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MICROWAVE SINTERING OF CALCIUM PHOSPHATE CERAMICS

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Specimens of a calcium phosphate powder, compacted at 44 MPa, were sintered at two sintering temperatures of 1000 °C and 1100 °C using a microwave furnace. Determination of the physical properties (shrinkage, porosity and density) and mechanical properties (hardness) of the specimens obtained were carried out, and compared to specimens of similar composition which had also been sintered at the same temperatures using a muffle furnace for comparative purposes. Microstructural examinations by scanning electron microscopy (SEM) were conducted to ascertain the differences in the properties observed.

Keywords : Microwave sintering, Calcium Phosphate, Precipitation, Hardness

INTRODUCTION

Bioceramic materials are widely used to repair and reconstruct damaged parts of the human skeleton [1]. Calcium phosphate ceramics materials based on hydroxyapatite (HAP) and tricalcium phosphate (TCP), due to their chemical composition, excellent biocompatibility, bioactivity and osteoconduction have received considerable attention as suitable bioceramics for the manufacture of osseous implants [2,3].There are many techniques for the production of such biomaterials, including wet chemical methods [4-7], hydrothermal processes [8–11], solid-state reaction [12–14], and sol–gel synthesis [5, 15].

Hydroxapatite has a hexagonal structure and is the most stable phase among the various calcium phosphates. Hydroxyapatite is stable in body fluid as well as in dry or moist air up to 1200 °C [16]. The high sintering temperatures and long sintering duration required for the consolidation of HAP powders often result in extreme grain coarsening and decomposition of the HAP, which is characteristic for conventional sintering methods and results in the deterioration of the mechanical properties of HAP ceramics [17, 18]. In order to overcome these problems, microwave sintering had
been shown to be of great potential in ceramics processing [19]

Microwave heating is a fast sintering process fundamentally different from conventional radiant element techniques in that the energy can be deposited volumetrically throughout the material rather than relying on thermal conduction from the surface. Proper use of the technique may lead to a series of benefits, including great microstructural control, improved product properties and reduced manufacturing costs due to energy savings and shorter processing times, and as such, microwave sintering shows promising potential in ceramics processing [20]. This research was conducted to ascertain the differences when using conventional and microwave sintering on hydroxyapatite powders synthesized at USM Rekagraf Laboratory.

MATERIALS AND METHODS

Synthesis of hydroxyapatite

Hydroxyapatite was synthesized using a Syriss Chemical Reactor by adding phosphoric acid, $H_3(PO)_4$ (Merck, 85%) at a pre-determined rate into calcium hydroxide solution, $Ca(OH)_2$ (Fluka, 96%) at 30-80 °C. The pH in the calcium solution was adjusted to be slightly alkaline. After the reaction was completed, aging was carried out for 1-3 days and the process was continued by filtering and drying. It took a minimum of 3 days to obtain the samples in powder form.

Then, the powder was compacted into pellets with a dimension of 13 mm diameter using 44 MPa of pressure. The pellets were separated into two batches for sintering using a muffle furnace and a microwave furnace. Sintering in both furnaces was also conducted at two different temperatures, viz 1000 °C and 1100 °C.

The arrangement and set up of specimens for microwave sintering are shown in Fig. 1 [20]. The samples were carefully placed in the furnace and covered with silicon carbide (SiC) plates to ensure the irradiation of microwave go through the specimens.

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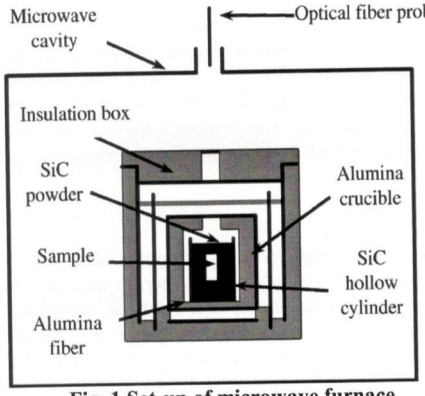

Fig. 1 Set-up of microwave furnace

CHARACTERIZATION

Compositional characterization

Compositional characterizations of the samples were carried out using x-ray diffraction (XRD). An x-ray diffractometer (D8 Advance, Bruker AXS) was used as the main analytical tool to confirm that HA was produced in all the reactions and to detect whether other phases might be present from the reaction.

Physical and mechanical characterization

For physical characterization, the shrinkage, porosity and density of the compacted specimens were measured. Scanning electron microscopy (Supra, Zeiss 35VP) was used to observe the grain size of specimens. These results were analysed to differentiate the outcomes of the two sintering methods. The mechanical characterization, i.e. hardness was also determined using a microhardness tester (Leco, LM 247 AT).

