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Phase transition mechanisms involved in the formation of structurally stable β-$Ca_3(PO_4)_2$-α-Al_2O_3 composites

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ABSTRACT

Composite powders comprising various proportions of β-Tricalcium phosphate [β-$Ca_3(PO_4)_2$] and α-Alumina (α-Al_2O_3) were synthesized by wet precipitation and then heat treated for drying and crystalline phase development. The phase formation mechanism was assessed through a set of characterization techniques including XRD, FT-IR and Raman spectra, and quantitative Rietveld refinement analysis. Al_2O_3 additions delayed the transformation kinetics from calcium deficient apatite to β-$Ca_3(PO_4)_2$ and preserved the thermal stability of β-$Ca_3(PO_4)_2 - \alpha$-Al_2O_3 composites till 1400 °C. Such enhancement of thermal stability was due to the occupancy of Al^{3+} at both $Ca^{2+}(4)$ and $Ca^{2+}(5)$ lattice sites of β-$Ca_3(PO_4)_2$. Beyond the occupancy saturation limit for Al^{3+}, the excess of aluminium crystallized as α-Al_2O_3. Morphological analysis revealed the growth of rod-like α-Al_2O_3 platelets on the surface of micron sized β-$Ca_3(PO_4)_2$ grains. The mechanical data obtained from indentation of bulk composites displayed enhanced hardness and Young's modulus with increasing α-Al_2O_3 content in the composites.

1. Introduction

Hydroxyapatite [HAP,$Ca_{10}(PO_4)_6OH)_2$) and β-Tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$] are the commonly used in dental and orthopaedic applications owing to their bioactivity and chemical similarities with bone mineral [1,2]. Due to their relatively poor mechanical properties, both HAP and β-TCP are preferentially used for filling bone defects and coating on metallic implants for hard tissue replacements. The reinforcement of these calcium phosphates (CPs) with bio-inert materials such as alumina (Al_2O_3) or zirconia (ZrO_2) to obtain stronger composites with superior bioactivity is a common strategy to expand their usage in load bearing orthopaedic applications [3,4]. Al_2O_3 is an important biomaterial in load bearing hard tissue replacements owing to its impressive mechanical features such as high elastic modulus, abrasion resistance and chemical stability, and moderate fracture toughness [5]. The α-Al_2O_3 phase is the most thermodynamically stable alumina polymorph due to its high activation energy, justifying its selection as constituent in CPs – Al_2O_3 composites [6].

Various synthesis routes have been attempted to obtain CPs – Al_2O_3composites, including solid state reaction, precipitation, mechanical mixing, sol-gel and hot-isotactic pressing, with greater attention being paid to HAP/Al_2O_3 composites rather than to β-TCP – Al_2O_3 composites[7,8]. However, the thermal degradation of bioactive component upon sintering HAP/Al_2O_3 composite mixtures is a serious drawback. HAP decomposes to yield $Ca_3(PO_4)_2$, CaO and H_2O. In the presence of Al_2O_3, the free CaO readily reacts with Al_2O_3 to yield calcium aluminates [9,10] and, as a consequence, the structural stability of Al_2O_3 is also not preserved in HAP/Al_2O_3 composites. The decomposition mechanism is given as follows:

$$Ca_{10}(PO_4)_6(OH)_2 \quad + \quad Al_2O_3 \quad \overset{>1150^\circ C}{\rightarrow} 3Ca_3(PO_4)_2 + CaAl_2O_4 + H_2O$$

The low temperature (T) polymorph of pure $Ca_3(PO_4)_2$ [β-$Ca_3(PO_4)_2$] is thermally stable up to 1180 °C and transforms into α-$Ca_3(PO_4)_2$ at T ≥ 1180 °C. Investigations also showed that the structure of β-$Ca_3(PO_4)_2$ is prone to host a wide variety of cationic substituents in its structure ranging from monovalent (M^+), divalent (M^{2+}) and trivalent ions (M^{3+}) [11–13]. The incorporation of such substituents in the crystalline lattice tends to increase its thermal stability, therefore delaying the allotropic β-$Ca_3(PO_4)_2 \rightarrow \alpha$-$Ca_3(PO_4)_2$ transformation till 1400 °C [14,15].

Both HAP and β-TCP are equally considered important for biomedical applications. In view of the above mentioned drawbacks of HAP – α-Al_2O_3 composites and the promising enhanced thermal stability of β-TCP with incorporated ionic substituents for

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Table 1
Molar concentrations of the precursors used in the synthesis of β-TCP – α-Al_2O_3 composites.

Sample Code	Molar concentration of the precursors			Ca/P ratio	(Ca + Al)/P ratio
	$Ca(NO_3)_2{\cdot}4H_2O$	$NH_4H_2PO_4$	$Al(NO_3)_3{\cdot}9H_2O$		
TCP	0.5 M	0.3333 M	–	1.5	1.500
1CPAL	0.5 M	0.3333 M	0.1 M	1.5	1.800
2CPAL	0.5 M	0.3333 M	0.2 M	1.5	2.100
3CPAL	0.5 M	0.3333 M	0.3 M	1.5	2.400
4CPAL	0.5 M	0.3333 M	0.4 M	1.5	2.700
5CPAL	0.5 M	0.3333 M	0.5 M	1.5	3.000

Ca^{2+}, the aim of the present study is to explore the feasibility of obtaining β-TCP – α-Al_2O_3 composites without the formation of undesirable products during thermal treatment. The concept relies on delayed allotropic transformation of β-$Ca_3(PO_4)_2$ due to the ionic replacement of calcium with aluminium. An *in situ* aqueous synthesis process has been deliberated to yield β-$Ca_3(PO_4)_2$ – α-Al_2O_3composites. The effects of increasing additions of alumina on the structure and thermal stability of β-$Ca_3(PO_4)_2$ – α-Al_2O_3 composites were evaluated to attain the combined features of bioactivity and mechanical strength, and upgrade the resulting composites for load bearing bone replacement applications.

