Effect of Microwave Conditions on Sintering of Hydroxyapatite Ceramics

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Abstract:
In this work, Hydroxyapatite (HAp) was sintered by microwave and compared with the sintered samples by conventional method. The power levels of microwave were 450, 600, 900 W and the sintering temperatures were in the range from 750 to 1000 ºC without isothermal holding. It was shown that the using of higher power level at the same heating temperature increases the density of sintered samples. Samples sintered in microwave at 1000 ºC by 900 W power reached a higher density of 95 % compared to the conventional process (85 %), however in the case of using 450 W power, the densification trend was almost similar to the conventional one. HAp to TCP phase transformation was not detected at 1000 ºC; however, the preferred growth of (211) planes corresponded to circular morphology was observed. Microstructural observations showed larger grains (500 nm) and porosities (300 nm) in the traditional sintered samples compared to the samples, which were sintered by microwave (200 nm and 100 nm, respectively).

Keywords: Microwave sintering; Hydroxyapatite; Grain size.

1. Introduction

According to previous researches [1] HAp Hydroxyapatite is a calcium phosphate composition that has application in different shapes for biomedical uses. It is inert in body reactions and it is able to create bonding with the bone. However, he has mentioned that, the synthesizing of well-defined orthophosphates even the most common ones is difficult. Asazuma [2] et al. (2005), used one dense hydroxyapatite (HAp) block grafted into the inter body space as in a sandwich. However, although they have observed the sinking and cracking in the segments, yet they suggested that, the dense HAp can be a suitable supernumerary for autogenous bone graft for PLIF.

Sintering is acute for HAp ceramic, shaping micro-structural properties. Tovstonoh, et.al [3] has researched on the sintering of bovine bone by calcination at 800 ºC for 3 h and sintering by microwave at 1000 ºC for 5 to 30 minutes. He has mentioned that the total porosity of biogenic hydroxyl apatite was not dependent on sintering time. He has obtained the sintered hydroxyapatite with 40 % porosity and 35 MPa compression strength. The power of microwave was not varied in his work.

Mangkonsu, et.al [4] have compared the usual furnace and microwave sintering of calcium phosphate at 1300 ºC and reached to 3.15 g/cm³ density, but due to the α-TCP formation the expansion and cracks on the surface of their samples were reported. They also showed that both conventional and microwave sintered samples were biocompatible.

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Wu, Q et al. [5] manufactured the HAp with the scaffolds structure by extrusion and microwave sintering (at 1200 °C for 30 min.). They showed that the microwave sintered scaffolds releases calcium ions through deprivation in saline, helpful in bone growth. Microwaves treating includes sintering of samples by transition of a microwave over them with an outer warming source, which coupled with the microwaves. Furthermore, microwave treating has the benefit of attaining the solid melting point temperatures in a short interval of time, causing in constant and dense structures [5].

Veljovic, et al. [6] used microwave sintering for nanosized HAp powders at 900-1200 °C for 15 min. Their samples were dense (1.35 g/cm³) and even with the mean grain dimension in the range of 130 nm to 1.559 μm. However, the effects of power levels of microwave sintering on hydroxyapatite sintering, according to the author knowledge were not studied. Therefore, more struggles are quiet wanted to well recognizing the consequence of different experimental conditions, for example: microwave power levels, heating conditions, holding time of sintering and sintering temperature, which have been investigated in the present work.

2. Materials and Experimental Procedures

The hydroxyapatite powders Ca₅(PO₄)₃OH (MERCK CAS No. 1306-06-5) were compacted by two-axial press by 200 MPa to form tablet-shaped samples with a 10 mm diameter and height of 11 mm. All specimens were sintered in microwave furnace under power of 900, 600, 450 W in air at temperatures of 750, 865, 965 and 1000 °C (time to reach the maximum sintering temperature was from 10 to 60 min.), without holding. The heating conditions of samples sintered in microwave were presented in Table I, while conventional sintering process was carried out at temperatures of 865, 965 and 1000 °C after 2 h with heating rate of 10 °C/min.

| samples | A | B | C | D | E | K | M | N | O | P | R | S | G | x  | u |
|---------|---|---|---|---|---|---|---|---|---|---|---|---|---|----|---|
| P.(W)*  | 900| 900| 900| 450| 900| 900| 900| 450| 600| 600| 450| 900-| 900| 600|
| T(°C)   | 1140| 965| 865| 1000| 1235| 860| 960| 1000| 750| 1000| 865| 865| 1000| 750| 965|
| S.t.(min)** | 14| 9| 7| 60| 20| 13| 9| 14| 60| 47| 22| 55| 8| 10| 37|

*Power level (W) 900,600,450)
**Sintering time to reach maximum temperature (min.)

