Influence of synthesis route on phase formation and sinterability of hydroxyapatite-zirconia composites

Lazar, D. R. R. [1, a]; Cunha, S.M [1,b], Ussui, V. [1, c]; Fancio, E. [2,d];
de Lima, N. B. [1,e]; Bressiani, A. H. A. [1,f]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN)
Av. Professor Lineu Prestes, 2242 – CEP 05508-000 - São Paulo – São Paulo - Brazil
[2] Instituto de Física da USP (IFUSP)
Rua do Matão, Travessa R, 187. CEP 05508-090 - São Paulo – São Paulo - Brazil
[a] drlazar@ipen.br, [b] smcunha@ipen.br, [c] vussui@ipen.br, [d] efancio@terra.com.br
[e] nblima@ipen.br; [f] abressia@ipen.br

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Abstract. Reinforcement with yttria stabilized zirconia (YSZ) is an alternative to improve mechanical strength of hydroxyapatite (HAp) ceramic. However, calcium may react with zirconium to form calcium zirconate. In addition, decomposition of HAp to tricalcium phosphate (TCP) occurs with water loss inhibiting ceramic densification. In order to minimize the formation of these compounds, two synthesis routes were compared in this work: coprecipitation of hydrous yttria stabilized zirconia in a calcium phosphate gel medium and powder mixture of individual calcined powders. Composite nominal compositions were fixed at 90 and 95 HAp wt%. Calcium, zirconium and yttrium chlorides and ammonium hydrogen phosphate were the employed precursors. Ammonium hydroxide was the selected precipitation agent. Calcination was performed at 800°C for 1 hour and pellets were sintered in the range of 1150 and 1350°C for 1, 3 and 5 hours. Ceramic samples were characterized by scanning electron microscopy and apparent density measurements. Crystalline phases were quantified by Rietveld analysis of X-ray diffraction patterns. Results indicate that powders prepared by coprecipitation can cause porosity formation due to the higher chemical reactivity during synthesis process.

Introduction

It is well known that synthetic hydroxyapatite (HAp – $CA_{10}(PO_4)_6(OH)_2$) is an important ceramic for bone restoration in medical and dentistry field due to its chemical and crystallographic similarity to human apatite. However, the worse mechanical properties of synthetic HAp, compared to the cortical bone, limits its use to nonload-bearing applications, such as maxillofacial bone grafts and reconstruction of ossicles in the middle ear, and as film coating on metallic prostheses. This behaviour is generally associated to the minor compositional differences between biological and synthetic apatites, which play an important role in the osseointegration process. Moreover, human bone is a composite material of an organic (collagen) and inorganic (carbonated apatite) constituents [1, 2].

In order to improve the mechanical properties of HAp ceramics, some bioinert oxides, including alumina, titania and stabilized zirconia can be added in form of powders or fibers [3-6]. Among then, 3 mol% yttria stabilized zirconia (3YSZ), that belongs to the family of transformation toughened ceramics, can be an interesting choice. Its specific feature consists in a microstructure formed by tetragonal grains that undergo transformation to a monoclinic phase with volume expansion of about 3-4%, giving a compressive stress field in the matrix which can stop a crack. The toughness of the ceramic is based on such dissipative energy mechanism [7]. There are, however, some problems concerning the ceramic processing of HAp-zirconia composite that should be solved. These problems are related to the influence synthesis and sintering conditions on phase stability of HAp and tetragonal zirconia. Calcium can be released from HAp and interact with zirconium, resulting in the formation of cubic zirconia or calcium zirconate, which inhibits the transformation toughening mechanism [8-12]. To minimize these reactions, some efforts have been made toward reducing the sintering temperature and holding time. One alternative is the use of HAp and zirconia nanopowders [13]. Another important procedure is the introduction of external pressure using the following techniques: spark plasma sintering (SPS), hot-pressing or hot isostatic pressing (HIP) [13-16]. However, considering the economical point of view, these methods are not cost-effective.

In this work it was compared the thermal stability and densification of hydroxyapatite-zirconia composite prepared by pressureless sintering, from powders obtained by coprecipitation route or mixed by mechanical technique. Sintering temperature and holding time was also evaluated.

