Structural and mechanical study of the sintering effect in hydroxyapatite doped with iron oxide

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ABSTRACT

Calcium phosphates are very important for applications in medicine due to their properties such as biocompatibility and bioactivity. In order to improve their properties, substitution of calcium with other ions has been proposed. Partial substitution of calcium by different ions has been made as a way to improve the properties of the calcium phosphates and also to allow new applications of apatites in medicine. In this work, hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$—HAP], prepared by high-energy dry milling (20 h), was mixed with different amounts of iron oxide (0.5, 1, 2.5 and 5 wt%). The mixtures were calcinated at 900 °C for 5 h with a heating rate of 3 °C/min in an attempt to introduce the iron oxide in the HAP structure. Small discs (12.5 mm $\varnothing$) were uniaxially pressed under a load of 2 t for 2 min. The pellets were sintered at 1000, 1200 and 1300 °C for 5 h in air. The main purpose of this work is to study why the iron oxide concentration and the heat treatment of the samples change the microhardness of the obtained ceramics. The sintered samples were characterized by X-ray diffraction (XRD), Vickers Microhardness and scanning electron microscopy (SEM).

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1. Introduction

The first materials used for implants frequently caused inflammations and rejections. For use in medicine they must not have a significant influence on the metabolism. Several materials and composites are used in the production of prosthesis, for example, metallic alloys, metallic materials covered with hydroxyapatite (HAP) films, alumina and polyethylene [1]. HAP is used in orthopedic and dental surgeries and odontological for wadding [2] or surface [3] coverings, despite their weak mechanical properties [3,4]. Due to these disadvantages considerable interest has recently been shown in the substitution of calcium in the HAP structure by metals [5,6] or ions, as for instance, silicon and magnesium [7], lead [8], titanium and zirconium [9] and aluminum [10] as reinforcing agents to improve the mechanical properties of the HAP. The presence of iron in the apatite structure seems to be important because iron is a vital element in the circulatory system and essential for the functioning of numerous proteins in cells [11]. Biomaterials containing iron oxide have a very important role to play in medicine. As an example,

ferrimagnetic bioglass ceramics (FBC) was introduced for hyperthermic treatment of bone cancer [12–15] and HAP, obtained by the sol–gel method, with different iron concentrations, after treatment at different temperatures has been used for hyperthermia treatment of bone tumors [16]. These materials are complex, multiphase, biocompatible and bioactive and motivate us to add this metallic ion in the HAP. The main purpose of this work is to study why iron oxide and heat treatment of the samples change the microhardness of HAP. A study by Kijima and Tsutsumi [17] highlights the changes of the insensitivity of the microhardness of HAP with increase in grain size. The measured Vickers values are between 6.3 and 6.5 GPa for monophase HAP calcinated at 1300 °C and with grain size between 1.6 and 6.5 μm, respectively. The main purpose of the work is to prepare ceramics of HAP with iron oxide and study the effect of concentration of iron oxide and heat treatment on microhardness of the materials. X-ray, scanning electron microscopy (SEM) and Vickers Microhardness measurements were done to characterize such ceramics.

2. Experimental

HAP crystalline powders were prepared by high-energy dry milling for 20 h. Eq. (1) represents the expected chemical reaction:

$$7Ca(OH)_2 + 6CaHPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 3CaO + 9H_2O \qquad (1)$$
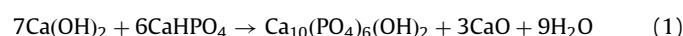
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The raw materials, $CaHPO_4$ and $Ca(OH)_2$, with the stochiometric proportionality for 10 g of total powder, were placed in a stainless-steel vessel inside a Fritsch Pulverisette 6 planetary mill system. The ratio between the powder and the ball mass was near 1/6. The reaction was performed using 370 rpm for 20 h. To avoid excessive heating the milling was performed in 30 min milling steps with 10 min pauses.

Iron oxide (Fe_2O_3) at different weight percentages (0.5, 1, 2.5 and 5 wt%) were added to the obtained HAP powder. Hereafter the samples will be named HAPFe0.5, HAPFe1, HAPFe2.5 and HAPFe5, where the number is the iron concentration. The mixtures were calcinated at 900 °C for 5 h with a heating rate of 3 °C/min. To prepare pellets (12.5 mm $\varnothing$) the obtained powder was uniaxially pressed under a load of 2 t for 2 min. Afterwards the discs were sintered at 1000, 1200 and 1300 °C, in air, with a heating rate of 3 °C/min for 1 h.

