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Hydroxyapatite–zirconia composites prepared by precipitation method

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Chemical routes to prepare ceramic precursor powders are frequently envisaged, especially when the aspects related to the microstructure are important and need to be controlled. An understanding of which parameters of synthesis and thermal treatment can influence the mechanical properties of hydroxyapatite compounds is essential for the production of such materials. Hydroxyapatite–zirconia composites have been prepared, in this study, by a precipitation method. This led to the formation of homogeneous powders with a very defined particle-size distribution. Ceramic pellets prepared from these powders were easily compacted and sintered without cracking. As expected, the presence of the zirconia phase improved composite densities and appeared to have an important role in thermal stabilization of the hydroxyapatite phase.

1. Introduction

Calcium hydroxyapatite (HA) is one of the most biocompatible materials with human bones and teeth [1, 2] but its mechanical properties, especially toughness, limits its utilization for hard tissues. Indeed, one of its major applications is as a covering material for titanium or other metals used in implants. In these cases the biocompatibility is assured by hydroxyapatite while the mechanical resistance is provided by the metal. One alternative implant material would be a ceramic composite, formed by one biocompatible hydroxyapatite phase and one mechanically resistant and bioinert phase, like alumina (Al_2O_3) or zirconia (ZrO_2).

Partially stabilized zirconia (PSZ), is a well-studied system that presents tested mechanical and thermal performances. Values of bending strength and fracture toughness of these systems are of the order of ten times of those of hydroxyapatite [1]. It can be described as a solid solution where the tetragonal phase of zirconia is stabilized by the introduction of a certain quantity of oxides, for example, CaO, Y_2O_3 and Mg_2O_3, into a ZrO_2 matrix at sintering temperatures of the order of 1000 °C. The composite synthesized in this work was formed by hydroxyapatite, as a dispersant phase, in which the zirconia–calcia partially stabilized phase, Z, had been dispersed.

The objective of this study was to improve the mechanical resistance of hydroxyapatite–zirconia composites prepared by chemical routes and to verify the influence of some parameters, such as the content and chemical form of the zirconium phase added, compaction pressure and sintering temperature, on the final densities of the composites.

2. Materials and methods

2.1. Samples preparation

Hydroxyapatite (HA) powder was prepared by precipitation of 1.0 M $Ca(NO_3)_2$ solution and 0.6 M $(NH_4)_2HPO_4$ solution in the presence of NH_4OH with vigorous agitation for 7 h followed by a resting period of 17 h at room temperature and a pH in the range 12–13 [3, 4]. The resulting precipitate was filtrated under vacuum and carefully washed with deionized water at 70 °C. Next, the material was dispersed and filtrated under vacuum, first in acetone and then in petroleum ether (Merck p.a reagents were used).

Calcia–zirconia powder of theoretical composition $(ZrO_2)_{0.95}(CaO)_{0.05}$ was prepared by mixing alcoholic solutions of $Ca(NO_3)_2$ and zirconium butoxide (Aldrich reagent) in an ammoniacal medium. The precipitated hydroxide was filtrated under vacuum and the residual water was removed by a distillation procedure using toluene. At this step, the formed hydroxide was divided in two portions. One portion was used in the composite synthesis as it was, that is, in hydroxide form, and the other was calcined at 750 °C in air for 3 h before being used in the composite synthesis. In this case, the formed product was in an oxide form.

Hydroxide–zirconia composites were prepared by mixing the hydroxyapatite slurry with the zirconium phase, in an ammoniacal medium, under vigorous agitation for 7 h, followed by a resting period of 17 h. After being dried at 90 °C for 24 h, the resulting fine powders were calcined at 800 °C for 3 h in air.

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Samples were pressed on cylindrical forms at 200 and 600 MPa and sintered at 900 and 1100 °C for 3 h. Two compositions (30% and 40% vol/vol of zirconia phase) were prepared. The influence of the chemical zirconium phase dispersed in the hydroxyapatite matrix was also studied for each composition.

The notations used to characterize the samples were HAZH*X* and HAZO*X*, where HAZ denotes the composite hydroxyapatite–zirconia, *X* is the content of zirconia (% vol/vol), and H and O represent the hydroxide and oxide zirconium phases, respectively. Samples symbolized by HA and Z were sometimes used for comparison and represent hydroxyapatite and zirconia powders, respectively.

