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Hybrid solid-porous titanium scaffolds

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Abstract: In the presented study novel hybrid solid-porous scaffolds were fabricated by selective laser melting from pure titanium powder enriched with oxygen. Unmelted powder particles removal, surface quality improvement and CAD model dimensions rendering were obtained by chemical polishing in a mixture of hydrofluoric and nitric acids. It was observed that the hardness of the samples increased with the energy density and varied in the range from 202±9 to 247±11 HV0,2. The obtained results show that selective laser melting combined with chemical post-processing is a perspective tool for fabrication of the hybrid titanium structures.

I. Introduction

Additive manufacturing (AM) has been recognized in medicine as facilitating the production of complexly-shaped, often patient-specific implants and surgical guides [1]. Among other AM technologies selective laser melting (SLM) is a powder-bed based technique that enables manufacturing of constructional elements with wide geometrical freedom. This method enables producing elements with gradient lattice structures and pre-designed mechanical properties [2]. It was studied, that the appropriate manufacturing parameters differ depending on the pore sizes and their volumes [3]. Thus, the computer-aided design (CAD), additive manufacturing parameters, and post-processing method in planning and producing patient-specific implants may need to be determined separately for each part's geometry. This becomes especially challenging for the complexly-shaped parts composed of areas with different shapes and porosities. The example of this type of solid-porous implants are titanium craniofacial meshes with the solid fixing plates. Some of them are commercially available, but they consist of solid struts with average size above 200 μm and pores with dimensions around 1 mm [4]. In contrast to industrial practice, most of the literature shows that optimal pore diameter should be around 250-750 μm for improved in-vitro cell adhesion and proliferation and in-vivo bone ingrowth [5]–[7].

The most popular metallic materials used in commercial AM systems for fabrication of patient-specific implants are Ti-6Al-4V and Co-Cr alloys. Nonetheless, Ti-6Al-4V contains potentially allergenic aluminum and toxic vanadium. For these reasons, pure titanium is a candidate for musculoskeletal devices. Technically pure titanium alloyed with oxygen during the SLM process can meet Ti-6Al-4V alloy tensile strength thanks to solid solution strengthening [8]. In this study, we have investigated the possibility of manufacturing hybrid solid-porous scaffolds by SLM method and the possibility of improving their dimensional accuracy by chemical polishing. The proposed approach could enable the production of bone implants using AM methods supporting cell adhesion and proliferation. Furthermore, oxygen-enriched titanium will posse high mechanical strength without allergenic and cytotoxic alloying elements.

II. Material and methods

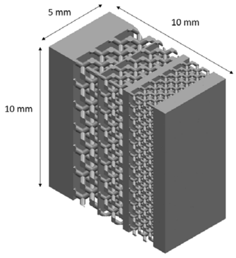

Figure 1. Samples visualization.

The hybrid solid-porous scaffolds CAD models (Fig. 1) were designed with outer dimensions of 5x10x10 mm and with three porous regions of 1.8x10x10 mm each (Magics 18.1, Materialise NV). The porous regions after being filled with diamond elemental structures had pore sizes of 500, 700 and 900 μm and were separated from each other with solid regions with the width of 2.0; 1.0; 0.5 and 0.1 mm. The set of 12 scaffolds was fabricated using Realizer SLM50 equipped with fiber laser of 120W in a protective atmosphere of argon with a controlled amount of oxygen under 0.5%. The titanium spherical powder Grade 1 with a mean diameter below 50 μm (TLS Technik, GmbH) was used for fabrication. Process parameters were set to achieve high CAD model accuracy along with defect-free builds. The energy density (E) delivered to the melted powder was in a range of 43-71 J/mm^3 obtained with constant scanning speed of 375 mm/s and different laser powers in range 45-60 W, and hath distances of 45-55 μm. Each layer was scanned by the laser using an alternating x–y scan strategy with 90° layer rotation while layer thickness was fixed at 50 μm throughout this study. The parameters used for the fabrication process are summarized in Table 1. After manufacturing samples were detached from the building platform and cleaned in the ultrasonic machine in a deionized water (2 times/15 minutes) to remove unmelted powder particles trapped in pores. Confirmation of the lack of powder in the pores was done with unaided eye, as the pores being transient at appropriate observation angles. After drying, solid-porous scaffolds were polished in 2.2% HF – 20% HNO_3 for 6 minutes in order to meet designed CAD model dimensions. The composition of polishing mixture was selected basing on our previous studies [9]. Scanning electron microscope (SEM) Hitachi 3500N was used to examine the dimensions of struts before and after chemical polishing, while optical microscopy observations on metallographic cross sections was done to confirm removal of powder from the struts.

