

Synthesis and Structural Characterization of Hydroxyapatite-Wollastonite Biocomposites, Produced by an Alternative Sol-Gel Route

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ABSTRACT

Hydroxyapatite is a type of calcium phosphate-based material with great interest for biomedical applications, due to the chemical similarity between this material and the mineral part of human bone. However, synthetic hydroxyapatite is essentially brittle; the practice indicates that the use of hydroxyapatite without additives for implant production is not efficient, due to its low strength parameters. In the present work, biocomposites of hydroxyapatite-wollastonite were synthesized by an alternative sol-gel route, using calcium nitrate and ammonium phosphate as precursors of hydroxyapatite, and high purity natural wollastonite was added in ratios of 20, 50 and 80 percent by weight immersed in aqueous medium. Formation of hydroxyapatite occurs at a relatively low temperature of about 350°C, while the wollastonite remains unreacted. After that, these biocomposites were sintered at 1200°C for 5 h to produce dense materials. The characterization techniques demonstrated the presence of hydroxyapatite and wollastonite as unique phases in all products.

Keywords: Hydroxyapatite; Wollastonite; Bioceramics; Biocomposites; Sol-Gel

1. Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), is the predominant mineral component of vertebrate bones and dental tissue: teeth and enamel. Its clinical applications are of great importance, because it is the calcium phosphate ceramic chemically more similar to the biological apatite crystals. For this reason, many processing routes have been developed for synthesizing fine hydroxyapatite and sintering the reactive powders to form a dense bioceramic. The most common approaches reported include precipitation, solid state reaction, sol-gel methods, hydrothermal route, emulsion and microemulsion techniques, mechanochemical reactions, and a combination of mechanochemical, hydrothermal, and ultrasonically assisted reactions [1-4]. The sol-gel process is one of the most important methods for the production of biomaterials, its advantages include the use of inexpensive and readily available reagents, and

it is an effective method for the preparation of highly pure powder due to the possibility of a strict control of the process parameters. This method offers a molecular mixing of calcium and phosphorus, capable of improving chemical homogeneity. Moreover, the high reactivity of the sol-gel powders allows a reduction of the processing temperature and of any degradation phenomena during sintering [5].

However, the mechanical properties of hydroxyapatite are not good enough to be used as an implant in load bearing situations, like artificial teeth or bones. One approach to solve this problem is to combine it with a suitable reinforcement phase, producing a biocomposite which provides optimum mechanical properties, by overcoming mechanical limitations. The ideal biocomposite should be the one that who combines their biological and mechanical properties, to provide adequate support for the hard tissues [6,7].

Wollastonite (CaSiO_3), is a calcium silicate which has

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been widely used as a filler to fabricate composites with improved mechanical properties. Moreover, it has also been used as a medical material for artificial bones and dental roots because of its good bioactivity and biocompatibility. Natural bone is a bioceramic composite made up of small hydroxyapatite crystal particles reinforced by organic collagen fibers. Because of its outstanding mechanical properties, researchers sought ways of duplicating its mechanical properties [8,9]. Kokubo and colleagues attempted to prepare a similar composite by the crystallization process, developing a clinically important glass ceramic (A-W glass-ceramic) [8,10]. A-W glass-ceramic is an assembly of small apatite particles, effectively reinforced by wollastonite in a glassy matrix. The bending strength, fracture toughness, and Young's modulus of A-W glass-ceramic are the highest among bioactive glass and glass-ceramics [11]. Many studies have involved the wollastonite phase in natural or synthetic forms to produce different composites in which its presence improved some mechanical properties as well as the bioactivity and porosity of the composites [12-14]. The application of extra-pure natural materials instead of synthetic materials reduces the cost of implant production. Also, as distinct from synthesized materials, natural wollastonite has a needle-shaped habit, with a ratio between the needle length and their diameter equal to 15 - 20 or more. This will presumably facilitate the production of an interwoven reinforcing mesh of wollastonite needles in the composite [6].