RESULTS AND DISCUSSION

Structural characterization

X-ray diffraction pattern of the Rekagraf calcium phosphate is presented in Fig. 2. This result illustrates the typical XRD pattern of hydroxyapatite powder.

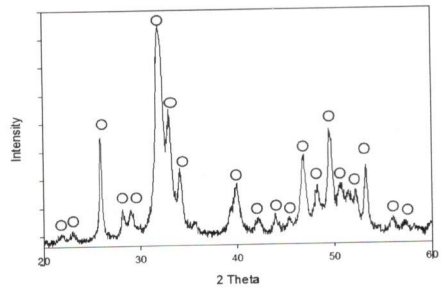

Fig. 2 XRD Pattern of as-synthesized Rekagraf Hydroxyapatite. The symbols (○) indicate ICDD 09-0432, $Ca_{10}(PO_4)_6(OH)$.

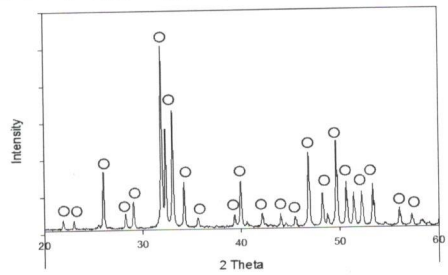

Fig. 3 XRD pattern of Rekagraf hydroxyapatite sintered at 1000 °C. The symbols (○) indicate ICDD 09-0432, $Ca_{10}(PO_4)_6(OH)_2$

Fig. 3 shows the diffractogram of Rekagraf hydroxyapatite which was sintered at 1000 °C. It is noted that the sintered bodies have relatively sharp XRD reflections than the as-synthesized samples. Sharp and narrow peaks refer to a good crystallinity and can be indexed as the hexagonal hydroxyapatite lattice with the lattice parameters a=b=9.418 Å, c=6.884 Å, α=β=90.0, γ=120.0 and space group P63/m which is in close agreement with the standard values for HA (ICDD, 09-0432). These results confirm, after several repeats, that the hydroxyapatite powders prepared in the Rekagraf Laboratory are that of pure hydroxyapatite of high crystallinity [21].

Physical and mechanical characterization

The first evaluation for the samples was the percentage of shrinkage that occurred to the compacted specimens upon sintering. The diameter and thickness of four specimens were measured before and after sintering using digital calliper. Fig. 4 shows the results of shrinkage using a conventional furnace (CF) and a microwave furnace (MF) at two different sintering temperatures. It is observed that the percentages shrinkage using a microwave furnace is higher than that using a conventional furnace by

about 5% at the same temperature. For example, the percentage value of diametral shrinkage using a sintering temperature of 1000 °C by the conventional furnace is 16.43% whilst that using the microwave furnace at the same temperature is 20.20%.

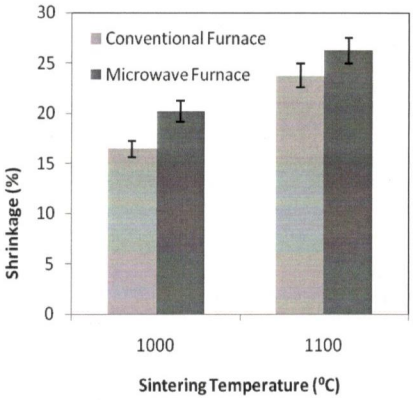

Fig. 4 Percentage of shrinkage after sintering.

The consequent differences in microstructure was observed using a scanning electron microscope (SEM). Fig. 5 shows the SEM micrographs of four different samples using the two different methods of sintering and at two different temperatures of sintering. It can be observed in micrograph 5(a) that the sample has less porosity compared to micrograph 5(b), where the difference was in the method of firing whilst the sintering temperature was the same at 1000 °C. It proved that microwave sintering can initiate the sintering process (or the coalescence of individual particles) much faster compared to the conventional sintering.

Fig.5(c) and 5(d) show the SEM micrograph at a sintering temperature of 1100 °C using the microwave furnace and the conventional furnace, respectively. It is observed that surface of the specimen sintered by using the microwave furnace is much smoother and flatter compared to that using the conventional furnace. This further reinforces the previous observations but Fig.5(c) and 5(d) are at a higher magnification. Admittedly, the tendency of grain growth in conventional sintering (due to higher sintering duration) can barely be distinguished in Fig.5(d) but it is expected that this phenomenon can be clearly revealed upon firing at a temperature higher than 1100 °C.

