



A novel ceramic material with medical application

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Abstract

Until now the basic methods used in manufacturing of wollastonite have been chemical (melting together with glass crystallization process, chemical coprecipitation) and sol – gel methods. A new and promising way of wollastonite fabrication is controlled pyrolysis of polysiloxane precursors with inorganic fillers. Heat treatment of such mixtures leads to the formation of wollastonite-containing ceramics already at about 1000°C. This is a relatively inexpensive and efficient method which enables to obtain complex shapes of the samples.

The aim of this work was to obtain sintered, wollastonite-containing bioceramics and determine its bioactive features. Samples were sintered at three different temperatures: 1000, 1100 and 1200°C. Then the bioactivity of the wollastonite-containing ceramics was investigated by the “in vitro” test in simulated body fluid. On the basis of the achieved results, it can be assumed that the obtained material possesses bioactive features.

Keywords: bioceramics, wollastonite, polymeric precursors, active fillers

I. Introduction

Wollastonite is a calcium metasilicate with the chemical formula CaSiO_3 [1]. It is commonly used in ceramic and cement industry [2]. Furthermore wollastonite is characterized by specific bioactive features in contact with living tissue what makes it an attractive material in manufacturing of artificial bone and in bone tissue engineering field [2].

The characteristic feature of bioactive materials is the ability to form a hydroxyapatite (Hap) layer on their surface, after immersion in simulated body fluid [3–6]. Moreover after comparing with bioglasses and apatite/wollastonite glass-ceramics, it was found that the rate of Hap formation on CaSiO_3 is faster [7].

Wollastonite-based ceramic can be manufactured by melting suitable raw materials followed by controlled crystallization of the glasses or by a sol-gel method [1,2]. The main drawbacks of the melting method are the multi-step preparation procedure and the relatively high processing temperatures (about 1500°C). The sol-

gel method offers lower processing temperatures (they do not exceed 1200°C), however it is expensive and has low efficiency [1].

A novel and promising method of wollastonite manufacturing containing ceramics is controlled pyrolysis of organosilicon precursors with adequate active fillers. Heat treatment of such mixtures, depending on the type of polymer precursor, the type of active fillers and the final heat treatment temperature, leads to formation of wollastonite-containing ceramic material already at about 1000°C [1,2].

II. Materials and Methods

Lukosil 901 poly (methylphenylsiloxane) resin (Lucebni Zavody, Kolin, Czech Republic), together with commercially available active fillers (powders of $\text{Ca}(\text{OH})_2$ and nano-grain sized SiO_2) were used. The resin was cured over the period of 7 days, in the temperature ranging from 100°C to 150°C. The cured resin was ground together with active fillers. Pellets were formed from the received powders and then heat-treated at 1000°C, in an inert atmosphere. The average heating rate was 0.7 °C/min and the total time of heat treat-

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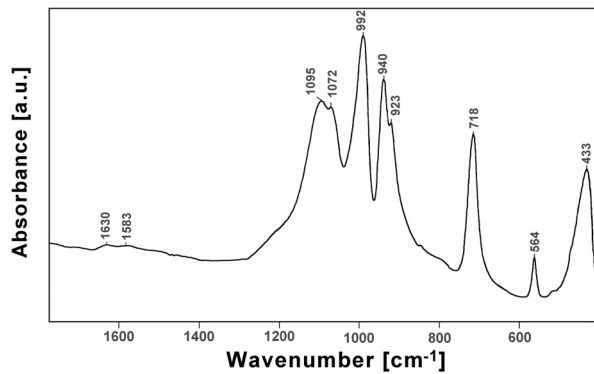


Figure 1. FTIR spectrum of wollastonite containing ceramics after controlled pyrolysis in 1000°C

ment 24 hours. The obtained samples were ground in a vibrating mill (milling time was 2h and mill frequency 12Hz) to a mean grain size of 0.5 μm . Pore size distribution was determined by the mercury porosimetry method (Poremaster 60, Quantachrome Instr.).

In the next step, bars were formed by isostatic pressing (200 MPa) and sintering at the following temperatures: 1000, 1100 and 1200°C (average heating rate was 5 °C/min and holding time at max. temperature 2 h).

The materials were investigated by using FTIR (Fourier transform infrared) spectroscopy. FTIR absorbance spectra were collected with FTS-60 V Bio-Rad spectrometer. Spectra were collected over the 4000 to 400 cm^{-1} wavenumber range, at a resolution of 4 cm^{-1} and 256 scans were summed. A standard KBr pellet technique was used.