2.2. Sample characterization

Powder X-ray diffraction (XRD) was used to identify the phases in the precursor powders and sample composites. All diffraction patterns were obtained on a Rigaku θ–2θ diffractometer using CuK_α radiation. Thermal studies were carried out using an SDT-2960 TA Instruments thermal analyser, under argon flux of 110 ml min^{-1}. Surface area measurements were determined by BET method, using nitrogen as an absorbate at 77 K. Sample morphology was analysed using a Jeol JMC 35C scanning electron microscope (SEM). Fourier transform–infrared spectroscopy (FT–IR) was also used for the characterization of the composites in a Galaxy-Mattson model 3020 spectrometer. Experimental densities were determined by a mercury picnometry method.

3. Results and discussion

Figs 1–6 show X-ray diffraction patterns of calcined composites for the different compositions of the zirconium phase, as well as those of hydroxyapatite and zirconia separately. The formation of a composite material with peaks corresponding to both precursor powders could be evidenced, and as expected, the formation of new phases was not detected.

FT–IR spectra of composite powders present absorption bands characteristic of hydroxyapatite phase in the region between 3600 and 560 cm^{-1}. It was not verified the presence of carbonate peaks. An absorption band characteristic of metal–oxygen vibration appears at 500 cm^{-1}.

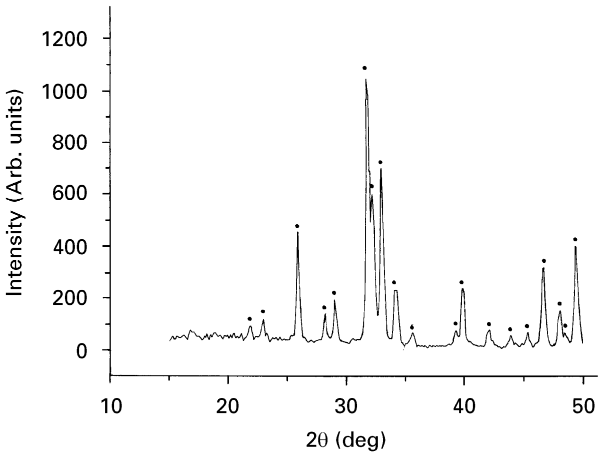

Figure 1 Powder X-ray diffraction pattern of HA. (●) HA.

The surface areas of composites, HAZH3, HAZO3, HAZH4 and HAZO4 are 52.4, 40.5, 73.2 and 48.8 m^2 g^{-1}, respectively. It can be noted that for the same content of zirconium phase, the composites

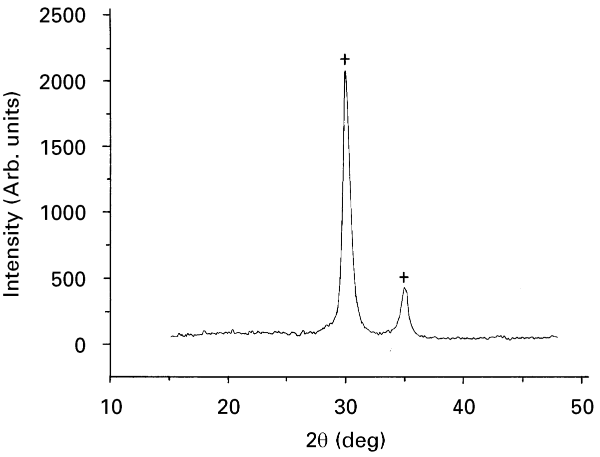

Figure 2 Powder X-ray diffraction pattern of Z. (+) Z.

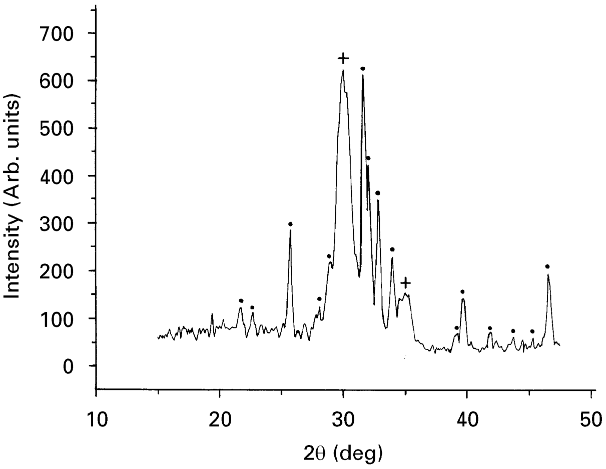

Figure 3 Powder X-ray diffraction pattern of HAZH3. (●) HA, (+) Z.

