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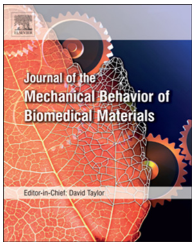

Research Paper

Effect of Mg and Si co-substitution on microstructure and strength of tricalcium phosphate ceramics

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ABSTRACT

Magnesium and silicon co-doped tricalcium phosphate (TCP) ceramics with compositions corresponding to 0, 5 and 10 wt% $CaMg(SiO_3)_2$ in the system $Ca_3(PO_4)_2$–$CaMg(SiO_3)_2$ were obtained by conventional sintering of compacted mixtures of $Ca_3(PO_4)_2$, MgO, SiO_2 and $CaCO_3$ powders at temperatures between 1100 and 1450 °C. Microstructural analyses were performed by X-ray diffraction and field emission scanning electron microscopy with energy dispersive spectroscopy. Major phases in the obtained ceramics were β- or α+β-tricalcium phosphate containing Mg and Si in solid solution. Certain amounts of liquid were formed during sintering depending on composition and temperature. There were found significant differences in distributions of strength determined by the diametral compression of disc tests (DCDT). Failure strengths were controlled by microstructural defects associated with phase development.

Mg and Si additions were found to be effective to improve densification and associated strength of TCP bioceramics due to the enhancement of sintering by the low viscosity liquids formed. The highest density and strength were obtained for the TCP ceramic containing 5 wt% $CaMg(SiO_3)_2$ sintered at 1300 °C. Cracking and porosity increased at higher temperatures due to grain growth and swelling.

1. Introduction

Tricalcium phosphate ($Ca_3(PO_4)_2$, TCP)-based bioceramics with the shape of granules, blocks (both dense and porous), and coating layers on metallic implants have been successfully used for bone repairing in dentistry, maxilla-facial and traumatology surgery for over 30 years. Their particular biological properties, mainly biocompatibility, bioactivity, osteoconductivity and biodegradability, are the reason for such a success (Carrodeguas and De Aza, 2011; Chevalier and Gremillard, 2009; De Aza et al., 2005; Dorozhkin, 2007a; Hench, 1998; LeGeros et al., 1995). There are three polymorphs of TCP the low temperature, β-TCP, and the high temperature forms, α- and α′-TCP. The last one lacks of practical interest because only exists at temperatures above ~1430 °C and reverts almost instantaneously to α-TCP by cooling below the transition temperature. The room temperature stable β-TCP undergoes reconstructive transformation at ~1125 °C to the high

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temperature polymorph, α-TCP, which can be retained during cooling to room temperature (Carrodeguas et al., 2008; Carrodeguas and De Aza, 2011).

α- and β-TCP are currently used in several clinical applications in dentistry, maxilla-facial surgery, and orthopaedics; β-TCP is the component of several commercial mono- or biphasic bioceramics and composites and α-TCP is the major constituent of powder component of various hydraulic bone cements (Bohner, 2000; Dorozhkin, 2008).

The main disadvantages of β- and α-TCP bioceramics are low toughness ($K_{IC}=1.2$ MPa m$^{1/2}$) that can affect reliability, and high elastic modulus ($E=90$–120 GPa) that can lead to stress shielding because of strain mismatch with bones (Carter and Norton, 2007). Moreover, TCP bioceramics are susceptible to fatigue failure when loading other than in compression occurs. Therefore, usage should be limited to filling bone defects or to reconstruct bony tissues at sites where only compression loading is expected (De Groot, 1983).

The main obstacle for the development of regenerative scaffolds for load-bearing bones is the achievement of bioactive composites with controlled bone-like composition and high mechanical strength (Sprio et al., 2013).

In the last years, intensive research has been devoted to prepare and characterise ion-substituted TCP-based materials to improve osteogenesis, bioreabsorption rate, and mechanical properties. Particularly, substitutions of Si for P (Bandyopadhyay et al., 2006; Dorozhkin, 2007b; Langstaff et al., 2001) and Mg for Ca (Bandyopadhyay et al., 2006; Manjubala and Kumar, 2001; Marchi et al., 2007; Otsuka et al., 2008) in TCP have received much attention. The interest in Si and Mg as substituents in TCP is that both are essential for bone metabolism and formation. As both polymorphs of TCP are biodegradable, substituted TCP release Si, Mg, Ca and P ionic species to the biological environment. Mg and Si significantly increase the range of thermal stability of β-TCP (Carrodeguas et al., 2008; Yoshida et al., 2005) and α-TCP (Reid et al., 2005), respectively. Moreover, controlled Mg doping has been proposed as a way to improve the mechanical strength of β-TCP bioceramics. In this sense, the systematic study of the phase development in Mg and Si substituted β-TCP bioceramics in relation with the mechanical behaviour is of prime interest to analyse their viability as constituents of scaffolds for regeneration of load-bearing bones.