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The built parts' density was determined by metallographic cross sections obtained during polishing of scaffolds on single wheel grinder and polisher Saphir 550 (ATM GmnH). The image analysis was performed using optical microscopy (Zeiss AxioVision Light Microscope) and MicroMeter software. Vickers microhardness (HV) measurements with 1.96 N were conducted using the Zwick/Roell ZHU 0.2 machine.

III. Results and discussion

All scaffolds were successfully manufactured with the proposed selection of SLM parameters, however some of them posed irregular or concave surfaces. It was observed that the surface quality is correlated to the value of energy density. In general, the smooth surface was obtained for samples produced with energy densities equal or below 53 J/mm^3, while energy densities higher than 64 J/mm^3 caused the concave surface of the fabricated samples. SEM observations of the as-printed elements showed powder particles attached to the surface, which caused dimensional inaccuracy with a CAD model (Fig. 2a). The measurement of struts and solid regions of each scaffold showed that the fabricated elements were about 20-170 µm thicker than in CAD models. The lowest dimensional inaccuracy was observed for sample no. 1 manufactured with an energy density of 53 J/mm^3, while the highest manufacturing inaccuracy was observed for sample no. 4 manufactured with the highest energy density (E=71 J/mm^3). Generally samples fabricated with energy density equal or bellow E=59 J/mm3 had good dimensional stability. Characterization results are summarized in table 1.

Table 1. Process parameters and characterization results.

No.	P [W]	h [mm]	t [mm]	E [J/mm^3]	v [mm/s]	Surface quality	Dimensional stability	Hardness HV 0.2
1.	45	0.045	0.05	53	375	+	++	212±13
2.	50	0.045	0.05	59	375	+/-	+/-	226±12
3.	55	0.045	0.05	65	375	-	-	233±15
4.	60	0.045	0.05	71	375	-	- -	247±11
8.	45	0.050	0.05	48	375	+	+	206±14
7.	50	0.050	0.05	53	375	+	+	212±19
6.	55	0.050	0.05	59	375	+/-	+/-	222±17
5.	60	0.050	0.05	64	375	-	-	221±10
9.	45	0.055	0.05	44	375	+	+	224±13
10.	50	0.055	0.05	48	375	+	+	221±18
11.	55	0.055	0.05	53	375	+	+	231±11
12.	60	0.055	0.05	58	375	+/-	+/-	202±9

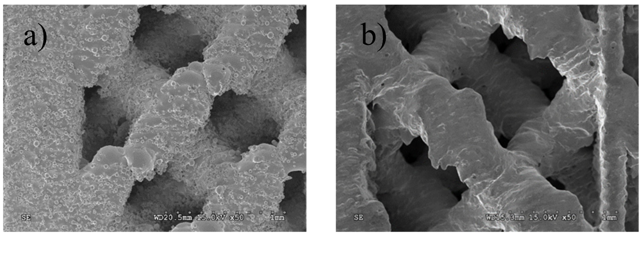

Figure 2. As-printed (a) and chemically polished sample (b) observed under the SEM microscope. Sample no. 1.

Chemical polishing in a mixture of HF-HNO_3 indicated a decrease of CAD model inaccuracy to 0-70 µm thanks to removing unmelted powder particles and thinning struts (Fig. 2b). Chemical polishing of the as-printed samples (Fig. 3a) improved the surface quality of interior and exterior regions as well. The continuity of the struts after the polishing process has not been disturbed (Fig. 3b). The porosity values for the majority of fabricated samples were lower than 0.79%. Some of the samples had single pores visible on the metallographic cross section in Fig. 3b. Only the sample no. 4 had the porosity higher than 1.5%. The lowest porosity was observed for samples no. 1 (E=53 J/mm^3), 3 (E= 65 J/mm^3) and 11 (E=53 J/mm^3). The hardness of the samples increased with the energy density and varied in the range from 202±9 to 247±11 HV0,2. The values of obtained microhardness are higher than for non-oxygen-enriched titanium [10].

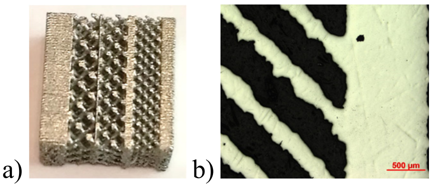

Figure 3. As-printed (a) and chemically polished sample observed under a metallographic microscope (b). Sample no. 1.

IV. Conclusions

We have successfully developed SLM parameters, which enabled the fabrication of the hybrid solid-porous titanium scaffolds with 3 regions of porosities (500, 700 and 900 µm); Chemical polishing in mixture of HF/HNO_3 improved the dimensional accuracy of fabricated elements by removal of the unmelted powder particles from struts; The SLM technique allows the production of parts from the pure titanium in a controlled atmosphere with oxygen addition and improving their mechanical properties.

AUTHOR'S STATEMENT

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