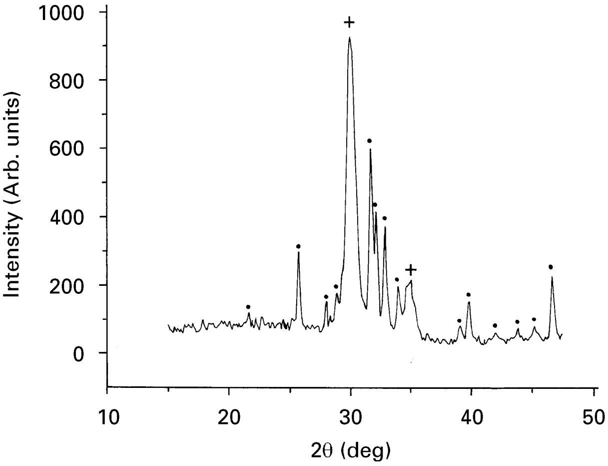

Figure 4 Powder X-ray diffraction pattern of HAZO3. (●) HA, (+) Z.

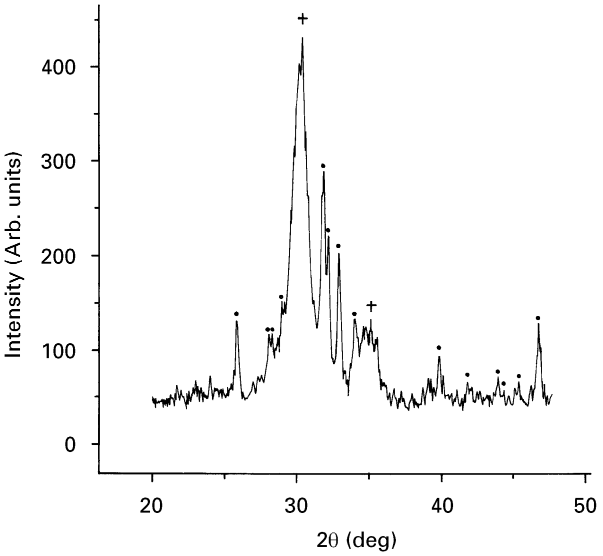

Figure 5 Powder X-ray diffraction pattern of HAZH4. (●) HA, (+) Z.

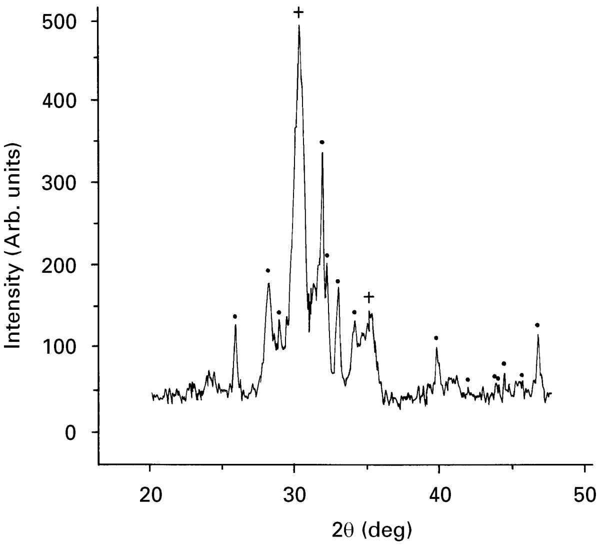

Figure 6 Powder X-ray diffraction pattern of HAZO4. (●) HA, (+) Z.

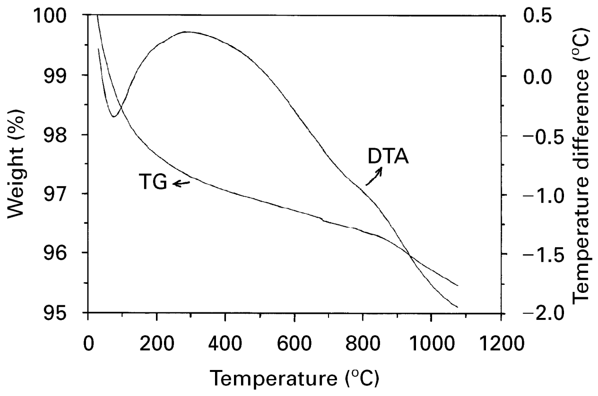

Figure 7 TG–DTA curves of HAZH3.

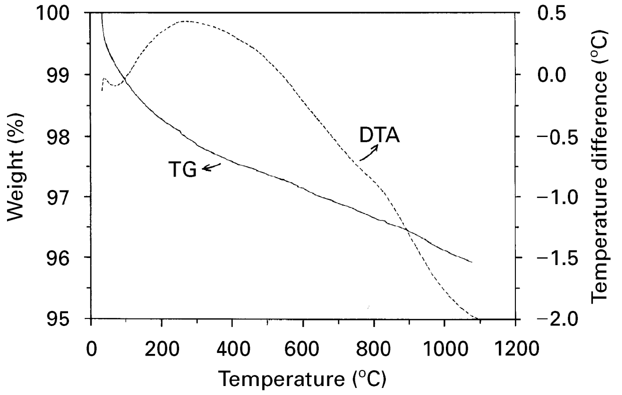

Figure 8 TG–DTA curves of HAZO3.

