RESEARCH ON INFILTRATING BIOCOMPATIBLE FILLERS TO PRODUCE COMPOSITE IMPLANTS

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Abstract: *This study evaluates the manufacturability of biocompatible composites and the adherence between the corresponding components. The composite materials consist of a metallic scaffold manufactured by Selective Laser Melting (SLM) from pure Titanium powder in which liquid biocompatible bone void fillers were injected. Two different types of materials were used : one based on hidroxiapatite, polymer and organic glass and the other on beta Tricalcium Fosfate and polymer. After solidification, a very good adherence between the titanium struts and the two biocompatible materials was observed.*
Key words: *lattice structure, bone void filler, selective laser melting, titanium, biocompatibility*

1. INTRODUCTION

The Selective Laser Melting (SLM) is one of the most spectacular technology, being among the few Additive Manufacturing (AM) processes, which allows to produce complex three dimensional (3D) parts made out of metallic powders. In some cases post processing operations are necessary onto the AM parts. In the last period, many researchers worked in developing some new technologies to produce scaffolds structures, as those porous skeletons provide preferential effect of promoting the bone ingrowth(Xiao et al, 2012). From the anatomical point of view, the outer geometry and the cell size has to be suitable to the bone defect area, for the individual patient, so that the customized implant could anchor to the healthy bone. The material for the implant needs to be designed to fulfill simultaneously multiple requirements: to be biocompatible, to have enough stiffness for loads bearings, but in the same time the necessary porosity. In many cases, the failure of the bone prosthesis solutions is caused by the stresses created due to the discrepancies between the mechanical characteristics of the bone and the implant. The bone tissues are basically natural composite materials, with variable architecture, complex structures with multiple functions and special properties. They are among most resistant components of the human body , but they could be seriously affected by the inadequate mechanical loads, with respect to the duration, way of acting or due to acute trauma, genetically or degenerative diseases, being necessary the replacement by different type of prosthesis. This situation appears often in day to day surgeries. These have a major impact onto the health and require a continuous effort to identify, develop and implement new techniques and mainly new materials, suitable for bone tissue reconstruction.

2. THE USE OF AM TECHOLOGIES TO PRODUCE CUSTOMIZED IMPLANTS

The current methods used up to now by the medical health services do not allow a complete reconstruction of all the anatomical functional and morphological characteristics of the native bone. In the last decade, the researches foreseen the obtaining of composite materials, polymer-inorganic with protein and cellular inserts. The purpose is that these composites should act as molds for bone ingrowth (Crane et al., 1995). The SLM is considered a viable alternative for achieving a precise control over the scaffolds architecture, the pore shape and especially interconnectivity, which is crucial for the bone ingrowth. In order to achieve this challenge, the structures must be manufactured from a biocompatible material and with high interconnected porosities, with a pore size in the range 100 - 700μm, porosity between 50% and 70%, compression strength >50Mpa (Otsuki et al, 2006). Titanium is the most biocompatible and corrosion-resistant metal, its elasticity modulus corresponds to the elasticity modulus of the bone more than any other metal does and for

this reason it can be used successfully for surgical implants.
In previous researches, the authors fabricated porous lattice structures in form of beams and cubes, with cell sizes in the range 0.5 – 1.2 mm. The corresponding porosities of the samples were in the range 51%-89 % (Mager et al., 2013).
The specimens were tested as following: beams at bending and cubes at compression. The flexure load at TS (Tensile Strength) and extension at TS were determined for the flexure tests, respectively the compression load for the compression tests.
The mechanical tests showed that by the increasing of the cell size, a decrease of the applied load appeared, together with an enhancement of the flexure extension. In particular, specimens with a cell size in the range 1-1.2 mm manifested an excellent flexibility by flexure tests.
The aim of the current research was to obtain a biocompatible composite material, based on a solid titanium scaffold, with a similar aspect to those of reinforced concrete.
To achieve this purpose, the novel idea was to fill up the empty gaps within the lattice structures built in the previous described manner with liquid biocompatible filler. We wanted to check, after solidification, the degree of adherence between the titanium struts and the injected biocompatible materials.
Through modifying the dimensions of the unit cell and filling different materials, we intend to obtain customized medical implants, which should possess improved mechanical characteristics, which should be adjusted according to the functional purpose of the reconstructed bone area, according to the age and the weight of the patient.

3. EXPERIMENTAL SET UP

This research included a case study, 50 discs with similar lattice structure and different porosities being manufactured, onto the MCP ReaLizer II SLM 250- at the Technical University of Cluj-Napoca/ROMANIA, illustrated in figure 1.
Commercially Pure Porous Titanium (CPPTi) powder was used, with a grain size distribution in the range 20 – 63 μm (TLS Technik GmbH-Germany). 80 W Laser power, 40 μm point distance (PD) and 50 μs exposure time (ET) as parameters for the machine and the ReaLizer Software were used.

