

Tricalcium Phosphate - Magnesium Interface: Microstructure and Properties

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Abstract. The fabrication of a composite material based on magnesium (Mg) and tricalcium phosphate is reported in this work. Rods of β -tricalcium phosphate (β -TCP) were processed and consolidated together with pure Mg powder through spark plasma sintering (SPS). The microstructure at the interface, the chemical composition and transformation of the components and the microhardness were analysed. The microstructure of the composite shows two zones with well-defined and continuous interface between them: a ceramic zone composed by β -TCP filled with Mg and the metallic zone constituted by Mg and Mg rich eutectic. Vickers hardness shows the excellent mechanical interaction between the two zones.

Introduction

Calcium phosphate biomaterials, such as β -tricalcium phosphate (β -TCP), has been widely used as bone substitute material in clinic applications because of their excellent biocompatibility [1]. Unfortunately, its poor mechanical behaviour limits its use for bone regeneration in load-bearing sites [2]. Recently magnesium (Mg) and its alloys have been attracted attention as biodegradable implants, as they have similar mechanical properties to natural bone [3,4].

The inconvenient of Mg and its alloys is the low corrosion resistance in body fluids. In this field, several researches have been focused in the coating of Mg bodies mainly with calcium phosphates, in order to improve the corrosion resistance [5,6]. In those studies, the physical, chemical and biological characterisation of the composite materials have been reported [6-8]. Nevertheless, into the knowledge of the authors, the interface between the calcium phosphate and Mg phases has not been extensively analysed.

Considering that the interface in any composite material is one of the most important features due to all the interactional phenomena take place in this region, the present study is focused in the characterization of the interface between β -TCP and Mg. To this end, β -TCP-Mg composites were consolidated through spark plasma sintering at 670 °C. The interface β -TCP - Mg has been analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and also the microhardness testing has been performed, either, in the metallic or ceramic component, or the interface between them.

Experimental Procedure

Materials. Pure β -TCP powder (VWR Chemicals, Belgium) was mixed with a binder (Pluronic F-127, Sigma Aldrich, Germany) for its extrusion into rods (250 μ m in diameter and 5 mm in

length). After that, the rods were sintered at 1100°C per 5 hours and placed together with pure Mg powder (Riedel de Haen S030195, Germany) inside of a graphite die for its consolidation.

Sintering conditions. Consolidation of TCP-Mg specimens was conducted using a commercial spark plasma sintering (SPS) system (Dr. Sinter 1050, Japan). The sintering temperature was set up at 670 °C in order to melt the Mg powder without thermal degradation of β -TCP. A heating rate of 100 °C·min⁻¹ was followed till reaching the sintering temperature under vacuum (15 Pa), in which, a holding time of 3 minutes was sustained. No load on the specimens was applied during sintering and the final dimensions of the consolidated specimens were 10mm in diameter and 20mm in length.

Characterisation. Sintered β -TCP-Mg cylinders were cut longitudinally and polished with SiC paper and diamond suspensions till 1-micron finished. The microstructure of polished surfaces was characterized by SEM (LYRA3 XMU, TESCAN). The Vickers hardness of polished samples was measured using a Vickers pyramidal microhardness indenter (STRUERS DuraScan-70), using 300 g of load for 10 sec. Minimums of seven measurements were practiced on each region of the samples, and the average was used to report Vickers hardness in MPa. XRD analysis was conducted on a Rigaku SmartLab 3 kW apparatus, using Cu-radiation to follow any phase transformation or reactions between the ceramic and metallic components.

Results and Discussions

The microstructure of the β -TCP – Mg composite revealed two main areas along the specimen (see Fig. 1). One area corresponds to the ceramic phase, composed mainly by β -TCP rods with metallic Mg inside its micropores. The microstructure of Mg inside β -TCP rods seems to correspond to pure Mg or solid solution of Ca in Mg (Mg can dissolve around 0.82 atomic % of Ca [9]). However, this could not be corroborated by EDS, because the minimum area that can be analysed with our system was larger than the size of this phase in the microstructure. The second area in the microstructure corresponds to the metallic phase, presenting pure Mg and Ca + Mg islets. More detail microstructural analysis of the islets reveal that are composed by pure Mg and Mg-CaMg₂ eutectic phase. Probably the CaMg₂ intermetallic was formed by partial dissolution and diffusion of Ca from the β -TCP component. In fact, the binary system Mg – Ca presents two eutectic points, the Mg-rich eutectic point is placed at 10.5 atomic % of Ca and 516.5 °C (eutectic melting point) [9]. Therefore, the formation of this eutectic during spark plasma sintering condition used in this work is thermodynamically feasible.

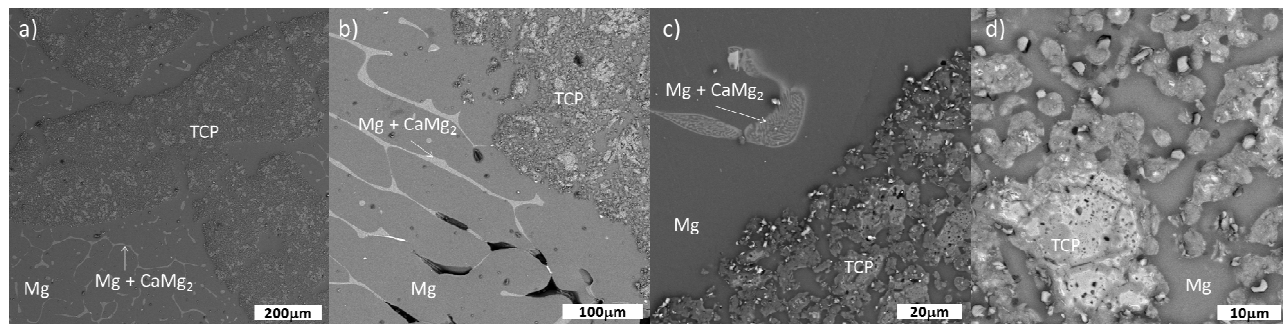


Fig. 1. Representative SEM pictures of β -TCP – Mg composite, after being consolidated by SPS during 3 min at 670 °C, under vacuum. In a) an overall view of the composite is showed, where ceramic and metallic components can be localized along the sample. In pictures b) and c) a detail of the interface between the Mg and the β -TCP is observed, revealing the presence of porosity in the metallic phase and also, the presence of the eutectic microstructure (Mg + CaMg₂). d) It is a detailed picture from the ceramic phase, the presence of Mg inside of the small porous of the β -TCP rod can be appreciated.

