MICRO-COMPUTED TOMOGRAPHY OF INTERCONNECTED β-TCP - Mg COMPOSITES OBTAINED BY CURRENT ASSISTED METAL INFILTRATION

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Abstract

Magnesium and calcium phosphates composites are promising biomaterials to create biodegradable load-bearing implants for bone regeneration. The present investigation is focused on the design of an interpenetrated magnesium - tricalcium phosphate (Mg-TCP) composite. In this study, TCP preforms were 3D-printed with a tip of 250 µm in aperture. Final preforms with parallel grids and internal pores of 150, 350, 500 and 1000 µm were obtained and sintered at 1100 °C for 5h. Later, the infiltration with commercial pure Mg was performed using a novel Current Assisted Metal Infiltration (CAMI) technique, which allows an effective and fast infiltration of brittle ceramic preforms with molten metal. Fast melting and final solidification of the Mg-TCP composite were achieved with the assistance of a pulsed electrical current as heating resource. The effect of pore size on the infiltration was analysed by X-ray computed microtomography (µCT). Virtual tomographic reconstructions were used to observe the components distribution and the remaining porosity of the composite after the infiltration. Results show a good penetration of the metal into the TCP preforms. Nevertheless, fracture of some TCP structures after the infiltration was observed, mainly in the preforms with a pore size of 150 µm. Some porosity after infiltration was registered, however, it does not exceed 5 % of the total volume of the specimen.

Keywords: Magnesium, tricalcium phosphate, current assisted metal infiltration, micro-computed tomography

1. INTRODUCTION

With the development of functional composites for the use in different areas of the science and technology, the necessity of novel processing techniques for their manufacture is constantly rising. Conventional methods of manufacture of metal-ceramic composites include such methods, as powder processing through chemical reactions, mechanical mixing of the components [1-3], or conventional infiltration process based on filling the existing open porosity of a structure (preform) with a second material, usually a molten metal [3, 4]. In contrast to them, with the development of the additive manufacturing techniques [5, 6], controlled pattern preforms with a homogenous distribution and equal size of pores can be obtained and later infiltrated with a second phase to get an interconnected composite with a controlled distribution of the phases [3, 6]. For the infiltration, there are several approaches nowadays, and among them, the Current Assisted Metal Infiltration (CAMI) is of greatest interest since it allows molten metal infiltration with the help of electric current as a heating resource [7].

Furthermore, characterisation of the obtained interpenetrated composites could represent a challenging issue, however, with the development of new techniques like X-ray computed microtomography (µCT), the analysis of the infiltration degree of the materials can be carried out without damaging the material. µCT allows getting phase distribution of the components [8], making easier the chemical and microstructural characterisation of composites with further simulation of their mechanical properties.

In biomaterials, functional composites are of great interest for tissue regeneration [9]. Currently, calcium phosphates porous scaffolds made of tricalcium phosphate (TCP) are studied and used in orthopaedic applications due to their similar chemical composition to the mineral phase of the bone that gives them a good osseointegration [10]. Infiltration of calcium phosphate preforms with non-toxic metal represents a novel alternative to increase the mechanical properties of such structures and to create a new generation of functional biomaterials. Magnesium (Mg) and its alloys are excellent candidates for the elaboration of functional composites with calcium phosphates, due to proper biodegradability and mechanical properties close to certain kind of bones in the human body [11].

Therefore, the main purpose of this research was the development and processing of functionally interpenetrated β-TCP - Mg composite, and its characterization using µCT for 3D imaging reconstruction. The β-TCP - Mg composite was produced using initial robocasting of grid-like cylindrical preforms with a different internal macro-pore size, which was followed by the infiltration of sintered preforms with a commercial Mg powder by means of CAMI technique. A special focus was put on the assessment of the effect of the pore size on the infiltration degree and the analysis of the integrity of ceramic preforms in the infiltrated composite by means of µCT.