Experimental Procedure

Hydroxyapatite - zirconia ceramic composites, containing 90 and 95 HAp wt% (sample codes 90H10ZY and 95H5ZY), were prepared via two synthesis routes: (a) coprecipitation from calcium, phosphorous, zirconium and yttrium solutions and (b) mechanical mixing (M) of hydroxyapatite (H) and 3 mol% yttria stabilized zirconia (3YSZ) powders prepared individually by chemical precipitation. Calcium chloride ($CaCl_2.2H_2O$ PA, CAAL, Brazil), ammonium hydrogen phosphate ($NH_4H_2PO_4$ PA, CAAL, Brazil) and ammonium hydroxide (UqB, Brazil) were the starting materials used to synthesize hydroxiapatite (Ca/P = 1.67). Zirconium oxychloride (IPEN, Brazil) and yttrium chloride, prepared by hydrochloric dissolution of 99,9% yttrium oxide (Aldrich, USA) were used as stabilized zirconia precursors.

Chemical coprecipitation was conducted by dropping $NH_4H_2PO_4$ 0.2 molar aqueous solution into a reactor containing $CaCl_2$ 0.5 molar solution. NH_4OH 5.5 molar was used to adjust at 10 the pH of the mixture. Temperature was maintained at 70°C for 1 hour, under agitation, to promote the reaction. After ageing for 24 hours the gel suspension was filtered and maintained in a NH_4OH 5.5 molar solution in order to receive the mixture of zirconium and yttrium solutions. After precipitation of zirconium and yttrium ions the suspension was stirred for 1 hour. The resulted gel was filtered and washed with water until no indication of residual Cl^-. To avoid the formation of hard agglomerates the precipitate was washed with ethanol and treated by azeotropic distillation with buthanol. The distilled powder was oven-dried at 80°C for 24 hours and calcination was carried out at 800°C for 1 hour. Ball milling in ethanol for 16 hours, using zirconia balls as milling media, was employed to eliminate large agglomerates.

Composite preparation of by mechanical mixing involved the preparation of each powder by precipitation in the same conditions described early, and the mixture by ball milling after calcination step. Green pellets were prepared by uniaxial pressing at 100 MPa and sintering was performed in air at the temperature range between 1150 and 1350 °C for 1, 3 and 5 hours.

Powders were characterized by scanning electron microscopy (SEM) (XL30, Phillips), gas adsorption (BET Nova 1200, Quantachrome), laser diffraction (granulometer 1064, Cilas), and X-ray diffraction (XRD) using Cu Kα radiation (D8 Advance, Bruker-AXS). The characterization of as-sintered samples was carried out by apparent density measurements (Archimedes method), SEM and XRD. Quantitative phase analysis of some powders and sintered samples were performed by Rietveld refinement of X-ray diffraction patterns. Data were collected from 5 to 80° 2θ with step of 0.02 ° and counting time 12 s. The DBWS-9807 program was used to refine the structures.

Results

SEM micrographs (Fig. 1) indicate that 3YSZ powder has a greater tendency to agglomeration compared to HAp powders (H sample), even though particles are in the nanoscale. Morphology and particle size of composite powders (95H5ZY and 90H10ZY) are very similar to H sample due to the high concentration of calcium phosphate constituent in these composites. Agglomerate mean size of these samples, determined by laser diffraction, is around 2μm and specific surface area values is in the range of 12 - 51 $m^2.g^{-1}$, for H and 3YSZ powders, respectively.