2.1. X-ray diffraction

X-ray diffraction (XRD) pattern data were obtained at room temperature using powder samples in an X'Pert MPD Philips difractometer (with K_α radiation, $\lambda = 1.54056$ Å) at 40 kV and 30 mA. Intensity data were collected by the step-counting method (step 0.02° and a time per step of 1 s) between 20° and 60° (2θ).

2.2. Scanning electron microscopy (SEM)

The microstructure of the free surface samples was studied using SEM (Phillips XL-30), operating with beams of primary electrons ranging from 12 to 20 keV. The pellets were covered with a layer of carbon of around 30 nm in thickness. From the micrographs the average grain size of the samples was calculated.

2.3. Microhardness

Microhardness measurements were made by Vickers indentations on the unpolished faces of the pellets using a standard Vickers microhardness tester (SHIMADZU HMV2). Loads of 9.81 N were applied with a 20 s loading time. In each sample between 10 and 15 indentations were made. The Vickers hardness (H_V) of the samples was calculated using the average diagonal length of the Vickers indentation according to the following expression [18]:

$$H_V = \frac{L}{2d^2} \tag{2}$$

where L is the indentation load in Newton and $2d$ the length of the indentation diagonal in meters.

3. Results and discussion

Fig. 1 presents the XRD pattern of the HAP with different weight concentrations of iron oxide (0.5, 1, 2.5 and 5 wt%) calcinated at 900 °C. HAP [19] and brownmillerite or srebrodolskite [20] ($Ca_2Fe_2O_5$) phases were detected in the XRD of all samples (Fig. 1). The presence of brownmillerite indicates that the added iron oxide has been inserted into $Ca_2Fe_2O_5$ phase [19]. It can be observed by the XRD that the $Ca_2Fe_2O_5$ phase increases with iron concentration, showing calcium–iron interaction. No substitution of calcium by iron ions is observed in the HAP structure. Another phase identified in the samples heat treated at 900 °C with 0.5 and 1 wt% of iron oxide was CaO. These phases are formed through the dissociation of excess $Ca(OH)_2$ [19] (Eq. (3)) during the preparation of HAP for milling (Fig. 2). The CaO phase decreases with a rise of the percentage of iron oxide and it
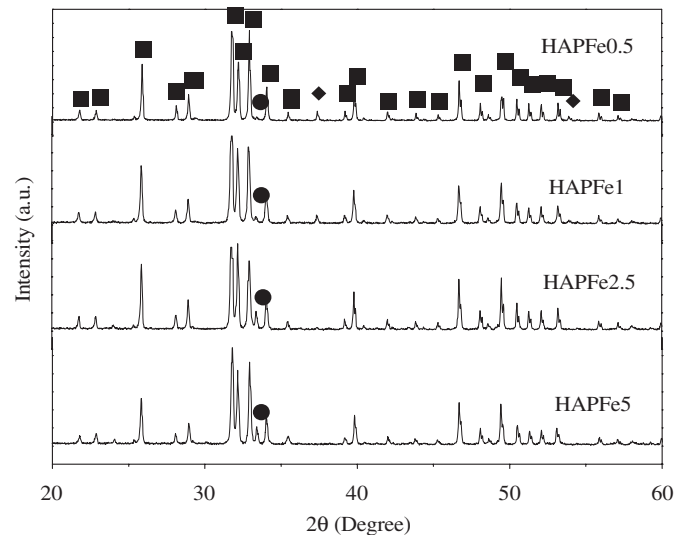

Fig. 1. XRD patterns of the HAPFe0.5, HAPFe1, HAPFe2.5 and HAPFe5 samples calcinated at 900 °C. HAP (■), $Ca_2Fe_2O_5$ (●) and CaO (♦) [17].
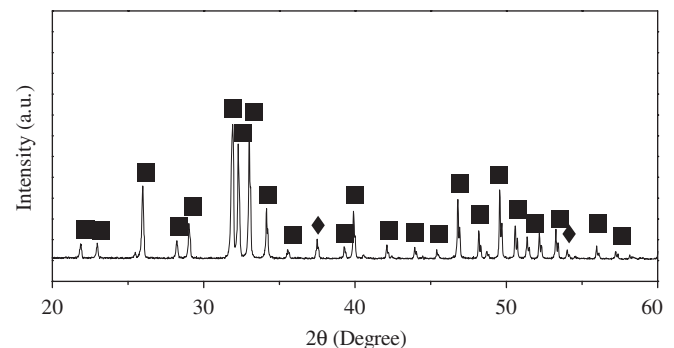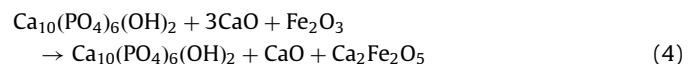

