

Physics/Solids, fluids: mechanical and thermal properties

Sintering and mechanical properties of magnesium-containing fluorapatite

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Abstract

Fluorapatite and magnesium-substituted fluorapatite powders synthesized by the precipitation method were pressureless sintered in the range 900–1300 °C. The results showed that both materials exhibited a good sinterability. Concerning fluorapatite, a relative density of about 97% was attained at 1050 °C for 1 h. Although the incorporation of Mg into the apatite framework induced a slight decrease in the density, the substituted samples presented slightly higher mechanical properties. The maximum values of flexural strength, fracture toughness, hardness and Young's modulus of these latter samples were about 50.8 ± 4.0 MPa, 1.36 ± 0.10 MPa m^{1/2}, 121.9 ± 2.4 MPa and 650 ± 8 Hv, respectively. **To cite this article:** *M. Hidouri et al., C. R. Physique 10 (2009).* © 2009 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Frittage et propriétés mécaniques de fluorapatites substituées au magnésium. Des fluorapatites substituées au magnésium et non substituées, préparées par précipitation, ont été frittées entre 900 et 1300 °C. Les résultats obtenus montrent que ces matériaux présentent une bonne aptitude au frittage. Pour la fluorapatite pure, une densité relative de l'ordre de 97 % a été obtenue après un traitement thermique à 1050 °C pendant 1 h. Bien que l'incorporation de Mg dans la structure apatitique induise une légère diminution de la densité, les échantillons substitués présentent une légère amélioration de propriétés mécaniques. Les valeurs maximales de résistance à la rupture, ténacité, dureté et module d'Young de ces derniers matériaux sont respectivement de l'ordre $50,8 \pm 4,0$ MPa, $1,36 \pm 0,10$ MPa m^{1/2}, $121,9 \pm 2,4$ MPa and 650 ± 8 Hv. **Pour citer cet article :** *M. Hidouri et al., C. R. Physique 10 (2009).*

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1. Introduction

During the last 30 years, calcium phosphates gained increasing importance due to their application in biomedical fields. Owing to its bioactivity and biocompatibility and thanks to its crystallographic structure and chemical composition matching those of hard tissues, hydroxyapatite (HA) was extensively investigated [1–4].

Although fluorapatite (FA) is known for delaying caries processes [5], enhancing the mineralization process [6,7] and for its lower solubility compared to HA [8,9], only a few works were devoted to the sintering and mechanical properties of this material [10–12]. As it is for HA, many ions can be substituted in different sites of the FA's structure [13–15]. Magnesium, whose concentration varies from 0.44 to 1.23 wt% [16], is one of the most abundant elements present in hard tissues. Its insertion in apatite compounds may lead to more biocompatible materials. The synthesis of Mg-substituted fluorapatite (MFA) and its thermal behavior were reported in a former work [17]. Accordingly, we intend to investigate in this Note the pressureless sintering and the mechanical properties of this material.

2. Experimental procedure

2.1. Starting powders

FA ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) and x MFA ($\text{Ca}_{10-x}\text{Mg}_x(\text{PO}_4)_6\text{F}_2$ with $0 \leq x \leq 1$) powders were prepared by the aqueous precipitation method from calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], diammonium hydrogenophosphate [$(\text{NH}_4)_2\text{HPO}_4$] and ammonium fluoride [NH_4F]. An amount of $\text{Mg}(\text{NO}_3)_2$ was introduced into the solutions containing Ca^{2+} at appropriate concentrations to obtain $\text{Mg}/(\text{Ca} + \text{Mg})$ molar ratios of 0.025, 0.05 and 0.10, respectively. The details of this synthesis route and the characterization of the obtained powders were reported elsewhere [17]. Notice that, the XRD patterns of the as-synthesized powders matched the ICCD standard of FA (JCPDS # 34-0011), and no secondary phases were detected. Moreover, it will be noted that the lattice parameters decreased with the increase of the Mg content that was used.

2.2. Sintering

Before sintering, the powders were calcined at 500 °C for 1 h and then uniaxially pressed at 100 MPa. Two types of compacts were prepared: those used for the densification study had a diameter of 13 mm and a 3 mm thickness, while those that were used for the mechanical characterization had a diameter of 30 mm and a 4 mm thickness. The pressureless sintering was performed in an argon flow at a temperature range 900–1300 °C and various holding times. The heating and cooling rates were 10 °C min⁻¹, respectively.