The Archimedes method was used to determination of the sintered sample's porosity. To calculate the shrinkage percentage the lengths of samples before and after sintering were evaluated. The phases of the sintered samples were characterized by X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., Netherlands). The size of the crystals has been calculated using the Scherer equation on the ≈31·5° 2θ (211) peak of HAp from the patterns scanned over the angular range 25–32° 2θ with a step length of 0·03° 2θ and a fixed counting time of 12 s/step. Hence D=G λ /B cos θ where D is the mean crystal size, G is a constant equal to 0·9, λ the wavelength of the x-rays, B is the corrected full width at half maximum of the peak and θ is the Bragg angle. The microstructure changes were observed using scanning electron microscopy (SEM, Quant a 200, FEI, Netherlands).
3. Results and Discussion
3.1 Microwave sintering process

Table II shows the change of relative densities of samples sintered in microwave at temperature of 1000 ºC using different power levels.

| Power level (W) | Density (g/cm³) |
|-----------------|-----------------|
| 450             | 2.26            |
| 600             | 2.66            |
| 900             | 2.92            |

From Table I, it is obvious that, there is a 29 % increase in density of composites sintered at temperature of 1000 ºC with the increasing of power level from 450 to 900 W, (despite the decreased sintering time from 60 to 14 min.). Momma [7] show that by the increased absorbed power P, all the power absorbed in the material is converted to heat, which the temperature increasing caused to high density, which is agree with our results.

Figs 1, 2 and Table III depicted to the change of densities, shrinkages and porosities of samples, sintered at 750-1000 ºC with 450 and 900 W power levels. Because of the constant heating rate, the meaning of shrinkage vs. temperature as shown in Fig. 1 is equivalent to shrinkage vs. time and can be considered as the sintering kinetics of HAp powder compact.

![Fig. 1. The change of densities and shrinkage of samples, sintered at 750-1000 ºC with 450 and 900 W power levels.](image)

In the case of 900 W, the sintering begins at a lower temperature and the temperature when densification stops is also lower. However, higher temperature is usually necessary for pore diminishing in the final sintering stage.

It can be seen from Fig.1 that the samples sintered by the power of 450 and 900 W obtained a low density at 750 ºC; since HAp absorbs little microwave energy at low temperatures while the sample heating is most closely linked to the absorption of microwave energy by SiC susceptor.

On the other hand, a sudden increase in the total shrinkage of the compacts by 900 W indicates that the 850 ºC sintering temperature is low for powders and makes the powder to densified at higher temperatures.

When the power level increased to 900 W, both SiC and HAp would absorb microwave energy powerfully. Thus, by comparing the relative density of HAp sections sintered with the two power levels of 450 and 900 W (Table III), it can be concluded that the
increase of power level from 450 to 900 W caused the increase in relative density from 70 % to 90 %, (at 950 ºC) respectively. Also, in the case of samples which start sintering by 450 W, first the shrinkage rate decreases, which indicates that higher temperature is necessary to reach the final stage of sintering.

Table III further reveals that, the increasing trend in the density and shrinkage of the samples which were sintered with power level of 900 W is higher comparing to the samples, sintered with power level of 450 W and in the former case, sintering almost completed at temperature of 1000 ºC.

**Table III** Relative densities, porosities and shrinkages of samples sintered between 750 and 1000 ºC by using 450 and 900 W power level.

| T (ºC) | Relative density% | Shrinkage % | Pore percentage | Relative density% | Shrinkage % | Pore percentage |
|--------|-------------------|-------------|-----------------|-------------------|-------------|-----------------|
| 1235   | 93.4              | 9.16        | 2.2             | 97.19             | 9.20        | 0.05            |
| 1140   | 90.2              | 9.16        | 3.2             | 97.00             | 9.21        | 0.8             |
| 1000   | 84.80             | 9.16        | 5.08            | 93.08             | 9.20        | 0.98            |
| 965    | 67.80             | 9.07        | 39.14           | 92.99             | 9.19        |                 |
| 865    | 58.91             | 9.06        | 82.48           | 9.08              | 15.74       |
| 750    | 59.87             | 9.10        | 38.52           | 61.14             | 9.08        | 36.70           |

Fig. 2 indicates the sample's microstructure sintered at temperature of 1000 ºC under different power levels. It has been shown that [8], the electric field in microwave sintering enhances the diffusion rate, and the diffusion rate depends on the input power level.

