The effect of manganese oxide on the sinterability of hydroxyapatite

S. Ramesha, C.Y. Tan, C.L. Peralta, W.D. Teng

Ceramics Technology Laboratory, University Tenaga Nasional, 43009 Kajang, Selangor, Malaysia
Ceramics Technology Group, SIRIM Berhad, 40911 Shah Alam, Selangor, Malaysia

Received 21 November 2006; received in revised form 7 February 2007; accepted 8 February 2007
Available online 3 April 2007

Abstract

The sinterability of manganese oxide (MnO₂) doped hydroxyapatite (HA) ranging from 0.05 to 1 wt% was investigated. Green samples were prepared and sintered in air at temperatures ranging from 1000 to 1400 °C. Sintered bodies were characterized to determine the phase stability, grain size, bulk density, hardness, fracture toughness and Young’s modulus. XRD analysis revealed that the HA phase stability was not disrupted throughout the sintering regime employed. In general, samples containing less than 0.5 wt% MnO₂ and when sintered at lower temperatures exhibited higher mechanical properties than the undoped HA. The study revealed that all the MnO₂-doped HA achieved >99% relative density when sintered at 1100–1250 °C as compared to the undoped HA which could only attained highest value of 98.9% at 1150 °C. The addition of 0.05 wt% MnO₂ was found to be most beneficial as the samples exhibited the highest hardness of 7.58 GPa and fracture toughness of 1.65 MPam¹/² as compared to 5.72 GPa and 1.22 MPam¹/² for the undoped HA when sintered at 1000 °C. Additionally, it was found that the MnO₂-doped samples attained E values above 110 GPa when sintered at temperature as low as 1000 °C if compared to 1050 °C for the undoped HA.

Keywords: Hydroxyapatite; Sintering additives; Manganese oxide; Sinterability; Mechanical properties

1. Introduction

The excellent review published by Hench [1] and Suchanek et al. [2] deliberated on the potential of using hydroxyapatite ceramic (HA) for medical implants due to its close chemical resemblance with the mineral components and crystal structure of apatite in natural bone and teeth. Moreover, its identical calcium to phosphorus (Ca/P) ratio to natural bone promotes strong bonding between bony tissues and the implant surface [3]. Evidence of rapid bone formation in the HA implant and subsequent healing around the damaged sites in the body were observed, thus demonstrating the potency of HA as a viable biomaterial for clinical usage [4,5].

The applicability of HA as a biomaterial in clinical orthopaedic and dental applications is, however, limited to non-load bearing regions mainly because of the brittle nature and the low fracture toughness (0.8–1.2 MPam¹/²) of the bioceramic [6]. Thus, the development of biocompatible HA that has enhanced mechanical properties is desirable. As a result, various studies focussing on the improvement of powder processing techniques, composition modification and experimental conditions were carried out with the aim of determining the most effective synthesis method and conditions to produce high strength sintered HA without sacrificing the biocompatibility nature of the ceramic [7–9]. Among these efforts, Suchanek et al. [10] found that HA composites, particularly that of HA/HA whiskers, could improve the reliability of HA ceramics. However, the authors observed the difficulty in densifying the HA-based composites by pressureless sintering. This problem associated with powder consolidation can be overcome by using unconventional techniques such as hot pressing [11] and hot isostatic pressing [12] but at the expense of high set-up cost.

An alternative economical technique to obtain highly dense HA body at low sintering temperature is by incorporating sintering additives or dopants during powder processing [13]. Several sintering additives such as silicon...
oxide [14] and lithium oxide [15] have been used in HA ceramics to improve the sinterability of the material. Although the densification of HA was enhanced with the inclusion of these dopants, decomposition of HA with the formation of tricalcium phosphate (TCP) or calcium oxide (CaO) was observed in the sintered body. These secondary phases are chemically dissimilar to apatite and are soluble in body fluids when compared to crystalline HA [16].

Other dopants such as zirconia, magnesia, alumina, ceria, iron, yttria and titania were also investigated [17–22]. For instance, Ryu et al. [20] reported that the sinterability of magnesia-doped HA, in particular the bulk density was greatly enhanced without any phase transformation even though the HA was sintered at elevated temperature of 1300 °C. Sato et al. [21] reported that yttrium-doped HA has improved osteoblast adhesion in human body when compared to the undoped HA.