2.3. Ceramic characterization

Both green and sintered densities of compacts were determined through dimension and weight. X-ray diffraction (XRD) patterns were recorded on a Philips PW 1800 diffractometer using Cu $K\alpha$ radiation. The phase identification of the sintered samples was carried out by comparing the experimental XRD patterns to the standards compiled by the joint Committee on Powder Diffraction Standards (JCPDS). The mechanical properties were investigated on compacts sintered at 1000, 1050, 1100 and 1150 °C for 1 h. The sample surfaces were properly polished using various grade silicon carbide paper (grade 400–1200) and a 3 μm diamond paste. Young's modulus (E) was determined by the propagation velocity of the longitudinal and transverse waves within isotropic materials using the pulse-echo method by means of a Grindo Sonic System (Lemmens, Germany). Flexural strength was obtained by a three-point-bending technique practiced on discs [18]. Measurements were carried out with a Wolpert 5TZZ 771 instrument using a 20 mm span and a crosshead speed of 0.2 mm min⁻¹. Five samples were used for each strength data point. Fracture toughness (K_{IC}) and hardness H_v were checked with Vickers indentation technique (durometer Zwick 3212, Germany). A load of 9.8 N was applied for 15 s to induce indentation. Polished specimens were indented in ten separated locations. K_{IC} values were calculated using the equation derived from the Evans and Charles model [19]:

$$K_{\text{IC}} = 0.0824 \frac{P}{C^{3/2}} \quad (1)$$

where P is the applied load and C is the length of the generated surface radial crack.

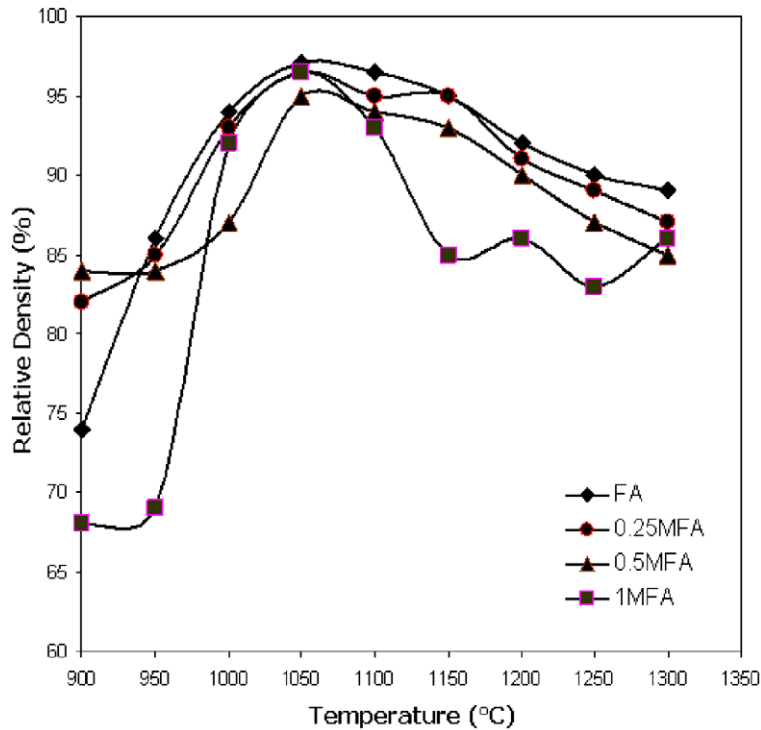


Fig. 1. Relative density of FA and MFA ceramics as a function of the sintering temperature.

Hv values were determined using the equation:

$$Hv = 1.854 \frac{P}{d^2} \quad (2)$$

where d is the diagonal of the indentation.

3. Results and discussion

3.1. Sintering

Fig. 1 illustrates the relative density as a function of the sintering temperature. As it is shown, the relative density of samples sintered for 1 h was found to rise with an increase of the sintering temperature; they reached their maximum values at 1050 °C and then decreased beyond this temperature. Compared to the pure FA, the substituted samples exhibited lower densities. Notice that, the density was much lower when the Mg content increased. This variation of density as a function of x was probably due to the decrease of the specific surface area, which is the driving force for the pressureless sintering [12]. The effect of the sintering time on the relative density was studied at 1050 °C only for both FA and 1.0MFA samples (Fig. 2). The results showed that the densification of both materials was very rapid. In fact, after only one minute, the samples had already sintered to 94% of the theoretical density. After 1 h, density attained its maximum value. Then, it was noticed that the densification decreased slightly for a longer time probably due to the grain growth.

