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Feature article

Phase and melting relationships of β, α and α′-$Ca_3(PO_4)_2$ polymorphs in the $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$ system

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ABSTRACT

In order to provide an exact knowledge of the phase transitions and melting relationships of $Ca_3(PO_4)_2$ (TCP) in the presence of zinc, a revisited version of the rich-$Ca_3(PO_4)_2$ region of the phase diagram of the system $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$ has been established in the present work. Experimental determination of this diagram was carried out by solid-state reactions of samples prepared from pure $NH_4H_2PO_4$, $CaCO_3$ and ZnO raw materials. X-ray Diffraction, Differential Thermal Analyses and Field Emission Scanning Electron Microscopy studies allowed to revise the α, β, α + β-TCP phase stability fields, delimitating for the first time the biphasic α + α′-TCP field and the melting relationships in the high temperature region of the system. The results allowed to determine two peritectic invariant points, at ≈1400 °C for 95 mol% $Ca_3(PO_4)_2$ and at ≈1490 °C for ≈99.5 mol% $Ca_3(PO_4)_2$.

1. Introduction

Tricalcium phosphate ($Ca_3(PO_4)_2$-TCP) based biomaterials are excellent candidates in hard tissue engineering due to its similarity to the natural bone composition and outstanding properties [1–6]. The presence of additives such as Zn^{2+}, Mg^{2+}, F^-, $CO_3{}^{2-}$ and/or $SiO_4{}^{2-}$ among others in solid solution in the structure of TCP affect the stability of its different polymorphs and therefore the properties of TCP based biomaterials. It is well known that the incorporation of zinc in TCP structure within the non-toxic level stimulates bone growth and its mineralization, hence its interest [7–9].

From the late–90s zinc substituted TCP based biomaterials have received a considerable attention from worldwide researchers, as regards the publications on the synthesis, obtaining, solubility, bioactivity and biological performance "in vitro" and "in vivo" of this family of materials [10–17]. Nevertheless none of these studies related their results with the information on the phases assemblage and microstructure available in the corresponding equilibrium phase diagrams. Recently our group has published results relating the effect of phase assemblage in Zn-TCP materials and physico-chemical properties and bioactive behaviour of Zn-TCP biomaterials [18–20]. These studies evidenced that consistent and detailed descriptions on the rich tricalcium phosphate region of $Ca_3(PO_4)_2$-ZnO phase diagrams are necessary to obtain, design and develop "smart" materials with tailored physic-chemical characteristics and biological performance "in vivo", able to replace and regenerate the mineral component of the bone.

TCP has three polymorphs β, α and α′ in order of increasing temperature. The low temperature phase β-TCP (Rhombohedral, R3CH) [21] is stable from room temperature up to 1125 °C and transforms reconstructively to α-TCP (Monoclinic, P121/A1) [22] phase. α-TCP phase is stable in the temperature range 1150–1470 °C. Moreover, α-TCP phase transforms rapid and reversible to α′-TCP (Hexagonal, P63/mmc) [23] at temperatures above 1470 °C. α′-TCP polymorph spontaneously transform to α-TCP on cooling and cannot be retained at room temperature even by quenching.

The presence of metal ions as solid solutions in the structure of TCP has significant consequences in the relative stability of these polymorphic forms, especially in the stabilization of β-TCP. As an example, the presence of Mg^{+2} increase the temperature of polymorphic transformation β-TCP → α-TCP in more than 300 °C as a function of magnesium content [24]. The dissolutions of different metals in the crystalline structure of β-TCP has been studied in various works [19,25–27] and solubility limit of divalent ions has been assessed ∼13.6 mol% [25].

The most detailed version of the $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$ multicomponent system was published by Kreidler et al. [28], back 1967. These authors, based on previous data [29–32] coupled with their own studies, published the first and most complete versions of the systems CaO-P_2O_5 [33], ZnO-P_2O_5 [34], and $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$ [29], (Fig. 1). Kreidler et al. [28] determined the phase relations

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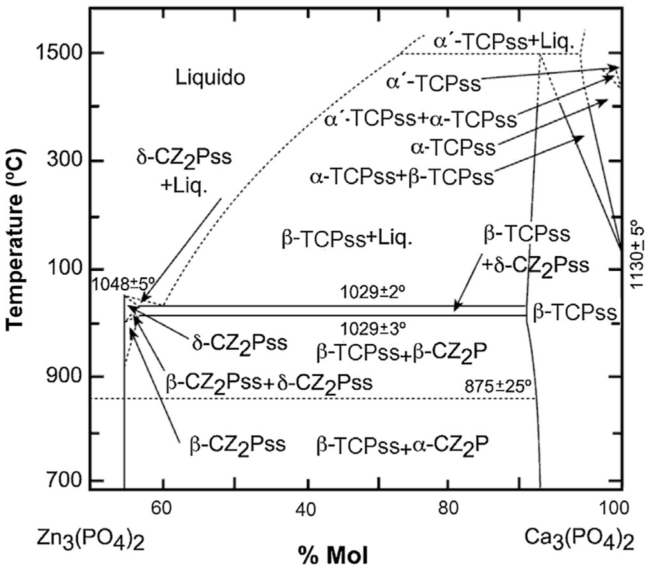

Fig. 1. Phase equilibrium diagram of the system $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$. (Redrawn from Kreidler et al. [28]). (CZ_2P : $CaZn_2(PO_4)_2$).

in the rich TCP region of the system concluding that β-$Ca_3(PO_4)_2$ allows a maximum of 10 mol% of $Zn_3(PO_4)_2$ into solid solution at 1000 °C producing a significant increase in the polymorphic transformation temperature β → α- $Ca_3(PO_4)_2$. However these authors did not established the polymorphic phase transitions and the melting relationships in the rich TCP region of the system at high temperature (≥1400 °C).

