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The Effect of Microwave Settings on HAp Sintering

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ABSTRACT

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), a calcium phosphate bio ceramic which is chemically similar to natural bone mineral, is widely used as a scaffolding material in bone tissue engineering. In this study, Hydroxyapatite (HAp) ceramics were sintered using microwave in one- and two-step heat treatment. The sintering temperatures in the first heat treatment step were in the range of 965-1000 °C without isothermal holding, and the power levels of the microwave were set at 600, 750, and 900 W. The temperatures in the second heat treatment step were 600, 735, and 860 °C. Of note, HAp-to-Tricalcium phosphate (TCP) phase transformation was not detected at 1000 °C; instead, the preferred growth of (211) planes corresponding to the circular morphology was observed. As observed in the XRD images, crystallite degradation occurred in two-step sintered samples. In addition, the SEM micrographs indicated that the open porosity in the two-step heat treated samples was more than that of samples which were heat treated in one step. In case the sintering temperature was set at 1000 °C, the maximum density values of 92 % and 95 % were obtained for one- and two-step sintered samples, respectively.

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1. INTRODUCTION

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is a calcium phosphate bioceramic that is chemically similar to the natural bone mineral which is widely used as a scaffolding material for bone tissue engineering [1-3]. Sintering is critical for porous HAp bioceramic scaffolds in that it determines their microstructural properties such as crystallinity, grain size density, and micro-porosity, which in turn affects their performance [4,5]. However, a significant concern regarding the HAp sintering is the necessity of providing lower sintering temperatures to ensure better bioactivity [5].

Higher temperature and longer sintering times are also required to ensure higher mechanical strength while sintering these materials. The conventional sintering methods, such as muffle sintering which is characterized by high temperature, slow heating rate, and long holding time, cannot solve this contradiction.

Microwave processing is defined as the sintering of specimens by putting them in a microwave equipped with an external heating source. It enjoys the advantage of reaching the required temperatures for material sintering within a short period of time, thus resulting in a uniform and dense microstructure [1-3]. Most HAp powders contain needle-like particles that hinder densification. Guo et al. [6] fabricated HAp nano-bioceramics based on Spark Plasma Sintering (SPS) approach. Bose et al. [7]

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also fabricated nano-crystalline HAp bioceramics through the microwave process. Chen [8] developed a new technique called Two-Step Sintering (TSS) method, a promising and straightforward approach to obtaining dense low-cost nanoceramics using typical ovens. To date, TSS has been successfully applied to sintering of Y_2O_3-Al_2O_3. In this regard, to better understand the effects of different experimental conditions, the current study investigated several involved criteria namely the microwave, heating rate conditions, sintering steps, and temperatures.

2. MATERIALS AND METHODS

The starting powder in this research was hydroxyapatite $Ca_5(PO_4)_3OH$ (MERCK, CAS No. 1306-06-5) (HAp) with the particle size of < 160 µm. The powder was pressed by two-axial cold pressing in a stainless-steel mold at 200 MPa to form disk-shaped samples of 10 mm in diameter and 11 mm in height, according to the British Standard for compression tests (No. 7253). All samples were first sintered in a high-temperature microwave furnace (600, 750, and 900 W) in the air at 750, 860, 965, and 1000 °C (heating rate was 60 °C/min) without holding the sintering time. Some samples were heat-treated by microwave in two steps, as reported in Table 1. A home-made microwave furnace (900 W and 2.45 GHz) with an Al_2O_3 insulation container was used for microwave heating. The temperature of the microwave furnace was controlled by an optical pyrometer (RAYR312MSCL2G temperature detector) with the temperature fluctuation of ± 5 °C.

TABLE 1. The Microwave Conditions for sintering of the different samples

Microwave Conditions	1	2	3	4	5	6	7
Power Level	750	900	600	600	900	900	900
First Sintering Temperature	750	965	860	1000	1000	960	860
Sintering Time To Reach Maximum Temperature (min.)	75	125	22	47	14	9	13
Second Step Sintering Temperature (°C)		860				600	735

The physical properties of the sintered samples were also investigated in this study. The porosity of each sintered sample was determined by Archimedes method using distilled water. The lengths of samples before and after sintering were measured to calculate their linear shrinkage. All samples were analyzed using PANalytical X'Pert Pro powder diffractometer (Panalytical B.V., Almelo, Netherlands). The required data was collected continuously using an X'Celerator RTMS detector and a counting time equivalent to 100 s per point over $2\theta = 5–70°$ with the step size of $2\theta = 0.03$ or 0.016°. The microstructure of the samples was then studied through Scanning Electron Microscopy (SEM, Quant a 200, FEI, Netherlands). The values of the magnification of the SEM parameters, accelerating voltage, and working distance were obtained in the ranges of 500-2000x, 3-20 kV, and 8-12 µm, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the samples sintered at 1000 and 965 °C according to which, the two-step heat treated samples were further heated followed by their first heating at 735 and 860 °C.