2. MATERIALS AND METHODS

2.1. Robocasting of β-TCP paste

In order to produce an injectable paste, commercial β-TCP powder (VWR Chemicals, Belgium) and 30 wt. % Pluronic F 127 (Sigma Aldrich, Germany) solution in distilled water were homogeneously mixed at a ratio of 0.6 (grams of powder per millilitre of pluronic solution) to make a paste able to pass through a tip with an aperture of 250 µm. Following robocasting of the paste using a direct ink writing system (Optimum® syringe barrels, Nordson EFD) was performed in order to build porous cylindrical preforms with the outward size of 7.5 mm in diameter and 15 mm in height (see **Figure 1a**). The porous structure of the preforms followed an orthogonal filling, doing a parallel grid in each circular layer of the cylinder, and varied in the pore size, i.e., 150, 350, 500 and 1000 µm. The robocasting was accomplished at room temperature at a speed of 8 mm/min. Later, the robocast preforms were dried at room temperature for 24 hours and after then, sintered at 1100 °C for 5 hours using a furnace (LH30/13, LAC, Czech Republic) to get the consolidation of the preform (**Figure 1b**).

2.2. Current Assisted Metal Infiltration, CAMI

Current assisted metal infiltration and consolidation of β-TCP - Mg specimens were conducted in a one-step process using a commercial SPS apparatus (Dr. Sinter 1050, Japan) with a special graphite mould designed for the infiltration, which consisted of two cylindrical chambers connected together by a reduced area (see **Figure 1c**). Prior to the infiltration procedure, 5 grams of pure pre-compacted Mg powder (Riedel de Haen S030195, Germany) were put into the upper chamber of 20 mm in diameter and of 20 mm in height, while the robocast β-TCP preform was placed into the lower chamber of the mould with a diameter of 10 mm and 20 mm in height. The mould was set inside the SPS machine, and the CAMI procedure was carried out at 670 °C in order to ensure the melting of magnesium (T_m = 650 °C) and to improve the fluidity of liquid Mg to infiltrate the porosity of the preform. A heating rate of 100 °C·min^{-1} was used to reach the infiltration temperature, at which the dwelling of 1 minute was maintained. A load of 1 kN (3.2 MPa) was applied to close the electric circuit. This load was borne by the Mg pellet and not by the ceramic preform due to the section with the reduced area and localisation of the preform inside the graphite mould. The infiltrated cylindrical samples had the dimensions of 10 mm in diameter and a variable height of around 20 mm.

2.3. 3D imaging reconstruction and microstructural characterisation

The volume of each of the phases, their distribution and the remaining porosity in the infiltrated β-TCP - Mg composite were analysed using 3D imaging reconstruction by micro-computed tomography (μCT) instrument (GE phoenix v|tome|x L 240) and VG Studio MAX 2.2.6 software. The analysed area delimited by the β-TCP preform was presented inside of the Mg screw-like sample (see **Figure 1d**), which was obtained after the CAMI. The degree of infiltration was calculated and expressed in percentage by means of the porosity volume before and after infiltration. The initial porosity in the preforms was assumed as the 100 % volume to be infiltrated and the remaining porosity after the infiltration was set as the lacking percentage to reach the full infiltration. The imaging reconstruction was supported with the microstructural and chemical analysis using scanning electron microscopy (SEM, LYRA3 XMU, TESCAN) and X-ray diffraction analysis (XRD, Rigaku SmartLab 3kW) on the samples, which were longitudinally cut and successfully polished with P800-P2000 grit SiC papers and 1-μm diamond suspension.

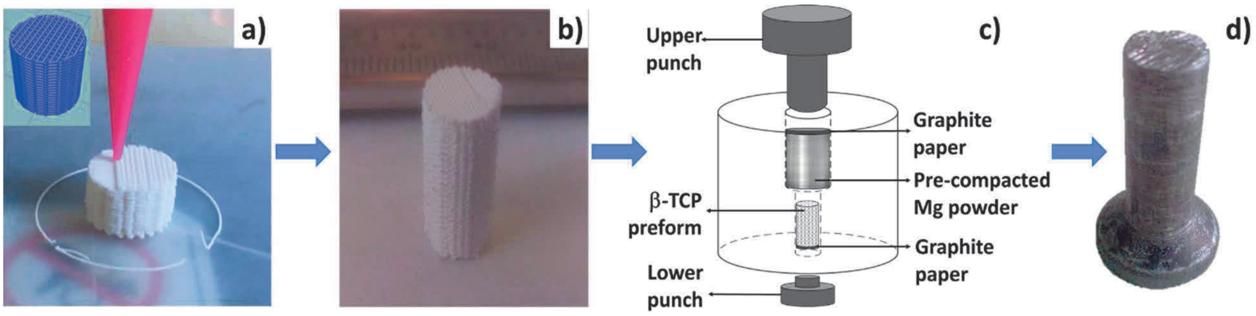

Figure 1 Methodology process for production of β-TCP - Mg composite. a) the appearance of the robocasting process of a cylindrical preform carried out using the computer model (presented in the left upper corner), b) sintered preform with a 150-μm-pore size, c) mould design and arrangement for CAMI process, and d) screw-like β-TCP - Mg composite obtained by CAMI

