

The Effect of Additives to the Densification of Natural Hydroxyapatite

Sri Asliza M. A, Shahrizal H, Zaheruddin K and Azida Azmi

Abstract __The effect of different additives to the microstructure and phase properties of compact natural hydroxyapatite was studied. Compact HA was fabricated from HA powder obtained from bovine bones via calcinations and grinding processes. The sintering temperatures 1150°C and 1200°C were applied to increase the densification behaviour of natural HA. In this study, the effects of MgO and BaO to the microstructure and mechanical properties of natural HA were also being investigated. From the result, BaO increased the densification and microstructure developments of sintered natural HA. The average grain size distribution of 1.5µm can be clearly seen from the microstructure at temperature 1200°C for specimen doped BaO. However the density of specimen doped MgO give lower value of 57 % compared to pure natural HA. Thus, from the microstructure results, the MgO decreased the sintering rate of natural HA. On the other hand, the BaO increased the sinterability of specimen.

Keywords: Hydroxyapatite, Natural, BaO, MgO, Temperature.

I. INTRODUCTION

Hydroxyapatite (HA) is widely used in medical fields especially as a bone substitute, due to its good biocompatibility, bioactivity, high osteoconductive and nontoxic properties [3]. The production of synthetic HA needs very complicated and sophisticated technique during synthesizing process. Whereas extraction of HA from the natural bone is biologically safe and economic since cow bone is easy to obtained. HA produced from natural bone inherits most properties of the origin bone such as its chemical composition and structures give advantage in surgical applications. Besides, its potential for bone grafting is better than synthetic HA [2]. Thus, the effect of

sintering temperature to densification process of compact HA from natural bone was investigated in order to produce dense HA for high load bearing application such as hip bone. In this study the effect of sintering temperature and different additives to the physical, microstructure and mechanical properties of dense natural HA were examined. The sintering additives should significantly enhance densification without decomposition of HA. Additionally, the sintering additives should introduce a weak interface for HA (easy path for debonding with consequent pull-out and/or bridging effects), which is of great importance in high toughness HA ceramics with precisely controlled microstructures. Moreover, the sintering additives could be used as structure stabilizers and/or to control grain size [6].

II. METHODOLOGY

This study was divided into two parts including extraction of natural HA powder and preparation of dense specimens with different parameters. In the first part of study a clean cow bones were cut into small pieces and treated into sodium hydroxide solution to remove organics and protein parts. After neutralized with distilled water, the bones were dried in oven and heat treated at 800°C for 3 hours to remove completely the organics part. Proteins free HA bone were then ground into fine powder by using planetary ball milling for several hour and sieve at 63µm.

In the second part of this study, dense specimens with different additive were prepared. In this study 2% of MgO and 2% of BaO were used as additive. At this stage, the fine cow bone powder was first mixed with distilled additive, water, calgon and polyethylene glycol PEG as binder for 16 hours and then dried in oven. After that, the compact bodies of cow bone were formed by compressed powder in rectangular steel bar mould by using cold pressed technique under 47MPa load pressure. The green bodies were fired at temperature 1150°C and 1200°C for 3h.

The chemical composition of natural HA was determined by EDS technique. The DTA/TG and Malvern Mastersizer analysis were carried out to determine the thermal properties and particle size of raw cow bone powder respectively. The FTIR analysis was carried out to examine the bonding character in natural HA powder. The

density was measured by using Archimedes' principle method and the specimen surface microstructure was examined by scanning electron microscope. Finally, the three point bending test was used to measure the fracture strength of sintered specimen.

III. RESULT AND DISCUSSION

Part A: Raw hydroxyapatite powder extract from cow bone

Figure 1a) presents the XRD analysis for raw cow bone. The result shows a high intensity of crystalline pattern with sharp narrower peaks. All the XRD peaks match with the standard JCPDS file no. 9-432 of pure HA and no impurity other than HA was detected. This result indicates that all organic substance was completely eliminated.