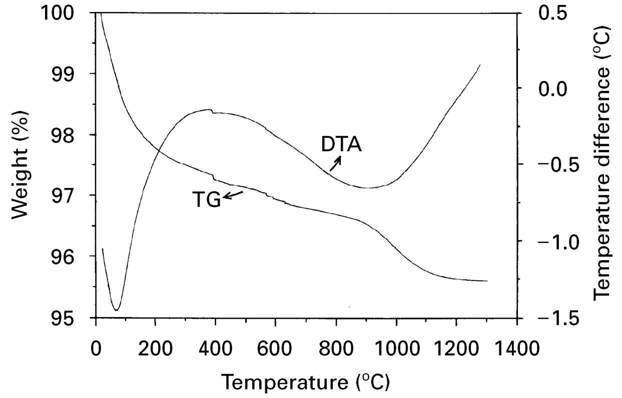

Figure 9 TG–DTA curves of HAZH4.

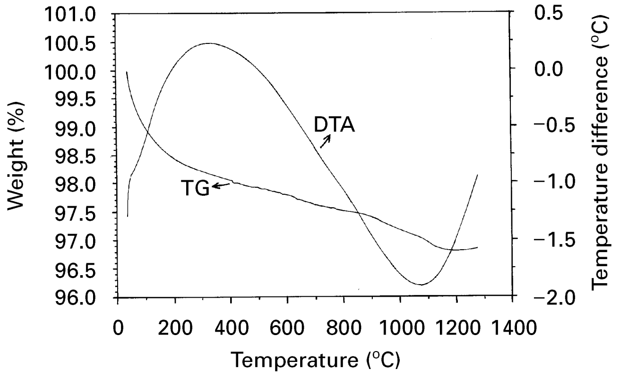

Figure 10 TG–DTA curves of HAZO4.

prepared from zirconium hydroxide present areas bigger than those prepared from zirconium oxide powders.

A very defined particle and agglomerated size distribution was obtained for precursor powders and their composites. The values of particle size varied from 0.20–0.35 μm with agglomerated medium size ranging from 1.60–2.00 μm. These results could explain the great morphological homogeneity of the composites produced by the precipitation method.

Thermal analyses revealed some important aspects related to the behaviour of different powders. TG and DTA curves of the composite powders are given in Figs 7–10. One important result shown by the TG curves is the fact that for all samples, the loss of weight was about 4%, when the temperature varied from 20–1300 °C. A relatively pronounced mass loss occurred between 20 and 200 °C with the corresponding endothermic peak attributed to adsorbed water. After this change, a progressive loss of about 1% occurs in the interval of 200 °C–900 °C. The exothermic peak

TABLE 1 Experimental density values for composite samples

Precursor powders	Sample	P (MPa)	% Z(vol/vol)	T_s(°C)	Density (g cm^{-3})
HAZH3	A	200	30	900	2.086
HAZH3	B	600	30	1100	2.959
HAZH4	C	200	40	1100	3.035
HAZH4	D	600	40	900	3.022
HAZX3	E	200	30	1100	2.630
HAZX3	F	600	30	900	2.706
HAZX4	G	200	40	900	2.470
HAZX4	H	600	40	1100	3.873

observed near 400 °C had already been seen and has been attributed to variations of the thermal conductivity of hydroxyapatite [5]. Another exothermic peak, near 1100 °C, is observed only for samples having a larger zirconia content. Finally, it could be noted that powders having more zirconia content also showed a stabilization step at temperatures above 1100 °C.

The influences of the compaction pressure, P, the content of the zirconia phase, % Z, and the sintering temperature, T_s, on the composite densities are given in Table I. Density values show clearly that all the investigated parameters influenced the composite densifications. The poorest densification was observed for sample A, which had the lowest values of the studied parameters. The best densification was observed for sample H, whose parameters were the largest ones. In general, the samples having a greater zirconia content presented higher densities than the others.

4. Conclusion

The chemical route proposed for the preparation hydroxyapatite–zirconia composites, in this study, leads to the formation of homogeneous powders with a very defined particle-size distribution. The resulting powders were easily compacted, without the addition of a ligant material, and the sintered pellets did not exhibit microcracking. The zirconia phase improves composite densities and appears to have an important role in the thermal stabilization of the hydroxyapatite phase.

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