FORMATION AND CHARACTERIZATION OF ANODIC TITANIUM OXIDE FILMS CONTAINING Ca, P AND Si IONS ON SELECTIVE-LASER MELTED Ti13Zr13Nb ALLOY

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Introduction

One of the directions to improve the mechanical properties of titanium alloy dedicated for biomedical application is to use newly β-type titanium Ti13Zr13Nb alloys known as low modulus and bioinert metals. Together with selective laser melting (SLM), it's possible to obtain preferable mechanical properties of implants [1,2]. Further, to enhance the bone tissue response, surface modification is obligatory. According to the literature, the addition of Ca, P, and Si ions can significantly improve the bioactivity of titanium implants [3]. Among the surface modification method, micro-arc oxidation (MAO), has gained special attention due to capability to produce dense oxide film that binds well to substrate, enhances biocompatibility and bioactivity, coat the complex-shape objects and can incorporate ions into the structure.

The main aim of this work was to investigate the formation and characterization of anodic titanium oxide films containing Ca, P, and Si ions on selective laser melted Ti13Zr13Nb.

Materials and Methods

The titanium specimens were manufactured by the Realizer SLM 100. The MAO process was performed at two voltages of 300 and 400 V with a constant value of time and current equal to 15 minutes and 32 mA respectively, in an electrolytic solution containing 0.1 mol/L of calcium glycerophosphate (GP), 0.15 mol/L calcium acetate (CA) and two various contents of Na_2SiO_3.: 0.02 and 0.06 mol/L. The MAO process characterization was analyzed by the time-dependent (PCD-300A; Kyowa Electronic Instruments) relations of voltage and current. To obtain the characteristics of coatings, the microstructure (SEM JSM-7800F), topography, surface roughness, pore diameter (LSM; Olympus LEXT OLS4100 3D), thickness (Elcometer, 456, Elcometer Inc), elemental composition (EDS; S-3400NX, Hitachi), crystal structure (XRD, Bruker D8 discover), and surface wettability (optical tensiometer Attention Theta Life) were evaluated. The nanomechanical properties were determined using nanoindenter, while MAO coating adhesion properties were estimated by the scratch test (NanoTest Vantage, Micro Materials Ltd., Wrexham, UK). The ability of calcium phosphate formation on oxide coatings was examined to obtain the bioactivity characterization (Immersion test in Hank's solution).

Results and Discussion

Macro-porous, Ca- and P-containing titania-based films were successfully formed on the Ti13Zr13Nb alloy substrates. The phase, Ca, P and Si content, morphology, roughness, thickness, nanomechanical properties, and adhesion of the MAO coatings were strongly dependent on the applied voltage. Due to the good ratio of structural and nanomechanical properties of the coatings, the optimal conditions of the MAO process were found at 300 V, which resulted in the predictable structure, high Ca/P ratio, the highest demonstrated early-stage bioactivity, better nanomechanical properties, elastic modulus, and hardness close to the values characteristic for bones. The addition of 0.02 M Na_2SiO_3 improves critical load of adhesion and total delimitation, while with increasing content of silica, the contact angle and the Ca/P ratio in the structure also increased.

Conclusions

The combination of SLM and MAO strategy is the perspective method to improve nanomechanical and bioactive properties of titanium alloys for biomedical application.

Acknowledgments

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References

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