3. RESULTS AND DISCUSSIONS

Figure 2a shows typical appearance of the printed and sintered preforms with a pore size of 150 μm. After sintering, β-TCP strands presented a characteristic microstructure for tricalcium phosphates (**Figure 2b**). SEM examinations of the scaffold surface revealed homogeneously distributed micropores with an average size below 5 μm in all the scaffolds (**Figure 2c**).

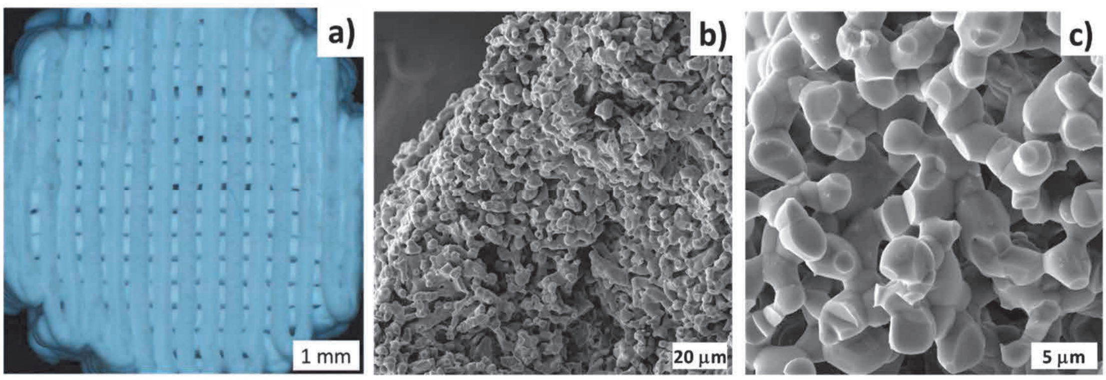

Figure 2 a) Typical appearance of a β-TCP preform with a 150-μm-pore size (light microscopy), b) representative microstructure of the sintered β-TCP strands, and d) detailed micrograph of the microporosity in the β-TCP strands of the robocast preforms.

Typical imaging reconstruction analysis of the quality of the infiltration in the interconnected β-TCP - Mg preforms by means of μCT shows the differentiation of the coexisting phases in the composite, where the metallic (Mg), ceramic phase (β-TCP), and the remaining porosity (locked air) were identified (**Figure 3**) and coloured in green, yellow and blue colours, respectively. Moreover, μCT technique also allows to obtain the longitudinal and transversal cuts of the 3D-computed reconstructions, where the effect of inner stresses generated during the infiltration process on the integrity of the ceramic preform could be analysed (**Figure 3**).

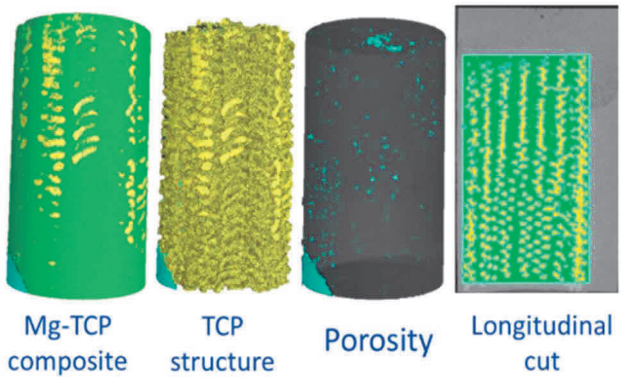

Figure 3 3D imaging reconstruction and phase differentiation for the infiltrated β-TCP - Mg composite obtained using a β-TCP preform with 500-μm-pore size

Analysis of the porosity shows that the larger the pore size, the better infiltration of the ceramic preforms together with a better preservation of the β-TCP preform shape. Samples with a pore size of 1000 μm presented the highest infiltration degree with a 97.5 % of infiltrated volume, followed by the scaffolds with 500-μm pores (96.3%). Higher remaining porosity was found in the samples with a pore size of 350 μm and 150 μm, exhibiting an average value of infiltration degree of 95.6 and 95.5 %, respectively (**Figure 4**).

