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Alumina based composites with possible medical applications

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The aim of this research is processing, characterization and testing of an alumina and a bioactive component based biocomposite. The biocomposite was designed as a multicomponent material, which has improved bioactivity compared with the alumina taken separately and better mechanical properties than the chosen bioactive component. By varying the type and the distribution of the reinforcing phase inside the composite, it will be possible to obtain a large range of mechanical and biological properties and, finally to optimize the structure of the implant and its interaction with the surrounding tissue[1]. After sintering, the phase composition, the specific ceramic properties, the mechanical properties, the chemical stability and the microstructure were investigated. The values of 50-400 MPa obtained for the compressive strength (similar or grater than those of the cortical bone) [2] and the positive result of the chemical stability test in physiological serum, recommends the composite for future tests, including possibility of its employment in medical applications.

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1. Introduction

Bioceramic materials are employed in the field of bioengineering for the production of temporary or permanent implant devices. For any given application, the ceramic material must have the necessary mechanical properties and biocompatibility with the corrosive environment of the human body, with high safety margin. Having selected a material for an implant application, it is not possible to simply adjust the mechanical properties to those of the removed living material, by making a direct replica of the removed part [3].

2. Materials and preparation techniques

The two components of the composite material, alumina and the bioactive component were obtained separately and mixed in different ratios. The samples have 50%Al_2O_3 (M1), 75%Al_2O_3 (M2) and 85%Al_2O_3 (M3) and the rest till 100 is represented by the bioactive component.

2.1 Obtaining the alumina

Al_2O_3 was obtained starting from $AlCl_3 \cdot 6H_2O$, from which the oxide was precipitate, in presence of ammonium dioxide at pH=10 - 12. The precipitate was dried at 120^0C/24h and grinded in a mill with alumina balls, and the result was a white powder. This powder was characterized using X ray diffraction. The X ray diffraction emphasizes the presence of only one crystalline phase - AlOOH (aluminum oxide hydroxide), as shown in Fig. 1.

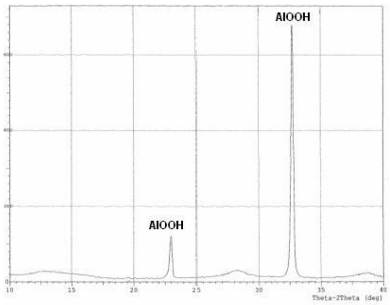

Fig. 1. X ray diffraction pattern of the alumina powder dried at 120^oC.

The powder obtained after calcination was evaluated using X ray diffraction, and resulted the pattern of γ-Al_2O_3 (fig. 2).

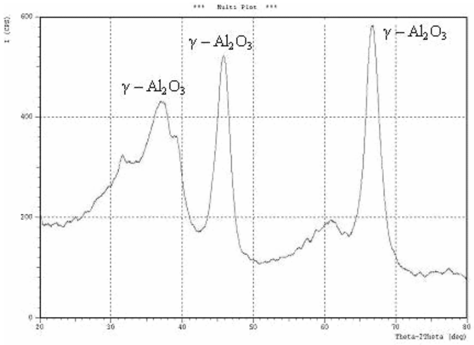

Fig. 2. X ray diffraction pattern of γ-Al_2O_3 obtained by calcination at $500\ ^0C$

The grain size analysis performed on the γ-Al_2O_3 powder emphasized a range of grain diameter of 0,151 - 1,908μm, an average diameter of 0,839μm and a surface area of 8,53m^2/g. The grain size distribution is single-modus with the highest proportion of the grains placed in the range of the average diameter.

2.2 Obtaining the bioactive component

The bioactive component was chosen in the SiO_2 – Na_2O – CaO – P_2O_5 system of Hench's diagram [4], on the curve where the bioactivity index I_b = 10. It's oxide composition is 42,62%SiO_2, 25,26%Na_2O, 22,12%CaO, 10%P_2O_5. In order to obtain the bioactive component, the raw materials were dissolute. The solutions were homogenized using magnetic mixing in the presence of NH_4OH, until pH = 11. On the obtained gel was ageing for 24h, and after that dried at 70^0C for 24h. The resulted powder was grinded for 1h in the ball mill at 180rot/min. Following, the powder was sieved and calcinated at 170^0C, in order to release all volatile compounds.

