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Synthesis and characterization of calcia partially stabilized zirconia-hydroxyapatite powders prepared by co-precipitation method

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Abstract

It was recently been reported that calcia partially stabilized zirconia can be used as a reinforcement phase in zirconia-hydroxyapatite composites. Composites prepared by a precipitation method lead to the formation of homogeneous powders, easily compacted without addition of other phases. In this work, hydroxyapatite-zirconia composites were prepared by a similar precipitation route previously used. Here, it was lightly modified in relation to steps of addition of precursors reagent solutions. Two powders, having different compositions, were prepared by this method. The modified route led to the formation of a mixture of tetragonal zirconia, t-ZrO_2, monoclinic zirconia, m- ZrO_2, and calcium zirconium oxide, $Ca_{0.15}Zr_{0.85}O_{1.85}$, as well as a hydroxyapatite phase. Fine powders with specific surface area of approximately 35 m^2/g were produced. Textural analyses revealed the presence of multiple generations of agglomerate, for both compositions. Thermal analyses showed the thermal stability of powders which presented weight losses of only 4%, for temperatures from 25 to 1400°C. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Powder; Hydroxyapatite; Partially stabilized zirconia; Synthesis; Co-precipitation method

1. Introduction

Synthetic hydroxyapatite (HA) has been envisaged for many kinds of medical applications due to its ability to form a bond with bone tissues. It is a very versatile material that can be used for repair bone, as well as a coating material in metal implants [1–5]. HA is a well-studied system, that normally is found associated with different phosphates produced during certain synthesis conditions [1]. The grade of the biological and chemical stability of these systems is closely associated with the amount and ratio of these different phases. For example, systems containing large amount of phosphate phase are very bioactive, but can dissolve easily in body fluids. For a given kind of application a specific system will be suitable.

However, synthetic hydroxyapatite presents low fracture toughness [6] due to its weakness and brittleness, which is an obstacle to its application in implant which must withstand higher loads [7]. Further improvement of the mechanical properties can be achieved by the incorporation of a resistant second phase as oxides or polymers [8,9].

In our previous work, it has been reported that calcia partially stabilized zirconia can be used as a reinforcement phase in zirconia-hydroxyapatite composites. Composites prepared by a precipitation method lead to the formation of homogeneous powders, easily compacted and sintered without cracking [10]. In this work, hydroxyapatite-zirconia composites were prepared by a similar precipitation route. Here, it was lightly modified in relation to the addition steps of the precursors reagent solutions. In the first preparation, the precipitation of

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hydroxides of calcium and zirconium, precursors of zirconia solid solution, was made in a reactor (step 1), separately of the HA precipitation (step 2). The two precipitates were then mixed (step 3). In the modification introduced in this study, the zirconia precursors were co-precipitated (step1) under a slurry of HA previously precipitated (step 2). Different phases and morphological properties are expected to be found for powders prepared by these methods.

The objective of this work is to optimize a chemical route for preparation of powders of zirconia- hydroxyapatite composites in order to improve mechanical properties of HA and verify the influence of precipitation steps of the precursors on the powders composition and morphology . The long-term goal of this study is to develop a biomimetic bone replacement material which consist of a synthetic bioactive phase (HA) and a reinforcement one (zirconia).

2. Experimental procedure

2.1. Sample preparation

Fine powders of calcia partially stabilized zirconia-hydroxyapatite composite were prepared by co-precipitation of a mixture of an alcoholic solution of calcium nitrate (Merck reagent) and zirconium butoxide (Aldrich reagent) [11] under an aqueous solution of calcium nitrate and ammonia monobasic phosphate (Merck reagent). This last solution was previously stirred for 7 h in ammoniacal medium and followed by resting [12]. Next the precipitate was left to stand for 17 h at room temperature. The pH was maintained in the range of 12–13. The resulting precipitate was filtered under vacuum, washed with isopropanol with agitation for 30 min, and again filtered under vacuum. The residual water, present in the precipitate, was removed by azeotropic distillation