Figure 2 presents the thermal gravimetric analysis for the cow bone. At 30°C to 200°C, there is a little weight loss due to moisture evaporation from the cow bone. At about 200°C to 700°C, the weight is lost rapidly cause by

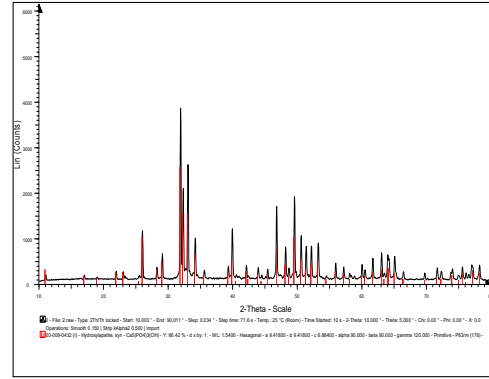


Figure 1: XRD pattern for cow bone powder after firing at 800°C

the elimination of organic parts. From 700°C to 1450°C, the weight continues to loss constantly. Figure 3 shows the EDS result of cow bone after fired at 800°C respectively. The result shows the present of Mg in the raw cow bone which is not exist in synthetic HA.

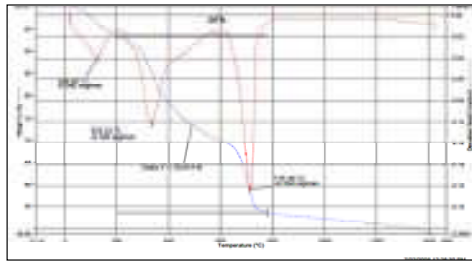


Figure 2: DTA/TG result of cow bone powder before firing

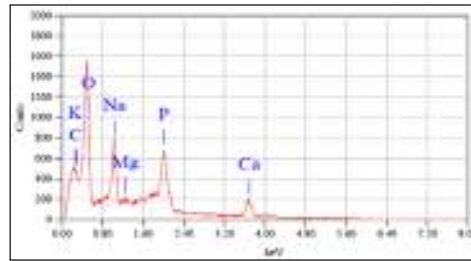


Figure 3: EDS result of cow bone powder after firing at 800°C

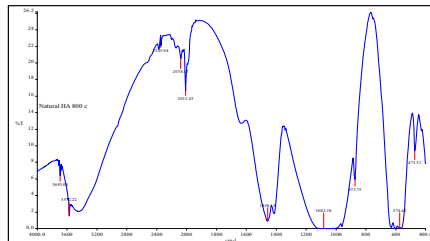


Figure 4: FTIR result of cow bone powder after firing at 800°C

From figure 4, the Fourier transform infrared spectroscopy (FTIR) spectrum indicated medium intensity band at 3693.08 cm^{-1} and 3572.22 cm^{-1} assigned to a

powder. From the result, the average particles size of cow bone powder was $10\text{ }\mu\text{m}$. The average particle size results of MgO and BaO were $9.2\text{ }\mu\text{m}$ and $13\text{ }\mu\text{m}$ respectively.