Fig. 2. XRD patterns of the HAP sample milled for 20 h. HAP (■) and CaO (♦) [17].

disappears in the 2.5 wt% sample due, probably, to the increase of concentration of CaO incorporated in the $Ca_2Fe_2O_5$ phase (Eq. (4)).

$$3Ca(OH)_2 \rightarrow 3CaO + 3H_2O \tag{3}$$

$$Ca_{10}(PO_4)_6(OH)_2 + 3CaO + Fe_2O_3$$
$$\rightarrow Ca_{10}(PO_4)_6(OH)_2 + CaO + Ca_2Fe_2O_5 \tag{4}$$

A shift of the XRD peak and a change in the relative peak intensities did not occur on increasing the iron oxide concentration and temperature of heat treatment. The absence of a shift in the apatite XRD peaks and a change in relative peak intensities suggest that iron is not incorporated into the apatite lattice, but it is used in the formation of the brownmillerite phase with CaO present in the initial powder composition.

The micrographs of the sample HapFe0.5 sintered at 1000, 1200 and 1300 °C are shown in the Figs. 3–5. An increase in the average grain size is observed on increasing the temperature of sinterization [21]. In these samples the grain has an average size between 0.7 μm (1000 °C) and 6.4 μm (1300 °C; Fig. 6). In the sample sintered at 1300 °C (Fig. 5) the presence of large agglomerates of particles showing well-defined grain boundaries is observed. Figs. 7 and 8 show, respectively, the micrographs of the samples HapFe1 and HapFe5 sintered at 1300 °C.
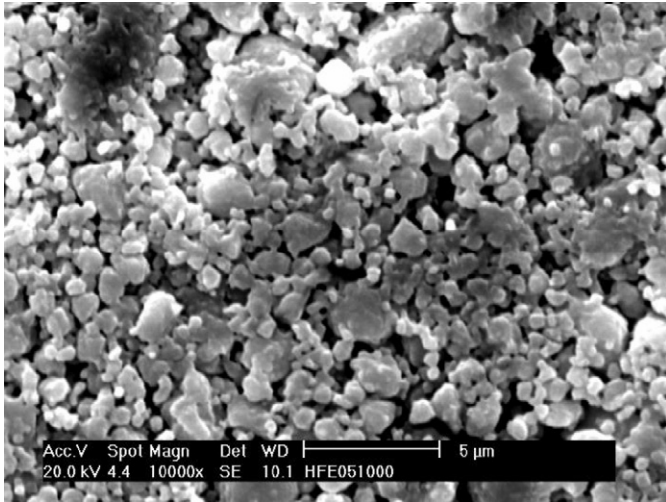
Fig. 3. SEM micrograph of the sample HAPFe0.5 with 10,000 × sintered at 1000 °C.
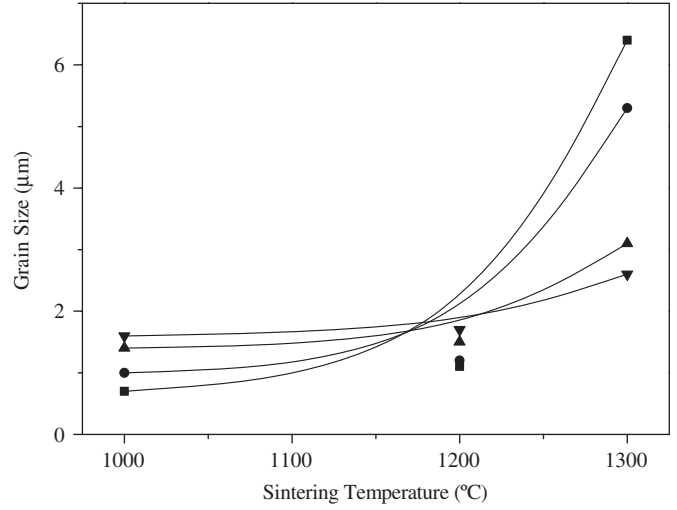