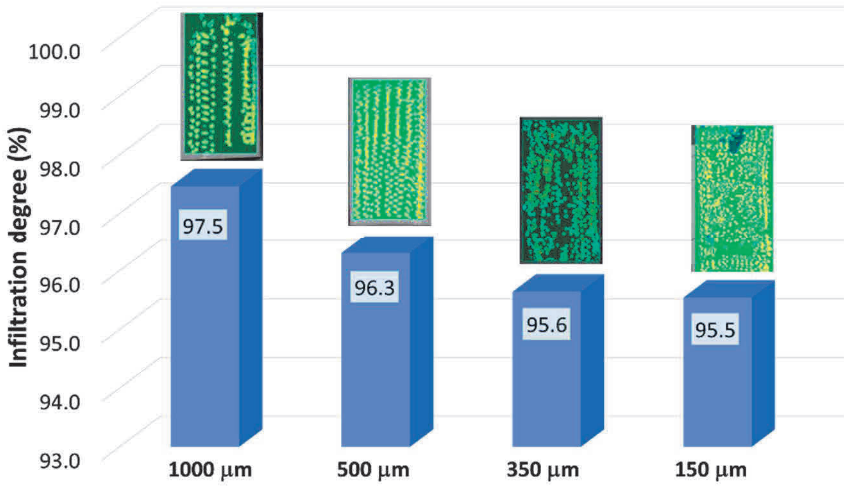

Figure 4 Average infiltration degree in the β-TCP - Mg composite depending on the pore-size of the initial preforms

The occurrence of the porosity during the infiltration can be connected with the difficulty of the molten Mg to penetrate and fulfil the pores of the ceramic preforms, which may also lead to their partial destruction if the molten metal exerts too high pressure to the β-TCP bodies. **Figure 5** shows the computed reconstruction and separation of the phases for one characteristic sample of each pore size in the ceramic preforms. Also, **Figure**

5 presents one longitudinal cut for each sample, where a clear evidence of the effect of the pore size in the restriction of the infiltration by the Mg is observed. Samples with a small pore size, i.e., 150 and 350 µm, tend to have more porosity after CAMI, which can be linked to a higher resistance for molten Mg to penetrate the pores. Therefore, they present higher tendency to lose the integrity of the porous preforms and to get destroyed during the infiltration in comparison with the preforms with a pore size of 500 and 1000 µm, where the initial structure is generally preserved in all the samples and the degree of infiltration is higher.

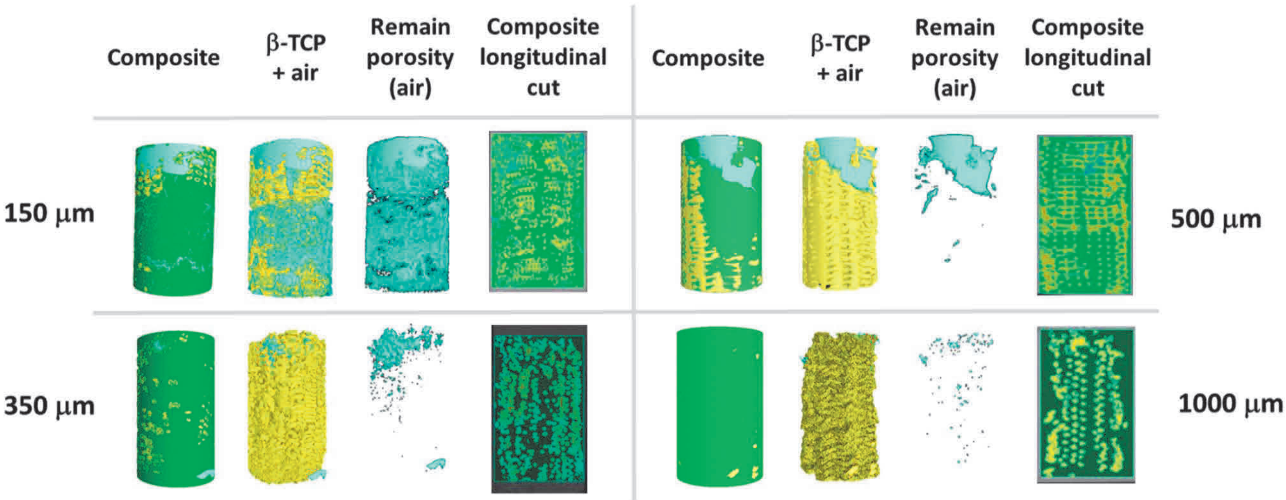

Figure 5 µCT reconstruction of Mg-infiltrated β-TCP preforms with different pore size