The aim of the present work was to synthesize and characterize hydroxyapatite-wollastonite biocomposite powders by a sol-gel route, using calcium nitrate and ammonium phosphate as precursors of hydroxyapatite, and high-purity natural wollastonite as a reinforcement element. These powders were processed by sintering to produce dense materials for the evaluation of their structural characteristics, whereas their bioactive and mechanical properties will be evaluated in a parallel study.

2. Experimental Procedure

2.1. Sol-Gel Synthesis of Hydroxyapatite-Wollastonite Biocomposite Powders

The biocomposites of hydroxyapatite-wollastonite were prepared by sol-gel processing from calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich USA) and ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$, Sigma, Japan) and high-purity natural wollastonite, NYAD M200 (CaSiO_3 , from NYCO's Pilares deposit in Hermosillo, Sonora, México), with 98.25% purity. **Table 1** shows the chemical analysis of the natural wollastonite used in this study [15]. The amounts of the precursors reagents were chosen in order

Table 1. Chemical composition of wollastonite NYAD[®] M200, produced by Minera NYCO S.A. de C.V. [15].

| Chemical composition | | CaSiO_3 |
|-------------------------|-------------------|------------------|
| Component | Typical value (%) | |
| CaO | 46.25 | |
| SiO_2 | 52.00 | |
| Fe_2O_3 | 0.25 | |
| Al_2O_3 | 0.40 | |
| MnO | 0.025 | |
| MgO | 0.50 | |
| TiO_2 | 0.025 | |
| K_2O | 0.15 | |
| wt% loss (1000°C) | | 0.40 |

to maintain the Ca/P molar ratio at 1.67 of stoichiometric hydroxyapatite, and the amounts of wollastonite were chosen in order to obtain 20, 50, and 80 wt%.

First, to produce about 1.0 g of pure hydroxyapatite powder, 0.1639 mol of calcium nitrate was dissolved in 10 mL of deionized water by ultrasonic stirring during 15 minutes, and then 0.0979 mol of ammonium phosphate was dissolved by ultrasonic stirring during 30 minutes.

The mixture of precursors was stirred at room temperature by magnetic stirring, while the pH of the mixture was controlled between 6 and 7 with liquid ammonia for approximately 2 h, until the gelation was observed. The gel was then dried at 120°C for 12 h.

To produce the hydroxyapatite-wollastonite biocomposites, a suitable amount of wollastonite to obtain 20 wt% (0.25 g), 50 wt% (1.0 g), and 80 wt% (4.0 g) was suspended, by ultrasonic stirring, in a proper volume of deionized water to keep the solid: liquid ratio at 1:2 (w/v) for all experiments. Then the same procedure, as described previously, was followed until the dried gels mixed with natural wollastonite were obtained.

Finally, the dried gels were ground to a fine powder and heat treated in a furnace at 750°C in air for 3 h; the heating was done at a rate of 10°C/min. The flow chart in **Figure 1** outlines the complete experimental procedure.

2.2. Sintering of Hydroxyapatite-Wollastonite Biocomposites

For sintering experiments, the powders were ground using tungsten carbide milling balls in a 50 mL tungsten carbide container with a Fritsch Pulverisette 6 planetary mono mill (Idar-Oberstein, Germany). Cylindrical tablets were produced by uniaxial pressing of powders (0.5 g) into a 10 mm diameter die in a Carver press Hydraulic Unit 3912 (Carver, Wabash, IN). Sintering tests were carried out in a Lindberg/Blue M high temperature fur-