Fig. 6. Graph of temperature vs. grain size of samples. HAPFe0.5 (■), HAPFe1 (●), HAPFe2.5 (▲) and HAPFe5 (▼); the lines are drawn as guide for the eye.
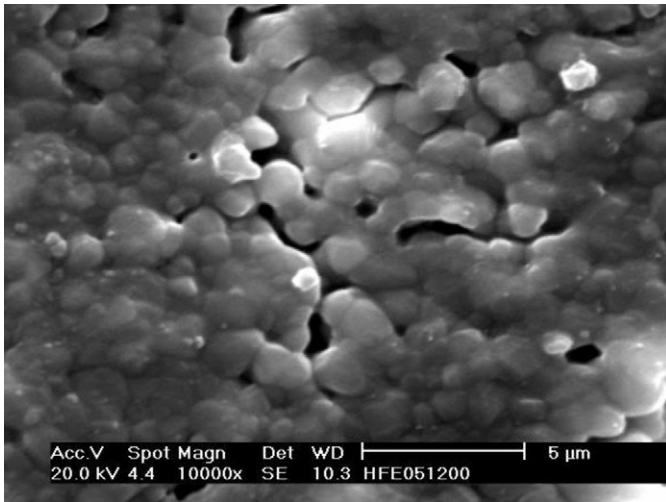

Fig. 4. SEM micrograph of the sample HAPFe0.5 with 10,000 × sintered at 1200 °C.
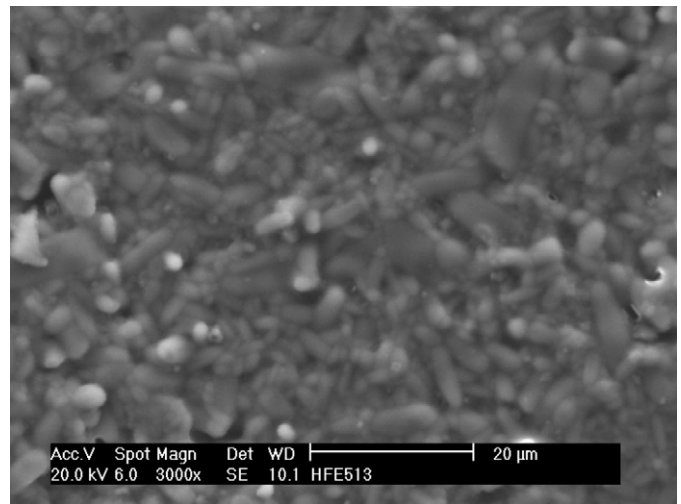

Fig. 7. SEM micrograph of the sample HAPFe1 with 3000 × sintered at 1300 °C.
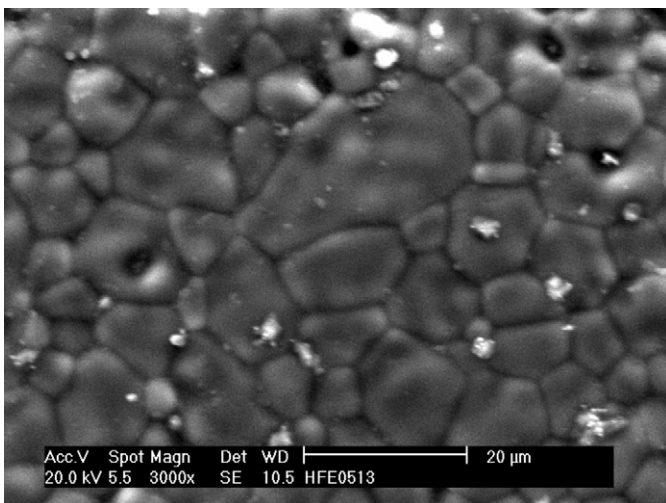

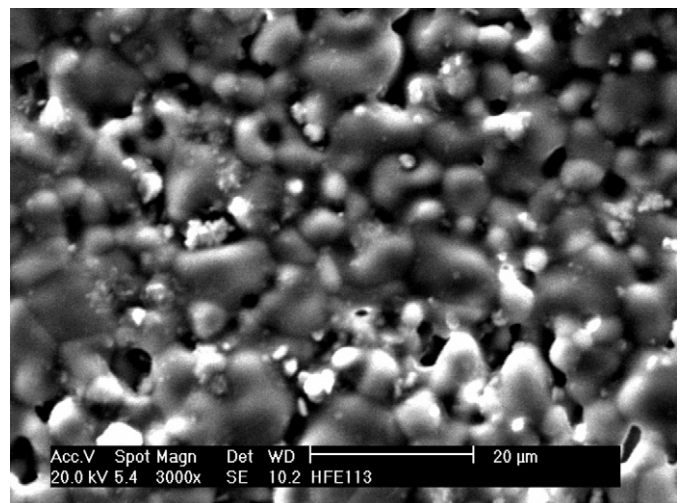**Fig. 5.** SEM micrograph of the sample HAPFe0.5 with 3000 × sintered at 1300 °C.