Fig. 3 presents selected XRD patterns of 1.0MFA samples sintered at different temperatures for 1 h. All the samples showed the FA characteristic peaks (JCPDS # 34-0011). In Figs. 3a–3b, two weak peaks were observed corresponding to Mg_2FPO_4 phase (JCPDS # 45-1060). This phase which crystallized from an amorphous phase was formed in a small amount [17]. As it is mentioned in this latter work, the intensity of its peaks decreased at 1120 °C (Fig. 3c) and vanished at 1300 °C (Fig. 3d). Two assumptions were suggested to explain its disappearance: its dissolution in the liquid phase corresponding to an eutectic between CaF_2 present in the powder as impurity and MFA or its incorporation into the apatite structure consecutive to its reaction with the MFA via a solid state reaction [17]. Moreover,

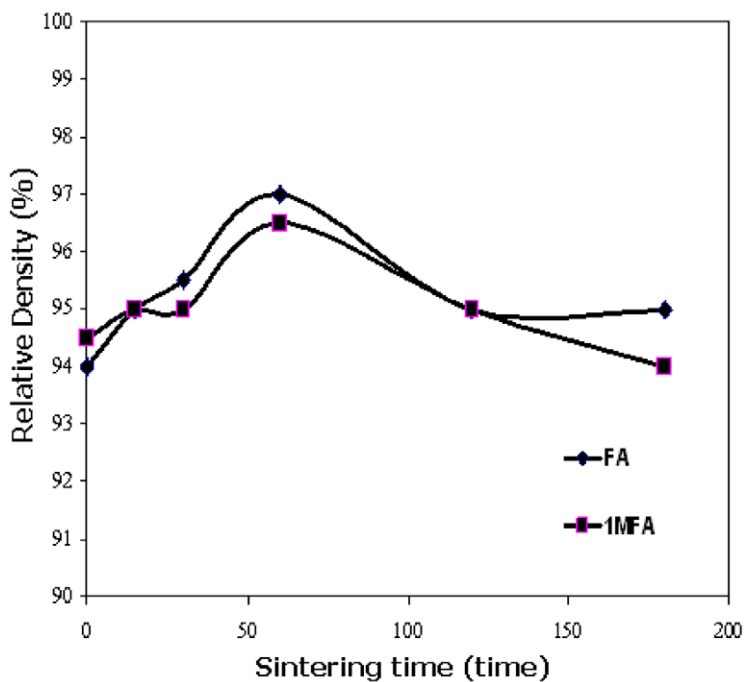


Fig. 2. Effect of sintering time (at 1050 °C) on relative density of FA and MFA samples.

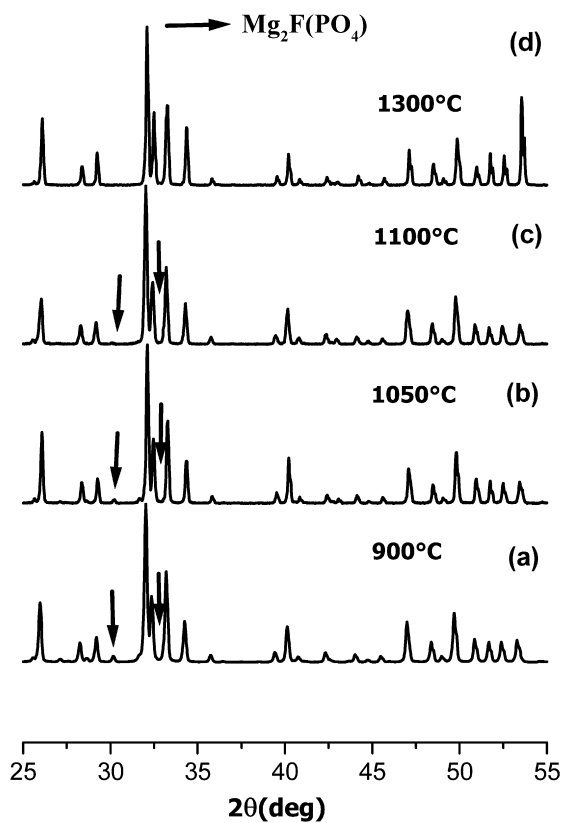


Fig. 3. XRD patterns of 1.0MFA samples sintered at various temperatures for 1 h.

Table 1
Characteristics of FA and MFA powders [17].

Samples	$\frac{\text{Mg}+\text{Ca}}{\text{P}}$ molar ratio	SSA (m ² /g) (as-dried)	SSA (m ² /g) (calcined at 500 °C)	Relative density of green compacts
FA	1.65(6)	28.4	24.3	0.59
0.25MFA	1.67(5)	28.8	13.3	0.49
0.50MFA	1.67(1)	29.2	11.7	0.48
1.0MFA	1.66(3)	29.5	7.6	0.48

whatever the used temperature was, the XRD patterns did not exhibit any sign of the materials' decomposition. Also, XRD analysis did not reveal any significant evolution of the phases change with the sintering time.