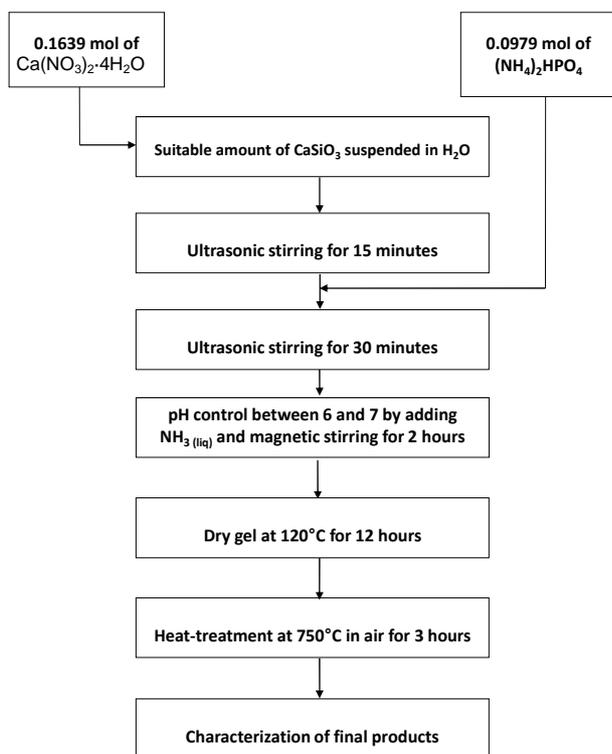


Figure 1. Schematic flow chart for the sol-gel procedure for synthesizing hydroxyapatite-wollastonite biocomposites.

nance (ThermoScientific, Asheville, NC) at 1200°C. The powders were ground in isopropanol for 30 min at a rotation speed of 200 rpm. The milled powder was dried at 120°C to remove the isopropanol and produce a fine powder. Cylindrical tablets were produced by pressing the powders under a pressure of 220 MPa for a 5 min dwell time and then sintered at 1200°C. The sintering procedure was performed at a heating rate of 2°C/min from room temperature to the sintering temperature, with a dwell time of 5 h at the maximum temperature followed by cooling at 2°C/min. The tablets produced contain 0, 20, 50, 80, and 100 wt% of wollastonite, coded as 100 H, 80 H - 20 W, 50 H - 50 W, 20 H - 80 W and 100 W, respectively.

2.3. Characterization Techniques

Thermal analysis was used to detect changes occurring during the heat-treatment process. Thermogravimetric (TGA) and differential thermal analyses (DTA) were carried out using a TA Instruments SDT 2960 Simultaneous DSC-TGA (New Castle, DE). Heating to 1000°C was performed in an alumina crucible, with air flow (23 cm³/min) at a rate of 10°C/min. The samples' weight was 3 mg of dried xerogel. XRD analysis was carried out by means of a Phillips X'PERT XRD diffractometer (Phillips Electronics, Eindhoven, The Netherlands). CuK α

radiation was used (40 mA, 40 kV). The 2 θ range was from 10° to 80° at a scanning speed of 1.2°/min. Identification of the crystalline phases was performed by comparison with JCPDS files 09-0432 and 84-0654 for hydroxyapatite and wollastonite, respectively. For FT-IR absorption analysis, the samples in KBr pellets were analyzed in the transmission mode using a PerkinElmer Spectrum GX System FT-IR spectrometer (Boston, MA) over the range 4000 - 400 cm⁻¹.

Morphological studies of the samples were performed using a JEOL SEM 5300 scanning electron microscope (JEOL, Tokyo, Japan). TEM studies of the samples were done on a JEOL JEM-2010F instrument. Sample specimens were prepared by dispersing the powders in distilled water to form very dilute suspensions. A drop of suspension was transferred onto a carbon mesh supported on a conventional copper microgrid.

3. Results and Discussion

3.1. Synthesis of Hydroxyapatite-Wollastonite Biocomposite Powders

Figure 2 shows the thermogravimetric analysis (TGA) combined with differential thermal analysis (DTA) for the dried gel of calcium nitrate and ammonium phosphate in water from room temperature to 1000°C. The dried gel trace displays a thermal transition in the temperature region 180°C - 350°C, which corresponds to a weight loss of about 40 percent by weight with an exothermic peak at about 280°C. This weight loss could be associated to the formation of hydroxyapatite in the early stages of crystallization. A further thermal process between 500°C and 700°C, corresponding to a negligible weight loss, and represented by an exothermic peak at about

