JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **10** (1999) 715–719

Zirconia-toughened hydroxyapatite ceramic obtained by wet sintering

J. A. DELGADO§, L. MOREJÓN
Centro de Biomateriales, Universidad de La Habana, 10400-Ciudad Habana, Cuba
S. MARTÍNEZ*
Dept Cristallografia, Mineralogia i Dip. Minerals, Fac. Geologia, Universitat de Barcelona, C/Martí Franquès, s/n, 08028-Barcelona, Spain
M.P. GINEBRA, N. CARLSSON, E. FERNÁNDEZ, J. A. PLANELL
CREB, Department of Materials Science and Metallurgical Engineering, Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028-Barcelona, Spain
M. T. CLAVAGUERA-MORA, J. RODRÍGUEZ-VIEJO
Grup Fìsica dels Materials I, Dept. Fìsica, Universitat Autònoma de Barcelona, 08193-Barcelona, Spain

A toughened hydroxyapatite (HA) ceramic has been obtained through the incorporation of magnesia partially stabilized zirconia (Mg-PSZ) under uniaxial pressing and sintering in wet oxygen at 1250 °C for 4 h. The powder X-ray diffraction (XRD) patterns and infrared spectra (FT-IR) show that HA is the only calcium phosphate phase present. The composite (MgPSZ-HA) has a density of 94% the theoretical value. The bending strength and the fracture toughness are around 50% higher for Mg-PSZ reinforced than for HA. The grain size and the fracture surface were studied by scanning electron microscopy (SEM). The influence of the Mg-PSZ particles on the fracture mechanism of the HA ceramic is discussed.

1. Introduction

The low fracture strength and fatigue resistance of HA ceramics are the main limitations to potential applications in which the implant must withstand certain loading levels [1]. It is well known that the brittle behavior of ceramics can be improved by the incorporation of partially stabilized zirconia (PSZ) or tetragonal zirconia particles (TZ) [2, 3]. Since PSZ presents high strength, high resistance to fracture and is inert in biological environments, its incorporation may enhance the mechanical properties of HA ceramics without adversely affecting its biocompatibility [4, 5].

However, the major drawback to this approach is that at high temperature the calcium, which is the main component of the HA, diffuses into zirconia and changes its structure into the stable cubic phase, hindering the transformation toughening mechanism [4]. Furthermore, calcium diffusion promotes the decomposition of HA, leading to the formation of β-tricalcium phosphate (β-TCP) and calcium zirconate (CZ). These phases reduce the mechanical properties of the ceramic [6, 7].

Commonly, yttria partially-stabilized zirconia (Y-PSZ) has been used as the reinforcing phase, and the decomposition associated to calcium diffusion appears mainly when pressureless sintering is used.

In this work we propose a new method, which prevents the decomposition of HA, to obtain a toughened HA ceramic by incorporation of Mg-PSZ particles. For that purpose we study the sinterability and the mechanical behavior of a (MgPSZ-HA) composite obtained by uniaxial pressing and sintering in humid environment.

2. Materials and methods

HA powder was prepared in the laboratory by reaction between $Ca(OH)_2$ and H_3PO_4 in aqueous solution. The precipitates were filtered, washed with distilled water and dried in air at 105 °C for 24 h. The dried product was calcined at 700 °C for 2 h and ground for 1 h. The Mg-PSZ powder was obtained mixing zirconia (Merck) and magnesia (Panreac) (8 mol %), heating at 1450 °C for 4 h and then grinding for 1 h. The particle sizes in the HA and Mg-PSZ powders were examined by laser diffraction (Coulter® LS) using a sodium pyrophosphate solution as defloculant.