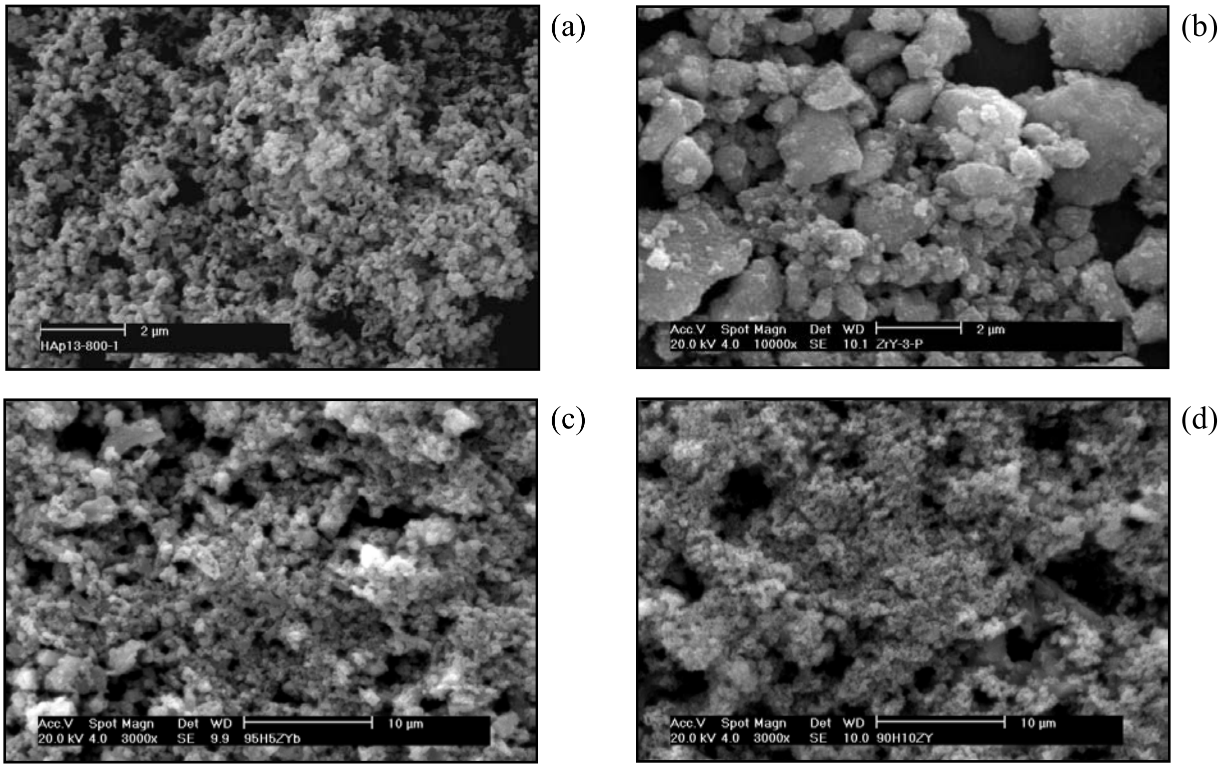

Figure 1: SEM micrographs of powders: (a) H; (b) 3YSZ, (c) 95H5ZY and (d) 90H10ZY.

XRD results (Table 1) show that the major phase present in HAp powder (H sample) is hydroxyapatite (hexagonal symmetry). β-tricalcium phosphate (β-TCP) with chemical formula $Ca_3(PO_4)_2$ and rhombohedral symmetry is also present in this sample as a minor phase. According to the previous work [17] β-TCP is normally obtained by heating HAp at temperatures as low as 600°C and has high resorbability in physiological medium [1,2]. Therefore, the porosity generation upon contact with body fluids will induce in situ formation of biological apatite, improving bone reconstruction and regeneration. On the other hand, 3YSZ powder has as a major phase tetragonal structure. Composite powders are mixtures of calcium phosphate powders (HAp and β-TCP) and calcium zirconate ($CaZrO_3$), indicating the great reactivity between zirconium and calcium ions during synthesis process.

Table 1: Phase composition of powders, determined Rietveld analysis of XRD patterns.

Sample	Phase composition (wt%)				
	HAp	β-TCP	$CaZrO_3$	ZrO_2 (m)	ZrO_2 (t)
H	81.0 ± 0.5	19.0 ± 1.3	—	—	—
3YSZ	—	—	—	14.0 ± 0.1	86.0 ± 0.1
95H 5ZY	90.5 ± 0.4		9.5 ± 0.1	—	—
90H 10ZY	75.1 ± 0.4	10.5 ± 0.2	14.4 ± 0.1	—	—

Phase composition analysis of ceramics samples (Table 2) shows that the amount of tricalcium phosphate increases with sintering temperature. In this case it is observed the formation of α-TCP, which has monoclinic symmetry and is characterized by a higher resorbability in physiological medium and lower density (2.86 g.cm^{-3}), compared to β - TCP (3.07 g.cm^{-3}). Calcium zirconate was also formed (4.62 g.cm^{-3}). Stabilized zirconia almost disappeared, restraining transformation toughening mechanism. In spite of this, HAp-zirconia composites containing calcium zirconate phase showed potential clinical application as structural implants [18].

Some authors [8-11] report that the CaO release, due to HAp decomposition to TCP, enhances the formation of calcium zirconate and zirconia-calcia solid solution, according the following reactions :

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3\ Ca_3(PO_4)_2 + CaO + H_2O \qquad (1)$$

$$Ca_{10}(PO_4)_6(OH)_2 + ZrO_2 \rightarrow 3\ Ca_3(PO_4)_2 + CaZrO_3 + ZrO_2{:}CaO + H_2O \qquad (2)$$

Adolfsson et al. [16,19] observed, by thermal analysis, that the release of water increases gradually with increasing temperature creating vacancies in HAp structure (former OH^- positions is replaced by O^{2-} ions and vacancies). When a specific fraction of vacancies has been created, HAp will not be stable and it will decompose. However, if water loss is maintained at a low level, the equilibrium of these reactions is shifted to the left and decomposition into TCP, $CaZrO_3$ and cubic zirconia will not occur. In order to prevent water loss, it is recommended the use of a close system and atmosphere control for sintering (HIP, for example), or incorporation of F^- ions in HAp structure. If fraction of vacancies formed is suppressed the temperature stability will be extended.