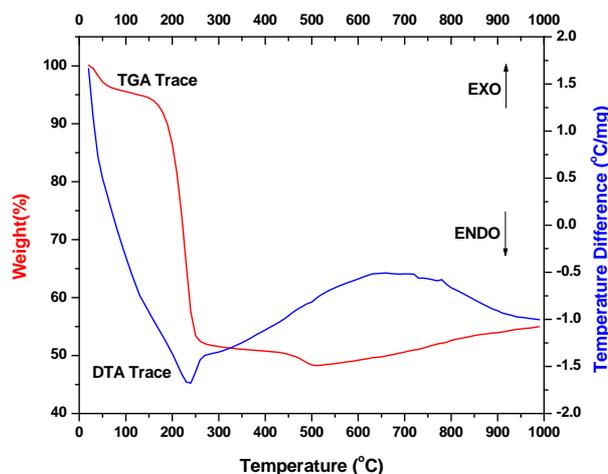


Figure 2. Thermogravimetric and differential thermal analyses trace for dried gel of calcium nitrate and ammonium phosphate in water from room temperature to 1000°C at a heating rate of 10°C/min.

650°C, could be due to formation of hydroxyapatite in advanced crystallization stages. **Figure 3** demonstrated that wollastonite does not exhibit any thermal transition in the whole temperature range. This fact indicates that synthesized hydroxyapatite and natural wollastonite added to produce the biocomposites, both maintain their chemical integrity, even under severe thermal conditions.

Figure 4 shows the XRD patterns for dried gel of calcium nitrate and ammonium phosphate in water upon heat treatment at 350°C and 750°C. This figure indicates that gel treated at 350°C is transformed to hydroxyapatite in an early crystallization stage; when gel was treated at 750°C it is converted to perfectly crystallized hydroxyapatite. In both cases the analysis reveals the presence of hydroxyapatite as individual phase in the materials.

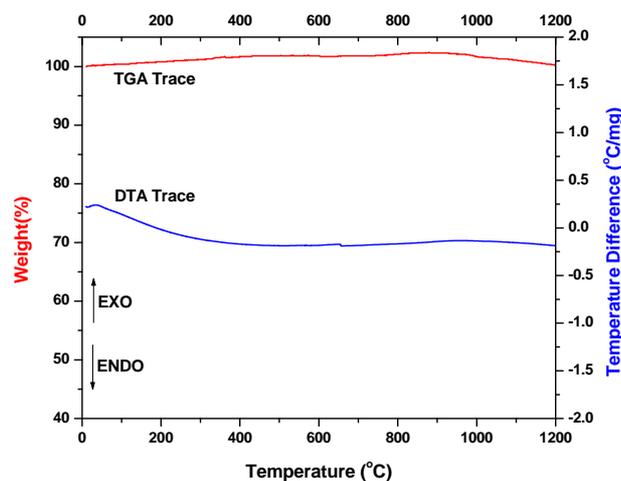


Figure 3. Thermogravimetric and differential thermal analyses trace for natural wollastonite from room temperature to 1200°C at a heating rate of 10°C/min.

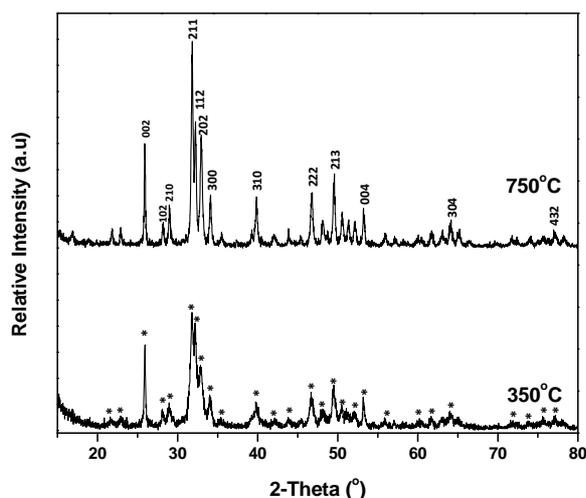


Figure 4. X-ray diffraction patterns for dried gel of calcium nitrate and ammonium phosphate in water upon heat treatment at 350°C and 750°C. (*) Hydroxyapatite.