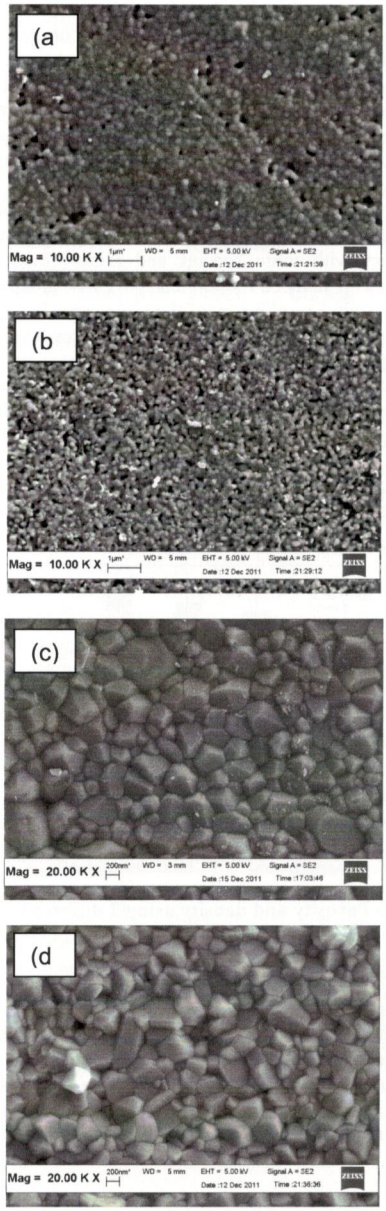

Fig. 5 SEM micrographs (a) Microwave sintering, 1000 °C (b) Conventional sintering, 1000 °C (c) Microwave sintering, 1100 °C and (d) Conventional sintering, 1100 °C.

Fig. 6 shows the comparative values of porosity and density achieved using both sintering methods. It can be seen that specimens obtained by

conventional sintering have a higher porosity than those by using microwave sintering. Consequently, the densities observed show a corresponding inverse relationship. These results further corroborate the previous findings, viz. sintering is achieved much faster and/or much more efficiently by using the microwave sintering as compared to the conventional sintering.

It had been reported [22] that microwaves, which are high frequency electromagnetic waves, interact with ionic species and induce motion in them. This induced motion tends to cause a departure from natural equilibrium of the system and is resisted due to frictional, elastic and inertial forces. Owing to this resistance, the electric field associated with the microwave radiation is attenuated and causes volumetric heating of the material. Calcium phosphate ceramics such as HAP and TCP, being iono-covalent in nature, are also expected to be microwave sensitive. Hence this causes the densification to be better.

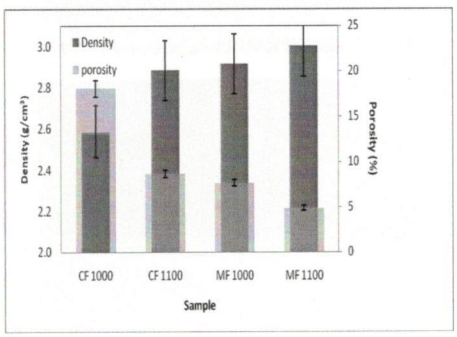

Fig. 6 Porosity and density using 2 different methods of sintering at 2 sintering temperatures.

The mechanical properties were measured by using a Knoop microhardness tester (Fig. 7). The hardness increases with increasing sintering temperature for each separate sintering mode. This can be related to the increase in density as well as the reduction in porosity for the respective corresponding specimens.

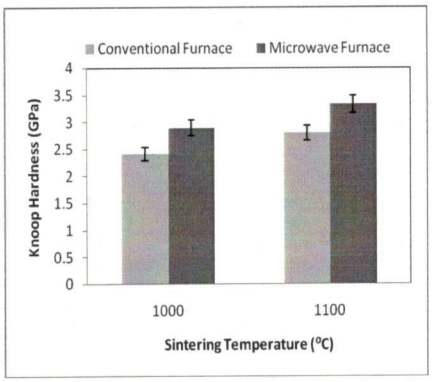

Fig. 7 Comparison of hardness values for conventional sintering and microwave sintering at 2 sintering temperatures.

CONCLUSION

This work has proven that there are apparently a number of benefits to be reaped by using microwave sintering as compared to the conventional sintering normally adopted for sintering of ceramic products. Based on the work conducted in the Rekagraf Laboratory, Universiti Sains Malaysia, the following attributes have been confirmed when using microwave sintering, viz. shrinkage is higher by 5%, smaller grain size, porosity less by 8%, density higher by 0.6 gcm^{-3}, and higher hardness values.

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