class 4B, according to ASTM B3359B) independent of the concentration of CuO in the suspension. The coatings were characterized by average surface development, for example Ra (the average roughness) = 0.14 ± 0.03 μm, Rq (the root mean square roughness) = 0.21 ± 0.04 μm and Rmax (maximum vertical distance between the highest and lowest point) = 8.8 ± 2.2 μm for the coating deposited from the suspension containing 0.2 g/l of CuO. The coatings exhibited a hydrophilic character. For instance, the contact angle of coatings deposited from the suspension containing 0.2 g/l of CuO with water and diiodomethane equaled 12.2 ± 0.4° and 37.6 ± 1.5°, respectively. The SFE equaled 75.6 ± 1.1 mN/m (40.8 ± 0.7 mN/m for the disperse component and 34.8 ± 0.4 mN/m for the polar component). The CuO/GtO/HA/SA coatings deposited from a suspension containing 0.4 g/l CuO showed enhanced antibacterial activity against Gram-negative *E. coli*, comparing with the HA/SA coating obtained from a suspension without GtO and CuO. In case of Gram-positive *S. aureus* no significant difference between the coatings deposited from the suspension containing 0.4 g/l CuO and those deposited from the suspension without GtO and CuO can be found.

Conclusions

Composite CuO/GtO/HA/SA coatings were successfully deposited on titanium alloy. Macroscopically uniform coatings were obtained at a potential difference of 7 V during 5 min. All CuO/GtO/HA/SA coatings exhibited high adhesion to the alloy substrates. Coatings were dense, exhibited average surface development and a hydrophilic character. Further optimization and characterization of the coatings are in progress.

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