Fig. 8. SEM micrograph of the sample HAPFe5 with 3000 × sintered at 1300 °C.
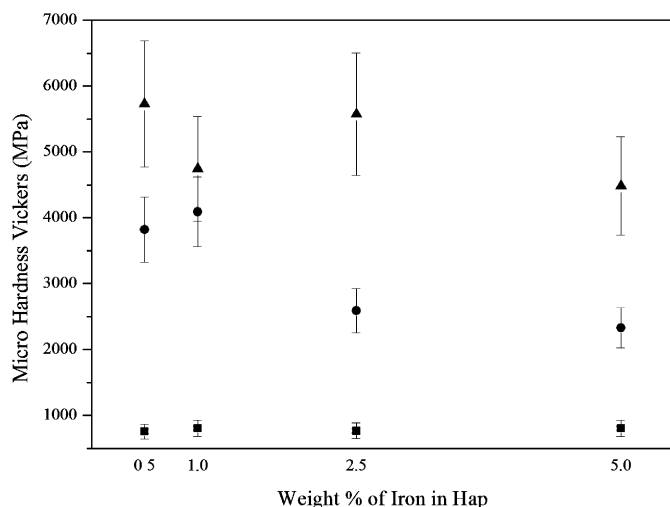
Fig. 9. Error graphic of measurements of Vickers microhardness for the samples HAPFe0.5, HAPFe1, HAPFe2.5 and HAPFe5; (■) samples heat treated at 1000 °C, (●) samples heat treated at 1200 °C and (▲) samples heat treated at 1300 °C.

Table 1
Measurements of Vickers microhardness for the samples HAPFe0.5, HAPFe1, HAPFe2.5 and HAPFe5 in MPa

Samples	Vickers microhardness (MPa)		
	Sintering temp. (°C)		
	1000	1200	1300
HAPFe0.5	754 ± 91	3820 ± 433	5733 ± 938
HAPFe1	801 ± 111	4089 ± 174	4746 ± 991
HAPFe2.5	767 ± 115	2589 ± 434	5574 ± 76
HAPFe5	802 ± 78	2329 ± 288	4484 ± 723
HAP	192 ± 47	1395 ± 256	1423 ± 260

Fig. 9 shows the values of Vickers microhardness for the samples after sinterization at 1000, 1200 and 1300 °C with the error bars. For each concentration of iron it is observed that the microhardness increases with a rise of the sintering temperature. This behavior can be related to the change in the superficial morphology of the samples (Figs. 3–7 and Table 1).

Comparing the microhardness results of the samples heat treated at 1000 and 1200 °C with those of the HAP prepared at the same temperature, an increase of the microhardness in the samples with iron oxide is verified. This behavior can be associated with the increase of the average grain size due to the incorporation of iron oxide in the $Ca_2Fe_2O_5$ phase (see Fig. 8). The addition of iron oxide changes the microhardness values for the samples heat treated at the same temperature. For example, for the sample heat treated at 1000 °C the microhardness changes between 754 ± 91 (HAPFe0.5) and 802 ± 78 (HAPFe5), while the sample of HAP has a microhardness of 192 ± 47. However, the principal factor of the rise of the microhardness is due of the densification of ceramic due to the heat treatment at increased temperatures [22].

4. Conclusions

$Ca_2Fe_2O_5$ (brownmillerite) phase was obtained with 0.5% iron added to HAP (Fig. 1). The formation of brownmillerite showed that calcium was not substituted by iron ions in the HAP structure. The other phase obtained was CaO. This phase disappears in the 2.5 wt% sample, probably due to the increase of concentration of iron and CaO incorporated in the structure of $Ca_2Fe_2O_5$. The brownmillerite phase was formed by the reaction of iron oxide with CaO formed through the dissociation of $Ca(OH)_2$ during the preparation of HAP. The micrographs at different sintering temperatures showed different morphologies and unequal grain size. The microhardness results of the samples with iron oxide heat treated at 1000 and 1200 °C show an increase relatively to the HAP samples prepared at the same sintering temperature. This behavior can be associated with the increase of the average grain size due to the incorporation of iron oxide in the $Ca_2Fe_2O_5$ phase, changing the microhardness values for the samples heat treated at the same temperature. The increase of microhardness is due of the densification of ceramic ascribed to the heat treatment at increased heat-treatment temperature. The densification of the ceramic is greater than that obtained in the HAP monophase, at the same temperature of sintetization.

Acknowledgements

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