The Ca/P ratio in HA was measured by atomic absorption spectrometry (Jarrel ASH, Polyscan 61E). The X-ray diffraction (XRD) patterns of both powders were obtained in a Siemens D-500 XRD diffractometer. Two series of ceramics were prepared using the same

---

*Author to whom correspondence should be addressed.
§Present address: Grup Fìsica dels Materials I, Dept. Fìsica, Universitat Autònoma de Barcelona, 08193-Barcelona, Spain.

protocol: pure HA and HA containing 20 wt % of Mg-PSZ particles. The powder mixtures were ground by ball-milling in ethanol for 1 h. Subsequently, they were pressed at room temperature in a steel die under a uniaxial stress of 400 MPa for discs and 100 MPa for bars. An acrylic resin (Elvacite®) dissolved in acetone was used as binder. The green bodies prepared as discs (6 mm diameter and 3 mm high) and bars (6 × 4 × 50 mm) were sintered at 1250 °C for 4 h in wet oxygen and in air. The sintering was performed inside a tubular furnace. The green bodies were heated from room temperature to 800 °C at a heating rate of 1 °C min^{-1} and then heated to the top temperature at a rate of 3 °C min^{-1}. The humid atmosphere was produced by flowing oxygen through boiling distilled water at a rate of $0.07\,\text{m}^3\,\text{h}^{-1}$. After sintering the specimens were cooled down inside the furnace at a rate of 100 °C h^{-1}.

The thermal stability of HA phase when Mg-PSZ is present was determined by XRD and Fourier transform infrared spectroscopy (FT-IR) using potassium bromide discs (FT-IR spectrophotometer Bomen MB 120). To determine the densification produced by sintering, the specimens were diamond polished and finished with a 0.1 μm alumina slurry. Volume was measured with a micrometer and weight with a balance. The relative density was calculated using $3.16\,\text{g}\,\text{cm}^{-3}$ and $3.47\,\text{g}\,\text{cm}^{-3}$ for the theoretical densities of HA and MgPSZ-HA, respectively. To reveal the grain structure, the polished surfaces were etched with a mixture 1 : 1 of aqueous solutions of 85% lactic acid and 0.12 M ethyldiaminetetraacetic acid for 20 s. The average grain size was estimated from micrographs obtained by scanning electron microscopy (SEM; JEOL, JSM 6300).

The bending strength and the modulus of elasticity in bending were measured by a three-point bending test performed on a 30 mm span at a crosshead speed of 0.5 mm min^{-1}, using an electromechanical testing machine (Instron) equipped with a load cell of 1 kN. The dimensions of the specimens were 5 × 3.5 × 40 mm. The fracture toughness (K_{IC}) measurements performed using the single-edge notched bend (SENB) method, were done by the same three-point bending set-up. In each fracture toughness specimen (5 × 2.5 × 40 mm) a notch was sawn. For each series, five specimens were tested. The fracture surfaces of the specimens were examined by SEM.

The fracture toughness was also determined by indentation with a micro-Vickers hardness tester (Carl Zeiss), on polished discs embedded in acrylic resin, applying 1.96 N for 15 s. Niihara *et al's* equation was used for the calculations of toughness [8]. The same loading condition for the Knoop indentations was used to determine the Young's modulus, which was calculated according to the Evans formula [9].

3. Results and discussion

The Ca/P ratio in the HA powder was 1.69 ± 0.02, which agrees with the Ca/P ratio of stoichiometric HA (1.67). The powder XRD patterns show no traces of thermal decomposition at temperatures up to 1250 °C. Fig. 1 shows the XRD pattern of Mg-PSZ heated at 1450 °C for 4 h. The diffraction peaks corresponding to monoclinic, tetragonal and cubic phases are present. This is a typical XRD pattern of Mg-PSZ [10]. The proportion of the monoclinic phase ($X_m = 0.41 \pm 0.03$) was calculated using the equation proposed by Batchelor *et al.* [11]. No attempt was made to determine the relative amount of cubic and tetragonal phases since they cannot be obtained from the integrated intensities {1 1 1} in the diffraction angle of 2θ ≈ 30° [10]. Both calcined HA and Mg-PSZ present average sizes of ≈ 10 μm and ≈ 6 μm, respectively. The particle size distribution of the HA powder is considerably broader than that of Mg-PSZ, 80% of the HA particles and Mg-PSZ powders had sizes in the range 2–20 μm and 1–10 μm, respectively.