For the above, hydroxyapatite in the biocomposites of this study, was synthesized at 750°C to obtain this bio-ceramic material completely crystallized.

Figure 5 shows the FT-IR spectra for the base materials. **Figure 5(a)** shows the spectral characteristics of natural wollastonite and **Figure 5(b)** shows the spectral characteristics of dried gel of calcium nitrate and ammonium phosphate in water upon heat treatment at 750°C, in the range of 4000 cm^{-1} to 400 cm^{-1} . The broad band around 1000 cm^{-1} in **Figure 5(a)** is mainly attributed to the silicate IR absorption of wollastonite. The peaks observed around 3571 cm^{-1} and 632 cm^{-1} in **Figure 5(b)** arise from the stretching and librational modes, respectively, of OH^- ions. The peaks at 1048 cm^{-1} and 1090 cm^{-1} have been associated with the stretching ν_3 mode of the P-O bonds, and the 962 cm^{-1} band arises from ν_1 symmetric P-O stretching vibrations mode of the PO_4^{3-} group. Bands at 603 cm^{-1} and 571 cm^{-1} were caused by the triply degenerate ν_4 bending vibration of the PO_4^{3-} group. The clear presence of two peaks at 603 cm^{-1} and 571 cm^{-1} , along the well-resolved peak at $\sim 632 \text{ cm}^{-1}$ confirms the presence of hydroxyapatite as stoichiometric phase [6,7,16-18].

Figure 6 resumes the X-ray diffraction patterns for natural wollastonite (100 W), and dried gels with different percentages by weight of wollastonite (20 H - 80 W) 80 wt%, (50 H - 50 W) 50 wt%, (80 H - 20 W) 20 wt% (100 H) 0 wt%, upon heat treatment at 750°C. This figure indicates that hydroxyapatite and wollastonite appear as unique phases in the biocomposites. In all cases well-crystallized, hydroxyapatite was obtained. This fact demonstrates that the wollastonite remains unreacted, throughout the whole in situ synthesis of hydroxyapatite.

Figure 7 shows the transmission electron micrographs of natural wollastonite and dried gels with different per-

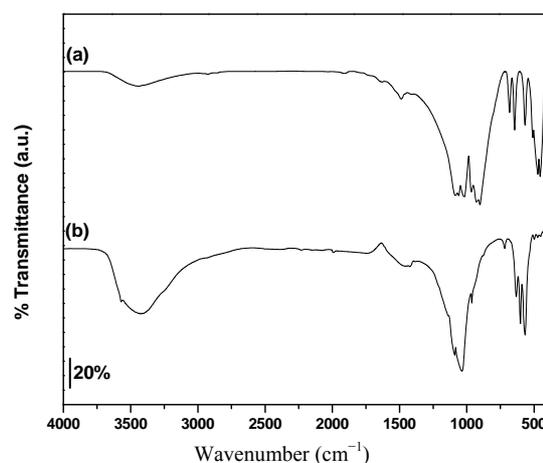


Figure 5. FT-IR spectra: (a) Natural wollastonite, (b) Dried gel of calcium nitrate and ammonium phosphate in water upon heat treatment at 750°C.

