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Preparation of hydroxyapatite ceramics for biomedical applications

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Hydroxyapatite (HA) is the main component of hard tissue and because of its high biocompatibility and bioactivity makes a strong bond with hard tissue. In this research, hydroxyapatite powders were uniaxially compacted at 86 MPa to form cylindrical shaped samples and sintered at 700-1300 °C with one hour soaking time. The density measured was between 2.89 and 3.49 g/cm^3. Phase analyses were performed using X- ray diffraction and the results revealed there was no sign of HA decomposition. Three and four point bending strengths were measured between 7 to 44 MPa. Microstructural studies with a scanning electron microscope (SEM) showed that hydroxyapatite ceramics formed a highly integrated structure with an increase in the sintering temperature up to 1300 °C. It was proved that the sintered samples of hydroxyapatite did not contain any unwanted phase. These results imply that the blocks prepared in this study have the potential for use as biomedical implants.

Key words: Hydroxyapatite blocks, Sintering.

Introduction

There is an increasing demand for materials to be used in biomedical and dental applications. These materials are currently implemented in different forms, depending on the part of the body which needs repair. Biocompatibility, biofunctionality, and availability are three significant factors in selecting materials [1].

Historically, ceramics are the oldest materials in medical applications. Tricalcium phosphate (TCP) was used for repairing bone defects in the early 20th century [2-4]. Although, ceramics are brittle by nature, they have excellent compressive strength and a high wear resistance. Calcium phosphate compounds such as hydroxyapatite (HA), tricalcium phosphate (TCP), dicalcium phosphate dihydrate (DCPD), dicalcium phosphate anhydrous (DCPA), and tetracalcium phosphate (TTCP) [1-7] have almost the same chemical compositions as bone minerals. When theseompounds are implanted into the living body (*in vivo*) for a period of time, they create a strong chemical bond with bone tissue [8, 9].

In replacing bone defects, besides all compatibility parameters, the material should possess the same porosity as the bone. Bone has a complex structure with macro- and micro-pores. Pores are mostly interconnected to allow body fluids to carry nutrients and provide a medium where interfacial reactions between hard tissue and soft tissue can occur. An implant material should generally present similar properties to that of the bone. However, mechanical requirements dictate a high strength for implants which is associated with the elimination of some pores from them. As a result, reducing the porosity should increase the mechanical properties of HA as with any other ceramics. It is therefore important to find an optimum porosity to maintain the mechanical strength while pores provide the bone implant with an acceptable channel for nutrition to obtain the best implant properties [10, 11].

The aim of the present study was to find the effect of sintering temperature on the microstructure, phase composition and the mechanical properties of hydroxyapatite ceramics.

Experimental Details

Medical grade hydroxyapatite powder was obtained from Sigma-Aldrich Chemical Company. The density of the powder was measured as 2.91 g/cm^3 using a ACCU-PYC 1330 (Micromeritics Gemini 2375). In order to determine the sintering temperature, a dilatometry test was performed. Also, the X-ray diffraction technique was employed using a Siemens, D500 diffractometer at each sintering temperature to estimate the probable phase transformations and the upper limit of the decomposition temperature. The particle size distribution was measured using a Fritsch Analysette22 system. The microstructures of the samples under different sintering conditions were studied using a Cambridge Stereosacn 360 scanning electron microscope. The starting powder was uniaxially compacted at 86 MPa to form cylindrical shaped samples 55 × 13 mm. The sintering was performed in air at 700-1300 °C with 1 hour soaking time. The rate of temperature increase was 10 °Kh^{-1} while the cooling was carried out in the furnace. The mechanical properties of sintered bodies were examined by 3 and 4 point bending techniques

