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Influence of Zn and Mg Doping on the Sintering Behavior and Phase Transformation of Tricalcium Phosphate Based Ceramics.

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Abstract. β-tricalcium phosphate based ceramics (β-TCP) are resorbable biomaterials used as bone substitutive materials. Several ions can substitute specific Ca positions in the crystalline structure of TCP, so that general Me-TCP can be obtained. Particularly, magnesium can increase the temperature of β-α-TCP transformation while zinc stimulates the bone formation. In this work, the influence of magnesium or zinc ions on the sintering behavior of Me-TCP was investigated. The powders were produced through wet chemical synthesis with a freeze drying process. The powders were calcined and subsequently uniaxially pressed into pellets. The pellets were sintered up to 1300°C/1h. The influence of Mg or Zn doping was investigated by dilatometric studies, thermal analysis and XRD. The microstructure was evaluated through SEM. The results suggest that Mg increased temperature of β-α-TCP phase transformation. The Me-doped TCP samples can be considered as promising biomaterials, having stimulatory effect of Zn or suitable densification due to Mg addition.

Introduction

Calcium phosphate based ceramics, such as β-tricalcium phosphate (β-TCP), are widely used as bone tissue reconstruction and replacement materials. These applications are possible because of its excellent biocompatibility with living tissue due to the similarity with the mineral phases of calcified tissues in terms of chemical composition and crystallographic structure [1, 2].

β-TCP phase, with the general formula Ca3(PO4)2, has a high absorption rate in human body, allowing bone growth during the progressive reabsorption of such ceramic materials [3]. However, at high temperature (~1125^{o}C) the β-TCP phase transforms into α-TCP phase, which induces to excessive dissolution rate and can reduce the mechanical properties of the final compounds [4]. Such phase is not suitable for biomaterials bone tissue replacement. The β-α phase transformation can be postponed to higher temperatures if suitable additives (and respective amounts) are added to the TCP lattice. Thus, the ionic substitution studies involving calcium phosphate phases, particularly TCP phase, deserves a great attention. In these cases, it is possible to sintering the β-TCP phases in temperatures higher than 1125^{o}C without the phase transformation into α-TCP structure [5]. Amongst the major ions studied as calcium substitute into TCP crystalline lattice are magnesium and zinc.

Magnesium has been studied in order to increase the mechanical strength of TCP. Studies have shown that Mg doping on β-TCP increased the thermal stability of the powder [4, 6]. On the other hand, zinc is known as its direct stimulatory effect on bone mineralization *in vitro*. Moreover, this ion acts as a bone metabolism activator [7]. Tricalcium phosphate ceramics doped with zinc proved to be biocompatible and suitable zinc delivery [5].

This paper evaluates the influence of magnesium or zinc substitution on the densification and phase transformation of tricalcium phosphate based ceramics synthesized by wet chemical procedures. The physical and chemical characterizations were performed in order to support such study.

Materials and methods

TCP doped synthesis was realized by neutralization method, as described in previous study [8]. The precursors used was calcium hydroxide ($Ca(OH)_2$, 0,1M, VETEC, Brazil), phosphoric acid (H_3PO_4, 85%, 0,3M, CAAL Reagentes Analíticos, Brazil), magnesium hydroxide ($Mg(OH)_2$, CAAL Reagentes Analíticos, Brazil) and zinc oxide (ZnO, IMPEX, Brazil). Three compositions were studied: pure TCP (TCP); TCP with 4.5 mol% magnesium (Mg-TCP) and TCP with 1.125 mol% zinc (Zn-TCP). The final precipitated cakes were freeze dryed in order to have fine powders.

The synthesized powders were calcined in an electric furnace (Lindenberg/Blue) at 800 ^oC/1h, with a heating rate of 10^oC/min. These Me-TCP powders were analyzed by x-ray diffraction technique (XRD, Multiflex, Rigaku) using 2θ range between 10º and 40º and 2º/min scan step. The spectra were analyzed using Search-Match software and compared with ICDD database to phase identification. Powder morphology was evaluated though High-Resolution Scanning Electron Microscopy (HR-SEM, JSM 6701S, JEOL).