The results revealed the HAp peaks in the prevailing crystalline phase. Of note, α-to-β transformation of hydroxyl apatite, which was previously reported by Fu Xu [9], was not observed in the present study probably due to lack of isothermal heating at the sintering

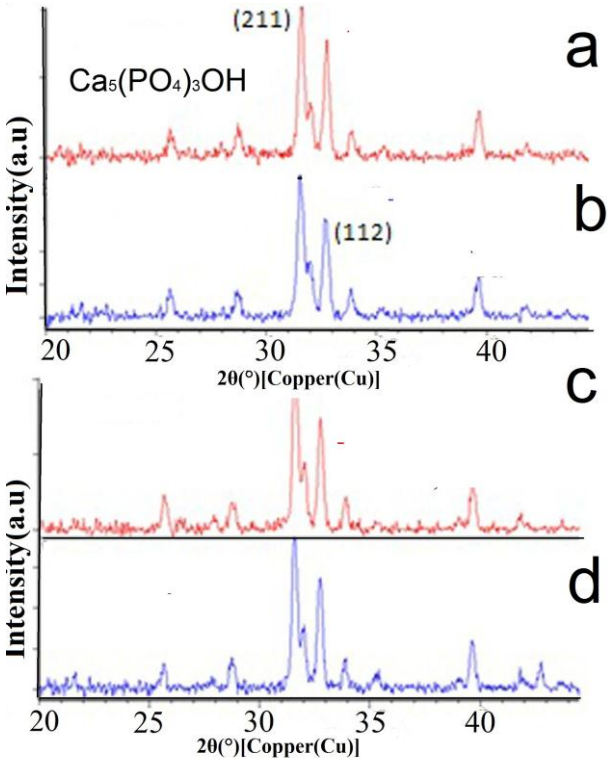


Figure 1. XRD patterns of sintered samples by microwave at (a) one step (965 °C-900 W), (b) two steps (965 °C, 900 W-750 °C, 300 W), (c) one step (1000 °C, 900 W), and (d) two steps (1000 °C, 900 W-965 °C, 300 W)

temperatures which suppressed this transformation. Sinitsyna [10] had already reported this phenomenon.

As observed, the peak intensity of (211) and (112) lattice planes decreased in the second heating step (Figure 2). In addition, the peak corresponding to (112) Millers plane family (at 2θ =32.45°) is weaker than other ones in the case of two-step heat treatment, indicating the decreasing trend of the a-axis length in the HAp structure, as already mentioned in Reference [5]. In this regard, it can be concluded that the OH^- vacancy increases upon increasing the steps of microwave sintering (OH^- groups absorb the microwave radiation more than other ones). Pajchel [11] reported that OH^- in nanocrystalline apatite would decrease by decreasing crystal size.

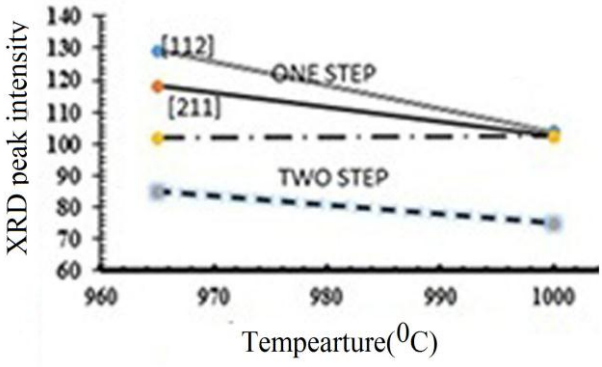


Figure 2. The relative intensities of the XRD peaks in (211) and (112) indexes of the sintered samples by microwave at 900 W in one- and two-step heat treatments

Figure 3 compares the relative density values of the samples sintered by both one- and two-step microwave heating. The obtained results revealed that one-step sintered samples were characterized by a higher density at all sintering temperatures than two-step sintered samples. At the sintering temperature of 1000 °C, the maximum density of 92% and 95% were obtained for one- and two-step sintered samples, respectively.