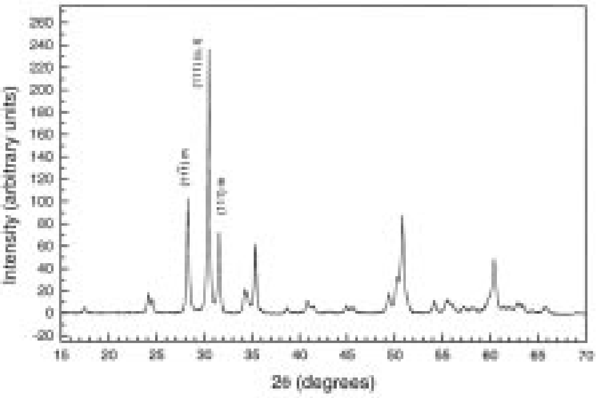

Figure 1 XRD pattern of Mg-PSZ obtained by heating at 1450 °C for 4 h.

No decomposition of the HA phase is detected in the XRD patterns of both the HA and the MgPSZ-HA materials sintered in moisture at 1250 °C for 4 h. No peaks corresponding to phases such as β-TCP or CZ are seen.

In contrast, when the MgPSZ-HA is sintered at 1250 °C for 4 h in air, the HA phase transforms into β-TCP and the CZ appears, probably due to the reaction of the Mg-PSZ and the calcium oxide (CaO) released by the decomposition of HA [12] (Fig. 2).

The FT-IR spectra of the MgPSZ-HA composite sintered in wet oxygen show the typical HA absorption

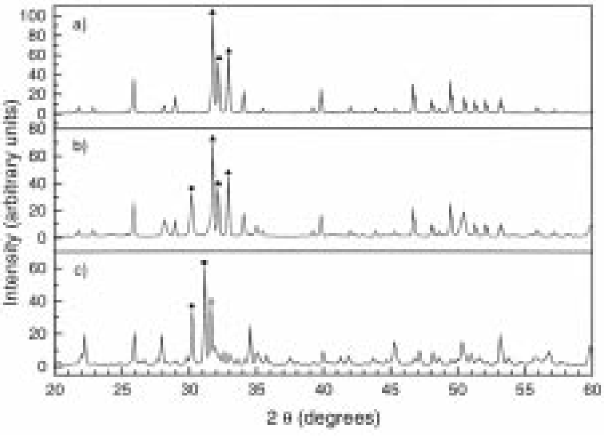

Figure 2 XRD patterns of HA and MgPSZ-HA ceramics: (a) HA sintered at 1250 °C for 4 h in wet oxygen; (b) MgPSZ-HA sintered at 1250 °C for 4 h in wet oxygen; (c) HA-MgPSZ sintered at 1250 °C for 4 h in air; (▲) HA; (●) Mg-PSZ (c, t); (■) β-TCP; (○) CZ.

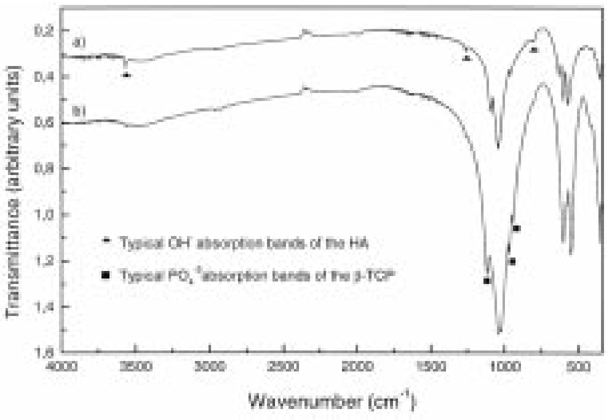

Figure 3 FT-IR spectra of MgPSZ-HA sintered at 1250 °C for 4 h; (a) sintered in wet oxygen; (b) sintered in air.

bands at 3560, 1090, 1034, 601 and 565 cm^{-1} [13] (Fig. 3). On the contrary, in the samples sintered in air the absorption bands at 1119, 972 and 948 cm^{-1} corresponding to the β-TCP are clearly detected.

The influence of the moisture content on the stability of HA at high temperature was demonstrated by Wang and Chaki [14]. In our case the sintering in humid oxygen prevents HA decomposition even when the Mg-PSZ particles, which promote the thermal decomposition of HA, are present.