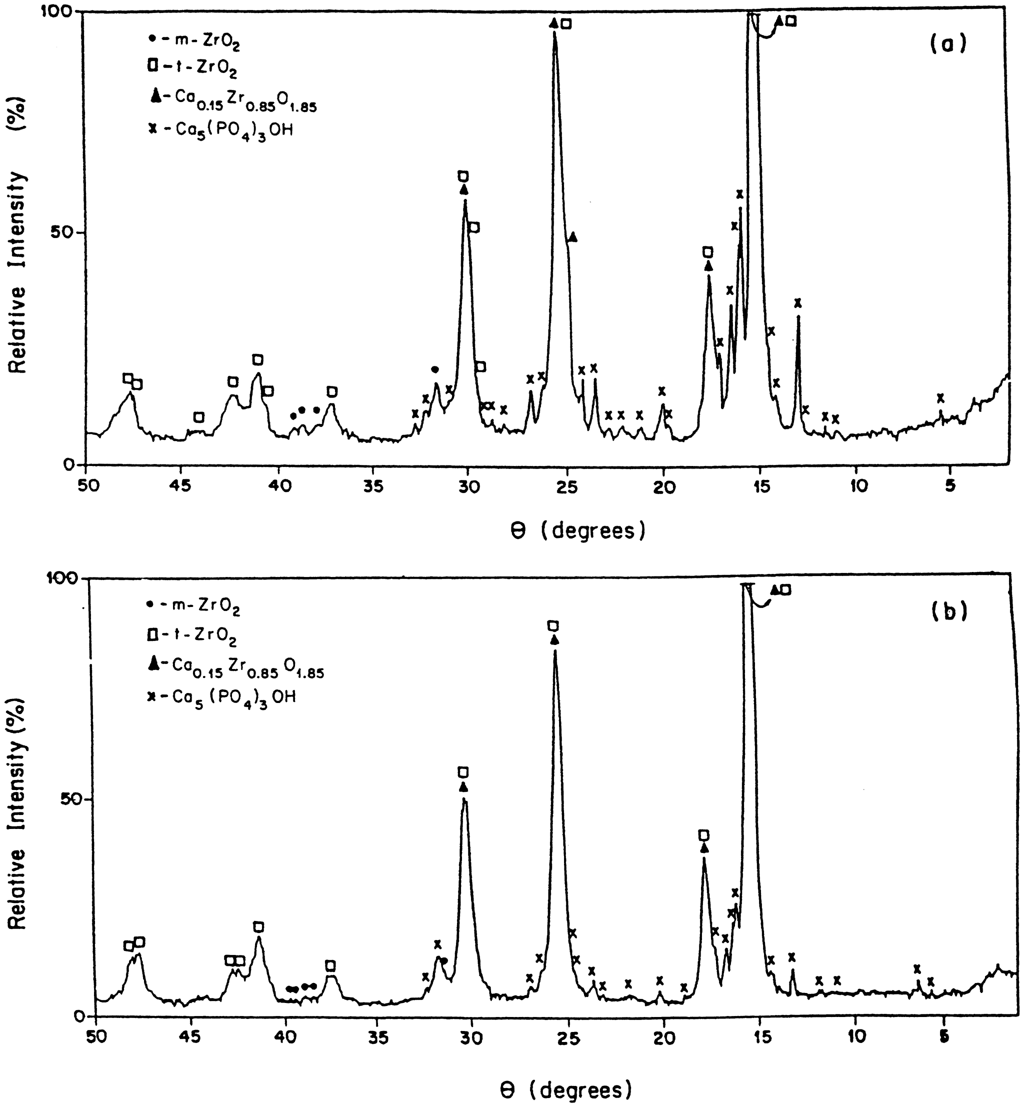

Fig. 1. X-ray diffraction patterns of (a) Z4H6 and (b) Z6H4.

using toluene and isopropanol. After drying at 90°C for 24 h, the resulting fine powders were calcined at 800°C for 3 h in air.

Two compositions were prepared: one with 40 and another with 60 vol.% in zirconia phase. These powders were noted as Z4H6 and Z6H4 respectively.