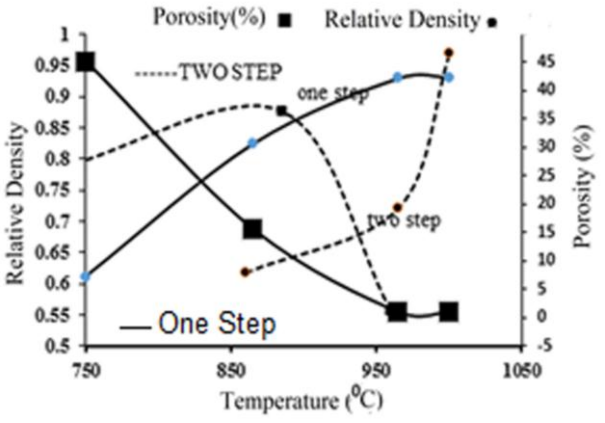
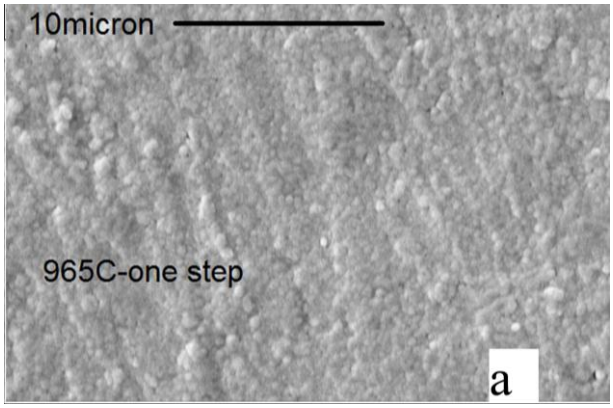
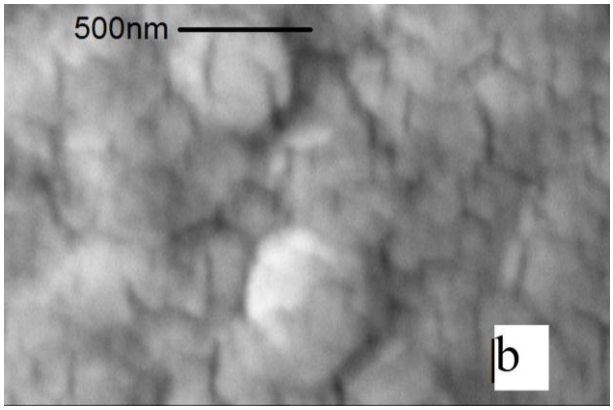


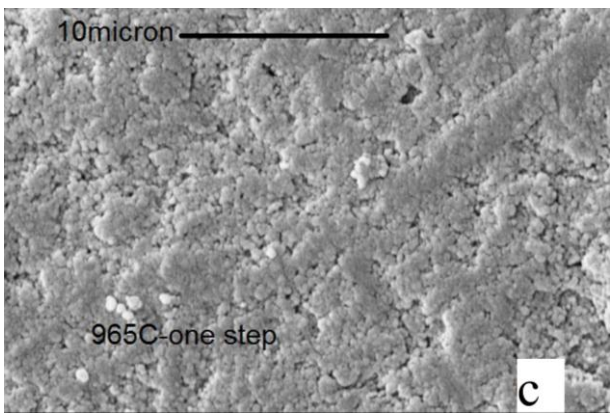
Figure 3. The relative densities and porosities of the one- and two-step microwave sintered samples

According to Fig. 3, the open porosity of the samples in the two-step heat-treatment process is more than that in the samples with one-step heat-treatment process. In addition, two-step heat treatment led to degraded crystallite phases and weak densification in the samples. Figure 4 makes a comparison between the microstructures of one- and two-step heating by microwave.

As observed in Figure 3, the two-step sintered samples did not achieve full densification. Of note, even at such a low temperature and a short holding time, the HAp grains were merged with each other [12-13]. At the triple junction points of the HAp grains, some nano pores were detected. Apparently, the appearance of pores would







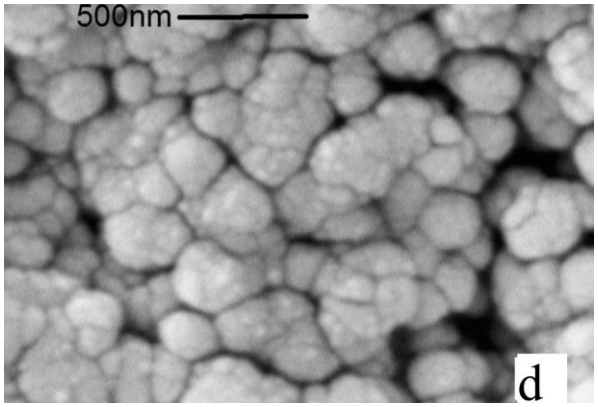


Figure 4. The micrographs of the microwave sintered samples at top one step heat treating at 965 °C by two different magnification (a) ×1000, (b) ×50000, (c) by two steps heat treating at 960-860 °C by ×1000 magnification, and (d) by two steps heat treating at 960-860 °C by ×50000 magnification

increase the diffusion distance between the HAp grains, thus reducing the driving force on the pore shrinkage of the sintered ceramics [6]. Therefore, in the case of the two-step heating, the porosity values decreased sharply. According to Figure 3, the dashed line curve corresponding to the two-step heating shrinkage shows a sharper trend than the one-step case. However, as observed in Figure 2, the crystallite size decreased (or degraded) in the case of two-step heating which can be related to the crystallite degradation, as approved by the XRD patterns demonstrated in Figure 1.