The samples, obtained through uniaxially pressing of powders at 100 MPa, were characterized by differential thermal analysis (DTA, STA 409, Netzsch), in a dynamic air flow at 1450^oC/1h, heating rate of 10^oC/min, using alumina as reference material. For the evaluation of sintering behavior, dilatometric analysis (DIL E7/402, Netzsch) were performed, using the same conditions for DTA experiments.

The samples were also sintered in air (Lindenberg/Blue) at 1200^oC/1h or 1300^oC/1h, both with a 10^oC/min heating rate. Sintered samples were characterized through density measurements, and microstructure characterization through XRD and HR-SEM analysis.

Results and discussions

As synthesized powders, it is known that the predominant phase is the calcium phosphate deficient in calcium with an amorphous structure (CDHA, ICDD 460905) [9]. Fig. 1 shows the XRD patterns of Me-TCP powders after calcination at 800^oC/1h. It can be observed that β-TCP phase (ICDD 090169) was identified in all powders. This temperature was, thus, suitable for the complete CDHA→β-TCP phase transformation.

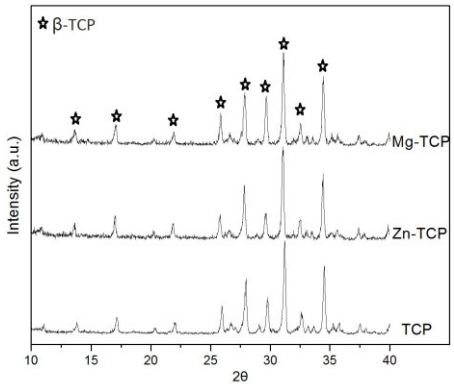

Fig. 1: XRD pattern of pure and doped Mg- or Zn-TCP powders after calcination at 800^oC/1h.

The morphology of the TCP powders calcinated at 800^oC/1h was evaluated by HR-SEM (Fig. 2). It can be seen the influence of Mg or Zn doping on the distribution and size of the TCP particles. It can be seen that all powders are agglomerated. The particle size distribution in all samples is homogeneous and narrow. It seems that doped powders (Figs. 2b and 2c) shows a decrease in particle size. Moreover, Mg doping (Fig. 2c) seems to be more effective for this behavior.

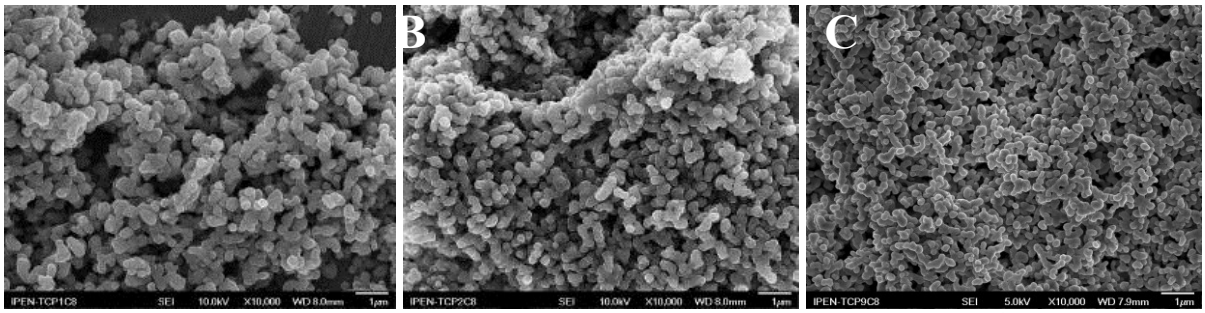

Fig. 2: Scanning electron micrographs of TCP powders after calcination at 800°C/1h: a) TCP, b) Zn-TCP, c) Mg-TCP.