According to Fig. 2 in the sample sintered with 450 W power, probably, few mass transfer of matter was happened during sintering process, while in the case of sample sintered with 900 W power, the mass moving of material occurred from particle volume or grain boundary between particles. In addition, it was shown that there is a significant direct interaction between the crystals in polycrystalline ceramics and microwaves, and so microwave coupling cannot be attributed solely to grain boundary effects. The pores between grains of the samples sintered with 900 W could be relates to the low grain growth tendency in this power level.
compared to the samples with 450 W power level. A trace expansion in the case of samples sintered with 450 W (in Fig. 1) could be relate to the grain growth as well [9]. Aoki, [10] has shown that, this phenomenon increases the shrinkage and reduces the porosity.

Fig. 3 shows the changes of relative density under two powers as a function of the microwave sintering heating rate. (The time to reach the maximum temperature).

![Graph showing the sintering time vs. relative density at different temperatures and two power levels.]

Fig. 3 The sintering time vs. relative density at different temperatures and two power levels.

It was seen that, in the case of applied 600 W power, the time (40 minutes) needs for sample's densification, takes shorter time compared to the sintering at 450 W (60 minutes) at the same sintering temperature.

It is well known that densification is a method of particles packing and integration and whole removing by the driving force of temperature. HAp is a microwave-sensitive ionic-covalent ceramic and when microwave energy (600 W) is spread over the HAp samples, the kinetic energy of internal molecular increases (compared to 400 W), that decreases the activation energy of sintering and improves the diffusion power. FuXu, et.al [11] have shown that, according to Eq.1, a higher densification can be achieved by increasing the heating rate. By comparing the heating rate of samples which sintered in 450 W or 600 W microwave power level it can be seen that, the faster heating rate (dT/dt) causes the larger volumetric heating ($P_v$):

$$P_v = \rho C_v \left( \frac{dT}{dt} \right) + P_{hl}$$

where $\rho$ is density, $C$ is specific heat capacity of the material of the sample, $P_{hl}$ is the power in heat losses, $(dT/dt)$ is the rates of heating and cooling before and after the microwave power switch off, respectively. As follows from Equation (1), the value of $P_v$ is higher (at 965 °C), the higher the heating rate (as long as the thermal insulation conditions are the same). Therefore, it can be argued that the experimental results depend on the microwave-heating rate, and electromagnetic power. In general, the power in heat losses, $P_{hl}$ is the total power lost by thermal conduction, convective and radiative heat flows. The power in heat losses increases as the power level of microwave increased. Therefore, at a constant temperature (865 °C) the microwave power deposited per unit volume of the sample increases by heating rate. (compare the relative densities of samples with 18 and 40 minutes heating time by 450 and 600 W respectively).
3.2 Phase evaluation

Figs 4 displays the XRD patterns of samples sintered at 750-1235 °C using 900 W power and exhibits HAp peaks as the prevailing crystalline phase. It can be seen that the α to β transformation of hydroxyl apatite (which was reported previously by Fathi, [12]) was not detected in the present work, this can be related to the lack of isothermal heating at the sintering temperatures. Sinitsyna, et.al; [13] before, reported this occurrence.

They have shown that stoichiometric HAp has a hexagonal crystal system, with the two major ‘a’ and ‘c’ crystal planes: Chen, et.al [14] believed that the ‘a’ plane is rich in calcium ions with positive charge, while the ‘c’ plane is rich in P5+ and OH- ions and hence negatively charged. Therefore, HAp surfaces exhibit anisotropic characteristics, caused to anisotropic microwave absorption and hence anisotropic growth.

![Fig. 4](image)

**Fig. 4.** (a) The XRD patterns of Hydroxyapatite sintered in the range of 750-1235 °C and at 900 W power, no phase transformation was detected (b) comparing of (112) planes (c) comparing of (200) planes (d) comparing of peak intensities of (112) and (211) planes at different sintering temperature.

In Fig. 4a, the diffraction peaks at 2θ=31.76º, 32.45º and 25.63º correspond to HAp peaks for the (211), (112) and (002) planes, respectively. In all cases the diffraction peak intensity of (002) plane is lower than (211) plane. It was shown that due to the granules morphology of HAp particles the diffraction peak intensity of (002) plane is lower than (211) plane [15]. SEM evidences in Fig. 3 confirm this morphology. The crystallite size of obtained phases was compared in Fig. 4d as well.

