

Effect of Mg²⁺ Addition During HA Nanoparticles Synthesis Using Ultrasonic Irradiation

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Abstract. Nanocrystalline hydroxyapatite was prepared by a precipitation method with add of ultrasonic irradiation. In this work the effect of H₃PO₄ addition rate during synthesis and the influence of the magnesium incorporation into apatite were studied. The results revealed that the morphology and cristalinity of synthesized nanopowders are significantly affected by ultrasonic irradiation. Monophase hydroxyapatite was obtained when magnesium was added into HA lattice during the synthesis with ultrasonic irradiation.

Introduction

Synthetic HA is a bioactive ceramic widely used as powders or particulates forms in bone repairs and as coating of metallic prosthesis to improve their biological characteristics. The properties of HA, including bioactivity, biocompatibility, solubility and adsorption properties can be tailored over a wide range by modifying the composition through ionic substitutions [1]. Magnesium is one of the most important bivalent ions associated to biological apatite [2]. The addition of magnesium to apatite phase has attracted the researches due to its significant impact on the mineralization process and also its influence in the HA crystal formation and growth [1, 3]. However, the Mg incorporation in synthetic HA is limited at about 0.4 wt% of Mg [1]. In previous works synthesis by neutralization method was reported to be suitable to obtain HA [2, 4]. Ultrasonic irradiation was shown to be a promising tool to facilitate the reactions to prepare homogeneous and fine ceramic powders from aqueous solution [5,6]. The aim of this work was study the influence of ultrasonic irradiation during the H₃PO₄ and magnesium addition throughout HA synthesis. The cristalinity and morphology was available.

Materials and Methods

HA nanopowder was synthesized by neutralization method as described in literature [4]. The synthesis was accomplished in ultrasound bath (USC 2850, Unique) that produces acoustic waves in a frequency of 25Khz. The phosphoric acid solution (0.3 M) was added in the calcium hydroxide suspension (0.5M) in the rates 8.0 mL.min⁻¹ (US8) and 15.0 mL.min⁻¹ (US15). After complete H₃PO₄ addition, the ultrasound was turned off. In other experiment, different amounts of Mg²⁺ were added in US15 synthesis. The chemical composition Ca_{10-x}Mg_x(PO₄)₆(OH)₂ (x = 0.0; 0.1; 0.15; 0.17 and 0.2 mols) was fixed that corresponds to 0.0; 0.24; 0.36; 0.41 and 0.49 wt% of Mg²⁺. The molar ratio (Ca+Mg)/P = 1.67 was kept. During all experiment the pH was monitored with a pH meter.

The as-prepared powders were characterized by thermogravimetric analysis (TGA; Setaram Model SETSYS 16/18) with a heating rate of 10° C.min⁻¹ in current of air up to 1250°C. The calcined powders at 800°C/3h were characterized by X-ray diffraction technique (XRD; Rigaku, Multiflex model; CuKα). The specific surface area was measured by BET method (Micrometric model ASAP 2000). Chemical analysis for Ca, Mg and P was evaluated by ICP-OES technique and the powder morphology was assessed by transmission electron microscopy (TEM; Philips-CM 200).

Results and discussion

The pH variation during the phosphoric acid addition in the suspensions is showed in Fig.1. When the addition rate was performed at $8.0 \text{ mL}\cdot\text{min}^{-1}$ (US8) the pH of the suspension, after 24 hours, was near 5.6 and when the addition rate was $15.0 \text{ mL}\cdot\text{min}^{-1}$ (US15), a more alkaline suspension was achieved, with pH near to 7.3. The ultrasound chemical effects on the liquid solution (sonolysis) produce hydroxyl radicals ($\bullet\text{OH}$) and atomic hydrogen (H) [7]. The ultrasonic waves can stimulate the reactivity of chemical species, resulting in the effective acceleration of heterogeneous reactions between liquid and solid reactants [8]. The heterogeneous species formation tends to influence the pH during synthesis. When Mg was added into HA lattice, the pH value was near to 8.0 for all compositions. According to literature the HA phase is known to be stable at high pH (>8.0) [9].