When heated at high temperature, HA transforms into β-TCP and tetracalcium phosphate (TetrCP) according to the scheme [15]

$$Ca_{10}(PO_4)(OH)_2 \rightarrow 2Ca_3(PO_4)_2 + Ca_4O(PO_4)_2 + H_2O$$

In our experiments, the high pressure of water vapor in the sintering environment prevents the decomposition of the HA by reversing the chemical process and stabilizing the HA phase. Therefore, the reaction with Mg-PSZ particles is minimized. Moreover, the sintering of the MgPSZ-HA ceramics in moisture avoids the calcium diffusion into the Mg-PSZ particles.

Table I shows the density and the mechanical properties obtained by indentation methods of the HA and MgPSZ-HA samples sintered at 1250 °C for 4 h in humid environment. The relative density values obtained are higher than those reported by Wang and Chaki [14] for HA sintered in moisture at 1250 °C for 4 h, indicating that the sinterability of our material is good.

The fracture toughness values for the MgPSZ-HA materials are around 2.5 times higher than those obtained for HA sintered at the same conditions (Table I). In Table II the K_{IC} of the MgPSZ-HA is compared with the values reported by Takagi *et al.* [5] and Ioku *et al.* [16] for Y-PSZ containing HA ceramics prepared by hot isostatic pressing (HIP). The toughness values obtained in this work were only slightly lower than those obtained when HIP is used. In all cases Niihara's equation was used to calculate the K_{IC}. The bending strength of the MgPSZ-HA (168 MPa) is very close to 170 MPa, the value reported by Takagi *et al.* using Y-PSZ (20 wt %) and HIP.

The mechanical properties obtained by three-point bending are shown in Table III. The fracture toughness and Young's modulus are lower than those obtained from the indentation measurements. The main cause of this difference may be attributed to the porosity and the compacting defects, which can reduce the values measured in conventional tests, whereas the micro-indentation tests are carried out on well-compacted surfaces of the specimen [17]. The values obtained are significantly higher than those reported by Wang and Chaki [14] for HA sintered in the same conditions. The morphological characteristics of the powder, the good stoichiometry, and the crystallinity of the calcined powder may be some factors which provide a good sinterability even when the sintering atmosphere presents high humidity contents. From FT-IR spectra, the

TABLE I Density and mechanical properties obtained by indentation methods of HA and the Mg-PSZ containing HA sintered at 1250 °C for 4 h in humid environment. The green bodies were pressed as discs at 400 MPa

Ceramic	Density (%)	Hardness (*H*) (GPa)	Young's modulus (*E*) (GPa)	Fracture toughness (K_{IC}) (MPa m$^{1/2}$)
HA	96.27 ± 0.43	4.14 ± 0.28	213 ± 26	0.72 ± 0.07
MgPSZ-HA	94.35 ± 0.52	2.94 ± 0.20	112 ± 17	1.73 ± 0.09

TABLE II Comparison between the value of the K_{IC} obtained in this work with those reported for similar materials. In all cases the content of PSZ was 20 wt %

Ceramic	Sintering method	K_{IC} (MPa m$^{1/2}$)
MgPSZ-HA	Uniaxial pressing and sintering	1.73 ± 0.09
YPSZ-HA [5]	Hot isostatic pressing	2.1
YPSZ-HA [16]	Post-sintering by hot isostatic pressing	2.1

TABLE III Density and mechanical properties obtained by three-point bending and the SENB method. Green bodies were pressed as bars at 100 MPa

Ceramic	Density (%)	K_{IC} (MPa m$^{1/2}$)	Bending strength (MPa)	Young's modulus (GPa)
HA	96.6 ± 0.54	0.98 ± 0.03	103 ± 11	90 ± 6
MgPSZ-HA	93.9 ± 0.49	1.46 ± 0.19	168 ± 10	108 ± 5

decreasing of the hydroxyl absorption bands suggest some dehydroxylation in the sintered material, which promotes the densification of HA ceramics [18]. In addition, the small grain size measured $(1.68 \pm 0.55\,\mu m)$, can also contribute to the good mechanical properties. It is worth mentioning that the incorporation of Mg-PSZ into the HA matrix does not significantly affect the grain size $(1.56 \pm 0.48\,\mu m)$.