The XRD analysis of the consolidated β -TCP – Mg composites (Fig. 2) corroborate the presence of the CaMg₂ intermetallic observed by SEM. It may be expected that the loss of Ca can lead on the partial phase transformation into other calcium phosphates or the decomposition of β -TCP.

Nevertheless, no characteristics pics of other phases were found by XRD. It is probable that ionic exchanges occurred during sintering leading on the substitution of Ca with Mg in the β -TCP crystalline lattice. In fact, Mg is considered as a stabilizer of the beta phase of tricalcium phosphate [10]. On the other hand, although the vacuum process, a partial oxidation of Mg was observed.

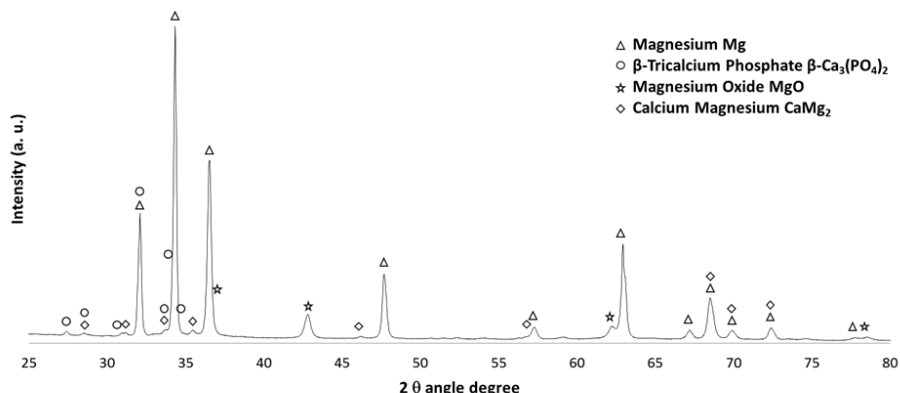


Fig. 2. XRD patterns of β -TCP – Mg composite after being consolidated by SPS during 3 min at 670 °C, under vacuum.

The interface between the metallic and ceramic components was well defined in the microstructure (see Fig. 1 b and c). The trabecula forming the β -TCP rods define a clear boundary between β -TCP and Mg. Nonetheless, Mg penetrates into the ceramic filling its micropores. In other words, Mg forms a continue matrix that envelops the β -TCP rods but as well infiltrates into the rods. The penetration of Mg in β -TCP microporosity produced a good contact between the two components. This can represent a significant advantage from the mechanical point of view, because the metallic component can tough the ceramic component, leading on improved mechanical strength respect the metallic component in close contact with the ceramic but without penetration in its microstructure.

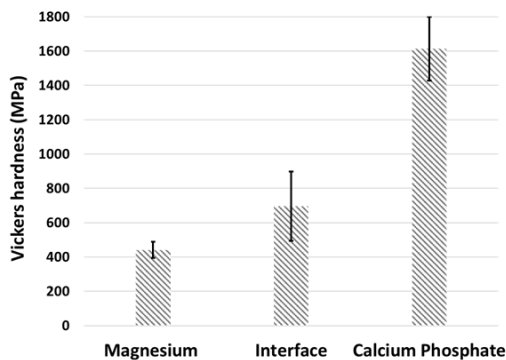


Fig. 3. Vickers hardness of β -TCP – Mg composite in the three different points: ceramic, metallic and the TCP – Mg interface. Bars indicate the standard deviation of the experimental data.

The hardness of the composite was measured in the ceramic and metallic areas as well as in their interface. The results are shown in Fig. 3. The highest hardness corresponds to the β -TCP component with average of 1614 MPa. Besides, no cracks propagation in the ceramic part has been perceived, this can be also attributed to the presence of Mg in the microporosity of the β -TCP rod. In contrast, the lowest hardness corresponds to the Mg component with an average value of 441 MPa (44.9 HV). In this case, the experimental hardness is a little bit higher than the one reported for pure Mg (around 40 HV, 392.3 MPa) [11]. An intermediate hardness, average value of 695 MPa, was measured in the β -TCP – Mg interface, showing a mixed mechanical behaviour but as well a good mechanical contact between ceramic and metallic components of the composite. The

higher standard deviation in hardness were observed for the interface and the β -TCP component. This behaviour is assigned to the microstructure of β -TCP rod with pores of heterogeneous size filled with Mg, which jeopardize the result depending on the area in which the hardness measurement was performed.

Conclusions

The microstructure of the β -TCP – Mg composite revealed two zones with well-defined and continuous interface between them: a ceramic zone composed by β -TCP filled with Mg and the metallic zone constituted by Mg and Mg rich eutectic. The formation of this eutectic is ascribed to Ca diffusion from the β -TCP rods. Vickers hardness corroborate the excellent mechanical interaction between the two zones. Besides, no crack propagation in the ceramic zones was observed during indentation, due to the presence of Mg in the microporosity of the β -TCP.

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