These findings confirm the good sinterability of FA against the HA, which was pointed out by Senamaud et al. [20], who noticed that the sintering of FA and HA at 1000 °C for 10 min leads to relative densities of 0.93 and 0.61, respectively. Senamaud et al. related the densification height of FA to the higher mobility of the species especially fluoride, which were responsible of matter transfer. With respect to the FA, the slight decrease of the density of the MFA may be due to the particle size of their powders. Indeed, as shown in Table 1, the calcination reduced the specific surface areas of the substituted powders more than it did for the non-substituted FA, and as expected, the density of the corresponding samples decreased respecting Herring's law of sintering [21]. Furthermore, the grain growth with an increasing sintering temperature would be elicited. Ben Ayed et al. [10] study of the densification of FA had shown that at high temperature an exaggerated grain growth occurred. In the case of the substituted FA, we can assume that the grain growth was more evident than that of the non-substituted FA. This occurrence is due to the high mobility of diffusing species such as Mg at high temperature.

3.2. Mechanical characterization

The mechanical characterization was performed on the FA and 1.0MFA samples sintered at various temperatures for 1 h (Fig. 4). The flexural strength of both FA and 1.0MFA materials with respect to the sintering temperature is shown in Fig. 4a. The trend of the curves is the same as in Fig. 1. When temperature increased, two concomitant phenomena occurred: densification and grain growth. Before exaggerated grain growth occurred, it was obvious that the higher the relative density was, the higher the strength would be, agreeing with the Duckworth–Knudsen model, which correlated the mechanical properties such as strength, toughness, hardness and elastic modulus of the ceramics to their porosity, i.e., to their density [22]. Thus, for the pure FA the highest flexural values were found to be at 1050 °C of 46.7 ± 5.0 MPa, which is very close to those reported [2,23]. At 1150 °C, the value decreased to around 32 ± 7 MPa. This decrement might be due to the grain growth and to the formation of a closed porosity. For 1.0MFA, there was a slight increase in the flexural strength, in spite of the relative density being lower than that of FA. At 1050 °C, the strength was 50.8 ± 4.0 MPa. This aspect could be related to the presence of the secondary phase Mg₂FPO₄ on the particle surface, which might limit the progression of the failure cracks. As Fig. 4b shows, the behavior of fracture toughness was similar to that of flexural strength for both materials. The toughness of FA ceramics was enhanced as the sintering temperature increased until 1050 °C reaching 1.16 ± 0.10 MPa m^{1/2}. This value is comparable to that obtained by Gross and Bhadang [12]. Then, the toughness decreased with the increase of the sintering temperature. After incorporating Mg, a slight enhancement of the toughness occurred. The maximum value of 1.36 ± 0.10 MPa m^{1/2} was obtained for the sample sintered at 1050 °C. Being higher than that of FA, this value might have resulted from the presence of the secondary phase Mg₂FPO₄. Above 1050 °C, the difference in the toughness values for both materials tended to decrease. As for flexural strength, the trend of toughness with the temperature should be related to that of density and grain size, which affected significantly its mechanical properties [24]. Notice that, contrasting the previous result, below 1050 °C, K_{IC} of FA was higher than that of MFA. The dependence of the hardness on the sintering temperature is illustrated in Fig. 4c. In this case too, the hardness followed the same trend as density did. The hardness of MFA was found to be higher than that of FA. Their highest values were 650 ± 8 and 619 ± 6 Hv, respectively. The Young's modulus as a function of the sintering temperature is given in Fig. 4d. As observed, its variation with the temperature was also in correlation with the densification. Like the preceding properties, 1.0MFA showed statistically 10% higher results than those of FA with a maximum of 121.9 ± 2.4 MPa obtained at 1050 °C. This value is more important than that previously reported [12].