Fig. 3 shows the differential thermal analysis results for pure and doped TCP with different ions. It can be seen the influence of Ca-Zn/Mg doping on the phase transformation of TCP based ceramics. At lower temperatures, it is observed endothermic processes related to absorbed and structural water losses, as (1) and (2) respectively indicated. The CDHA → β–TCP phase transformation is characterized by an exotermic-endotermic process (peak 3) related to the CDHA desydroxilation, and, consequently, β-TCP phase formation [8]. The last endotermic peak (peak 4, enlarged shown in Fig 3b) is associated with the β-TCP→α-TCP phase transformation. It can be seen that the Zn-TCP showed lower temperature of this phase transformation as compared with pure or Mg-TCP. Marchi et al [8] showed that the addition up to 1.5 mol % magnesium increased the β→α phase transformation and accelerated the densification process during sintering of β-TCP.

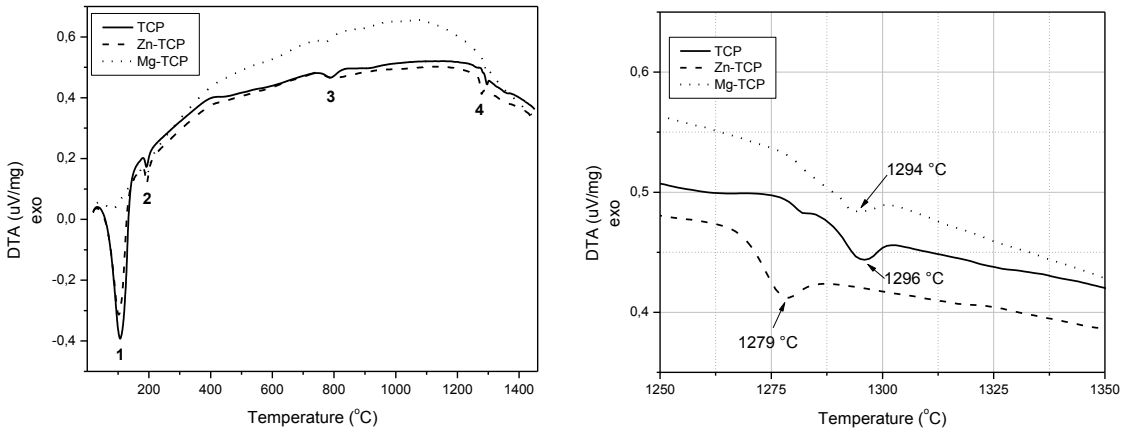

Fig 3: a) Differential thermal analysis results for TCP powder with different compositions. b) Enlarged region between 1250 – 1350°C, showing the detailed peak 4.

Thermal behavior was also analysed through dilatometric experiments (Fig. 4). The results of linear shrinkage as a function of temperature can indicate the temperatures of CDHA→β-TCP →α-TCP phase transformation. Pure TCP sample shows a great shrinkage at ~ 100°C due to loss of absorbed water. Up to ~ 800°C, pure TCP and Zn-TCP showed shrinkage with an stable behavior. The same phenomena can be observed up to ~ 700°C to Mg-TCP. At such temperatures, the TCP samples show the beginning of linear shrinkage, corresponding to the particle rearrangment due to the CDHA→β-TCP phase transformation. It is worth to mention that the theoretical densities of CDHA and β-TCP phases are 2.97 g/cm^3 and 3.07 g/cm^3, respectively. At around 1200°C two concorrent phenomena are observed: retraction due sintering process and expantion due to β-TCP→α-TCP phase transformation. The theoretical density of α-TCP is lower than β-TCP (2.86 g/cm^3). Mg-TCP sample show the lower final linear shrinkage, indicating that Mg doping inhibits the retraction at temperatures higher than 1300°C.