4. CONCLUSION

Sintering the HAp samples by two-step heating using microwave confirmed that the relative density of all samples was similar; however, their open porosity was more than that of the samples which were heat-treated in one step. Two-step heating led to degraded crystallite (due to the OH vacancy) and weak densification.

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REFERENCES

1. Fang, Y., Agrawal, D. K., Roy, D. M., Roy, R., "Microwave sintering of hydroxyapatite ceramics", ***Journal of Materials Research***, Vol. 9, No. 1, (1994), 180-187. https://doi.org/10.1557/JMR.1994.0180
2. Yang, Y., Ong, J. L., Tian, J., "Rapid sintering of hydroxyapatite by microwave processing", ***Journal of Materials Science Letters***, Vol. 21, No. 1, (2002), 67-69. https://doi.org/10.1023/A:1014250813564
3. Ehsani, N., Sorrell, C. C., Ruys, A. J., "Microwave Hybrid Processing of Hydroxyapatite", ***Journal of Biomimetics, Biomaterials & Tissue Engineering***, Vol. 18, No. 1, (2013), 108. https://doi.org/10.4172/1662-100X.1000108
4. Wu, Q., Zhang, X., Wu, B., Huang, W., "Effects of microwave sintering on the properties of porous hydroxyapatite scaffolds", ***Ceramic International***, Vol. 39, No. 3, (2013), 2389–2395. https://doi.org/10.1016/j.ceramint.2012.08.091
5. Tovstonoh, H., Sych, O., Skorokhod, V., "Microwave sintering of biogenic hydroxyapatite ceramics for reconstructive surgery", ***Processing of Applied Ceramics***, Vol. 8, No.1, (2014), 1–5. https://doi.org/10.2298/PAC1401001T
6. Gu, Y. W., Loh, N. H., Khor, K. A., Tor, S. B., Cheang, P., "Spark plasma sintering of hydroxyapatite powders", ***Biomaterials***, Vol. 23, No. 1, (2002), 37–43. https://doi.org/10.1016/S0142-9612(01)00076-X
7. Venkateswarlu, K., Bose, A. C., Rameshbabu, N., "X-ray peak broadening studies of nanocrystalline hydroxyapatite by Williamson-Hall analysis", ***Physica B: Condensed Matter***, Vol. 405, No. 20, (2010), 4256-4261. https://doi.org/10.1016/j.physb.2010.07.020
8. Chen, C., Huang, Z., Yuan, W., Li, J., Cheng, X., Chi, R. A., "Pressure effecting on morphology of hydroxyapatite crystals in homogeneous System", CrystEngComm, Vol. 13, No. 5, (2011), 1632-1637. https://doi.org/10.1039/C0CE00090F
9. Pajchel, L., Kolodziejski, W., "Solid-state MAS NMR, TEM, and TGA studies of structural hydroxyl groups and water in nanocrystalline apatites prepared by dry milling", ***Journal of Nanoparticle Research***, Vol. 15, (2013), 1868. https://doi.org/10.1007/s11051-013-1868-y
10. Xu, G. F., Lloyd, I. K., Carmel, Y., Olorunyolemi, T., Wilson, O. C., "Microwave sintering of ZnO at ultra high heating rates", ***Journal of Materials Research,*** Vol. 16, No. 10, (2001), 2850-2858. https://doi.org/10.1557/JMR.2001.0393
11. Sinitsyna, O. V., Veresov, A. G., Kovaleva, E. S., Kolen'ko, Y. V., Putlyaev, V. I., Tretyakov, Y. D., "Synthesis of hydroxyapatite by hydrolysis of α-$Ca_3(PO_4)_2$", ***Russian Chemistry Bulletin***, Vol. 54, No. 1, (2005), 79-86. http://doi.org/10.1007/s11172-005-0220-9
12. Ţălu, S., "Special Issue: Characterizations of Three-Dimensional Surfaces at Micro/Nanoscale", ***Applied Sciences***, Vol. 12, No. 15, (2022), 7729. https://doi.org/10.3390/app12157729
13. Mwema, F. M., Akinlabi, E. T., Oladijo, O. P., Fatoba, O. S., Akinlabi, S. A., Ţălu, S., "Chapter two - Advances in manufacturing analysis: fractal theory in modern manufacturing", In Kumar, K., Davim, J. P., (Eds.), ***Woodhead Publishing Reviews: Mechanical Engineering Series, Modern Manufacturing Processes***, Woodhead Publishing, Cambridge, UK, (2020), 13-39. https://doi.org/10.1016/B978-0-12-819496-6.00002-6