The structure of the obtained ceramic samples was examined with the use of the Philips X'Pert Pro MD powder diffractometer ($\text{K}\alpha_1$ radiation from Cu anode, Ni filtered). Data analysis and the peak profile fitting procedure were carried out using Philips X'Pert High-Score Plus (PW3212) Release 2.1 software. The patterns were acquired in the 2θ range from 3 to 90° at the room temperature.

In the bioactivity “in vitro” test, sintered samples were immersed in simulated body fluid (SBF) solution. During the experiment time, the pH of SBF was controlled. The samples were immersed for 30 days at 37°C. The simulated body fluid solution was changed every 3–4 days to provide constant chemical composition of solution. Scanning electron microscopy (SEM) with EDS analysis (JEOL 5400 with LINK AN 10000 point microanalyzer of X-ray radiation) was used to study morphology and chemical composition of the prepared samples before and after the bioactivity test.

III. Results and Discussion

The FTIR spectrum (Fig. 1) of the sample obtained by controlled pyrolysis of polysiloxane resin with addition of active fillers at 1000°C shows bands characteristic for α -wollastonite [1]. The characteristic stretching vibrations of Si-O-Si bonds at 718 cm^{-1} can

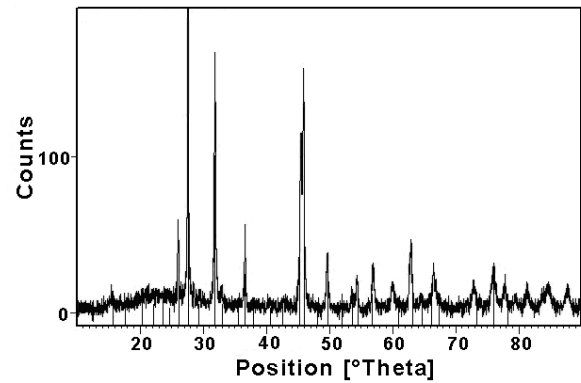


Figure 2. XRD pattern of wollastonite containing ceramics obtained at 1000°C

be observed. Furthermore, vibrations, associated with the bond mentioned above, are visible at 1072 and 1095 cm^{-1} . The bands at 923, 940 and 992 cm^{-1} corresponds to stretching vibrations of Si-O bond. Typical bending vibrations of -O-Si-O- bond can be seen at 563 cm^{-1} [8-10].

XRD analysis (Fig. 2) confirmed the presence of α - CaSiO_3 . The mean grain size of crystallites measured according to the Scherrer equation is about 52 nm.

Fig. 3 shows cumulative pore size distribution curves in green samples made of wollastonite powder produced by controlled pyrolysis. Pore size distribution in the sample made from the non-grounded powder was relatively wide, in the range of 0.5 to 2 μm , indicating that the powder consisted of particles of various sizes. In contrary, pore size distribution in the sample made from the ground powder was narrow with modal pore diameter of about 0.5 μm . This suggests that the grinding process was effective and produced particles of the similar size. Narrow pore size distribution in a green sample indicates homogenous particle arrangement, which is advantageous for its sintering process.

The SEM micrographs of the pressed samples sintered in 1000, 1100 and 1200°C are shown on the Fig. 4. Significant differences on surface morphology can be

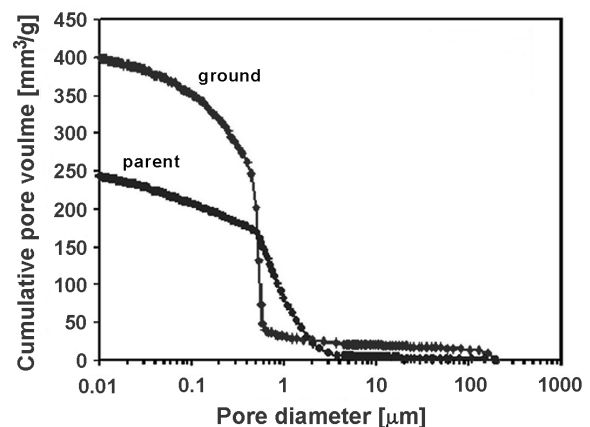


Figure 3. Pore-size cumulative curve of the powder before and after grinding process