2.2. Powder characterization

Powder X-ray diffractometry (RIGAKU θ-2θ diffractometer using nickel-filtered CuK_α radiation) was used to identify crystalline phases present in all powders. X-ray patterns were recorded in the range of $5° < \theta < 50°$.

The chemical functional groups were characterized by Fourier Transform Infrared Reflection (FTIR) spectroscopy, using a GALAXY-MATTSON model 3020 spectrometer. For these analyses, the powders were grounded and mixed with previously dried KBr powder in a concentration close to 1 wt.%.

The textural and microstructural morphology of powders, (particle, agglomerate and pore sizes) was determined by SEM and BET. Average agglomerate sizes were obtained from SEM observations (JEOL CO., JMC-35C microscope) and also from image processing using a microstructural analyzer (QUANTIKOV) [13]. The specific surface area and pore size were measured by the multipoint BET (QUANTACHROME CORP. Nova-1200 BET surface area analyzer) method using nitrogen gas as an absorbate. Before the analyses, samples were heated at 120°C, at reduced pressure, in order to eliminate the adsorbed water.

Average particle size was calculated with the equation:

$$d = 6/\rho S \qquad (1)$$

where d is the average particle size (μm), ρ is the theoretical density of the sample (g cm^{-3}) and S is the specific surface area (m^{2}g^{-1}). The particles were assumed to be spheres.