This work is a part of a broad study on the feasibility of using the solid state reaction sintering approach to obtain Mg and Si substituted $Ca_3(PO_4)_2$ based bioceramics for biomedical applications. In particular, it describes the preparation of materials within the compositional range: $(100-x)$ $Ca_3(PO_4)_2-x$ $CaMg(SiO_3)_2$; with $x=0$, 5 and 10 wt%, the analysis of their mineralogical composition and microstructure and the evaluation of their mechanical properties. Materials have been formulated on the basis of the information supplied by the equilibrium relationships in the $Ca_3(PO_4)_2$–$CaMg(SiO_3)_2$ pseudo-binary system ($CaMg(SiO_3)_2$=diopside=D, in which follows) According with this information, the three compositions are located in the TCP-rich region of the diagram. In vitro studies with Human Fetal Osteoblasts (HOb) using the MTT and Alamar blue essays demonstrated that these ceramics are not cytotoxic and stimulate cell proliferation (García-Páez et al., 2013).

2. Materials and methods

2.1. Processing

The starting raw materials were $CaCO_3$ and $CaHPO_4$ (>99.0 wt%, Panreac, Barcelona, Spain), amorphous SiO_2 (>99.7 wt%, Strem Chemicals Inc., Newburyport, MA, USA), MgO (>99.6 wt%, Fluka, Darmstadt, Germany), MgO was previously heated to 950 °C to remove adsorbed or hydration water.

$Ca_3(PO_4)_2$ was prepared by solid state reaction between $CaCO_3$ and $CaHPO_4$. Reactants were homogeneously mixed in an attrition mill during 45 min using isopropanol and 3 mm ∅ zirconia balls. The resulting slurry was dried at 60 °C overnight. Dry cake was disintegrated and sieved through 100 μm mesh and the powder was heated at 1100 °C for 4 h. Finally the product was grinded in a CW mill to a mean particle size of 2.3 μm. It was constituted of 45.4±0.03 wt% of P_2O_5, 54.6±0.03 wt% of CaO, 0.38±0.02 wt% of MgO, Ca/P molar ratio=1.52.

Three compositions, C0, C5 and C10, were prepared (100 wt% $Ca_3(PO_4)_2$, 95 wt% $Ca_3(PO_4)_2$–5 wt% $CaMg(SiO_3)_2$ and 90 wt% $Ca_3(PO_4)_2$–10 wt% $CaMg(SiO_3)_2$, respectively). The amount of 30 g of the mixture of raw materials ($Ca_3(PO_4)_2$, $CaCO_3$, MgO, and SiO_2) with the adequate proportions were attrition milled in isopropanol (powder:isopropanol 2:3; 3 mm ∅ YSZ balls Tosoh, Japan; balls:powder 5:1; Teflon® jar and propeller (1000 rpm; 1 h) to a final average particle size of ~2 μm (see Table 1). After milling, the slurry was dried at 60 °C overnight and the powder was sieved through a 100 μm mesh. The dried and sieved mixtures of powders were uniaxially pressed in a stainless steel mould at 125 MPa into discs of 10 mm ∅ and 3 mm of height. The pressed specimens reached 62±1% of their theoretical densities.

2.2. Characterization

The specific surface area of the powders employed as raw materials was determined by the single-point B.E.T.-N_2

Table 1 – Physical characteristics of raw materials.

	Particle size distribution				Density (g/cm^3)	Specific surface area (m^2/g)
	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Modality		
$CaCO_3$	16	31	47	Unimodal	2.67	0.03
MgO	3.3	7.3	15	Unimodal	3.20	29.5
SiO_2	49	120	228	Unimodal	2.22	0.04
$Ca_3(PO_4)_2$	0.4	2.3	4.6	Bimodal	2.98	1.1