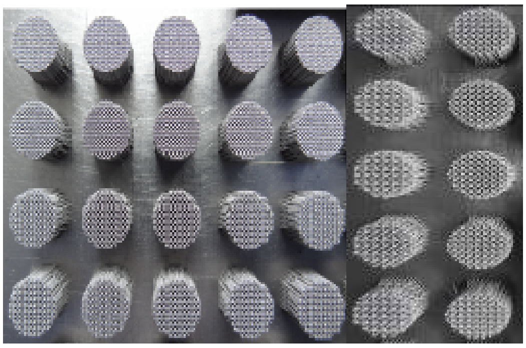


Fig.1. Discs with 5 different porosities, manufactured on the MCP Realizer II SLM 250

The dimension of each disc is Ø10 x 5 mm and the cell size unit is 0.6, 0.8, 1, 1.2, respectively 1.5 mm. In the Fig.2 is presented the used elementary cell- type (BBC= body-centered cubic).

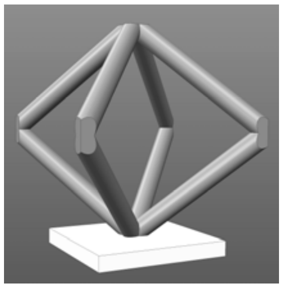
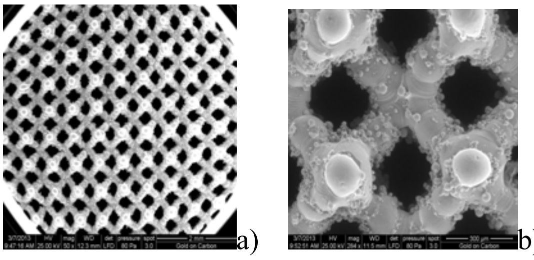


Fig.2. Topology of the BCC – unit cell

The porosity, calculated based on the relation-ship between the measured density of the samples and the material standard bulk density, is in the range 51 – 93 %, corresponding to the cell size unit-range 0.6 – 1.5 mm.
By the current fabrication of the samples, a special support structure was used (illustrated in the figure 3), which already proved their efficiency in our previous studies. Thus, the supports are built with a uniform distribution on the whole surface of the samples, taking over and transmitting in a proper manner the released heat towards the building platform and decreasing to the minimum the deformations which usually appear during the metal powder melting process.

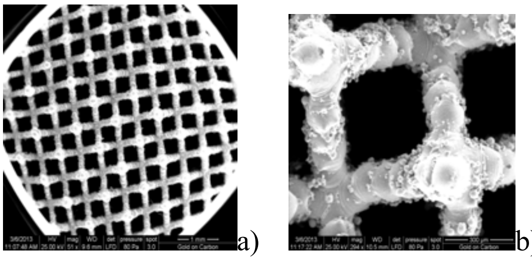
Fig.3. Supports for porous discs

In the Fig.4 and Fig.5 SEM images for the manufactured samples, with the cell size of 0.6 respectively 1 mm and different magnifies are presented. The images were obtained with the electronic microscope FEI Quanta 133 at the Chemical Institute from Cluj Napoca.



a) b)

Fig.4. Disc with cell –size 0.6 mm, before infiltration; a) 50x, b) 284x magnification



a) b)

Fig.5. Disc with cell–size1mm, before infiltration; a) 51x, b) 294x magnification

First step of the research was to manufacture the titanium porous discs onto the SLM –machine. Within the second stage of our research we infiltrated the disc frames with two different biocompatible mixtures, which were solidified by polymerization and become filled up discs. We cooperated with the Chemistry Insitute from Cluj Napoca, where there is a strong experience in developing biocompatible materials (Moldovan et al., 2007). The filler materials P1 and P2 where obtained by mixing A +B, respectively C+D components, there chemical composition being presented in table1.
The liquid solutions L1 and L2 were prepared sepparately in advance. The composition of L1 and L2 is presented in the table2. Different additives were added to L1 and L2, before L1 and L2 were mixed and solidified together.
The mixed composite materials were injected into the titanium disc frames, using syringes.

Table 1. Pastes composition

Paste	A	B	C	D
L1 [%]	74,07	-	71.43	-
L2 [%]	-	74.07	-	71.43
ßTCP [%]	25.93	25.93	-	-
TCP with chitosan [%]	-	-	14.29	14.29
HA-ZnO [%]	-	-	7.14	7.14
Glass with Sr [%]	-	-	7.14	7.14
Hardening time at 22°C [min]	P1=A+B 16		P2=C+D 10	

In table 1, the accronims are:
TCP = Tricalcium phosphate
HA = Hydroxylapatite

Table 2. Monomers composition

Monomers (liquids)	L1	L2
Bis-GMA [%]	70	70
TEGDMA [%]	30	30
DHEPT [%]	1	-
BHT [%]	0.035	0.035
BPO [%]	-	1.08
Hardening time at 22°C [min]	L1 + L2 11	

In table 2 , the accronims are:
Bis-GMA= Bisphenol A-glycidyl methacrylate
TEGDMA = Trietilenglicol dimetilacrilat
DHEPT = Dihydroxyethyl-P-Toluidine
BHT = Butylhydroxytoluene
BPO = Benzoyl peroxide
We produced anf infiltrated two separate discs for each of the 5 cell sizes, being 20 discs in total. We obtained in this way filled up discs based onto a pure titanium frame.

