3D printed porous stainless steel for potential use in medicine

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Abstract. 3D printing technologies like Selective Laser Melting (SLM) or Electron Beam Melting (EBM) produce components of very complicated shapes from various kinds of materials. In this work a highly porous (porosity of almost 90 vol. %) stainless steel component was manufactured by SLM. The material was characterized in terms of structure, surface chemistry and mechanical properties. It was observed that mechanical properties of the material were similar to those of trabecular human bone. The tests realized in this work confirmed suitability of the porous material prepared by SLM for the use in medicine, for example, for scaffolds designed to repair bone defects.

1 Introduction

With the constant progress in development of biomaterials and availability of new technologies, regenerative medicine keeps achieving greater success. However, there are still many challenges that are hoped being overcome in the near future. One of them is the design of bone scaffolds and implants which would replicate the biomechanical properties of the host bones perfectly.

For the bone applications, especially metals have been used for many years. Among them, stainless steel, cobalt alloys and titanium along with its alloys are well established for permanent implants. These materials are biocompatible, have good mechanical properties and express high corrosion resistance in the body environment [1]. Such characteristics are very important and even fundamental for the use of biomaterials, but do not guarantee flawless operation of the final implant. Although mechanical strength of over-mentioned metals is high enough to bear physiological loading, much higher stiffness over natural bones is the main source of bone tissue loss and eventual implant failure. The extent of such negative influence depends especially on the difference in elastic moduli between natural bone and the implant material. When a bone is coupled with an implant, it begins to share its load-carrying capacity. As a consequence, the bone is subjected to reduced stresses, which is perceived as a stimulus for bone resorption. Such a phenomenon, termed ‘stress shielding’, was observed decades ago and since then scientists have been searching for possible solutions [2-4].

An effective method is to introduce porosity into bulk materials and change their relative density [5]. When damaged bone must be repaired or even replaced, porous metals present suitable candidates as their stiffness and porosity can be adjusted on demands. In case when pores are opened towards the implant surface and interconnected, metallic replacements also allow the bone tissue to grow into and, thus, accelerate the osseointegration process [6,7]. The fabrication of
porous metals has been studied intensively and many methods have been developed. Four main manufacturing routes - solid state processing, liquid state processing, vapor deposition and electron deposition – can be classified according to the state of matter in which the metal is processed. In addition, first two approaches cover tens of various methods, e.g. use of blowing agents, gas injection, powder metallurgy techniques, sintering of fibers etc. [8]. Despite a high number of available traditional techniques, only limited control over the internal architecture is provided. Although pore size and shape can be adjusted to some extent by the set-up of process parameters, pores distribution remains rather random [9]. However, current boom in additive manufacturing (AM) opens new horizons. Thanks to a layer-by-layer additive principle, complex structures that were impossible to be prepared by conventional techniques can be nowadays achieved [10].

New era in manufacturing is highly appreciated especially in the field of regenerative medicine, where newly prepared customized implants may already meet the increasing demands on implant performance [11]. Metallic materials satisfying requirements for mechanical load in the human body can be processed by several AM techniques among which selective laser melting (SLM) and electron beam melting (EBM) are the most widespread [12,13]. This paper is, therefore, focused on characterization of stainless steel 316L porous scaffold prepared by SLM which could potentially serve as a bone scaffold or an augmentation in the vicinity of joint replacements.

2 Experimental

Studied scaffold was prepared by selective laser melting technology using a M2 Cusing machine (ConceptLaser, Germany) equipped with 200W Yb:YAG fiber laser. As an input material a gas-atomized powder of stainless steel AISI 316L (Misan GmbH) with particle size in the range of 15-50 µm was used. An initial powder layer thickness of 30 µm was selected to be processed in a layer-by-layer manufacturing process. In each manufacturing step processing parameters were kept constant: laser power of 200 W, scanning speed of 200 mm s⁻¹ and hatching distance of 1 mm. With hatching distance set to 1 mm and cross-scanning strategy, a geometrically defined lattice structure was obtained. Final product (shown in figure 1) was in the form of 50 x 30 x 20 mm³ block and possessed square-shaped pores of an average size of 750 µm separated by 250 µm thick struts. The total porosity was determined to be 87 vol.%.  

![Figure 1. AISI 316L scaffold manufactured by means of 3D printing.](image)

Macrostructure and surface morphology of the produced scaffold were studied by scanning electron microscope TESCAN VEGA-3LMU equipped with an Oxford instruments INCA 350 EDX analyzer (SEM-EDX). Material microstructure was observed on metallographic cross-sections using an Olympus PME3 light microscope and SEM-EDX. Cross-sections were grinded up to P4000, polished on a diamond paste D2, final polished with colloidal alumina and etched electrochemically in 10 wt.% oxalic acid (6 V, 80 s).

X-ray photoelectron spectroscopy (ESCAprobe P, Omicron Nanotechnology Ltd. equipped with an Al Kα (λ = 1486.7 eV) X-ray source) was used to study the surface chemistry. To assess the influence of SLM technology, obtained surface was compared with a reference sample of AISI 316L steel produced conventionally by means of hot forging. The spectra were measured with an energy step of 0.05 eV and normalized to the adventitious carbon (C1s peak, 285.0 eV). NIST X-
ray Photoelectron Spectroscopy Database was used to evaluate chemical states of detected elements. Prior the spectroscopy measurement, the specimens were thoroughly cleaned with distilled water, ethanol and acetone.

Compressive tests were carried out on a LabTest 5.250SP1-VM universal loading machine to determine basic mechanical properties. Tests were performed at room temperature, with a strain rate of 0.001 s⁻¹, on three rectangular samples cut from the manufactured scaffold.

