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Effects of plasma electrolytic oxidation process on the mechanical properties of additively manufactured porous biomaterials

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ABSTRACT

Metallic porous biomaterials are recently attracting more attention thanks to the additive manufacturing techniques which help produce more complex structures as compared to conventional techniques. On the other hand, bio-functional surfaces on metallic biomaterials such as titanium and its alloys are necessary to enhance the biological interactions with the host tissue. This study discusses the effect of plasma electrolytic oxidation (PEO), as a surface modification technique to produce bio-functional layers, on the mechanical properties of additively manufactured Ti6Al4V scaffolds based on the cubic unit cell. For this purpose, the PEO process with two different oxidation times was applied on scaffolds with four different values of relative density. The effects of the PEO process were studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), optical microscopy as well as static and dynamic (fatigue) mechanical testing under compression. SEM results indicated pore formation on the surface of the scaffolds after oxidation with a thickness of 4.85 ± 0.36 μm of the oxide layer after 2 min and 9.04 ± 2.27 μm after 5 min oxidation (based on optical images). The static test results showed the high effect of relative density of porous structure on its mechanical properties. However, oxidation did not influence most of the mechanical properties such as maximum stress, yield stress, plateau stress, and energy absorption, although its effect on the elastic modulus was considerable. Under fatigue loading, none of the scaffolds failed even after 10^6 loading cycles at 70% of their yield stress.

1. Introduction

In bone tissue engineering, scaffolds play essential roles in mimicking bone characteristics and supporting the formation of new tissue. Not only should bone-mimicking scaffolds be biocompatible and capable of inducing bone ingrowth and osseointegration, they should also have proper mechanical properties relative to the surrounding tissue [1–3]. Hence, fabrication of scaffolds with biomechanical properties similar to those of the surrounding bone is one of the main concerns in bone tissue engineering [4].

Due to the higher strength of metallic scaffolds as compared to other materials, they have become the key material in load-bearing applications such as orthopedic and dental implants [5]. One of the most well-known metallic biomaterials applicable in dental and orthopedic implants are titanium and its alloys due to their excellent properties such as biocompatibility, high strength-to-weight ratio, and closer elastic modulus to bone as compared to some other metallic biomaterials [6]. However, even for implants made of titanium, aseptic loosening may happens due to stress shielding which is the result of mismatch between the elastic moduli of bone and metallic implant as well as the micro-motions of the implant in the implanted zone. Porous implants have been introduced as one of the most suitable solutions to overcome this deficiency. Porosity within porous implants decreases the elastic modulus of the metallic structure to values around those of bone which balances the load transfer through the implant leading to decreased effect of stress shielding. The interconnected hollow pores with adequate pore size inside porous structures also provide space for nutrient delivery, vascularization, and finally bone ingrowth and implant fixation [7–9]. Additive manufacturing (3D printing) is one of advanced techniques for fabrication of porous metallic scaffolds. This method allows for manufacturing of interconnected porous structures with desired micro-architectures. By applying this method and controlling the porosity and designing pore morphology and size, predictable mechanical properties are achievable [10,11].

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Another way to overcome aseptic loosening is improving bone ingrowth which is feasible through surface treatment. Improvement of the biological properties of scaffolds is possible through surface modification and inducing new surface properties [5]. Plasma electrolytic oxidation (PEO) is an effective surface modification technique for synthesis of bio-functional oxide layers with interconnected micro/nano porosity on titanium materials. This surface layer is beneficial for increasing cell affinity and growth, which in turn results in better bone-scaffold integration [8]. Overall, surface modification might influence the mechanical properties of porous structures more than those of bulk materials due to the much higher surface area of the porous structures [12]. Previous studies [13,14] on bulk titanium alloys have shown that the presence of the PEO layer may affect the fatigue behavior of these materials. Currently, there are no reports addressing the effect of PEO layers on the mechanical behavior of additively manufactured titanium scaffolds.