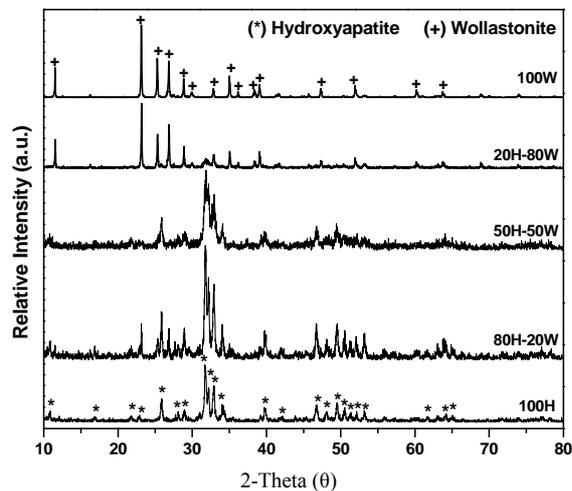


Figure 6. X-ray diffraction patterns for natural wollastonite (100 W), and gels of calcium nitrate, ammonium phosphate in water with different wt% of wollastonite upon heat treatment at 750°C: (20 H - 80 W) 80 wt%, (50 H - 50 W) 50 wt%, (80 H - 20 W) 20 wt% (100 H) 0 wt%. (*) Hydroxyapatite; (+) Wollastonite.

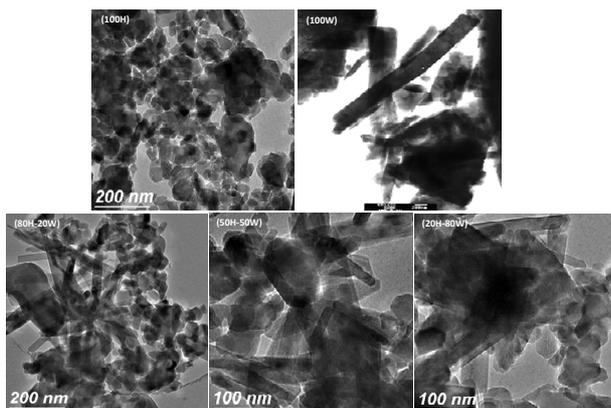


Figure 7. Transmission electron microscopic images of base materials powders: hydroxyapatite (100 H) and wollastonite (100 W), and hydroxyapatite-wollastonite biocomposites powders (80 H - 20 W, 50 H - 50 W, 20 H - 80 W).

centages by weight of wollastonite upon heat treatment at 750°C. This figure shows the typical lath shape and acicular (needle like) morphology of wollastonite fibers, while hydroxyapatite grains exhibit their typical shape and its hexagonal growth morphology [6]. Almost all of these grains are between 50 nm and 100 nm in size. In all biocomposites the grains of hydroxyapatite appear inserted among the wollastonite fibers, with the same shape and size than the observed in the base materials. The particles of synthesized hydroxyapatite agglomerate homogeneously on the surface of the wollastonite fibers, which assures an efficient interaction of both phases in the biocomposites. Additionally, the different amounts of wollastonite involved in the formation of the biocomposites

do not affect the stages of synthesis and the final characteristics, such as the structure and morphology of hydroxyapatite produced. These morphological characteristics of these biocomposites can avoid direct fiber-to-fiber interaction because the surfaces of wollastonite fibers are covered thoroughly by hydroxyapatite. Any further treatment such as pressing and sintering will produce materials with mostly fiber-hydroxyapatite interactions, because when the fibers interacted with themselves, other studies [12-14] have reported that these interactions affect some of the physical and mechanical properties of the materials.

3.2. Sintering of Hydroxyapatite-Wollastonite Biocomposites

Figures 8 and 9 show the scanning electron micrographs for cylindrical tablets of natural wollastonite (100 W), and synthesized hydroxyapatite (100 H), and biocomposites of hydroxyapatite-wollastonite with different percentages by weight of wollastonite (20 H - 80 W) 80 wt%, (50 H - 50 W) 50 wt%, (80 H - 20 W) 20 wt%, sintered at 1200°C for 5 h. When the powders were sintered, the surfaces in all materials show a compact microcrystalline appearance with clear crystal boundaries and some micropores. This fact demonstrates that the sintered hydroxyapatite-wollastonite biocomposites were not completely dense in the processing conditions of this study. Although it could be thought that this porosity could