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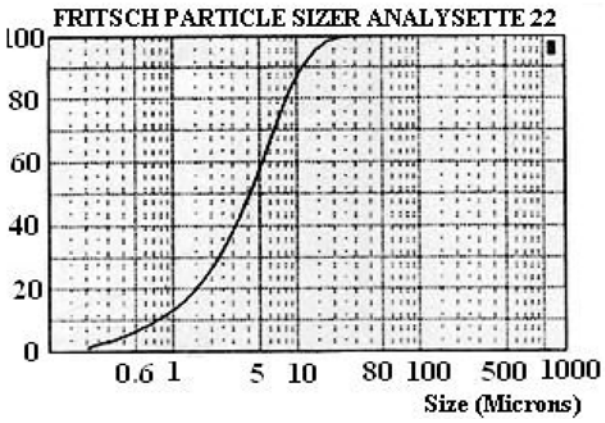

Fig. 1. Particle size distribution of the hydroxyapatite powder.

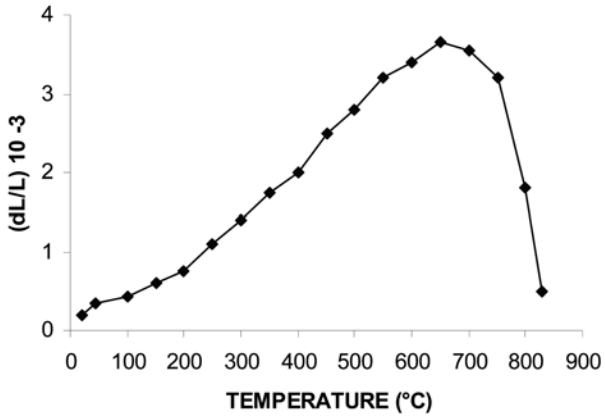

Fig. 2. Dilatometry measurement for a hydroxyapatite sample.

using an Instron Universal Testing Machine 1196 was used with a cross head speed of 0.5 mm/min and maximum load application of 5 kN.

Results and Discussion

Fig. 1 shows the particle size distribution. It is evident that the average size of the powder was around 4 micrometre. The particle size and specific surface area of the starting powder are the most important parameters affecting the sintering behavior of ceramics. By reducing the particle size and increasing the specific surface area, the same degree of sintering can be achieved at much lower temperatures.

The specific surface area of the starting powder was measured as 52.3 m^2/g which compared with other commercial powders can be considered as an active powder. The molar ratio of Ca/P is another important parameter which is 1.5 in tricalcium phosphate, 2 in tetra calcium phosphate, and 1.67 in stoichiometric hydroxyapatite [12]. The molar ratio of the Ca/P in the present powder was measured with the ICP technique at around 1.62. A ratio less than 1.64 will be interpreted as the creation of pores and voids in a sintered body. A ratio higher than 1.67 means that the rate of absorption