Besides the formation of calcium zirconate, it was observed in the present work that the composite preparation by mechanical mixing inhibits TCP formation.

Table 2: Phase composition of ceramic samples as a function of synthesis procedure and sintering conditions , determined Rietveld analysis of XRD patterns.

Sample	Phase composition (wt%)					
	HAp	β-TCP	α-TCP	$CaZrO_3$	ZrO_2 (t)	CaO
H-1250-1	83.1 ± 0.6	16.9 ± 1.2	—	—	—	—
H-1350-1	46.0 ± 0.9	18.0 ± 0.4	36.0 ± 0.2	—	—	—
95H 5ZY-1250-1	76.9 ± 0.3	14.8 ± 0.1	—	8.3 ± 0.1	—	—
95H 5ZY-1250-1M	89.7 ± 0.3	2.5 ± 0.7	—	7.6 ± 0.7	<1	—
95H 5ZY-1350-1	52.9 ± 0.5	—	37.2 ± 0.1	9.9 ± 0.1	—	—
95H 5ZY-1350-1M	64.0 ± 0.1	< 1	26.4 ± 0.7	7.4 ± 0.4	1.7 ± 0.3	—
90H10ZY-1250-1	28.7 ± 0.9	54.8 ± 0.1	—	16.5 ± 0.1	—	—
90H10ZY-1250-1M	49.7 ± 0.1	32.9 ± 0.7	4.6 ± 0.9	11.8 ± 1.3	<1	<1
90H10ZY-1250-3	42.1 ± 0.1	27.3 ± 1.3	14.6 ± 0.8	16.0 ± 0.1	—	—
90H10ZY-1250-3M	66.7 ± 0.7	19.2 ± 0.8	<1	13.0 ± 0.9	< 1	<1
90H10ZY-1350-1	45.8 ± 0.5	11.0 ± 0.1	39.7± 0.1	—	3.5 ± 0.1	—
90H10ZY-1350-1M	56.9 ± 0.1	1.1 ± 0.4	27.1 ± 0.6	13.4 ± 0.3	1.5 ± 0.1	<1

Considering that theoretical densities of HAp and 3YSZ are 3.1 and 6.1 g.cm^{-3}, respectively, the expected density of HAp-3YSZ composites should be around 3.3 g.cm^{-3}. Based on this assumption, apparent density results of sintered samples (Table 3) reveal that the addition of stabilized zirconia powder was not effective to increase the density of ceramics prepared from coprecipitated powders. However, ceramics prepared by solid state reaction, especially sample 95H5ZY1350-1 M showed a better densification, compared to H sample. This behaviour is confirmed by SEM micrographs of ceramics sintered at 1250°C for 1 hour showed in Fig. 2.

Table 3: Apparent density of ceramic samples as a function of synthesis procedure and sintering conditions.

Sintering conditions T(°C) – t (h)	Apparent density ($g.cm^{-3}$)				
	H	95H 5ZY	95H 5ZY M	90H 10ZY	90H 10ZY M
1150-1	3.06 ± 0.01	2.25 ± 0.02	2.57 ± 0.03	2.11 ± 0.02	2.14 ± 0.02
1250-1	3.09 ± 0,01	2.80 ± 0.01	3.06 ± 0.01	2.52 ± 0.01	2.66 ± 0.02
1250-3	—	2.82 ± 0.02	3.12 ± 0.01	2.28 ± 0.01	2.71 ± 0.19
1250-5	—	2.78 ± 0.01	3.12 ± 0.01	2.23 ± 0.05	2.74 ± 0.01
1350-1	3.08 ± 0.01	2.94 ± 0.03	3.15 ± 0.02	2.15 ± 0.05	2.98 ± 0.01
1350-3	—	2.96 ± 0.04	3.14 ± 0.02	2.16 ± 0.06	3.00 ± 0.03