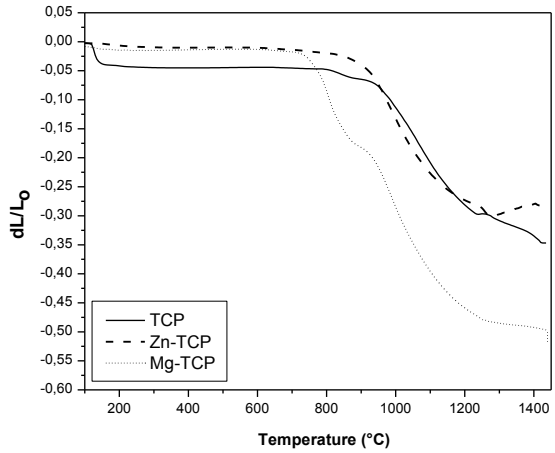

Fig. 4: Linear shrinkage of TCP samples after dilatometric experiments

Fig. 5 shows the XRD patterns of TCP samples after sintered at 1200°C/1h (Fig. 5a) and 1300°C/1h (Fig. 5b). It can be seen that all samples sintered at 1200°C/1h presented only the β-TCP phase (ICDD 090348). When higher temperatures were applied, both β-TCP and α-TCP phases were identified as crystalline phases for all TCP samples.

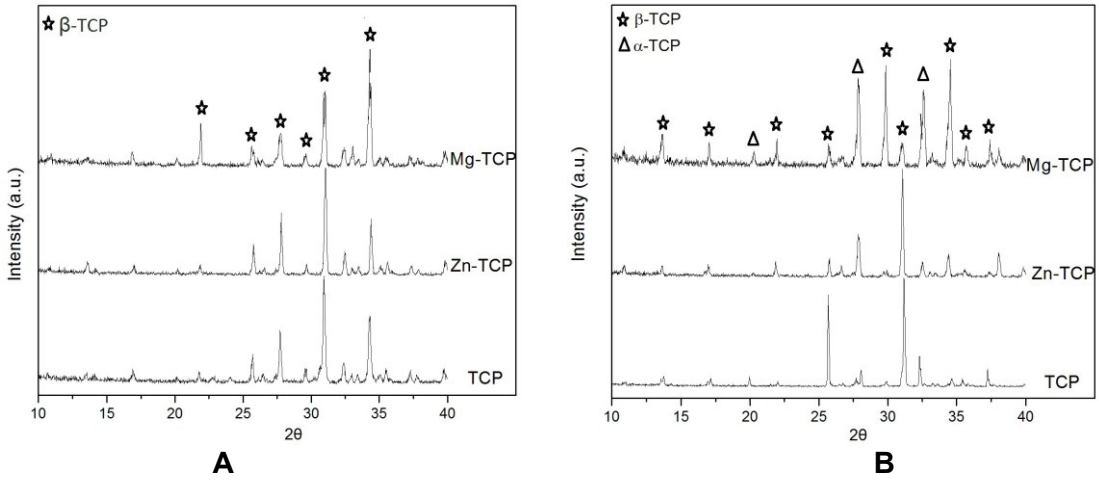

Fig. 5: XRD patterns of TCP samples sintered at different temperatures: (a): 1200°C/1h; (b): 1300°C/1h

Fig. 6 show the density of TCP samples sintered at 1200°C/1h or 1300°C/1h. Before sintering, the samples showed low densification, with a percentage lower than 60% theoretical density. After sintering, it can be seen that all samples density higher than 90% theoretical density. This results sugests that the zinc or magnesium incorporation on the TCP crystalline lattice does not present a significative influence on the density of the samples. Moreover, the samples sintered at 1300°C/1h present lower densities as compared to 1200°C/1h, due to the partial β-TCP→α-TCP phase transformation, and, thus, presenting a significative amount of α-TCP phase with lower density as compared to β-TCP.

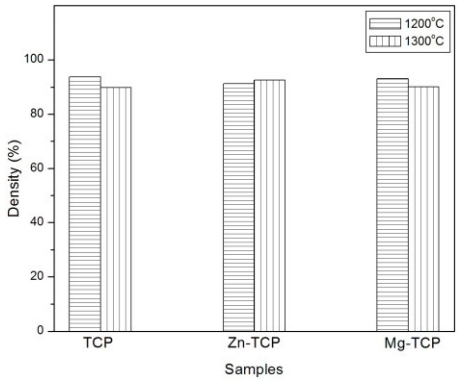

Fig. 6: Densities of TCP samples after sintering at different temperatures.