In the present work a complete experimental mapping of the rich tricalcium phosphate region of the equilibrium phase diagram of the system $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$ has been performed through experimental studies. The phase stability regions β, α and α + β were revised, and, for the first time, α + α′-TCP stability region, melting relationships of β, α, and α′-TCP polymorphs and two peritectic invariant points were established in the system. The exact knowledge and understanding of the effect of zinc on the stability, phase transitions and melting relationships of TCP polymorphs was mandatory towards the design of zinc doped TCP based biomaterials with controlled phase composition and physico-chemical and biological properties [18–20].

2. Experimental procedure

In order to study the rich-TCP region of the $Ca_3(PO_4)_2$-$Zn_3(PO_4)_2$ system, different compositions with a molar relation (Zn + Ca/P) = 1.50 were designed and synthesized from pure $NH_4H_2PO_4$ (≥99.0%-Fluka), $CaCO_3$ (99.0%-Panreac) and ultra-pure ZnO (99.9%-Agalsa), raw materials.

All compositions were synthesized by conventional solid state sintering process with a previous calcination step [18–20]. In this sense, as a preliminary step the reagent powders were previously optimized and therefore milled individually in an attrition-mill for 4 h using ZrO_2 balls and isopropyl alcohol as suspension media, in order to obtain an appropriate distribution of the particle size. Then, stoichiometric amounts of the milled reagent powders were weighted in an analytical balance to obtain the selected compositions (14) (Table 1) and hand milled three times in an agatha mortar using isopropyl media for homogenization. After the milling step, the powders were oven dried at 60 °C for 24 h, passed through a 63 μm sieve and isostatically pressed. The pellets were first calcined in platinum crucibles at 900 °C for 4 h to remove H_2O, NH_3 and CO_2 and subsequently reactivated by crushing and remilling, in order to improve the surface reactivity for the subsequent solid state reaction sintering process. The powders were pressed again into pellets (10 mm Ø × 2 mm high) and a second heat treatment in the temperature range 1150 up to 1470 °C for 12 h was carried out, followed by air-quenched at room temperature.

To ensure that the equilibrium conditions were achieved, the soaking time was held for a longer period of time (72 h) in some of the samples, appreciating no changes by X-ray diffraction in the mineralogy of the samples.

The (Ca + Zn)/P molar ratio determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) for all thermal treated compositions was 1.50 ± 0.01.

The collection of X-ray diffraction (XRD) patterns used to identify the crystalline phases in all the thermal treated powdered samples (angular range: 2θ = 10–90, step scan = 0.0197) were performed with a Vantec D8 Advance (Bruker Germay). To evaluate the thermal processes associated to the polymorphic transitions and the phase relationships in the high temperature region ≥1400 °C of the rich TCP zone of the binary system, Differential Thermal Analysis (DTA) measurements were carried out using a Netzsch STA-409 device coupled with a TASC 414/2 Netzsch temperature controller. Measurements were performed on 80–100 mg of powder, in a platinum crucible, over the range 25–1500 °C, at a heating rate of 3 °C/ min, under an air flux of 0.04 l/min.

Field Emission Scanning Electron Microscopy (FE-SEM) (Hitachi S-4700 Japan) equipped with an energy dispersive spectroscopy (EDS) was employed for the characterization of the samples. A complete study of the microstructures of either polished or chemically etched samples (with diluted acetic acid 1:9) and its phase distribution was carried out in order to detect the possible presence of secondary or minoritary phases.

3. Results and discussion

Experimental studies were performed in the range of 1150–1470 °C for 14 rich-TCP compositions. Composition of the designed samples studied (1)–(14) is reported in Table 1 in terms of $Zn_3(PO_4)_2$ (Z3P) and $Ca_3(PO_4)_2$ mol% content.

3.1. X-ray diffraction studies

Phase assembles coexisting in equilibrium in the samples after the solid state heat treatments are listed in Table 1, according to the crystalline phases detected in the XRD patterns at each sintering temperature. Characteristic diffraction peaks of β-TCP and α-TCP phases were identified in the XRD according JCPDS card 9-0348 and 70-0364 respectively.

A detailed analysis of the compositions (4), (8) and (11) is subsequent discussed for a better understanding of the phases stability, the reactions involved and the character and compositions of invariant points.

In Fig. 2 the XRD patterns obtained for composition (4) (0.64 mol% Z3P), heat treated at 1150, 1200, 1250 and 1350 °C, respectively are shown. At 1150 °C (Fig. 2a) only diffraction peaks attributed to β-TCP phase were observed, while at 1200 °C (Fig. 2b) phase transformation begins obtaining diffraction peaks attributed to β and α-TCP.

At 1250 °C (Fig. 2c) α-TCP polymorph is the majority phase in the composition. Finally at 1350 °C, the phase transformation β → α-TCP has already been completed, obtaining only diffraction peaks attributed α-TCP phase (Fig. 2d).

In the case of composition (8) (2.56 mol%Z3P) Fig. 3, β → α-TCP polymorphic transformation takes place at temperatures higher than in composition (4). At 1250 °C only diffraction peaks attributed to β-TCP phase were observed while at 1350° and 1400 °C mixtures

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