3 Results and Discussion

3.1 Scaffold macrostructure

Macrostructure of the manufactured scaffold is shown in figure 2. Struts thickness of about 250 µm corresponds to the laser beam spot diameter. Struts are inclined by 45° from the building direction. Every four struts enclose a square-shaped pore, altogether forming a structure with fully interconnected open porosity. In higher magnification (figure 2b) a joint where four struts converge is displayed. One can also observe the surface is not completely smooth, but is roughened by adhering spherical particles. These are indicated by white arrows in figure 2b. As the diameter of these particles falls into the range of the initial powder diameter (15-50 µm), it can be supposed it concerns unmelted particles which were sintered to the final product due to the thermal diffusion effects. As the inclined struts were partially built on the loose powder, particles below each layer were partially melted and bonded to its bottom [14]. Therefore, it can be noticed that the adhering particles prevail on the bottom part of the struts. Figure 2c brings a strut surface in detail. Arrows are pointing at arcs representing overlapping layers.

![Figure 2](image-url)  
**Figure 2.** Macrostructure and surface morphology of the SLM scaffold. Arrows in b) show unmelted powder particles and in c) overlapping layers.

3.2 Microstructure of SLM AISI316L stainless steel

Figure 3a represents a cross-section through 4 scaffold struts. Here, dark arcs can be also observed. The distance between these is about 80-150 µm, which significantly exceeds the powder layer thickness setting indicating that the material is melted also in several precedent layers and a strong interlayer bonding is formed. In agreement with other works [15-17], material exhibits microstructure typical for laser-treated austenitic steels that undergo rapid cooling. Austenitic grains are elongated in the building direction as they grew through several melted layers and possess very fine cellular-dendritic substructure (shown in figure 3b).
3.3 Surface chemistry

XPS analysis was carried out on SLM scaffold as well as hot forged reference for which the 316L stainless steel biocompatibility is well known. The aim was to assess changes brought about by the laser melting process and estimate if the observed changes may have negative effect on interactions with cells. Survey spectra for both materials are given in figure 4. Except from main constituting elements (Fe, Cr, Ni, Mo) adventitious carbon, oxygen and nitrogen were also detected. Binding energies declare that, in both cases, the surface layers are formed by a mixture of iron and chromium oxides particularly (Fe$_2$O$_3$, Fe$_3$O$_4$, FeCr$_2$O$_4$ and Cr$_2$O$_3$). The changes in surface composition induced by SLM process are shown in figure 5. Nickel and molybdenum were detected only in the passive oxidic layer of hot forged reference (in the form of NiO and MoO$_3$, respectively). Within SLM surface a strong enrichment in chromium was observed. Such an enrichment occurred due to a high affinity of chromium to oxygen at high temperatures induced by laser melting, as some oxygen residues remained in the protective argon atmosphere.

![Figure 3](image1.png)

**Figure 3.** a) Microstructure of the scaffold struts and b) cellular-dendritic substructure.

![Figure 4](image2.png)

**Figure 4.** Survey spectra for a) SLM scaffold and b) hot forged reference obtained by XPS.

From observed facts, it can be concluded that SLM should not exert any negative effect on biocompatibility. Although high Cr content could represent a toxic hazard, all the Cr is present in the form of chromium (III) oxide or chromite which are almost insoluble in the body environment and, conversely, play the key role in the stainless steels corrosion resistance.
3.4 Mechanical behaviour in compression

Compressive tests yielded stress-strain curves, one of which is given in figure 6. It exhibits a high level of plasticity, with compressive strain reaching $56.8 \pm 0.1\%$. A plateau in between 5 and 35% can be observed which is related to a high plastic deformation with only low increase in stress. Afterwards, a densification stage occurs, where the stress increases sharply. Such a phenomenon is often observed in case of highly porous metallic materials. It is caused by the collapse of struts followed by complete collapse of cells accompanied with compaction of the porous structure [18,19]. Table 1 summarizes mechanical properties subtracted from the curve. To illustrate the impact of porosity introduced into the material on its mechanical properties, table 1 also lists values achieved in our previous study [20] with nonporous AISI 316L stainless steel prepared equivalently by SLM technology under comparable conditions. Since the aim of this paper is to show if the studied scaffold is suitable for medical use, also a comparison with human bone is given.

![Figure 5](image-url)  
**Figure 5.** Surface chemical composition of SLM AISI 316L stainless steel in comparison with hot forged reference (only metallic elements included).

![Figure 6](image-url)  
**Figure 6.** Compressive stress-strain curve for SLM scaffold.

|                          | CYS (MPa) | UCS (MPa) | $\varepsilon$ (%) | $E$ (GPa) | Ref.   |
|--------------------------|-----------|-----------|-------------------|-----------|--------|
| **Scaffold**             | 3.01±0.13 | 10.6±0.6  | 56.8±0.1          | 0.15±0.03 | this study |
| **Compact**              | 497±24    | 981±20    | 18.1±6.1          | 187±5     | [20]    |
| **Cortical bone**        | ~170-193  | ~1.85-2.60| 7-27              |           | [21]    |
| **Trabecular bone**      | ~2.4-11.6 | ~0.1-0.4  |                   |           | [22]    |

*Table 1.* Mechanical properties in compression for SLM AISI 316L scaffold, compact material and human bone (CYS = compressive yield strength, UCS = ultimate compressive strength, $\varepsilon$ = maximal compressive strain, $E$ = Young’s modulus in compression).
4 Conclusion
By SLM technology AISI 316L stainless steel scaffold was successfully prepared. In this study, basic characterization was carried out. As mechanical properties in compression approached those for human trabecular bone and the surface chemistry seems not to negatively influence material biocompatibility, prepared scaffold appears to be a promising tool for bone defects repair.

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