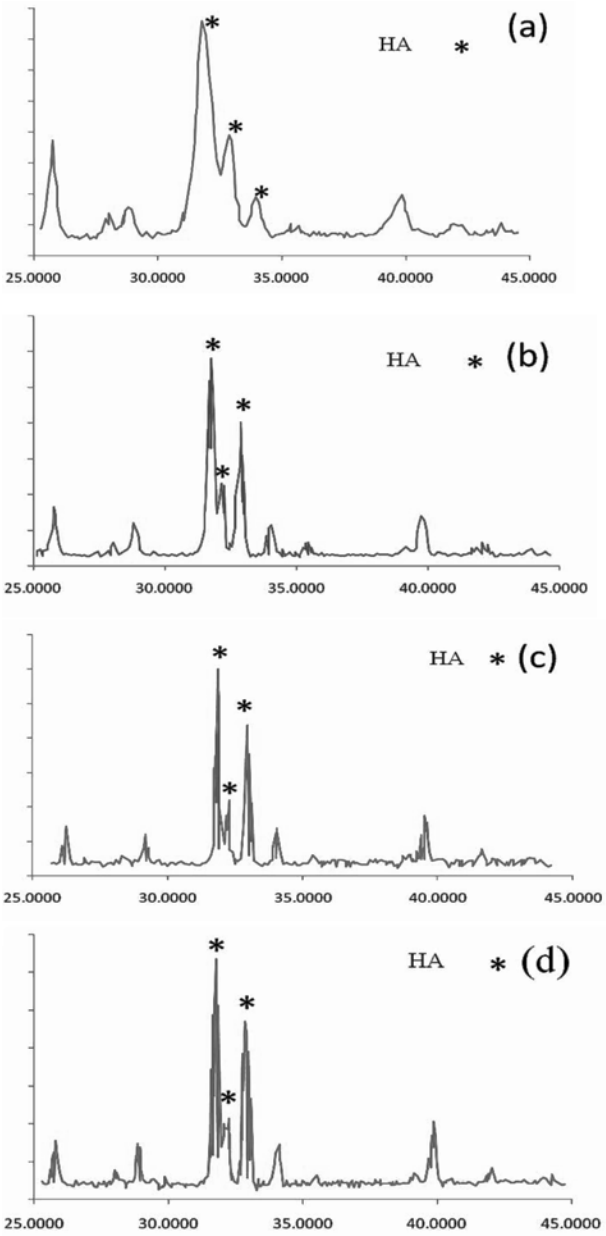

Fig. 3. X-ray diffraction pattern of: (a) starting powder, (b) fired at 900 °C for 1 hour, (c) fired at 1100 °C for 1 hour, (d) fired at 1300 °C for 1 hour.

in vivo will be increased [13].

In order to gain insights into the sintering behavior of hydroxyapatite, dilatometric tests were carried out. Fig. 2 shows a typical curve which indicates the shrinkage starts at about 700 °C and the sintering temperature is estimated to be between 900 and 1300 °C [14-24].

XRD results of the sintered samples are shown in Fig. 3(a) to 3(d). As it is evident from these patterns, within the sintering range of 700-1300 °C, no other phases could be detected by XRD. Also, the CaO phase was checked for in particular to be absent since this phase has been shown to have negative effects on the growth of bone cells [14].