Finally, the results of the microstructural characterisation of the β-TCP - Mg composite are presented in **Figure 6**. X-ray diffraction analysis of the composites determined the occurrence of a chemical reaction between the β-TCP and Mg, leading to the formation of intermetallic compound characterised as $CaMg_2$ (reach in Mg). This phase is commonly precipitated in the Ca-Mg system [12]. While the ceramic phase remained chemically as β-TCP, the presence of magnesium oxide was registered, even though the infiltration by means of CAMI is performed under vacuum (**Figure 6a**).

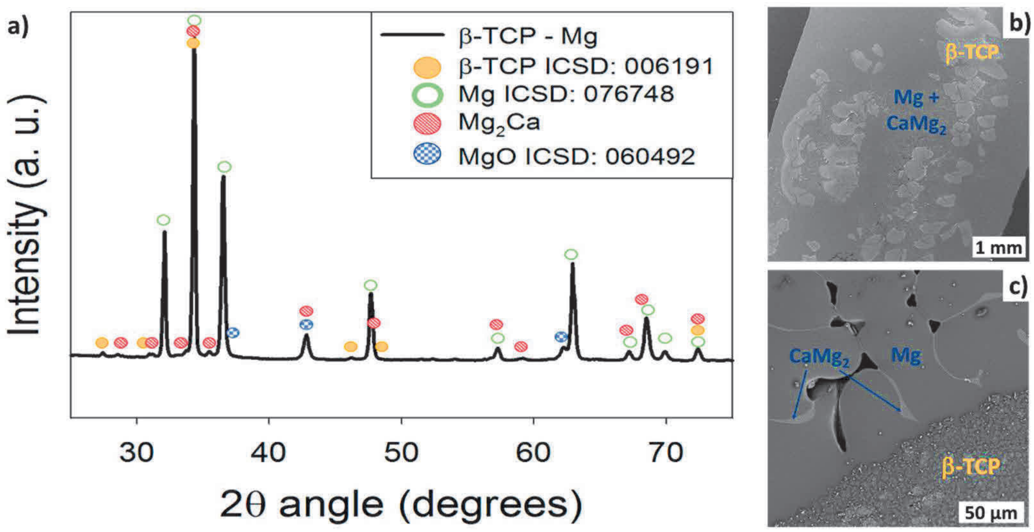

Figure 6 a) Representative X-ray diffraction pattern of the β-TCP - Mg composite obtained by CAMI, b) SEM micrograph of the composite microstructure, and c) the detailed view of the β-TCP - Mg interface

Figure 6b shows an overall view of the microstructure of the β-TCP - Mg composite. Some of the β-TCP strands, observed in the way of islets, are labelled in the picture and recognised by the light grey phase in the micrograph, meanwhile, the metallic Mg phase is surrounding the ceramic islets. A detailed view of the β-TCP - Mg interface is showed in **Figure 6c**, the presence of the intermetallic $CaMg_2$ phase is indicated. The observed porosity is attributed to delamination of the $CaMg_2$ phase during the metallographic preparation. An important fact that can be clearly detected in this micrograph is the presence of Mg in the micropores of the β-TCP strands, which were previously showed in the microstructure of the ceramic preforms (**Figure 2c**).

4. CONCLUSION

In the present study the interconnected β-TCP - Mg composites were successfully obtained by using the novel current assisted metal infiltration (CAMI) technique, which represents a prospective technology to infiltrate porous ceramic preforms. The pore size and the microstructure of the preforms play an important role in the infiltration process and the final microstructure of the composite. β-TCP porous preforms with the pore size larger than 350 μm did not perform high resistance against the infiltration by molten Mg, nevertheless, due to the chemical compatibility between the components, it is possible to fill some micro-porosity around the 5-μm size.

μCT is a novel technique for the characterisation and differentiation of phases in interconnected composites. The calculation of the volume of the analysed area allows to determine the percentage of phases, therefore, in infiltration process, the degree of the penetration of a phase into another can be easily measured. From the obtained results, CAMI allows a decent infiltration for a wide range of pore sizes with the infiltration degree above the 95% for all composites studied.

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