The inclusion of manganese oxide (MnO2) in HA has not been studied extensively although numerous workers have reported the significant role of manganese oxide in promoting densification in other ceramic systems [23–25]. Thus, the primary objective of the present work is to study the effect of MnO2 on the mechanical properties of sintered HA bioceramics.

2. Experimental details

In the current work, the HA powder was prepared according to a wet chemical method comprising precipitation from aqueous medium by slow addition of orthophosphoric acid solution to a calcium hydroxide suspension. The precipitate was aged overnight and subsequently washed and filtered to obtain a sticky cake, which was then dried overnight and ground to powder [26]. Manganese-doped hydroxyapatite powder (MHA), ranging from 0.05 to 1 wt% MnO2 additions, was prepared by wet milling. After the mixing, the wet slurry was dried, crushed and sieved to obtain soft MHA powders.

The green samples, in the form of rectangular bar (4 × 13 × 32 mm) and circular disc (20 mm diameter), were prepared by uniaxial compaction at low pressures (1.3–2.5 MPa). The green compacts were subsequently cold isostatically pressed at 200 MPa. This was followed by consolidation of the particles by pressureless sintering at temperatures ranging from 1000 to 1400 °C, with a ramp rate of 2 °C/min (heating and cooling) and soaking time of 2 h being adopted for each firing. All disc-sintered samples were then polished to a 1 μm surface finish prior to testing.

The calcium and phosphorus content in the HA powder was determined by using the inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique. The particle size distributions of the powder were determined using a standard Micromeritics Sedigraph 5100 X-ray particle size analyzer. The phase present in the powders and sintered samples were determined using X-ray diffraction (XRD, Geiger-Flex, Rigaku, Japan). The microstructural evolution of the HA under various sintering temperature was examined by using the scanning electron microscope (SEM) and the grain size was determined from scanning electron micrographs using the line intercept analysis [27]. The bulk densities of the compacts were determined by the water immersion technique. Five measurements were taken for each temperature and the percentage error was found to be consistent for each temperature and was very small, i.e. less than 0.1%. The average density was taken and the relative density was calculated by taking the theoretical density of HA as 3.156 g cm−3. Young’s modulus (E) by sonic resonance was determined for rectangular samples using a commercial testing instrument (GrindoSonic: MK5 “Industrial”, Belgium). The instrument permits determination of the resonant frequency of a sample by monitoring and evaluating the vibrational harmonics of the sample by a transducer. The modulus of elasticity or Young’s modulus was calculated using the experimentally determined resonant frequency [28]. The microhardness (HV) and fracture toughness (KIC) of the samples were determined using the Vickers indentation method. The indentation load (∼200 g) was applied and held in place for 10 s. Five indentations were made for each sample and the average value was taken. The indentation fracture toughness was determined from the equation derived by Niihara [29].

3. Results

The results of the chemical analysis as well as the particle size analysis that were carried out on the synthesized HA powder are shown in Table 1. The individual HA particle is very small and this is evident from the SEM micrograph of the powder agglomerates shown in Fig. 1.

X-ray diffraction (XRD) analysis shows that the synthesized HA powder produced only peaks which corresponded to the standard JCPDS card for stoichiometric HA as shown in Fig. 2. No other phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP) or calcium oxide (CaO) were detected in the synthesized powder.

Similarly, the XRD signatures of the MnO2-doped powders corresponded to the standard JCPDS card No: 74-0566 for stoichiometric HA. Estimates of crystal size from peak broadening for these powders indicated that the HA crystal size did not vary very much with dopant addition as shown in Table 2. From the evidence provided, it is clear that the addition of manganese oxide and the processing technique employed to incorporate the dopant had negligible effect on the HA phase stability and crystallite size.

Table 1

| Properties of the starting HA powders |
|--------------------------------------|
| Ca/P molar ratio | 1.67 ± 0.02 |
| Average particle size | 3.20 ± 0.54 μm |
| Colour | White |
The XRD phase analysis for compacts that were sintered between 1000 and 1400°C revealed the presence of HA phase. In general, there were no secondary phases present in the HA lattice and the XRD signatures of all the samples, regardless of sintering temperature, as typically shown in Fig. 3, belong to that of stoichiometric HA. These results indicate that the phase stability of HA was not disrupted by the dopant addition and sintering temperature.