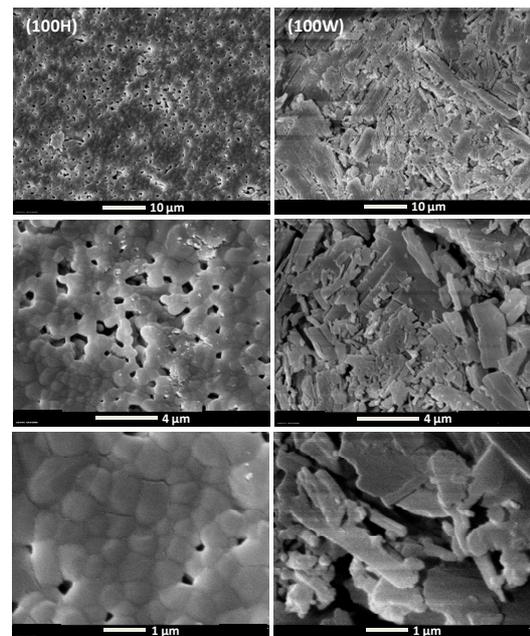


Figure 8. Scanning electron micrographs of sintered base materials: hydroxyapatite (100 H) and natural wollastonite (100 W) sintered at 1200°C for 5 h, at different magnifications.

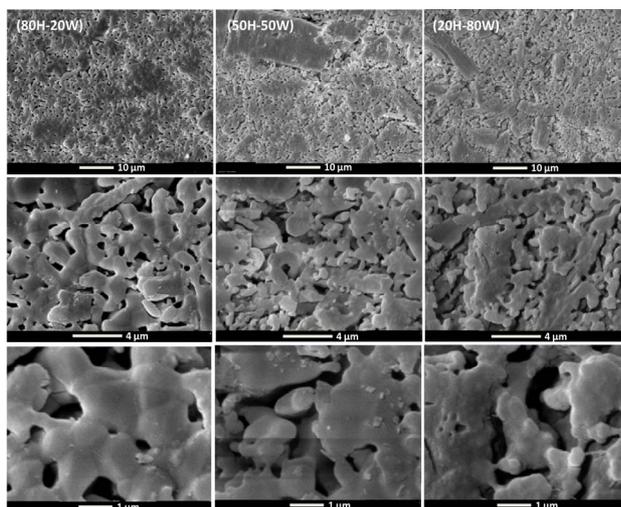


Figure 9. Scanning electron micrographs of sintered hydroxyapatite-wollastonite biocomposites (80 H - 20 W, 50 H - 50 W, 20 H - 80 W) sintered at 1200°C for 5 h, at different magnifications.

have a negative effect on the mechanical properties, the porosity actually enhances the bioactive properties, because the pores increase the penetration of physiological solutions in the specimens and permit the crystal growth of the bone-like apatite towards the surface, resulting in more efficient bioactive properties [7,19]. Therefore, the appropriate relationship between porosity and mechanical behavior in these materials has important implications in bone regeneration. Consequently, in a complementary study the porosity effect will be analyzed, and its relationship with the microstructure and mechanical properties of the materials will be evaluated.

4. Conclusion

Hydroxyapatite-wollastonite biocomposites were synthesized using an alternative sol-gel route using calcium nitrate and ammonium phosphate as hydroxyapatite precursors, and high purity natural wollastonite as reinforcement phase in aqueous medium. Formation of hydroxyapatite in the biocomposites occurs at the relatively low temperature of about 350°C, in the early stages of crystallization. A further thermal treatment of about 750°C produces completely crystallized hydroxyapatite, while wollastonite remains unreacted. The particles of hydroxyapatite appear agglomerated on the surface of wollastonite fibers. The hydroxyapatite-wollastonite biocomposite powders sintered at 1200°C for 5 h, experience no significant decomposition upon this heat treatment. The hydroxyapatite and wollastonite remain as single phases in the sintered biocomposites, exhibiting a certain grade of porosity. Although this porosity could have a negative effect on the mechanical properties, it is

important for ensuring the efficient integration of these materials with bony tissues, which could be modulated to vary the amounts of base materials in the biocomposites.

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