2. Experimental methods

2.1. Powder synthesis

The starting powders to prepare the β-$Ca_3(PO_4)_2$ – α-Al_2O_3 composites were synthesized by aqueous precipitation using analytical grade $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $NH_4H_2PO_4$ as reactants. The concentrations of $Ca(NO_3)_2$ and $NH_4H_2PO_4$ were maintained constant for all the synthesis whereas those of $Al(NO_3)_3$ were varied to yield five different compositions. Table 1 presents the concentrations of the precursors and the respective sample codes hereafter used throughout the manuscript. In brief, a discretely prepared $NH_4H_2PO_4$ stock solution was added in a drop wise manner to the stock solution comprising $Ca(NO_3)_2$ under constant stirring (250 rpm) at the operating temperature of 100 °C. After the completion of addition, the pH was enhanced to 8.0 by adding the required amounts of concentrated NH_4OH solution and allowed for 30 min stirring. This was followed by the addition of appropriate amount of $Al(NO_3)_3$ solution to the aqueous suspension and then left for 2 h stirring. The as obtained precipitate was separated by vacuum filtration and then dried at 120 °C overnight. The dried precipitates were crushed to fine powders and hereafter designated as starting powders.

2.2. Characterization

The phase purity and composition of the starting powders after heat treated for 4 h at different temperatures within the range of 800 – 1400 °C were assessed through a set of characterization techniques. The phase analysis of the powders was determined using a high resolution X-ray diffractometer (Rigaku, Ultima IV, Japan) with Cu Kα radiation (λ = 1.5406 Å) produced at 40 kV and 30 mA to scan the diffraction angles (2θ) between 10 and 80° with a step size of 0.02° 2θ per second. Phase determinations were made using Standard ICDD (International Centre for Diffraction Data) card Nos. 00-009-0169 for β-$Ca_3(PO_4)_2$, 01-080-0786 for α-Al_2O_3, 00-009-0348 for α-$Ca_3(PO_4)_2$ and 00-009-0432 for HAP. The functional groups in the powders were determined using Fourier transform infrared spectroscopy (FT-IR) in the transmission mode using a FT-IR spectrophotometer (Perkin-Elmer, USA) in the infra region ($4000 – 400\ cm^{-1}$). The vibrational modes of the composite powders were determined using back scattering geometry of Confocal Raman microscope (Renishaw, United Kingdom). All the powder samples were excited at a wavelength of 785 nm by semiconductor diode laser (0.5% of power) with the data acquiring time of 30 s. The microstructural features of β-$Ca_3(PO_4)_2$ – α-Al_2O_3 composites were determined through High resolution scanning electron microscope (FEI-Quanta, HRSEM, FEG-200, Netherlands).

Quantitative phase analyses through Rietveld refinement for selected compositions were performed using GSAS-EXPGUI software package. The initial refinement of pure β-$Ca_3(PO_4)_2$ was done with the standard CIF (Crystallography Information File) from Yashima et al. [16]. The structural parameters of β-$Ca_3(PO_4)_2$ taken for refinement were given as space group *R3c*, Z = 21, *a* = 10.4352 Å and *c* = 37.4029 Å, 18 independent atomic positions: five Ca positions (three in site *18b* and two in site *6a* at one-half occupancy), three P positions (two in site *18b* and one in site *6a*), and ten O positions (nine in site *18b* and one in site *6a*). The CIF file from Newnham and Dehaan [17] was taken as standard for refining the α-Al_2O_3 (corundum). The structural parameters of α-Al_2O_3 taken for refinement were given as space group *R3c*, *a* = 4.7589 Å and *c* = 12.9910 Å.

2.3. Cytotoxicity tests

Cytotoxicity analysis was performed in accordance with the procedure detailed in the previous report by the authors [18,19]. The viability of human osteosarcoma cell line MG-63 (National Centre for Cell Science, India) in the presence of stoichiometric β-$Ca_3(PO_4)_2$ and selective β-$Ca_3(PO_4)_2$-α-Al_2O_3 composites was evaluated through the MTT assay. Cells were cultured in Dulbecco's modified Eagle's medium supplemented with 10% fetal calf serum and incubated at 37 °C with 5% CO_2. In brief, 10,000 cells were seeded in 96 well plates and various concentrations (as 10, 50, 100 and 200 μg/ml) of selected compositions were supplemented in culture media and finally incubated for 96 h at 37 °C. The potent proteosomal inhibitor MG-132 (Sigma-Aldrich) at the concentration of 48 μg/ml, was taken as negative control. The assay was carried out in accordance with the protocol using EZ count MTT cell assay kit (Himedia, Cat. No. CCK003). All the data are expressed as mean ± standard deviation.

2.4. Mechanical evaluation

The hardness and Young's modulus of the β-$Ca_3(PO_4)_2$ – α-Al_2O_3 composites at room temperature were assessed by nanoindentation measurements (Nanoindenter CETR, USA) on fine polished surfaces of sintered samples. The starting powders were firstly heat treated at 700 °C to eliminate all the volatile impurities, milled in a high energy ball mill (Retsch, Germany), and pressed into pellets (13 mm diameter and 1 mm thickness) using a semi-automatic hydraulic press machine under the applied force of 10 N for 60 s. The as obtained pellets were then sintered at 1400 °C for 2 h followed by fine polishing using diamond paste. The hardness and Young's modulus measurements were performed with a triangular pyramid (Berkovich) diamond tip indenter with a radius of

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