In order to make microscopic studies, samples were

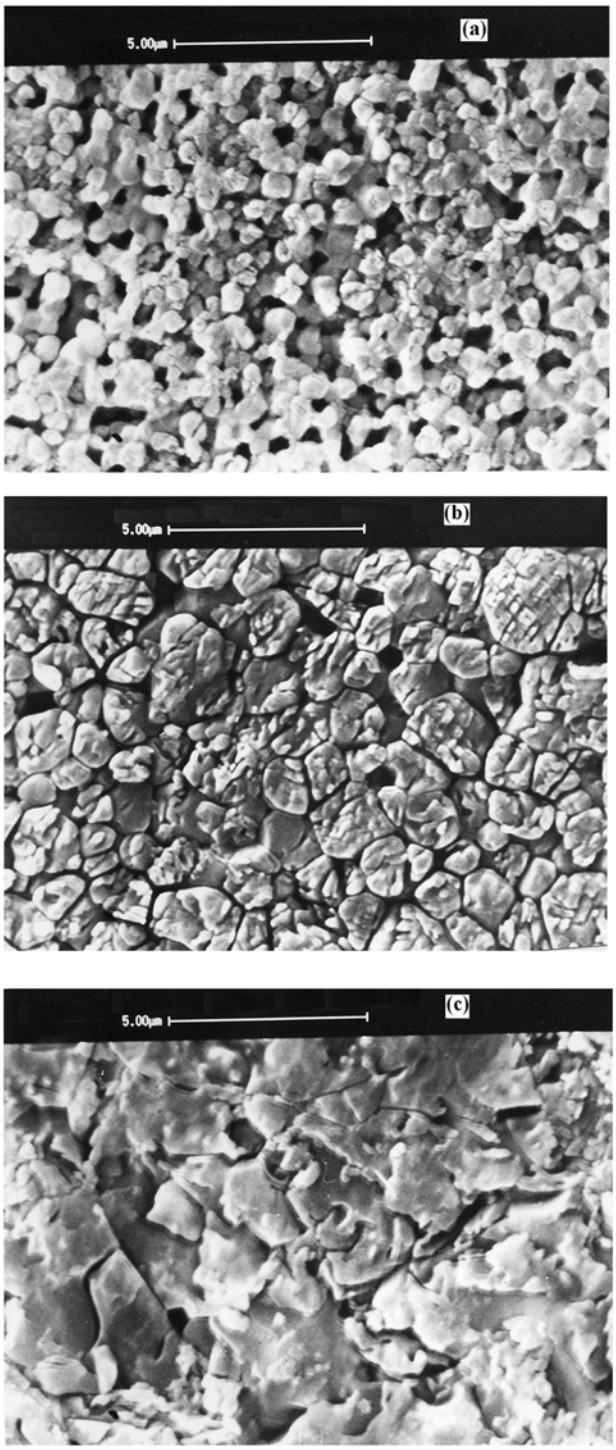

Fig. 4. Scanning electron micrographs of hydroxyapatite sintered for one hour at (a) 1100 °C (b) 1200 °C and (c) 1300 °C.

etched in 1% phosphoric acid and gold sputtered prior to study by SEM studies. Fig. 4 shows scanning electron microscope images of hydroxyapatite sintered at different temperatures. In all cases, the sintered samples were highly polished with different grades of polish; the last one being 1 micrometre of diamond paste.

As is evident from Fig. 4(a), when the samples were fired at 1100 °C, hardly any changes in grain size could

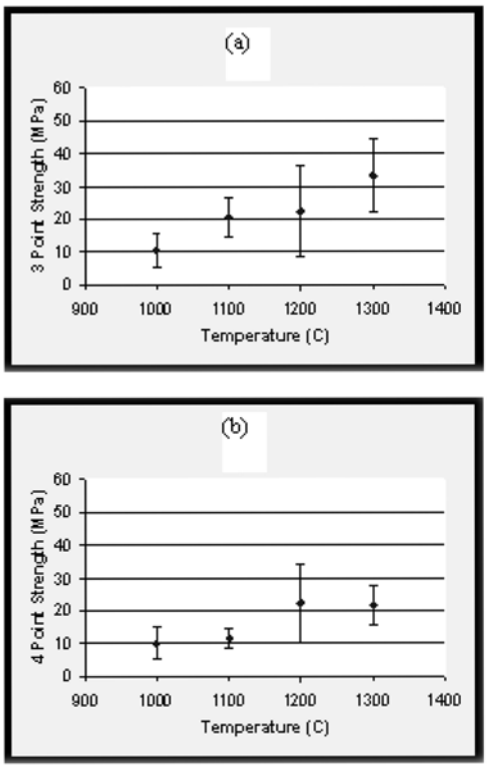

Fig. 5. Bending strength against sintering temperature (a) 3 point and (b) 4 point.

be observed. Sintering at 1200 °C results in grain growth as is shown in Fig. 4(b). The grain growth is also associated with a reduction in the apparent porosity which is a favorable condition as far as the mechanical strength of the part is concerned Fig. 4(c) shows an electron micrograph of a sample sintered at 1300 °C. Further grain growth is evident and a higher mechanical strength is expected for this sample.

The mechanical properties of sintered bodies were examined by 3 and 4 point bending techniques after samples polished with emery paper and diamond paste. An Instron Universal Testing Machine 1196 was used with a cross head speed of 0.5 mm/minute and maximum load application of 5 kN. In fact, in many cases, the mechanical properties of the samples were improved when they were fired at higher temperatures as is demonstrated in Figs. 5(a) and (b).

Conclusions

The present study shows that the sintering of hydroxyapatite at 1100-1300 °C results in an essentially porous body which can be used as an implant. XRD diffraction patterns of the sintered ceramics proved that no additional phase formation takes place even at elevated temperatures.

Mechanical measurements showed that the bending strength of the sintered bodies were between 7-44 MPa which improved proportional with sintering temperature. Microstructural studies showed that while the grain size

of the bodies sintered at 1100 °C remained basically comparable to the particle size of the starting powder, ceramics fired at 1200 to 1300 °C showed an increase in grain size in line with the increased temperature.

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