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Incorporation of Ca ions into anodic oxide coatings on the Ti-13Nb-13Zr alloy by plasma electrolytic oxidation

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ABSTRACT

The present work concerns the surface modification of The Ti-13Nb-13Zr alloy by electropolishing and plasma electrolytic oxidation (PEO) process in Ca-containing electrolytes: calcium formate and calcium lactate solutions (0.1–1.0 mol dm^{-3}) under voltages of 200 and 400 V. As a result of the PEO process, a porous oxide layer containing incorporated calcium compounds was formed on the Ti-13Nb-13Zr alloy surface. The morphology and chemical composition of the modified Ti-13Nb-13Zr alloy were investigated using scanning electron microscopy (SEM + EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). An increase in the applied voltage caused an increase in the number of pores and an increase in the amount of calcium incorporated in the oxide layer. Analysis showed that all samples were covered by titanium oxide, which was present in the form of anatase and/or rutile. In course of the experiments, it was showed that the proposed procedure has a positive effect on the overall bioactivity of the Ti-13Nb-13Zr alloy. Bioactivity investigations using simulated body fluid (SBF) confirmed the formation of apatite on the anodized surfaces. The cell adhesion results obtained by the use of human bone marrow mesenchymal stem cells (hBMSC) demonstrated that the PEO coatings on the Ti-13Nb-13Zr alloy remarkably enhanced the cytocompatibility of the substrate, indicating a potential application in orthopedic surgeries. The incorporation of Ca into the oxide layer proceeded to a higher extent when the PEO treatment was performed in the calcium lactate bath. The oxide layers formed in the calcium lactate solution exhibited also superior biological behavior towards hBMSC. This can be ascribed to the presence of carboxylic groups onto coatings' surface (as identified by XPS), which facilitated the anchoring of cells and tissues.

1. Introduction

Ti-6Al-4V is a well-established metallic alloy for biomedical applications [1–3]. However, studies have shown the alloy has a possible toxic effect resulting from the release of aluminum and vanadium ions by corrosion or wear processes after long-term implantation. These metallic ions in contact with adjacent tissues might cause adverse health issues. Vanadium causes various allergic, cytotoxic and mutagenicity effects, while aluminum is associated with potential neurological disorders [4]. For this reason, research and development on titanium alloys composed of non-toxic elements were started, and vanadium- and aluminum-free alloys are getting much attention in biomedical applications [5,6]. Primarily, to overcome the potential toxicity of titanium alloys, vanadium was replaced by niobium or iron, leading to the development of new Ti-6Al-7Nb and Ti-5Al-2.5Fe α + β-type alloys with good mechanical and metallurgical behavior comparable to those of Ti-6Al-4V [7]. Recently, low modulus β-type titanium alloys have been extensively developed [8] to avoid the stress shielding effect and eventual implant failure. The Ti-13Nb-13Zr ternary alloy is one of the most promising titanium alloys demonstrating superior properties to those of conventional load-bearing α and α + β biomaterials. Thanks to niobium alloying, the Ti-13Nb-13Zr alloy demonstrates better biomechanical compatibility than Ti-6Al-4V alloy. Its Young's modulus (60–90 GPa) is closer to the bone modulus (~30 GPa)

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