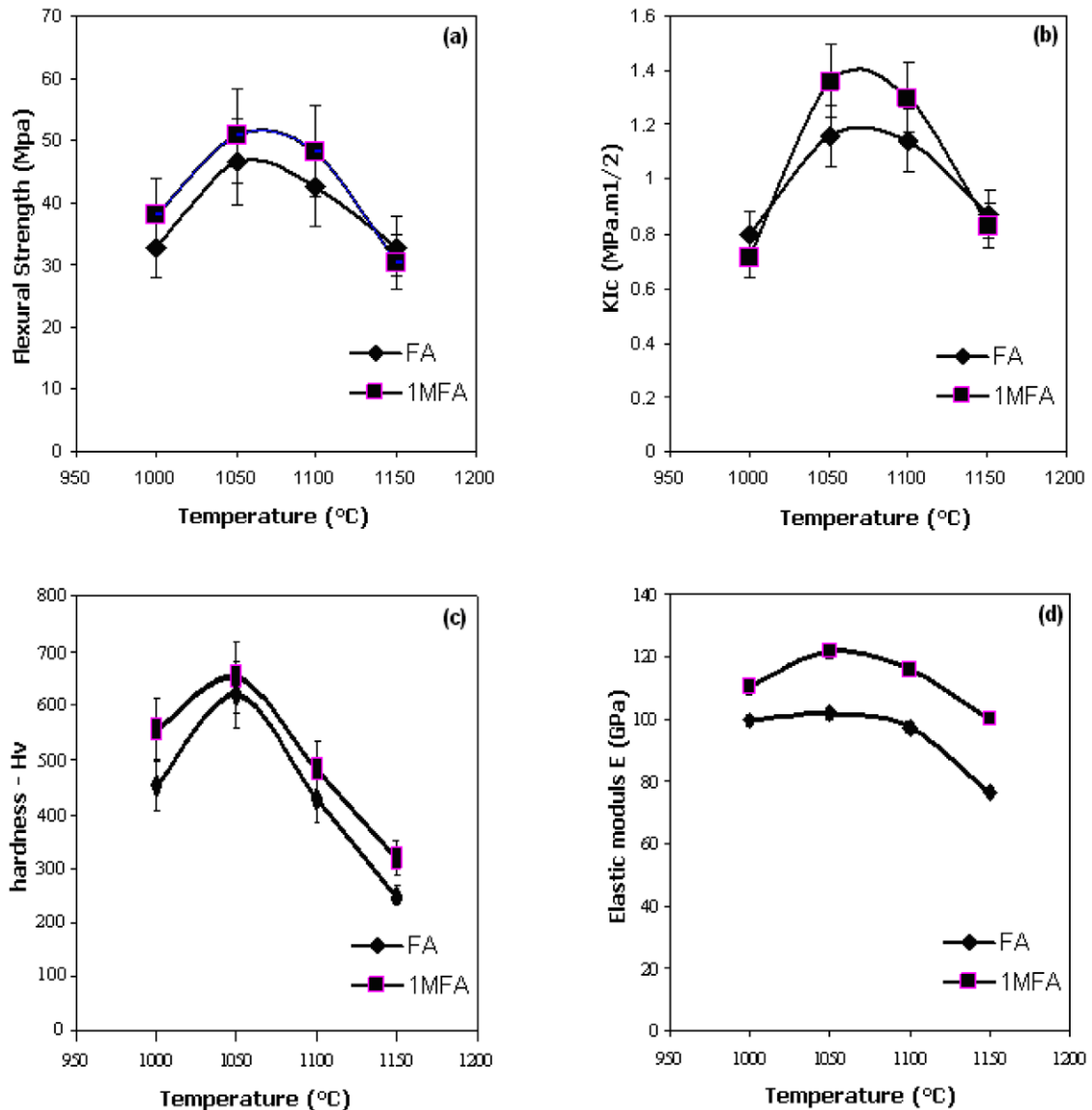


Fig. 4. (a) Flexural strength, (b) fracture toughness, (c) hardness, (d) Young's modulus of FA and MFA ceramics as a function of the sintering temperature.

4. Conclusion

In the present study, FA and MFA synthesized using a wet precipitation method were pressureless sintered under argon flow at temperatures ranging from 900 to 1300 °C and their mechanical properties were investigated. We can conclude that:

1. FA and x MFA ($0 \leq x \leq 1$) compacts exhibited a good sinterability. For all the materials, the highest density was obtained at 1050 °C. However, the sintered density of the substituted samples was lower than that of non-substituted FA. The decrease of density with increasing of the Mg content used was related to the surface area of the powders and the grain growth during the densification.
2. In spite of the relative density which was lower than that of FA, 1.0MFA material exhibited slightly higher strength, toughness, Young's modulus and hardness values. Concerning the latter material, their maximum values

were 50.8 ± 4.0 MPa, 1.36 ± 0.10 MPa m^{1/2}, 121.9 ± 2.4 MPa and 650 ± 8 Hv, respectively. These mechanical properties were correlated with the density of the samples. Nevertheless, the secondary phase Mg₂FPO₄, which crystallized from an amorphous phase, certainly played on the mechanical properties a significant role that should be identified and determined.

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