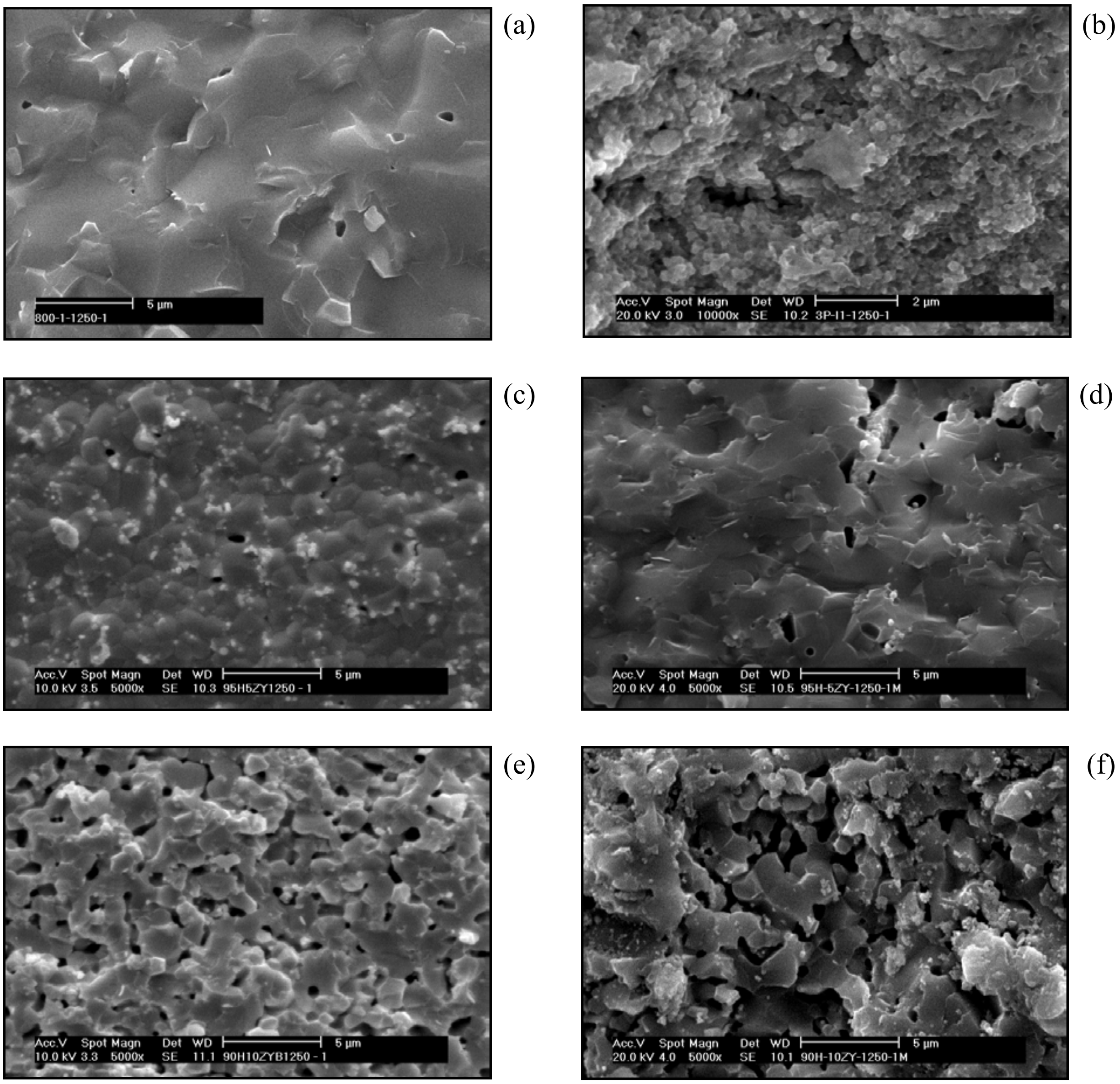

Figure 2: SEM micrographs of ceramic samples sintered at 1250°C for 1 hour: (a) H; (b) 3YSZ, (c) 95H5ZY , (d) 95H5ZY – M, (e) 90H 10ZYand (f) 90H 10 ZY – M.

Conclusions

The synthesis of hydroxyapatite – zirconia composite by coprecipitation route allowed the preparation of powders with adequate physical properties for ceramic processing. However, phase analysis results has demonstrated that reactions between calcium and zirconium started during powder synthesis steps (coprecipitation/calcination) and continue during sintering process, creating porosity due to water loss. Moreover, it is known that the bioresorbable characteristic of tricalcium phosphates induce porosity formation when in function. In the case of composite preparation by mechanical mixing, a better densification was observed for sintering temperatures above 1250^{o}C, in spite of the presence of calcium zirconate phase. As the influence of calcium zirconate on transformation toughening mechanism has not been elucidated, further investigation are needed. In order to preserve hydroxyapatite and stabilized zirconia phases in the composite, it will be important to control sintering atmosphere and to use pressure sintering techniques, such as hot-pressing or hot isostatic pressing.

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