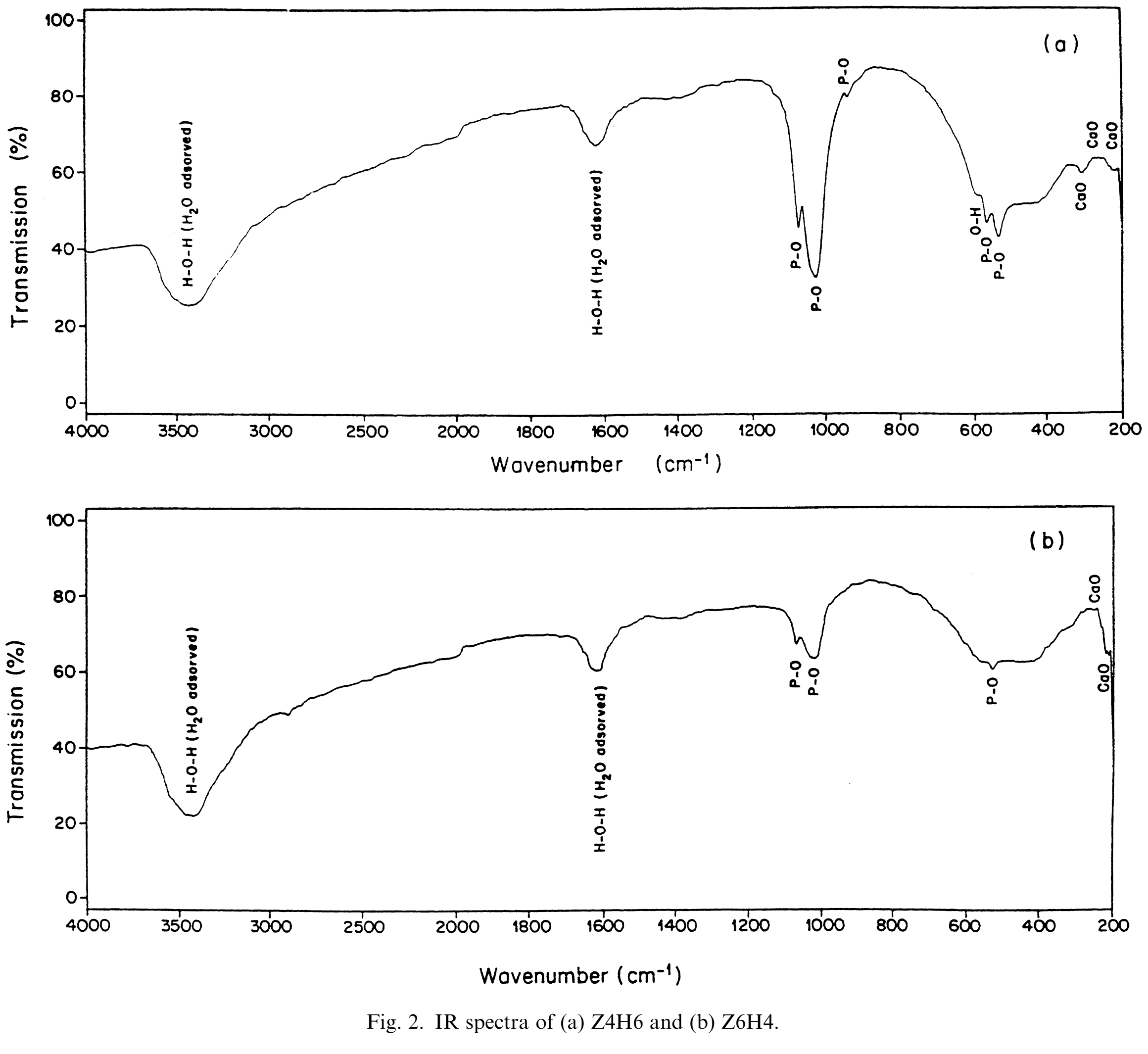

Fig. 2. IR spectra of (a) Z4H6 and (b) Z6H4.

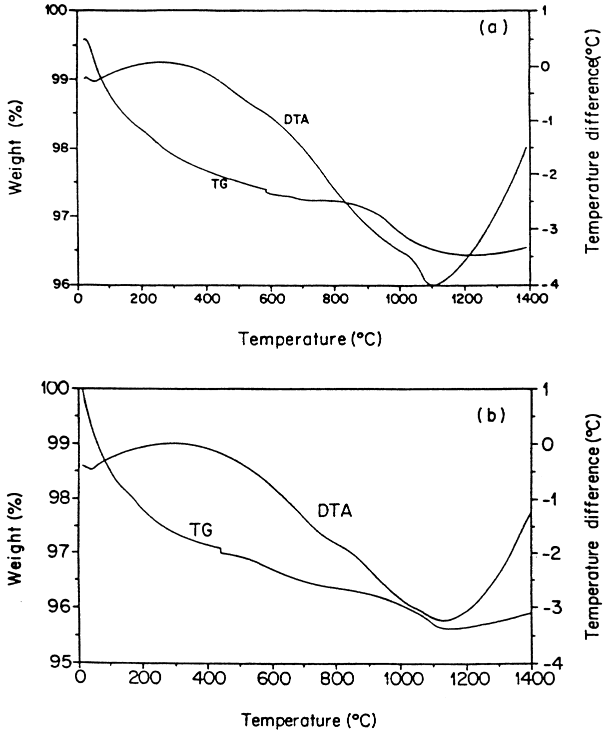

Fig. 3. TG-DTA curves of (a) Z4H6 and (b) Z6H4.

3. Results and discussion

3.1. X-ray diffraction patterns

Fig. 1(a and b) show XRD patterns obtained for Z4H6 and Z6H4 powders, respectively. A mixture of monoclinic zirconia (m-ZrO_2), tetragonal zirconia (t-ZrO_2) and calcium zirconium oxide ($Ca_{0.15}Zr_{0.85}O_{1.85}$) phases were found in both powders, as well as, hydroxyapatite peaks. The major peaks of t-ZrO_2 and $Ca_{0.15}Zr_{0.85}O_{1.85}$ (111, 200, 220 and 311 planes) indicated that these phases coexist. The presence of the t-ZrO_2, and the $Ca_{0.15}Zr_{0.85}O_{1.85}$ could be explained by the high concentration of calcia in solution. Probably Ca^{+2} ions, belonging to HA phase, diffused to zirconia matrix. Calcia-zirconia phases having larger Ca content than expected, as well as, other phases consisting of amorphous calcium deficient HA, were formed. The effect of the zirconia content in the composite spectra can also be noted. The sample Z6H4 has HA diffraction peaks less pronounced than Z4H6. However, it is important to note that zirconia phases seem to be the same, independently of zirconia or HA content and no other crystalline phosphate phases were detected in the spectra.