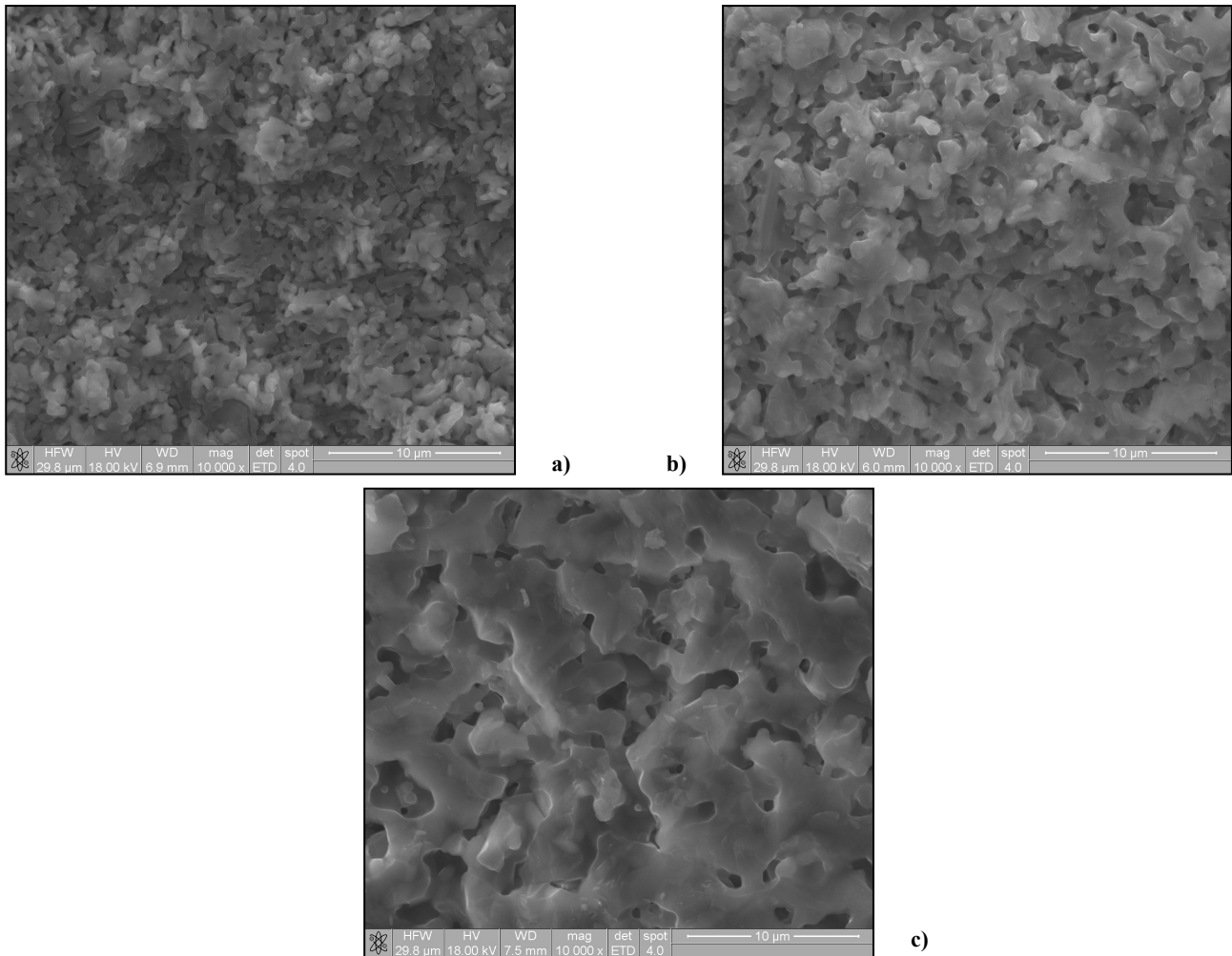


Figure 4. SEM micrographs of samples obtained at: a) 1000°C, b) 1100°C and c) 1200°C