The densification curves as a function of sintering temperatures are shown in Fig. 4. The bulk density variation of all the composition studied exhibited a similar trend with increasing sintering temperature. All the samples attained above 98% of theoretical density when sintered above 1000°C. Nevertheless, all the MnO₂-doped HA achieved above 99% rel density when sintered at 1100–1250°C if compared to the undoped HA which could only achieve the highest value of 98.9% at 1150°C. These results were in agreement with the SEM analysis, which showed the presence of intergranular pores for all samples sintered ≥1150°C as typically shown in Fig. 5.

The variation of the average Vickers hardness of samples sintered at various temperatures is shown in Fig. 6. The beneficial effect of MnO₂ (up to 0.5 wt% addition) in

![Fig. 1. SEM micrographs of synthesized HA powder revealing the presence of loosely packed fine particles.](image)

![Fig. 2. Comparison of XRD patterns of synthesized HA with the standard JCPDS card for stoichiometric HA.](image)

| MnO₂ content (wt%) | Crystal size (Å) |
|-------------------|-----------------|
|                   | (2 1 1) reflection | (0 0 2) reflection |
|                   | 2θ = ~31.9°     | 2θ = ~25.9°       |
| 0 (undoped)       | 108             | 319               |
| 0.05              | 106             | 319               |
| 0.10              | 107             | 301               |
| 0.30              | 114             | 328               |
| 0.50              | 115             | 304               |
| 1.00              | 114             | 274               |
enhancing the hardness of HA sintered at low temperatures has been revealed. A general observation that can be made from Fig. 6 is that the hardness of all the MnO₂-doped samples revealed a similar trend, i.e. the hardness decreased slowly with increasing sintering temperatures. In contrast, the hardness of the undoped HA increased rapidly to a maximum value of 7.21 ± 0.17 GPa at 1050 °C and thereafter decreased with increasing temperature. Fig. 6 also shows that the addition of 1 wt% MnO₂ was detrimental as samples exhibited the lowest hardness throughout the sintering regime employed. The addition of 0.05 wt% MnO₂ was found to be most beneficial as the samples exhibited the highest hardness when sintered at 1000–1100 °C.

The effect of MnO₂ addition (up to 0.5 wt%) on the fracture toughness of HA with respect to sintering temperature is shown in Fig. 7. The toughness of the
1 wt% MnO₂-doped samples was not measured due to the low bulk density of the material. The fracture toughness of all compositions in Fig. 7 exhibited very similar trends as the sintering temperature increased.

The variation in Young’s modulus with sintering temperature of all composition studied was in good agreement with the variation in bulk density. In general, it was found that the MnO₂ addition had a marginal effect on Young’s modulus. All the doped samples attained E values above 110 GPa when sintered at temperature as low as 1000 °C if compared to 1050 °C for the undoped HA. Furthermore, it was found that Young’s modulus of all samples varied linearly with increasing sintered bulk density as shown in Fig. 8.

4. Discussion

The HA powder consists of a mixture of small agglomerates ranging from 1 to 3 μm diameter and larger agglomerates of 5–10 μm diameter which composed of loosely packed fine particles as shown in Fig. 1. The drying of the filter cake was ground and sieved, this has resulted in the formation of soft agglomerates that break up easily during powder compaction. Thus, it is evident that the synthesized crystals were single-phase HA and is believed to be very small as reflected by the peak broadening [30] of the diffraction patterns shown in Fig. 2.

Estimates of crystallite size from peak broadening based on Scherrer’s formula [31] for the HA powders taken at the most prominent HA peaks were 108 Å at (2 1 1) reflection corresponding to diffraction angle 2θ = ~31.9° and 319 Å at (0 0 2) reflection corresponding to diffraction angle 2θ = ~25.9°. In general, the XRD results of the powders correlated well with that of the particle size analysis and SEM observation.

