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Influence of MgO doping in hot-pressing tricalcium phosphate

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Abstract. Tricalcium phosphate ceramics (TCP) has been widely investigated. The main advantage of this bioresorbable ceramic is its bioresorbable behavior. The factor that still limits the application of these materials as temporary implants is the low strength resistance of the TCP sintered material. The tricalcium phosphate presents an allotropic transformation β to α phase around 1250 ºC that degrades its resistance, limiting the sintering temperature of the compacted samples. The objective of this work is to study the physical and mechanical properties of hot-pressed tricalcium phosphate with MgO additions. The results obtained have shown that the hot-pressed process increases significantly the mechanical properties of TCP materials. The addition of MgO has not improved the sintering process and the properties of hot-pressed tricalcium phosphate.

1. Introduction

Tricalcium phosphate biomaterial (TCP) has a good potential to be used for bone implant applications, owing its bioactivity, high solubility and high bioresorption rate. The sintering behavior of TCP (Ca₃(PO₄)₂) has shown to be dependent on some factors such as the processing method and the resulting microstructure, the presence of additives and of crystal structures (α or β) [1-3]. The formation of α-TCP phase at sintering temperatures higher as 1200 ºC causes micro-cracks, reducing significantly the strength of the sintered material and making the α-TCP the main crystalline phase to be used for implant applications. Several studies have been developed in order increase the high-temperature limit of the β domain, producing a denser material and to improving the mechanical properties of α-TCP [4-13]. It is difficult to densify β-TCP ceramics because high densification requires high temperatures, but a high temperature induces the β→α phase transformation.

The incorporation of additives such as MgO, Al₂O₃, CaO, SiO₂ and TiO₂ into TCP has not improved the densification process and the mechanical properties [4-8, 13]. Contrary to that, some works report that the presence of some metal oxides causes an increase of the flexural strength [8,9]. The improvement observed can be basically attributed to: a) promotion of the densification due the formation of a liquid phase b) the stabilization of α-TCP phase at higher temperatures and also c) the small size of the tests samples. Mn-containing β-TCP was also investigated [15,16]. The incorporation of MnO has improved the densification process of the TCP matrix [15]. EPR spectroscopy analyses indicated that the Ca site in the TCP structure is occupied by Mn²⁺ [16]. Magnesium oxide is an efficient additive to increase the high-temperature limit of the β-TCP phase [7]. This study has shown that a new compound Ca₃Mg₆(PO₄)₁₂ is formed below 1175 °C when more than 0.6 mol of MgO to 1 mol P₂O₅ is incorporated into the phosphate. Calcium phosphate apatites with variable Ca/P atomic ratio was investigated [5]. This research showed that a high amount of β-TCP is detrimental to the densification and mechanical properties [5]. Although a phase diagram for the TCP-MgO is not available in the literature, an analysis of the corresponding Ca₃(PO₄)₁₂-Mg₆(PO₄)₁₂ diagram revealed the formation of a liquid phase at temperatures as low as 1120 °C and no presence of MgO single phase [17]. The phase diagram indicates that substitution of Mg to Ca leads to the formation of MgO-TCP phase (Ca₃Mg₆(PO₄)₁₂). The mechanical properties of TCP materials are governed basically by two parameters: porosity and grain size. Studies have shown that is difficult to densify TCP bodies because
a grain growth occurs during the sintering process and that the temperature is limited by the $\beta \rightarrow \alpha$ transformation. Hot pressing method allows enhancing the densification at lower temperatures, producing dense specimens and reducing the grain size growth.

As innovation, this work investigates the influence of MgO addition and hot-pressing method on the densification and mechanical properties of TCP material, with the objective to improve the final properties of tricalcium phosphate.

2. Experimental Procedure

A commercially available tricalcium phosphate powder ($\beta$-TCP) with an average particle size of 3.61 microns was doped with MgO content ranging from 0.5 to 5 wt. %. The chemical composition of the TCP was obtained by X-ray fluorescence (Shimadzu EDX 700). The tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and the MgO powders were mixed in a ball mill and uniaxially hot pressed at 1070 °C in a argon atmosphere under a load of 30 MPa. Water absorption and porosity values of the sintered samples were calculated by using the Archimedes water displacement method, as specified by the European standard EN 99. Crystalline phases were identified by X-ray diffraction (Shimadzu XRD 600) in the 2θ range of 15 to 45 ° with a scanning rate of 2° min$^{-1}$. The strength values (average of five bodies for each value) were evaluated in three-point bending tests on a 20 mm span at a constant cross-head speed of 0.4 mm /min$^{-1}$. The microstructure of the sintered specimens was revealed on a polished surface by chemical etching the TCP material with phosphoric acid ($\text{H}_3\text{PO}_4$).

