FABRICATION AND CHARACTERIZATION OF MULTICOMPONENT HA/MoS2/PEEK COATINGS ON THE Ti-13Nb-13Zr ALLOY

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Introduction

Among all structural metallic materials, titanium alloys are the most prominent in contemporary implantology. They are characterized by a high strength to weight ratio, superior electrochemical corrosion resistance and a relatively low modulus of elasticity [1]. However, titanium alloys, including the Ti-13Nb-13Zr alloy, exhibit relatively poor tribological properties and are inert to the human body. Polyetheretherketone (PEEK) is a promising material for a bioactive coating matrix. PEEK is a semi-crystalline thermoplastic polymer with good tribological properties and relatively high strength. It is commonly used in biomedical engineering as a replacement for metallic, orthopaedic, long-term implants due to its high performance and biocompatibility [2]. Despite its advantages, its bioactivity is low but may be improved by the addition of bioactive particles. Synthetic hydroxyapatite (HA) is a commonly known and widely applied osteointegrated agent. It is a primary non-organic bone component. The effectiveness of the bone bonding capability and enhanced implant stabilization of HA have been widely proven clinically [3]. To elicit the bioactive properties of titanium alloy substrates, HA nanoparticles and MoS_2 nanosheets were co-deposited with PEEK microparticles in this work.

The goal of the present work was the fabrication of multicomponent HA/MoS_2/PEEK coatings on the Ti-13Nb-13Zr alloy through duplex treatment consisting of electrophoretic deposition (EPD) and post heat treatment. The microstructure and adhesion of the coatings to the titanium alloy were also characterized.

Materials and Methods

Composite coatings were deposited by EPD on Ti-13Nb-13Zr alloy disks with a diameter of 27 mm and thickness of 4 mm. Specimens were ground with 1200 grit sandpaper and subsequently washed in distilled water and ethanol.

The HA used for EPD was delivered in the form of nanopowder with elongated particles and with the average size of 43 nm and specific surface area of 46 m^2/g. To prepare a suspension for the EPD of coatings, 1.5 g of PEEK704, varying amounts of HA nanoparticles of 1 g, 0.5 g or 0.3 g and 0.1 g with 0.02 g of MoS_2 powders in 50 ml of an electrolyte composed of ethanol and 25 vol. % of colloidal chitosan solution were mixed. The suspension was prepared gradually. Firstly, by dispersing the suspension containing PEEK and MoS_2 in an ultrasonic bath for 20 minutes. Then, by adding HA powder, magnetic stirring at 300 rpm for 10 minutes and dispersing for 5 minutes. Electrodes were immersed at a constant distance of 10 mm apart in the EPD cell.

Coatings were deposited at a constant voltage in the range of 50-120 V with 10 V changes and a constant deposition time of 30 s. The specimens were exposed to heat treatment at a temperature of 380ºC for 40 min and cooled with rate of 2ºC /min.

Coatings were subjected to initial macroscopic observation. After that, the morphology of selected samples was characterized by scanning electron microscopy (SEM). The chemical composition of coatings was investigated by Energy Dispersive X-ray Spectroscopy (EDS) microanalysis. A cross-cut tape test in accordance with ASTM D3359-17 was performed to investigate the adhesion of coatings to the substrate.

Results and Discussion

It has been observed that macroscopically homogeneous coatings were obtained for cathodic deposition in the voltage range of 80-100 V. Coatings deposited at voltages below 80 V were too thin and often inhomogeneous. Application of higher voltages resulted in the deposition of coatings with uneven thickness and numerous pores. Therefore, the voltage of 90 V was finally adopted as optimal for obtaining macroscopically homogeneous coatings. The optimal time of deposition was determined at 30 seconds. Coatings deposited below that time were too thin, often not completely covering the alloy sample. Longer deposition times increased the probability of inhomogeneity.

Macroscopic evaluation of the coatings deposited from the suspension containing 1 g or 0.5 g or 0.3 g of HA revealed numerous inhomogeneities, such as cracks and pores with a diameter up to 100 μm. SEM investigation of the coating morphology after heat treatment revealed net-shaped microcracks appearing on their surfaces. Moreover, many unmelted PEEK particles covered by HA nanoparticles occurred on the surface of the coatings. It is supposed that the HA nanoparticles hindered the melting of the PEEK particles. EDS microanalysis confirmed the presence of calcium, phosphorus, molybdenum, sulphur, oxygen and carbon in the coatings. The Ca/P atomic ratio in the HA particles evaluated from the EDS spectra was close to 1.6.

It was found that the coatings deposited from the suspension containing 0.1 g of HA at the voltage of 90 V during 30 seconds were macroscopically homogeneous without any defects. After heat treatment, the PEEK changed its morphology from particles to a continuous and dense coating matrix. The tape-test conducted for the heat-treated coating revealed that this coating exhibited very high adhesion (class 5B) to the titanium alloy substrate. Detailed investigation of the coating using SEM showed that the edges of the cut were continuous. No detachment of the square of the coating from the incision grid was observed.

Summary

Macroscopically homogeneous HA/MoS_2/PEEK coatings were successfully obtained by EPD from a suspension containing 0.1 g of HA at a voltage of 90 V, during the deposition time of 30 seconds. Heat treatment densified the coatings and significantly enhanced their adhesion to the titanium alloy substrate. Further optimization and characterization of the coating microstructure, surface topography and properties are in progress.

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