The introduction of MnO₂ in the starting powder, however, was observed to have a distinct colour change, i.e. from white for the as-received HA powder to grey for the MnO₂-doped powders. However, after sintering in oxidizing (air) atmosphere above 1000 °C, the undoped HA remained white whereas HA containing MnO₂ turned blue. In addition, it was found that the intensity of the blue hue increased with both increasing MnO₂ content and sintering temperature. It was reported by Yubao et al. [32] that the origin of theapatite blue colour was due to the presence of Mn²⁺ or MnO₂⁻⁻ ions at the PO₄⁻⁻ sites in the apatite crystal structure. According to these authors, the high temperature not only increases the intensity of oxidation in the oxidizing atmosphere, but also provides enough energy for the oxidized manganese ion (Mn²⁺ to Mn⁵⁺) to facilitate their migration within the crystal lattice. This change in colour in the present work was found to have negligible effect on the HA phase stability as confirmed by XRD phase analysis, even when samples sintered at 1400 °C as shown in Fig. 3.

The high-temperature stability of the HA phases, particularly for samples sintered at 1400 °C, is not in agreement with the findings of Royer et al. [33] and Wang et al. [34]. Both these authors reported that decomposition of HA started at about 1300 °C. In general, sintering of HA can lead to the partial thermal decomposition of HA into TCP and/or TTCP [35]. The thermal decomposition is accompanied in two steps, i.e. dehydroxylation and decomposition. Dehydroxylation to oxhydroxyapatite proceeds at temperatures about 850–900 °C by the fully reversible reaction in accordance to [35]

\[ \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_{2-2x} \text{O}_x + x \text{H}_2\text{O}_{\text{gas}}. \]  

(1)

The decomposition to TCP and TTCP occurs at temperatures greater than 900 °C according to the reaction [25]

\[ \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow 2\text{Ca}_3 (\text{PO}_4)_2 + \text{Ca}_4 \text{P}_2 \text{O}_9 + \text{H}_2\text{O}_{\text{gas}}. \]  

(2)

According to these equations, both the dehydroxylation and decomposition reactions include water vapour as a product. The rates at which these reactions proceed depend...
on the partial pressure of H$_2$O in the sintering atmosphere [35]. Thus, in theory the secondary phases could be suppressed by controlling the moisture content in the sintering atmosphere. The high moisture content present in the sintering atmosphere has the tendency to slow down the decomposition rate by preventing the dehydration of the OH group from the HA matrix. The difference in result obtained in the present work with that reported in the literatures [33,34] could in part be attributed to the difference in relatively humidity in the sintering atmosphere and also the nature of the starting synthesized HA powder used in the experiments.

Ruys et al. [36] inferred that the formation of porosity as observed in the present work (Fig. 5) could be in part due to dehydroxylation within the HA matrix. Dehydroxylation is characterized by the release of OH ions at high temperatures [37], which does not occur instantly but over a wide temperature range and has been reported to be dependant on the partial H$_2$O pressure during heating [38]. Based on the SEM observation and the XRD analysis of the HA in the present work, it is hypothesized that during sintering, a mild dehydroxylation could have occurred and continued slowly passing the point at which maximum density (~98%–99% relative density) was attained at about 1000–1100 °C. With further increased in temperature, dehydration of HA could have continued and result in the build up of internal vapour pressure in closed pores located near the free surface of the HA sample. Once the intensity of the internal vapour pressure exceeds the strength of the closed pore structure, the release of pressure could accompany by an open pore as observed in Fig. 5. Since dehydroxylation is associated with HA decomposition and the fact that no secondary phases were detected in the present HA matrix, the partial pressure build up as well as the degree of dehydroxylation could have been mild, i.e. lower than the limit required for decomposition to proceed. For the purpose of evaluating the effect of density on the hardness, some samples were sintered at 900 °C and measured. In general, the increase in hardness of all samples sintered below 1100 °C could be attributed to the increase in bulk density as typically shown in Fig. 9. In contrast, the decline in hardness with further increase in sintering temperature was not due to decomposition of HA nor can be related to the bulk density of the sintered HA. For example, Fig. 9 shows that the hardness of the 0.05 wt% MnO$_2$-doped HA increases with increasing bulk density up to 1000 °C and thereafter decreases with increasing sintering temperature despite still having high relative density of 98.5–99.2%.