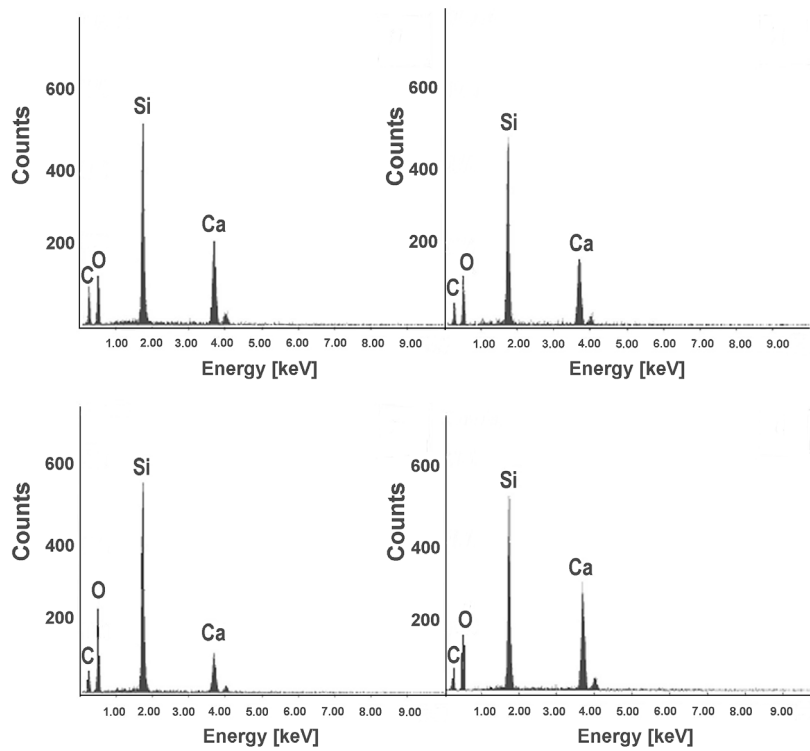


Figure 5. EDS point analysis of the samples sintered at: a) 1000°C, b) 1200°C, c) 1100°C (one position) and d) 1100°C (another position)

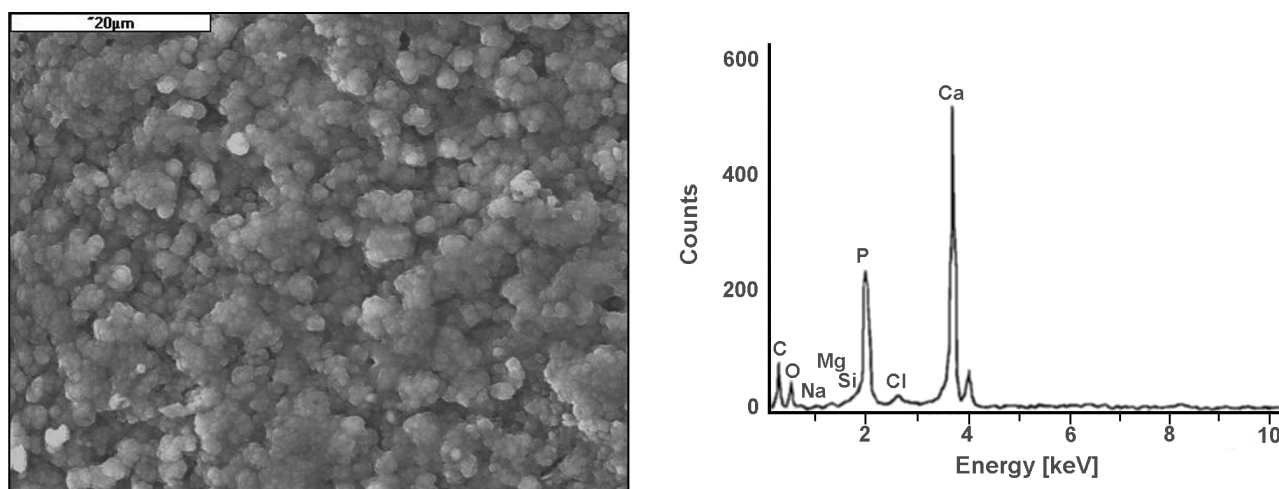


Figure 6. SEM micrograph (bar=20 μm) with EDS point analysis of the samples after bioactivity test in SBF

observed with the sintering temperature changes. The mean grain size of the material sintered at the 1000°C is about 0.6–1.2 μm. When the sintering temperature increases, grain growth is visible and the morphology of material surface changes. The mean grain size for the samples sintered in 1100°C is about 2–5 μm and for the 1200°C, 4–10 μm. EDS analysis (Fig. 5) shows that during the sintering, changes in chemical composition of investigated materials can be observed. The samples sintered at 1000 and 1200°C contain wollastonite as the main phase. However, the samples sintered at 1100°C have an additional phase, consisting significantly lower quantities of calcium. At temperature of 1100°C wollastonite can be partly dissolved, creating another silicate (metastable phase). EDS spectra of the sample sintered at 1100°C (Fig. 5c,d) confirmed existing of peaks with different intensity of particular elements when analysis at different points was carried out.

Fig. 6 shows surface micrographs of the sample surface after immersion in SBF for 30 days, together with EDS analysis. All the samples show very good bioactivity. Surface is totally covered by the dense so-called cauliflower shape crystalline layer characteristic for hydroxyapatite. The EDS analysis confirms that this layer consists mostly of calcium and phosphorus atoms. The ratio Ca/P is similar to that in bone apatite.

IV. Conclusions

The results show that thermal treatment of organo-silicon precursors with active fillers leads to obtaining ceramic material which contains nanocrystalline wollastonite. Moreover sintering of such powders leads to obtaining of the samples with bioactive features, as indicated by the results of the „in vitro” test in simulated body fluid.

On the basis of the achieved results it is assumed that the material obtained can be useful in the regeneration of the bone tissue.

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