The micrographs of the fracture surfaces show a mainly transgranular mechanism of fracture for the HA ceramic (Fig. 4). For the MgPSZ-HA the fracture mechanism seems to be less transgranular (Fig. 5), as expected because of the increased toughness of the material. The brittleness index (H/K_{IC}) is $5.75 \times 10^{-3} m^{-1/2}$ for HA and $1.6 \times 10^{-3} m^{-1/2}$ for MgPSZ-HA. The fracture toughness increases can be attributed to two mechanisms, which may be operative in MgPSZ-HA ceramics, the transformation toughening of the Mg-PSZ particles and the presence of microcracking [5]. In fact, the difference of thermal expansion coefficients of HA and Mg-PSZ $(13.8 \times 10^{-6}$ and $10.9 \times 10^{-6}\,{}^{\circ}C^{-1}$, respectively) promotes microcraking in the HA matrix (Fig. 6).

4. Conclusions

We conclude that it is possible to obtain toughened HA reinforced with Mg-PSZ particles by employing uniaxial pressing and sintering in humid environment. The wet sintering environment prevents the decomposition of the HA phase. The characteristics of the starting HA powder seem to be a key factor to achieve high sinterability in the MgPSZ-HA composite. The method proposed in this work can be useful to enhance the mechanical behavior of HA-based materials.

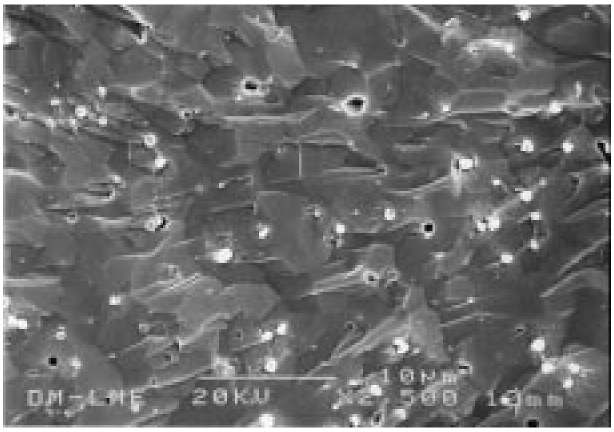

Figure 4 SEM micrograph showing the transgranular fracture mechanism in HA ceramic sintered at 1250 °C for 4 h in wet oxygen.

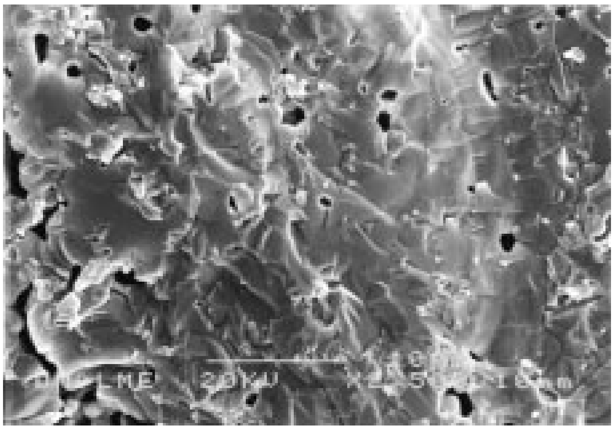

Figure 5 SEM micrograph of a fracture surface of MgPSZ-HA sintered at 1250 °C for 4 h in wet oxygen.

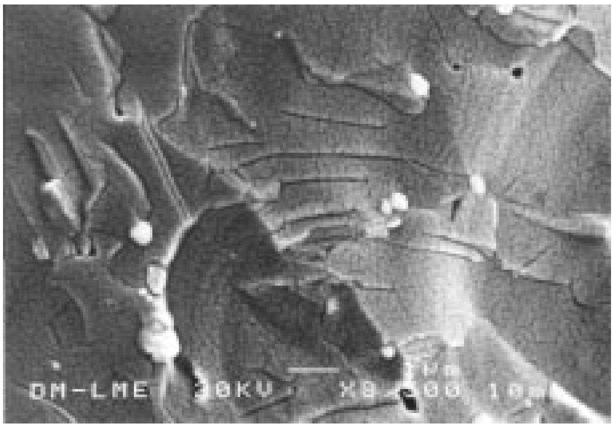

Figure 6 SEM micrograph showing the presence of microcraking in MgPSZ-HA ceramic sintered at 1250 °C for 4 h in wet oxygen.