4.RESULTS AND DISCUSSION

After the final hardening, the titanium discs filled up with biocompatible composite materials, were polished manually, in order to be analised under the EM . Figures 6, 7,8 and 9 ilustrate the SEM images of the infiltrated discs, with different magnitudes. We produced and analized many samples using the described method. Two examples were selected and are presented in this paper, for a disc with a cell size of 0.6 mm, infiltated with P1 composite material and for the second with a cell size of 1 mm infiltated with P2 mixture.
It can be observed a good adherence of the fillers to the titanium skeleton, in both cases. Many pores could be observed within the structure of the fillers, due to the small air bubbles traped, because the infiltration process could not have been done under vacuum, due to technical difficulties.

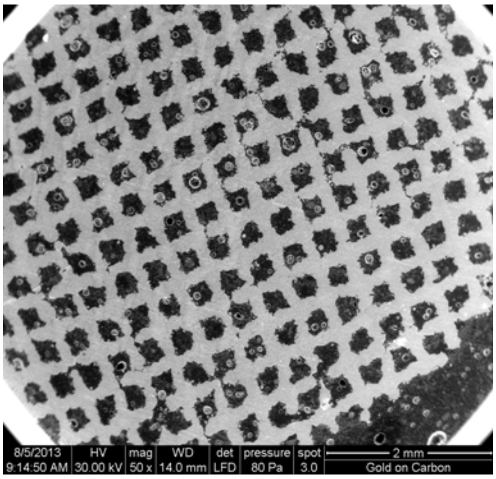


Fig.6. Disc with cell –size 0.6 mm, after infiltration with paste P1; 50x magnify

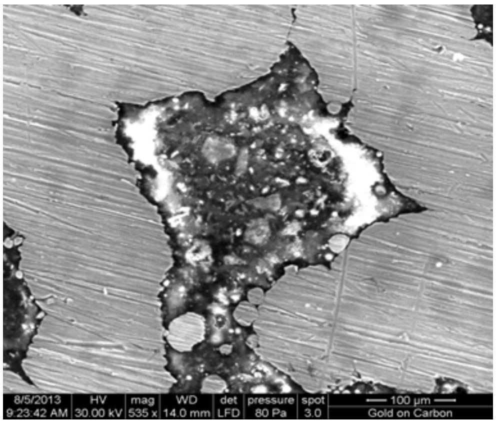


Fig.7. Disc with cell –size 0.6 mm, after infiltration with paste P1; 535x magnify

5. CONCLUSION

A good adherence could be obtained between the titanium frames made by SLM and the biocompatible composite materials fillers, which were injected as liquid mixtures and solidified by polymerization in between the titanium porous implants.

Further research should improve the infiltration technology, to be done under vacuum, in order to avoid the small but many air bubbles trapped within the fillers structure.

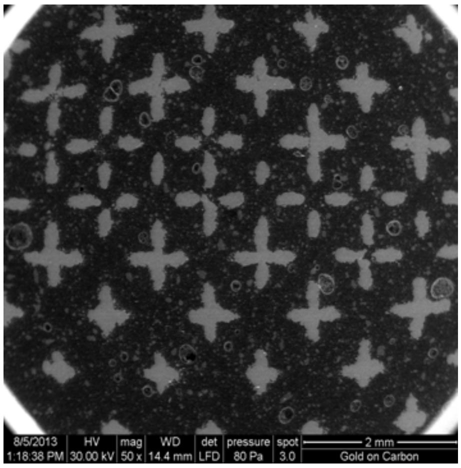


Fig.8. Disc with cell –size 1 mm, after infiltration with paste P2; 50x magnify

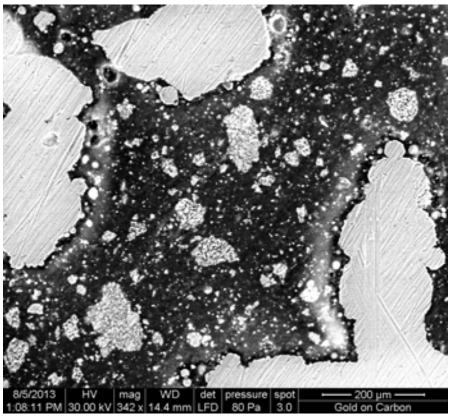


Fig.9. Disc with cell –size 1 mm, after infiltration with paste P2; 350x magnify

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