3. Results and Discussion

The TCP raw material is constituted basically by $\text{Ca}_3(\text{PO}_4)_2$, showing also a high MgO content (0.425 wt.%) and minor amounts of SiO$_2$ and Na$_2$O. Figure 1 depicts the shrinkage behavior of pure and added TCP. The results from the dilatometric tests indicate that the presence of MgO did not change significant the dilatometer behavior of the TCP material, suggesting that the presence of magnesium oxide did not contributed to the densification process of TCP. This behavior indicated that the added MgO content did not form a liquid phase. The pressureless sintering process of this material may take place at sintering temperatures higher as 1200 °C. Figure 2 shows the X-ray diffraction pattern of TCP + 5 wt. % MgO. The X-ray analysis show only the presence of $\beta$-TCP phase, suggesting that the amount of 5 wt. % MgO is presented as a solid solution in the TCP material. The presence of $\text{Ca}_3\text{Mg}_3(\text{PO}_4)_4$, suggested in the $\text{Mg}_2(\text{PO}_4)_2-\text{Ca}_3(\text{PO}_4)_2$ diagram phase [17] or other crystalline phases were not detected, indicating that the solid solution limit of MgO in the TCP was not reached. Recent work has showed that the substitution of 50% of calcium by magnesium results in the formation of the brushite phase [18]. Figure 3 shows the effect of the incorporation of MgO on water absorption and porosity values of hot-pressed TCP. The hot-pressed method has produced dense samples. As can be seen, the incorporation of MgO was produced specimens with higher porosity and water absorption values, especially for the highest TCP + 5 wt.% MgO. The observed porosity value of TCP is considerable superior as compared to sintering pressureless process (10-20 %), overlapping the effect of the additive. Figure 3 also indicates that the presence of MgO do not improve the sintering process as observed in others works for pressureless sintering [4,7,14]. Figure 4 shows the dependence of the hardness and flexural strength on the MgO content. The addition of MgO content degrades the properties of TCP doped material. The TCP with 0.5 wt. % shows practically a slight influence on the strength has compared to pure TCP. Higher MgO content causes a marcant drop of the strength and hardness, showing the TCP + 5 wt. % a strength and hardness decrease from 150 to 30 MPa and from 6.1 to 4.3 GPa, respectively. The decrease of the mechanical properties is in agreement with the measured physical properties (figure 3). It can be emphasized that the strength of hot-pressed observed in this work shows a standard deviation of about 14% and is considerable superior as the
similar pressureless sintering TCP material [15]. The difference founded between the various investigations can be associated to: a) sample size  b) tests (three or four points) and c) superficial condition. The three-point bending strength values founded in this work is comparable to the hot-pressed calcium phosphate [5] and significant superior to the β-TCP produced by gel-casting method (σ≤ 20 MPa) [13]. Calcium phosphate samples have showed strength values ranging from 50 to 150 MPa, depending on the Ca/P atomic ratio. The results of microstructural investigations of TCP and TCP with MgO additions are presented in figure 5. The microstructural analysis didn’t show any evidence of the formation of a liquid phase at 1070 °C, what is in concordance with the phase diagram [17]. The magnesium content investigated in this work form a solid solution into the TCP matrix. All hot-pressed materials show a dense and homogeneous microstructure, with no pores, quite different from the pressureless sintering TCP [4,7,14]. The microstructural investigations have also shown that the increase of the MgO content caused no marcant change on the grain size of TCP-grains. Further investigations are still under way to investigate the solid solution limit of MgO and its consequence on the mechanical properties of the sintered hot-pressed TCP-materials.

**Figure 1.** Shrinkage behavior of TCP.  **Figure 2.** X-ray diffraction pattern of TCP + 5 wt. % MgO.

**Figure 3.** Water absorption and porosity values.  **Figure 4.** Hardness and flexural strength values.
4. Conclusions

The results obtained in this study have evidenced that the hot-pressed TCP material shows superior properties as compared to pressureless sintering process. Hot-pressed technique has produced dense samples at 1070 °C, below that of the allotropic transformation of the TCP phase.

The addition of MgO has not improved the sintering process and the properties of hot-pressed tricalcium phosphate, suggesting that the magnesium oxide is not an effective sintering additive for hot-pressed TCP. The materials show a homogeneous and dense microstructure. The presence of MgO did not change significant the microstructure of the sintered samples. The bending strength values obtained for the hot-pressed samples is comparable to the better values indicated in the literature.

References