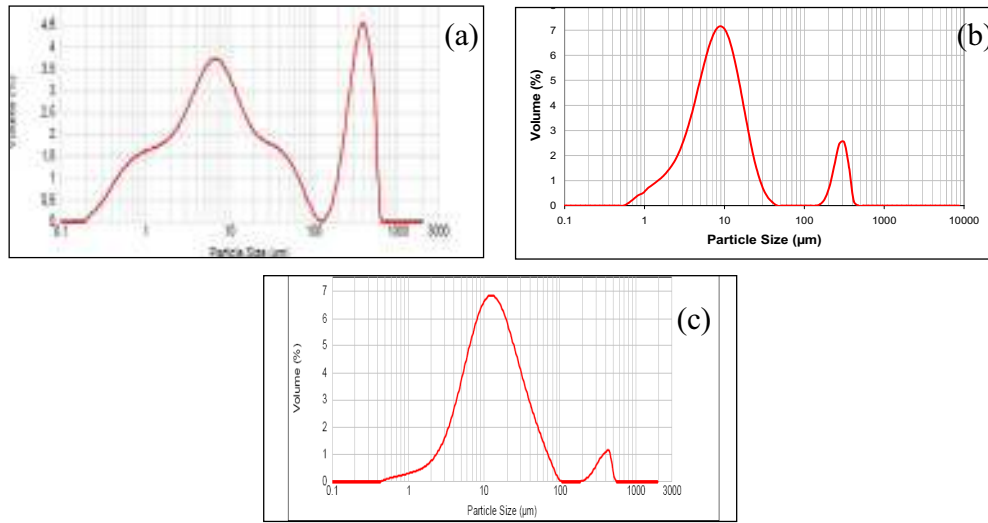


Figure 5: Particle size analysis of (a) cow bone powder at 800°C , (b) MgO powder and (c) BaO powder

hydroxyl (OH) vibration mode. Figure 5 present the particles size result of cow bone powder, MgO and BaO

Although the raw powder were sieve below $63\text{ }\mu\text{m}$ before testing, the higher particles size value and two peaks exist

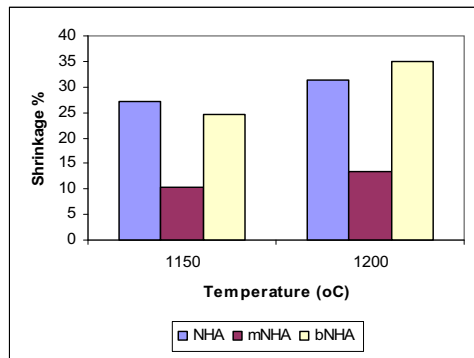


Figure 6: shrinkage percentage of specimen vs temperatures

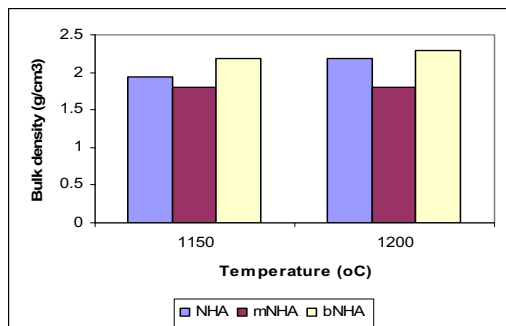


Figure 7: Bulk density of specimen vs temperatures

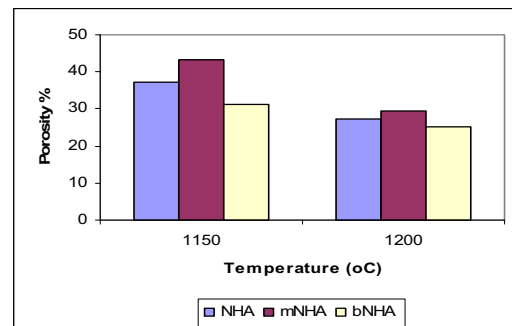


Figure 8: Porosity percentage of specimen vs temperatures

was due to the agglomeration of particles during testing and non uniform size distribution of particles during milling.

Part B: Specimens with different additives

Figure 6 shows the percentage of shrinkage for pure and doped natural HA at temperature 1150°C and 1200°C. Meanwhile figure 7 and 8 present the density and

porosity result of specimens at different temperatures. The bar chart presented in Figure 7 shows clearly that BaO dramatically enhanced densification of HA. On the other hand MgO inhibited densification significantly. The influence of the sintering additives was more strongly pronounced when sintering was carried out at 1200°C. However, a non-uniform distribution of the sintering additive and a larger size of the additive particles than the size of particles of the sintered material may have a negative influence on densification.