In the present study, we aim to investigate the effects of bio-functionalization of additively manufactured Ti6Al4V scaffolds through the PEO process on their static and dynamic mechanical properties. The PEO process with the same current density but two different oxidation times (i.e. 2 min and 5 min) in calcium acetate and calcium glycerophosphate electrolytes were applied to scaffolds with the cubic unit cell and with four different porosities (relative densities) produced using selective laser melting (SLM). Both the as-manufactured and oxidized scaffolds were characterized by SEM, energy dispersive X-ray spectroscopy (EDS), optical microscopy, and static and dynamic mechanical compression tests. Furthermore, we used the finite element (FE) method to predict the mechanical properties of the porous metallic biomaterials.

2. Materials and methods

2.1. Additive manufacturing of scaffolds

Porous scaffolds were additively manufactured using the selective laser melting (SLM) method (Layerwise NV, Leuven, Belgium). File preparation was performed using the Magics (Materialise, Belgium) and DMP Control (3D Systems, Belgium) software. A customized 3D Systems ProX DMP 320 machine was used to manufacture the specimens. The low oxygen level in this machine (<50 ppm) is ideally suited for production of Ti6Al4V-ELI scaffolds (according to ASTM B348, grade 23) on top of a rigid plate. All scaffolds were cylinders (approximately 7 mm length and 10 mm diameter) with a porous structure based on the cubic unit cell, but with four different strut sizes and porosities (designated as types A, B, C, and D in Table 1). The samples were scanned using a micro-computed tomography machine (micro-CT) (20 μm × 20 μm × 20 μm voxel size, 90 kV tube voltage, 180 μA tube current, 3600 projections, Quantum FX, Perkinelmer, USA). The 3D reconstructed images were then sliced into 2D stacks using Analyze 11.0 (in-built micro-CT software). The 2D stacks were locally segmented in imageJ v.1.47. The pore size and distribution, strut size, porosity, total surface area per unit volume, and volume of the as-manufactured scaffolds were determined using boneJ (plugin of imageJ) (Table 1).

2.2. Plasma electrolytic oxidation of scaffolds

In the first step, the additively manufactured specimens were degreased in acetone, ethanol, and deionized water (5 min each one). The PEO process was applied to the electrolyte prepared by dissolving 24 g/L calcium acetate (P99%, Sigma–Aldrich) and 4.2 g/L calcium glycerophosphate (Dr. Paul Lohmann, Germany) in demineralized water. A cylindrical stainless steel (Goodfellow, AISI 316 Hard) electrode was used as cathode whereas the scaffold was the anode. A current density of 20 A/dm^2 was supplied through an AC power supply (50 Hz) type ACS 1500 (ET Power Systems Ltd., UK) in galvanostatic mode. The temperature during PEO was controlled by using a cooling bath and a double-walled electrolytic cell to maintain the temperature at 9 ± 7 °C. More experimental details on the applied PEO process can be found in a previous study of our group [15]. Two different oxidation times (i.e. 2 min and 5 min) were considered for each group. The numbers 0, 2, and 5 were used to specify samples with respectively 0 min, 2 min, and 5 min of oxidation time (Table 2).

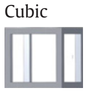
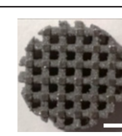
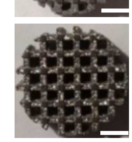
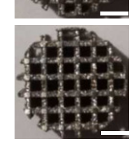
2.3. Surface morphology and chemical characterization

Scanning electron microscopy (SEM) (Dual Beam strata 235, EI, USA) was employed to image the topography of the scaffolds, and their elemental composition was determined by energy dispersive X-ray spectroscopy (EDS) (EDAX, UK).

2.4. Thickness of the TiO_2 layer

To measure the thickness of TiO_2 coating formed on the scaffold's struts, a specimen was embedded into a cold mounting epoxy resin (ClaroCit, Struers, Denmark). The mounted specimen was successively ground with SiC grit paper and polished with Chem cloth and colloidal silica paste (0.04 μm, OP-S suspension) after which the cross-section

Table 1
Physical properties of the additively manufacture scaffold.

Scaffold	Unit cell shape	Strut size (μm)	Pore size (μm)	Relative density (%)	Porosity (%)	Total surface area/volume (mm^{-1})	Macro structure (scale bar: 250 μm)
A	Cubic 	823 ± 230	1020 ± 311	37	63	46	
B		693 ± 200	1155 ± 354	28	72	51	
C		654 ± 190	1139 ± 359	24	76	58	
D		451 ± 147	1413 ± 366	13	87	77