It can be concluded that the crystallite size of Hap are increased with growing the sintering temperature up to 1000 °C (Fig. 4d).
As perceived, the peak corresponded to 112 Millers plane family (at 2θ = 32.45°) is sharper than other peaks. This shows a growing trend of \( a \)-axis of the HAp crystals as already mentioned in reference 16. The circular structure of particles shown in Fig.s 6 can be implied the growth of \( a \)-axis in HAp structure. In addition, the crystalline size has significantly decreased at sintering temperatures higher than 1000 °C. The crystalline size increased from 444 nm to 685 nm from 750 to 1000 °C, respectively. It is well known that, the (002) plane correspond to the \( c \)-axis and the full width at half maximum (FWHM) of this reflection is in reverse related to the crystallite length along the \( c \) unit cell direction (\( c \)-axis length). As the (002) reflection is gradually decreased with increasing sintering temperature from 1000 to 1235 °C, hence the crystalline size decreased from 685 to 437 nm respectively it is concluded that, the OH⁻ vacancy rises with increasing temperature of microwave sintered HAp samples. It has been proven experimentally that an increase of OH vacancy concentration accelerates cation transport in the HAp lattice thus accelerating the whole sintering process.

Pleshko, et.al [17] have verified this incidence by observation of the broad diffraction peak of (002) planes as well. Pajchel [18] also reported that OH⁻ in nano-crystalline apatite decreases with decreasing crystal size. The crystalline size in sintered samples with 450 W also is 23 % higher than the sintered samples in 900 W power level, which can be related to the lower OH vacancy in the case of low power level.

3.3 Comparing of the specimen's properties by furnace and microwave sintering

Results of Fig. 5 show that microwave sintered samples obtained a higher density at all sintering temperatures rather than conventionally sintered samples. Besides, the maximum density of 95 and 85 % obtained for microwave and conventionally sintered samples, respectively.
Fig. 5. The relative density of samples vs. sintering temperatures.

According to Anklekar, et.al [19], in \( \frac{\Delta T}{\Delta t} = \frac{P}{\rho C_p} \) relation, the decreasing in \( P \) (volumetric heating \( P \)) amount, causes to decreasing in \( \frac{\Delta T}{\Delta t} \) (heating rate in conventional heating), so it can led to the low sintered density in the case of conventional sintered samples.

The SEM evaluations of microwave and conventionally sintered samples compared in Figs 6.

Fig. 6. SEM micrographs of samples sintered in furnace (a) 865 (b) 965 (c) 1000 ºC and microwave (d) 865 (e) 965 (f) 1000 ºC.

The micrographs confirm the existence of HAp agglomerates in particles sintered by two sintering methods. However, in conventional sintering process the size of agglomerates increased from 0.5 to 1.5 \( \mu \)m with the increase in the sintering temperature from 965 to 1000 ºC. SEM investigations showed that the conventional sintered samples were porous and their microstructure was non-uniform in size. In addition, it seems that in conventional sintering most porosity is open especially in the case of sample sintered at 865 ºC, while in MW sintered samples most porosity is close and smaller. It was shown that the porosities in the
microwave-sintered samples have more rounded edges (Fig. 6f) compared to conventionally sintered samples which have more sharp edges (Fig. 6b). Fig 7 associates the XRD results of conventional and MW sintered samples at 1000 °C.

Fig.7. XRD patterns of conventional and MW sintered samples at 1000 °C.

It can be seen that, although the HAp peaks were detected in both sintering processes, but the splitting of (211) reflection is observed in conventional sintering. This event probably, was due to the higher crystallinity of the sample as the result of holding at 1000 °C (sintering temperature) for 2 h and lower heating rate compared to microwave sintering (without holding time and higher heating rate). The splitting of (211) reflection was reported by Hung, et.al [20].

4. Conclusion

Hydroxyapatite (HAp) has been made-up by microwave sintering and conventional method. The microwave sintering was carried out at different power levels of 450, 600 and 900 W and the sintering temperatures were in the range of 750-1000 °C without isothermal holding. Samples sintered in microwave at 1000 °C by using 900 W power reached a higher density of 95 % compared to conventional process (85 %), however in the case of using 450 W power, the densification trend was almost similar to the conventional one. The microstructure investigations confirmed the existence of 500 nm sized HAp particles agglomerates in both sintering method but the splitting of (211) reflection in conventional sintered samples pointed to the high crystallinity of these samples. However, in the case of conventional sintering the agglomerate sizes increased with the temperature increasing. XRD results also confirmed the (211) planes in the microwave sintered samples have higher intensity compared to conventional sintered samples. In addition, some trace of dehydroxylation in the case of sintered samples at 1140 and 1235 °C was detected which results in (002) planes intensities’ decreasing.
5. References

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