3.2. FTIR spectra

Fig. 2(a and b) correspond to FTIR spectra of Z4H6 and Z6H4 samples, respectively. For both samples, spectra recorded ill-defined and low-intensity absorption bands of P–O due to PO_4^{3-} groups at the 1080–1020 cm^{-1} region which are characteristic of hydroxyapatite. Two peaks, at 570 and 540 cm^{-1} due to P–O bending vibrations are present in the spectra for sample Z4H6. The HA characteristic peaks are better defined in Z4H6 than for Z6H4. O–H–O bands related with adsorbed water are observed for both samples. A small shoulder associated to the O–H vibrational mode around 600–610 cm^{-1} (found in pure hydroxyapatite spectra) is also seen for the Z4H6 sample, but it is absent for Z6H4. Bands or shoulders of O–H stretching at 3600–3580 cm^{-1} and of the ZrO_2 phase were not identified for these samples, although CaO absorption bands at 250–200 cm^{-1} were found in their spectra.

XRD patterns and FTIR spectra indicate that the higher the zirconia phase content in the composite, the stronger its effect on structural features of the HA phase.

3.3. Thermal analysis

TG and DTA curves of the composite powders are given in Fig. 3(a and b). There are no significant differences between thermal behaviors for both powders. Weight losses were 3.5 and 4.5% for Z4H6 and Z6H4, respectively, for temperatures from 25 to 1400°C. A relatively pronounced mass loss, occurs between 25 and 100°C with the corresponding endothermic peak attributed to release of water. From 100°C on, a slight decrease in TG curves corresponding to a loss of about 2.5% is verified up to 900°C. Another endothermic peak at 1100°C can be attributed to the partial decomposition of hydroxyapatite into oxyapatite that, in turn, converts into tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP). After this peak, no other thermal change was observed up to 1400°C. In other words, thermal stability was achieved for both materials at temperatures above 1100°C independently of the zirconia phase content.

3.4. Scanning electron microscopy and the BET method

Specific surface area, and pore and particle size measurements performed by the BET method and estimates of particle agglomerate sizes from SEM (Fig. 4) of the samples Z4H6 and Z6H4 are shown in Table 1. The Z4H6 and Z6H4 powders appear to be constituted of very fine and spherical particles that aggregate, forming multiple generations of agglomerate. These results are similar to other observations found in the literature [14–19]. According to theoretical and experimental investigations of diffusion-limited aggregation processes of individual particles and small groupings of particles [20–24], fine ceramic powders tend to form hard agglomerates during the synthesis process. In structures having multiple