Scanning electron micrographs of fracture surface of TCP samples sintered at different temperatures can be seen in Fig. 7.

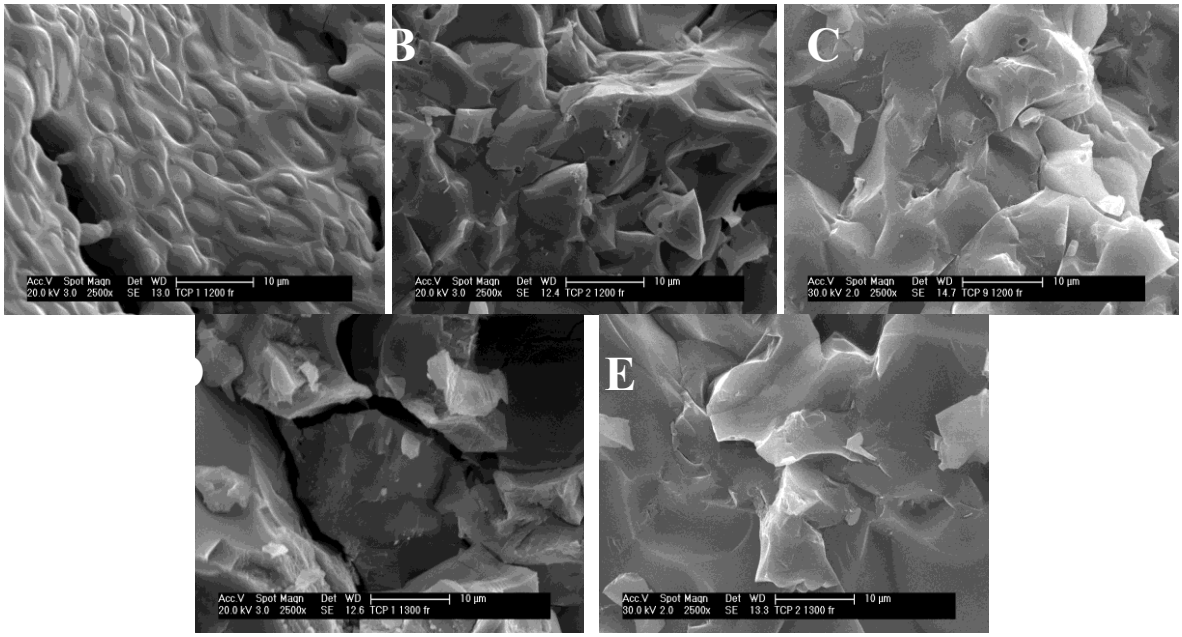

Fig. 7: Scanning electron micrographs of fracture surface of TCP samples sintered at different temperatures. (a): TCP sintered at1200^{o}C/1h; (b): Zn-TCP sintered at1200^{o}C/1h; (c): Mg-TCP sintered at1200^{o}C/1h; (d): TCP sintered at1300^{o}C/1h; (e): Zn-TCP sintered at1300^{o}C/1h;

From the overall micrographs, it can be seen the qualitative behavior of pore size and distribution presented on ceramic matrix. Analysing the TCP ceramics sintered at 1200°C/1h (Fig. 7 a-c), it can be seen that the Mg-TCP sample shows lower porosity than the other samples, sugesting that the Mg addition on TCP crystalline lattice increases the sinterability of the samples. Samples sintered at higher temperatures (Fig. 7 d-e) indicates higher porosity with larger porous as compared with the same compositions sintered at lower temperatures

Conclusions

Mg and Zn dopped TCP ceramics samples showed higher β-α-TCP phase transformation TCP samples, with a more pronounced effect using Mg as doped agent. Samples sintered at 1300°C/1h showed concomitant α-TCP and β-TCP phases, with a lower density and higher porosity as compared with lower sintering temperatures. The sintering procedure at 1200°C/1h is considered better conditions for having Me-TCP biomaterials. Future studies are in development in order to study the mechanical properties os such samples.

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