2.3 Obtaining the composite material

Combining the two types of oxide materials, in different proportions, the samples M1, M2 and M3 were obtained. The two components, as powder, were homogenized in ethylic alcohol, for 2h, at 180 rot/min. The resulting paste was dried at 40^0C for 12h and its grain size distribution was analyzed. In table 1, the values of surface area and average diameter are presented.

Following, cylinder shape samples (Φ=20mm and h=5mm) were formed, using single axis pressing. (150 MPa). The composite material was shaped using single axis pressing and thermally treated at temperatures between 1200^0C and 1400^0C, with 1 and 3 hours at the highest temperature.

Table 1. Results of the grain size analysis.

Samples	Surface area (m^2/g)	Average diameter (μm)
M1	4,75	6,515
M2	6,24	6,004
M3	6,02	4,825

3. Results and discussions

In order to identify the crystalline phase after the thermal treatment, the samples were studied using the X ray diffraction patterns. The sintered samples were analyzed in what it concerns the ceramic characteristics (apparent density, absorption, shrinkage and apparent porosity), the mechanical properties (compressive strength) and chemical stability (pH variation of some physiological serum solutions in which same quantity of the three samples was dissolved). Using the scanning electron microscope (SEM), the structure of the composite materials was studied.

3.1. Phase composition

Qualitative phase composition analysis was performed using a Shimadzu HZG-4A difractometer. In figure 3 are shown the X ray diffraction patterns of the three samples, influenced by the temperature and soaking time. One can see that the same crystalline phases are appearing, Al_2O_3, albite Ca rich $(Na,Ca)(Si,Al)_4O_8$ (sodium calcium aluminum silicate) and $(Na_{0.11}Ca_{0.89})(P_{0.11}Si_{0.89})O_3$ (sodium calcium phosphate silicate – identified at the detection limit of the difractometer) in all samples. The intensity of the diffraction lines increases when the proportion of alumina in the sample increases as well.

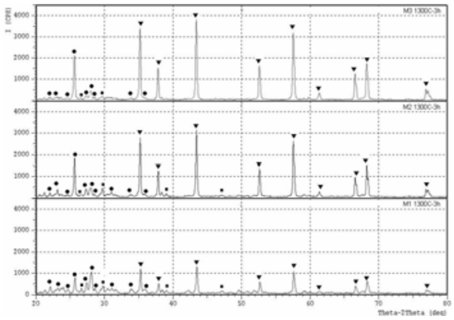

Fig. 3 X ray diffraction pattern for samples M1, M2 and M3 at 1300^0C 3h soaking time (● - $(Na,Ca)(Si,Al)_4O_8$ [ASTM 09-0456], ▼- Al_2O_3 [ASTM 46-1212, ASTM 10-0173], ■ – $(Na_{0.11}Ca_{0.89})(P_{0.11}Si_{0.89})O_3$ [ASTM 46-0163]).

3.2. Density and porosity

The apparent porosity of the sample was analyzed using a PASCAL 240/140 mercury porosimeter. Then, from its values, the apparent density was calculated. From the analysis of the data for apparent density (Fig. 4), one can see that the apparent density increases while the temperature and the soaking time are increasing, consequence of the intensification of the sintering – vitrification. The value of the apparent density increases during sintering and because of alumina's density, as this is the main component.

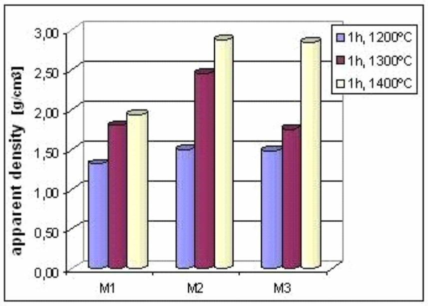

Fig. 4 Apparent density for the three samples, at different temperatures with 1h soaking time.

The evolution of the values for apparent porosity is shown in figure 5. The sintering at 1200^0C determines the highest values of porosity, as a result of a lower sintering degree, obtained for all compositions. The thermal treatment at 1400^0C reduces the values of porosity, as a result of the sintering – vitrification process.