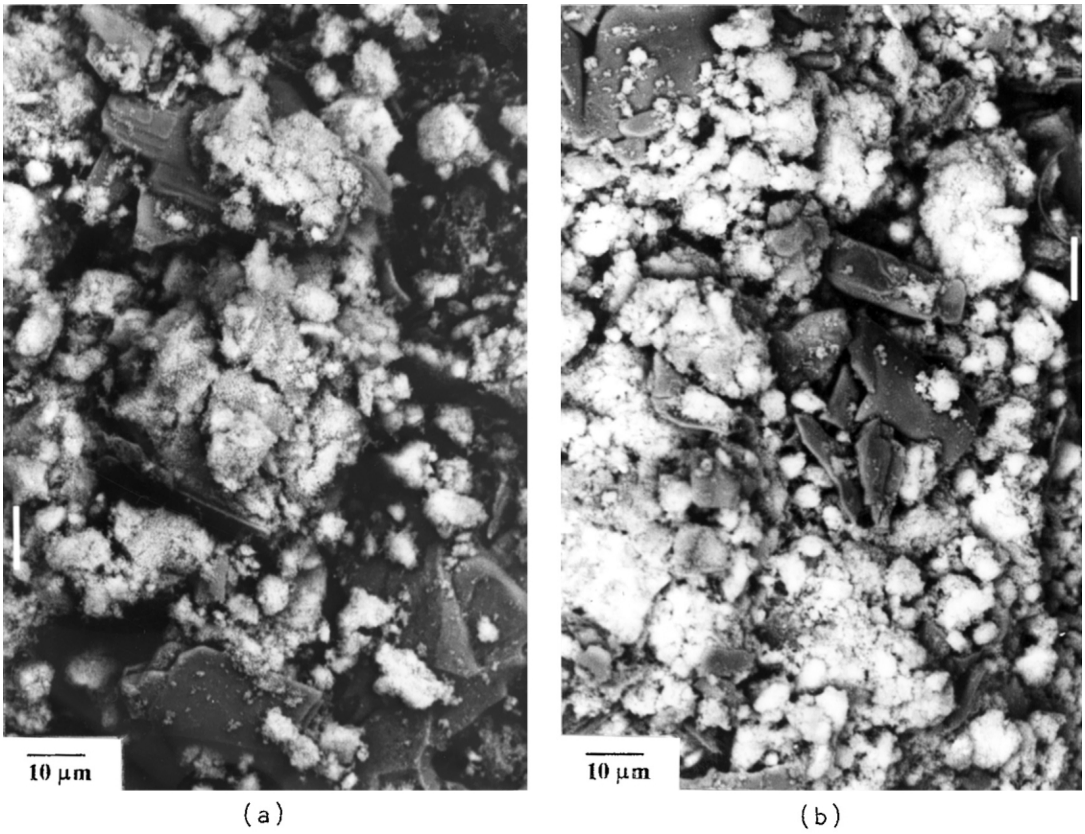

Fig. 4. Microstructures of (a) Z4H6 and (b) Z6H4.

Table 1
Physical and morphological characteristics of Z4H6 and Z6H4 powders

Sample	$\rho_{\text{theoretical}}$ (g/cm^3)	S_{BET} (m^2/g)	d_{pore} (nm)	d_{particle} (nm)	d_1 (μm)	d_2 (μm)	d_3 (μm)	d_4 (μm)
Z4H6	4.25	34.23	2.449	41.2	0.633	1.55	6.27	13.9
Z6H4	4.80	39.32	2.383	31.8	0.601	1.68	6.04	12.9

generations of agglomerates, the first generation is a cluster of primary particles or hard agglomerates, and the second generation is a cluster of these clusters. Successive generations are further clusters of clusters at higher scales. Such structures may occur because of the variety of clustering mechanisms (diffusion, convection, granulation and others) acting within a given powder. By image processing and analysis, four generations of agglomerates were considered in the morphological study of the composite powders synthesized. The values of agglomerate size for the first (d_1), second (d_2), third (d_3) and fourth (d_4) generations are shown in Table 1. Similar agglomerate sizes are also observed for a given generation.

4. Conclusion

Two calcia partially stabilized zirconia-hydroxyapatite powders were synthesized by the co-precipitation method. Powder XRD patterns and IR spectra for Z4H6 and Z6H4 revealed the presence of the different zirconia phases characterized as t-ZrO_2 and $Ca_{0.15}Zr_{0.85}O_{1.85}$. The presence of these phases, richer in Ca content than expected by the nominal composition of zirconia phase, could be explained by the high concentration of calcium ions in solution. Ca ions belonging to HA phase diffused to zirconia phase, and the calcia-zirconia phases and probably, other consisting of amorphous calcium deficient hydroxyapatite, were formed. The precipitation of hydroxides precursors of calcia-zirconia phase in a medium containing HA phase previously precipitated seems to promote the partial decomposition of hydroxyapatite. A cation diffusional mechanism appears to govern the formation of phases. Besides, higher is the zirconia phase content in the composite, the stronger is its effect on structural features of the HA phase. The great thermal stability is another interesting result. It suggests that these composites could be sintered at temperature as higher as 1300°C. Specific surface area, pore, particle and agglomerate sizes data present great similarity, independently of sample composition. The chemical route used in this work produced reproducible samples and, as expected, the precipitation steps of the powders precursors has a crucial role on the final powders composition.

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