One of the beneficial effects of MnO$_2$ additions was the enhancement in the fracture toughness as depicted in Fig. 8. The results show that the addition of MnO$_2$ (up to 0.5 wt%) was effective in enhancing the fracture toughness of the synthesized HA, particularly when sintered at 1000 °C. The 0.05 wt% MnO$_2$-doped HA samples exhibited the highest fracture toughness of 1.65 ± 0.01 MPam$^{1/2}$ as compared to 1.22 ± 0.11 MPam$^{1/2}$ measured for the undoped HA. Further comparison indicates that this trend is in good agreement with the variation in Vickers hardness as described earlier.

In an attempt to correlate the grain size with hardness, it was found that for all composition studied, the hardness of the HA increased with grain size and reached a maximum at a certain grain size limit ($d_c$) before decreasing. Table 3 shows the value of $d_c$ at which maximum hardness was attained for all composition studied. It is believed that below $d_c$ the hardness is governed by bulk density (or porosity) whereas above $d_c$ the bulk density is not the controlling parameter but grain growth.

### Table 3

| MnO$_2$ content (wt%) | Grain size, $d_c$ (µm) | Maximum Vickers hardness (GPa) |
|-----------------------|-----------------------|-------------------------------|
| 0 (undoped)           | 0.50                  | 7.21                          |
| 0.05                  | 0.47                  | 7.58                          |
| 0.10                  | 0.58                  | 7.00                          |
| 0.30                  | 0.52                  | 7.30                          |
| 0.50                  | 1.03                  | 7.04                          |
| 1.00                  | 1.56                  | 5.32                          |

5. Conclusions

The sinterability of the MnO$_2$-doped HA compacts was compared in terms of HA phase stability, relative density, Vickers hardness, fracture toughness and Young’s modulus. All the samples, regardless of sintering conditions, did not show any cracking or distortion after sintering. It was found that small addition of MnO$_2$ was beneficial in enhancing low-temperature densification of hydroxyapatite bioceramics coupled with improved mechanical properties without disrupting the HA phase stability.
All the MnO₂-doped HA achieved above 99% relative density when sintered between 1100 and 1250 °C whereas the undoped HA could only attained 98.9% at 1150 °C. The additions up to 0.5 wt% MnO₂ was effective in improving the hardness of HA especially for samples sintered at low temperature of 1000 °C. However, the hardness trend of all samples revealed that above a certain grain size limit, the hardness decreased as a result of grain growth.

The addition of 0.05 wt% MnO₂ was found to be most beneficial as the samples exhibited the highest hardness of 7.58 GPa, fracture toughness of 1.65 MPam¹/₂ and Young’s modulus above 110 GPa when sintered at 1000 °C. Young’s modulus measurement for all composition studied indicated that the HA matrix stiffness was governed by the bulk density of the sintered body.

Acknowledgements

This work was funded by MOSTI through the IRPA scheme (IRPA Grant no. 09-99-03-0002-EA001). The authors thank SIRIM Berhad and TNBR for providing the test equipment.