Acknowledgments

The authors gratefully acknowledge the collaboration of the Serveis Cientìfico-tècnics of the Universitat de Barcelona. We also thank Montserrat Marsal of Department of Materials Science and Metallurgical Enginering of the Universitat Politècnica de Catalunya for the SEM observations. J. A Delgado and L. Morejón thank the Programa de Becas Mutis, AECI, Spain, for financial support through a pre-doctoral fellowship.

References

1. K. DE GROOT, C. DE PUTTER and P. SMITT, *Sci. Ceram.* **11** (1981) 433.
2. A. G. EVANS, *J. Amer. Ceram. Soc.* **73** (1990) 187.
3. P. F. BECHER, *ibid.* **74** (1991) 255.
4. T. KASUGA, M. YOSHIDA, A. IKUSHIMA, M. TUCHIYA and H. KUSAKARI, *J. Mater. Sci.*: *Mater. Med.* **4** (1993) 3.
5. N. TAKAGI, M. MOCHIDA, N. UCHIDA, K. SAITO and K. UEMATSU, *ibid.* **3** (1992) 199.
6. J.-M. WU and T.-S. YEH, *J. Mater. Sci.* **23** (1988) 3771.
7. J. CAETANO-ZURITA, O. BERMÚDEZ, I. LÓPEZ-VALERO, E. B. STUCCHI, J. A. VARELA, J. A. PLANELL and S. MARTÍNEZ, in Proceedings of the 7th International Symposium on Ceramics in Medicine, Turku, July 1994, edited by Ö. H. Anderson and Yli-Urpo (Butterworth-Heinemann Ltd, Oxford, 1994) p. 267.
8. K. NIIHARA, R. MORENA and D. P. H. HASSELMAN, *J. Mater. Sci Lett.* **1** (1982) 13.
9. D. B. MARSHALL, T. NOMA and A. G. EVANS, *J. Amer. Ceram. Soc.* **65** (1982) C-175.
10. M. -O. GUILLOU, J. L. HENSHALL and R. M. HOOPER, *Mater. Sci. Eng.* **A 209** (1996) 116.
11. W. J. BATCHELOR, T. R. FINLAYSON and G. L. KELLY, *J. Amer. Ceram. Soc.* **79** (1996) 2477.
12. J. A. DELGADO GARCÍA-MENOCAL, S. MARTÍNEZ MANENT, J. RODRÍGUEZ-VIEJO and M. T. CLAVAGUERA-MORA, in Proceedings of the Topical Symposium XI ''Materials in Clinical Applications'' of the Forum on New Materials of the 9th CIMTEC-World Ceramics Congress and Forum on New

Materials, Florence, June 1998, edited by P. Vincenzini (Techna, Faenza, 1999) p. 259.

13. J. LI, H. LIAO and L. HERMANSSON, *Biomaterials* **17** (1996) 1787.
14. P. E. WANG and T. K. CHAKI, *J. Mater. Sci.: Mater. Med.* **4** (1993) 150.
15. J. R. VAN WAZER, in ''Phosphorus and its compounds. Vol I: Chemistry'' (Interscience Publisher, New York, 1958) p. 527.
16. K. IOKU, M. YOSHIMURA and S. SÔMIYA, *Biomaterials* **11** (1990) 57.
17. J. A. PLANELL, M. VALLET-REGÍ, E. FERNÁNDEZ, L. M. RODRÍGUEZ, A. SALINAS, O. BERMUDEŹ, B. BARADUC, F. J. GIL and F. C. M. DRIESSENS, in Proceedings of the 7th International Symposium on Ceramics in Medicine, Turku, July 1994, edited by Ö. H. Anderson and Yli-Urpo (Butterworth-Heinemann Ltd, Oxford, 1994) p. 17.
18. T. KIJIMA and M. TSUTSUMI, *J. Amer. Ceram. Soc.* **62** (1979) 455.

Received 6 May
and accepted 17 May 1999