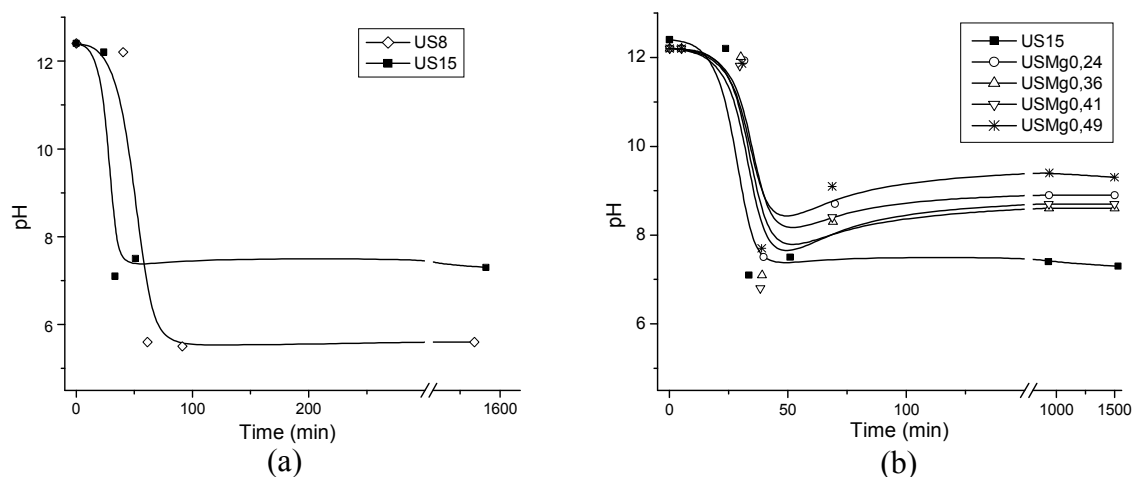


Fig. 1 pH variation for samples synthesized at (a) US8 = $8.0 \text{ mL}\cdot\text{min}^{-1}$ and US15 = $15 \text{ mL}\cdot\text{min}^{-1}$; and with (b) 0.0, 0.24, 0.36, 0.41 and 0.49 wt% of Mg.

TGA analyses of the as-prepared powders are shown on Fig. 2. In all the samples, significant weight loss up to approximately 450°C was due to the loss of adsorbed water (up to $\approx 200^\circ\text{C}$) and lattice water (up to $\approx 400^\circ\text{C}$) [1].

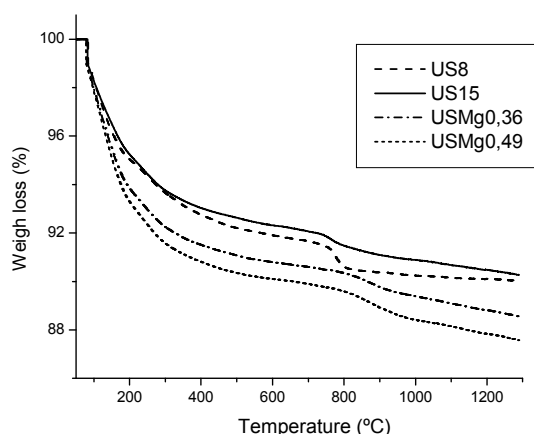


Fig. 2 Thermogravimetric curve of as-prepared powders for samples US8, US15, USMg0.36 and USMg0.49.

The samples, with nominally stoichiometric (US8 and US15), showed 9.9 and 9.7 % of total weight loss (Δm). Above 700°C , these samples exhibited a sudden weight loss which might indicate decomposition of HA in β -TCP phase [9]. With the rising Mg amount, the total weight loss (Δm) in-

creased to 11.4 and 12.4 wt% for USMg0.36 and USMg0.49. No significant weight loss was observed for these samples.

The X-ray diffraction of as-prepared powders without Mg addition (US8 and US15), calcined at 800°C/3h, was analyzed according to JCPDS card 9-342 and 9-169. Results of XRD analysis of these samples were in a good agreement with TGA analysis. β -TCP phase was identified in both samples as secondary phase. However, the majority phase of US15 sample is HA (Fig. 3-a). When Mg^{2+} was added into HA structure, the samples synthesized at 15.0 mL.min⁻¹, became thermally stable. Absence of any β -TCP peak in XRD samples with magnesium confirms that this ion helps to stabilize the HA phase. No significant change in XRD peaks was observed when the amount of magnesium varied between 0.24 and 0.49wt% (Fig. 3-b). The ultrasonic frequency favored the increase of the Mg^{2+} acceptance limit in the HA structure when compared with literature dates.

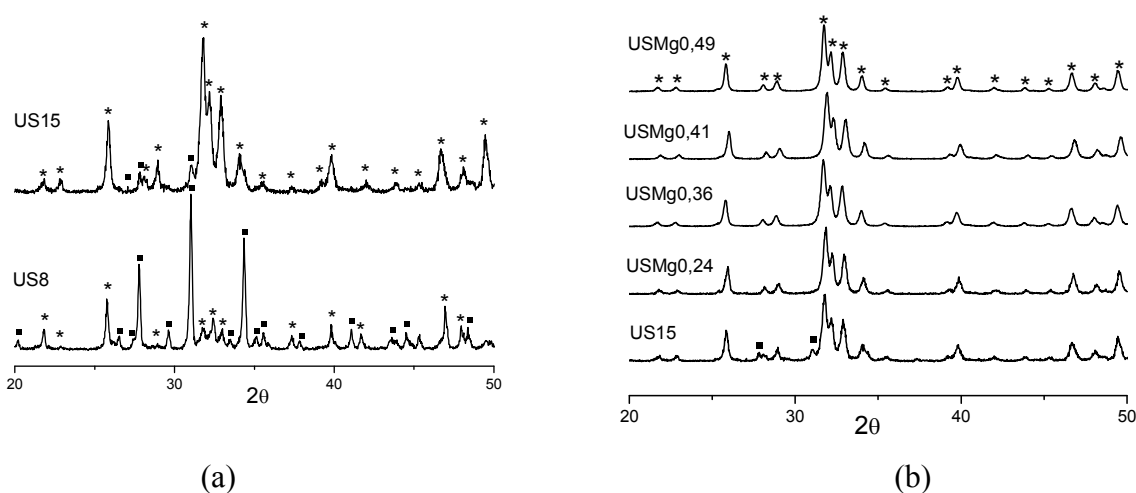


Fig 3 X-ray diffraction patterns of HA for the samples calcined at 800°C/3h: (a) H₃PO₄ solution added at 8.0 mL.min⁻¹ (US8) and 15.0 mL.min⁻¹ (US15); (b) samples with 0.24, 0.36, 0.41 and 0.49 wt% of Mg. Where (*) HA and (■) β -TCP.