References

[1] L.L. Hench, J. Am. Ceram. Soc. 81 (1998) 1705.
[2] W. Suchanek, M. Yoshimura, J. Mater. Res. 13 (1998) 94.
[3] K.A. Gross, C.C. Berndt, J. Biomed. Mater. Res. 39 (1998) 580.
[4] C.D. Cook, K.A. Thomas, F.J. Kay, M. Jarcho, Clin. Orthop. 232 (1988) 225.
[5] B. Fartash, H. Liao, J. Li, N. Founda, L. Hermansson, J. Mater. Sci. Mater. Med. 6 (1995) 451.
[6] J. Li, H. Liao, M. Sjostrom, Biomaterials 18 (1997) 743.
[7] L.M. Rodriguez-Lorenzo, M. Vallet-Regi, J.M.F. Ferreira, M.P. Ginebra, C. Aparicio, J. Planell, J. Mater. Sci. Mater. Med. 60 (2002) 159.
[8] T. Kokubo, H.M. Kim, M. Kawashita, Biomaterials 24 (2003) 2161.
[9] A. Ruys, J. Wei, M. Sorrell, C.C. Dickson, M.R. Brandwood, B.K. Milthorpe, Biomaterials 16 (1995) 409.
[10] W. Suchanek, M. Yashima, M. Kakihana, M. Yoshimura, Biomaterials 17 (1996) 1715.
[11] E. Champion, S. Gautier, D. Bernache-Assollant, J. Biomed. Mater. Res. 7 (1996) 125.
[12] K. Ioku, S. Somiya, M. Yoshimura, J. Ceram. Soc. Japan 99 (1991) 191.
[13] W. Suchanek, M. Yashima, M. Kakihana, M. Yoshimura, Biomaterials 18 (1997) 923.
[14] T. Kanazawa, T. Umegaki, K. Yamashita, H. Monma, T. Hiramatsu, J. Mater. Sci. 26 (1991) 417.
[15] A. Ababou, D. Bernache-Assollant, Euroceramics 8 (1995) 185.
[16] B.C. Wang, E. Chang, T.M. Lee, C.Y. Yang, J. Biomed. Mater. Res. 29 (1995) 1483.
[17] Z. Feng, Y. Liao, M. Ye, J. Mater. Sci. Mater. Med. 16 (2005) 417.
[18] R. Morrissey, L.M. Rodriguez, K.A. Gross, J. Mater. Sci. Mater. Med. 16 (2005) 387.
[19] H.W. Kim, Y.M. King, Y.H. Koh, H.E. Kim, J. Am. Ceram. Soc. 86 (2003) 2019.
[20] H.S. Ryu, K.S. Hong, J.K. Lee, D.J. Kim, J.H. Lee, B.S. Chang, D.H. Lee, C.K. Lee, S.S. Chung, Biomaterials 25 (2004) 393.
[21] M. Sato, M.A. Sambito, A. Aslani, N.M. Kalkhoran, E.B. Slamovich, T.J. Webster, Biomaterials 27 (2006) 2358.
[22] M.A. Fanovich, J.M.P. Lopez, J. Mater. Sci. Mater. Med. 9 (1998) 53.
[23] T. Zhang, P. Hing, H. Huang, J. Kilner, Mat. Sci. Eng. B 83 (2001) 235.
[24] S. Shimada, K. Kodaira, T. Matshusita, J. Mater. Sci. 19 (1984) 1385.
[25] H. Erkal, Z. Misirli, T. Baykara, Ceram. Int. 24 (1998) 81.
[26] S. Ramesh, Malaysia Patent, No. PI. 20043325 (2004).
[27] M.I. Mendelson, J. Am. Ceram. Soc. 52 (1969) 443.
[28] ASTM E1876-97, Standard test method for dynamic Young’s modulus, shear modulus and Poisson’s ratio by impulse excitation of vibration, Annual Book of ASTM Standards, 1998.
[29] K. Nihara, Ceram. Japan 20 (1985) 12.
[30] H.S. Liu, T.S. Chin, L.S. Lai, S.Y. Chiu, K.H. Chung, C.S. Chang, M.T. Lui, Ceram. Int. 23 (1997) 19.
[31] B.D. Cullity, S.R. Stock, Elements of X-ray diffraction, third ed., Prentice-Hall, New Jersey, 2001, pp. 170.
[32] L. Yubao, C.P.A.T. Klein, X. Zhang, K. de Groot, Biomaterials 14 (1993) 969.
[33] A. Royer, J.C. Vigue, M. Hughebaert, J.C. Hughebaert, J. Mater. Sci. Mater. Med. 4 (1993) 76.
[34] P.E. Wang, T.K. Chaki, J. Mater. Sci. Mater. Med. 4 (1993) 150.
[35] C.K. Wang, C.P. Ju, J.H.C. Lin, Mater. Chem. Phys. 53 (1998) 138.
[36] A.J. Ruys, K.A. Zeigler, O.C. Standard, A. Brandwood, B.K. Milthorpe, C.C. Sorrell, in: M.J. Bannister (Ed.), Proceedings of the International Ceramic Conference (Austceram), CSIRO, Australia, Avon Books, New York, 1992, p. 605.
[37] J.C. Trombe, G. Montel, J. Inorg. Nucl. Chem. 40 (1977) 15.
[38] B. Locardi, U.E. Pazzaglia, C. Gabbi, B. Profilo, Biomaterials 14 (1993) 437.