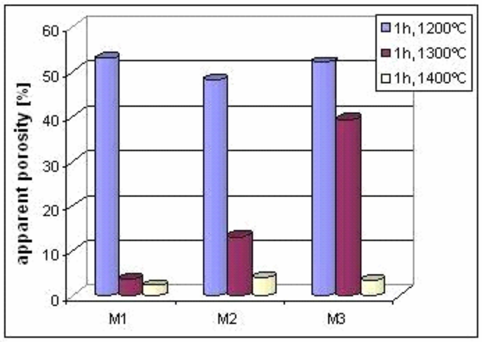

Fig. 5. Apparent porosity for the three samples, at different temperatures with 1h soaking time

3.3. Compressive strength resistance

The mechanical behavior was evaluated by compressive strength resistance, using the Walter Bai AG Testing Machine Lfm 50kN. The results of the resistance ranged between 50 MPa (M1 treated 1h at 1200^0C) and 400MPa (M3 treated 3h at 1400^0C). The mechanical resistance depends of the alumina content, and the soaking time determines increasing of the resistance with 1 – 5%.

3.4. Chemical stability (pH)

On a physiological serum suspension (rate composite: serum = 1:10) was measured the pH variation in time. The pH measurement was performed using an electronic pH – meter with electrode with integrated temperature measurement sensor. The evolution of the pH was studied for 14 hours, for the samples M1, M2 and M3, sintered at 1300^0C and 1400^0C, with 1h and 3h soaking time. The data are emphasizing the fact that the pH values of the studied solutions stabilized after about 7 hours, in the range 7.60 – 7.90, starting from 7.0-7.2.

3.5. Microstructure

In Figs. 6 – 8 are presented the scanning electron microscope images of samples M3, sintered for 3 hours at temperatures of 1200 – 1400 ^{0}C. The microstructure is homogenous, with submicron pores uniformly distributed. A few larger pores, of about 1 μm, can be noticed. The amount and dimensions of pores are reducing with higher temperature.

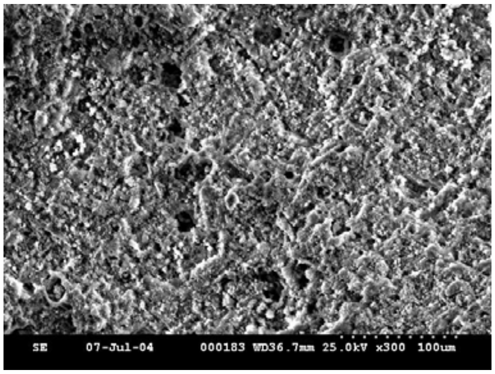

Fig. 6. SEM image of sample M3, sintered 3h at 1200^0C (x300).

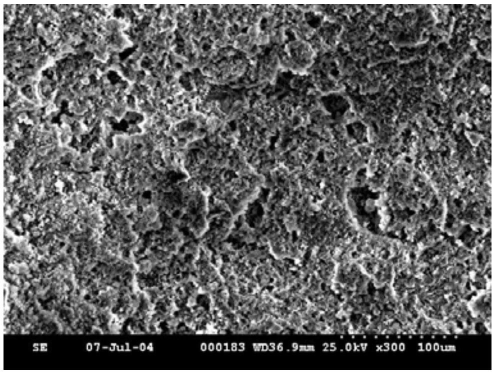

Fig. 7. SEM image of sample M3, sintered 3h at 1300^0C (x300).

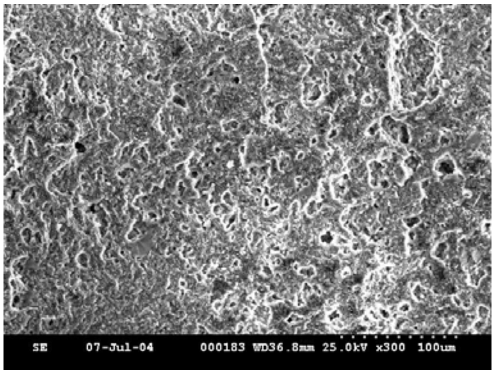

Fig. 8. SEM image of sample M3, sintered 3h at 1400^0C (x300).

4. Conclusions

The aim of this work was to obtain composite biomaterials, with a bioinert component – alumina, well known for its mechanical properties and a bioactive component, chosen in the SiO_2 – Na_2O – CaO – P_2O_5 system of Hench's diagram. The composite material was prepared using solid state reactions and the identified crystalline phases were alumina and albite. The sintered samples were analyzed in what it concerns the mineral composition, ceramic characteristics, the mechanical properties, and chemical stability. Using the scanning electron microscope (SEM), the structure of the composite materials was studied.

Considering the higher values of compressive strength of the sample M3, the fact that the chemical stability of the physiological serum is not affected by the higher amount of alumina of this sample and the bioactivity index I_b=10 of the chosen bioactive component from Hench's diagram, recommends this material for future test involving behavior in biological environment.

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