Chemical analysis and specific surface area results are summarized in Table 1. ICP measurements indicate that powders prepared without magnesium (US8 and US15) contain 0.03 mols of Mg. This Mg content results from magnesium impurities in commercial calcium hydroxide.

Table 1 Chemical analysis and specific surface area for samples calcined at 800°C/3h

| Samples | N° mols calculated | | | N° mols after calcination | | | (Ca+Mg)/P | BET (m ² /g) |
|----------|--------------------|---|------|---------------------------|------|------|-----------|-------------------------|
| | Ca | P | Mg | Ca | P | Mg | | |
| US8 | 10 | 6 | 0 | 9.93 | 6.38 | 0.03 | 1.56±0,05 | 13.70±0.04 |
| US15 | 10 | 6 | 0 | 9.70 | 6.13 | 0.03 | 1.59±0.00 | 21.43±0.14 |
| USMg0.24 | 9.9 | 6 | 0.1 | 9.22 | 5.79 | 0.13 | 1.60±0.01 | 8.41±0.03 |
| USMg0.36 | 9.85 | 6 | 0.15 | 9.68 | 6.04 | 0.18 | 1.62±0.05 | 20.39±0.12 |
| USMg0.41 | 9.83 | 6 | 0.17 | 10.21 | 6.11 | 0.20 | 1.64±0.02 | 22.17±0.12 |
| USMg0.49 | 9.8 | 6 | 0.2 | 10.31 | 6.10 | 0.23 | 1.72±0.01 | 23.90±0.05 |

The increase of magnesium amount, in mols, found in the samples USMg0.24, USMg0.36 USMg0.41 and USMg0.49 after calcinations at 800°C/3h confirms the Mg incorporation into HA structure, as observed in XRD analysis. The (Ca+Mg)/P molar ratio for this samples increased with

the increasing Mg amount. The BET analysis of these powders leads to an increasing in specific surface area, from 13.0 m²/g, for US8, to 21.0 m²/g, for US15. The specific surface area of samples with Mg²⁺ is between 8.41 m²/g for USMg0.24 to 23.9 m²/g for USMg0.49. Typical TEM micrographs of HA, USMg0.36 and USMg0.49 are shown in Fig. 4 (a), (b) and (c). It was observed a narrow particles size distribution. HA crystals display the characteristic acicular morphology. This is similar to the particle morphologies reported by other wet chemical methods [2].

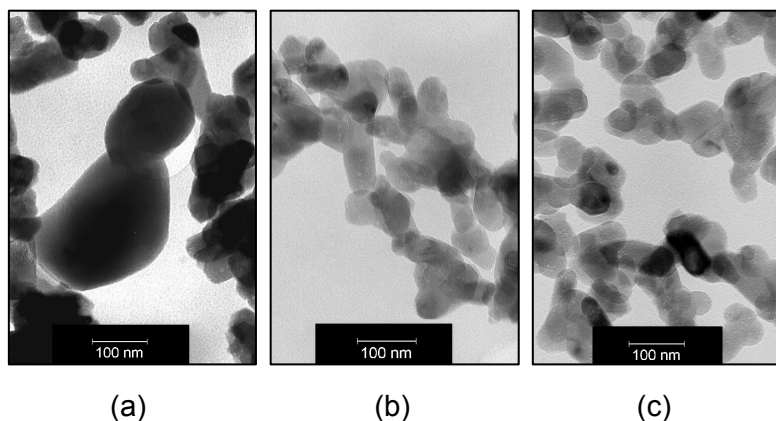


Fig.4 TEM for samples (a) US15 (b) USMg0.36 (c) USMg0.49 calcined at 800°C/3h.

Conclusions

Neutralization method with the ultrasonic irradiation addition in wet solutions provides a simple and economic route for the hydroxyapatite nanopowders synthesis. The rate of acid addition (8.0 and 15.0 mL.min⁻¹) and the amount of Mg wt% during the synthesis, influence both the morphology and the phase formation. HA monophase, with 15.0 mL.min⁻¹ H₃PO₄ addition, was obtained with magnesium addition into structure. The Mg²⁺ addition leads to pH near 8.0 where HA is known to be stable. The ultrasonic frequency favored the increase of the limit of the Mg²⁺ acceptance in the HA structure when compared with the literature dates. When 0.49 wt% of Mg²⁺ was added, the samples became thermally stable. The ultrasonic irradiation applied during the synthesis was helpful to synthesize HA finer particles.

References

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