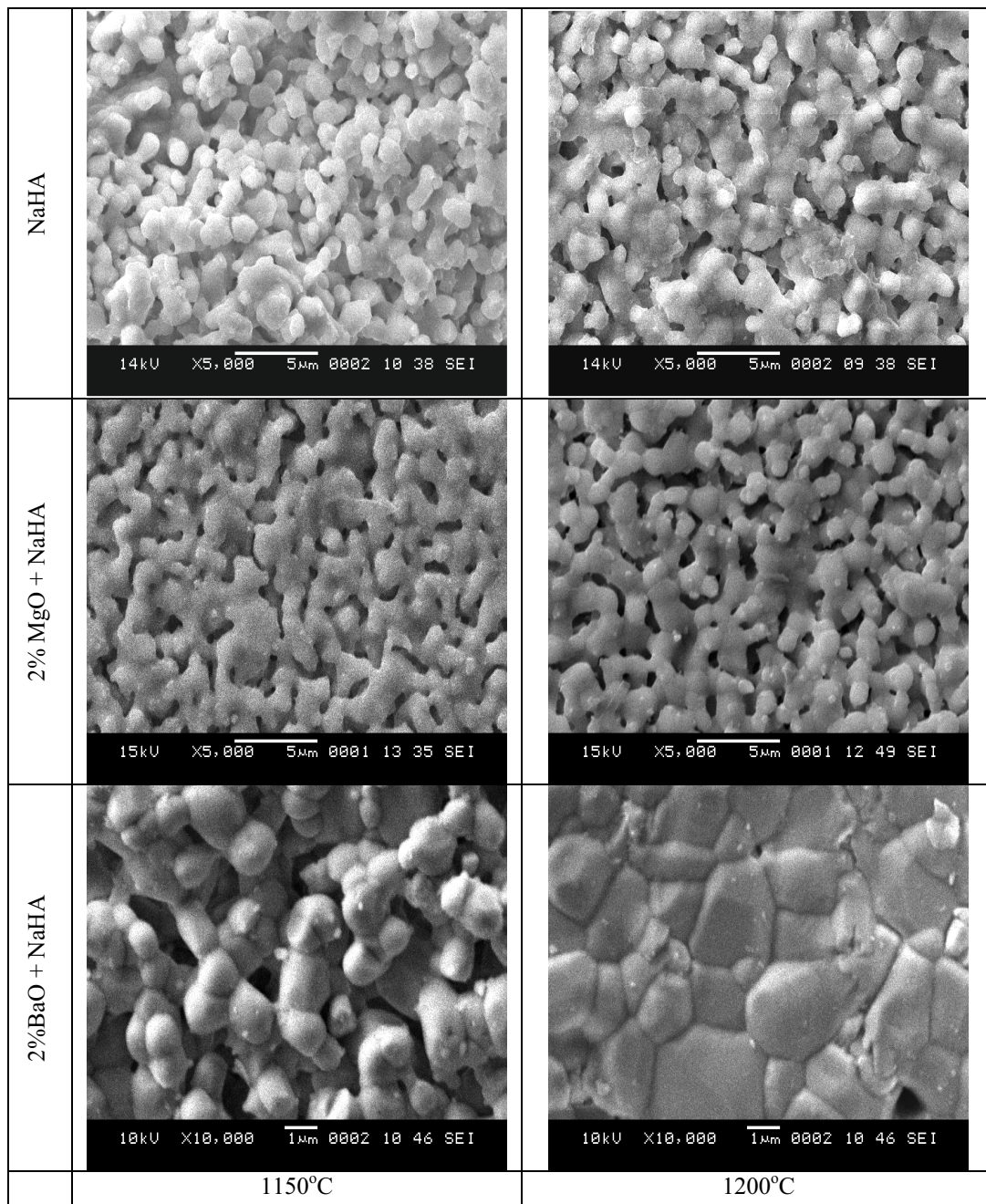


Figure 9: SEM micrographs of specimens at temperature 1150°C and 1200°C

Figure 9 shows SEM micrographs of specimens at temperature 1150°C and 1200°C. For both specimens pure and doped MgO, the microstructures show in the early stage of sintering. In this stage, the necking between particles could be observed especially at temperature 1200°C. It indicates that the addition of MgO reduces the sintering rate of the natural HA. The materials were inhomogeneous in most cases, suggesting nonuniform distribution of the sintering additives and the raw of HA itself. Average particle size distributions of ~1.5µm could be clearly seen only for specimen doped BaO additive. It shows that the sintering stage is almost complete which representing that the BaO increased the sintering rate of natural HA.

Pure and doped natural HA, sintered at 1150 °C and 1200°C, were subjected to 3 point bending testing to determine the failure strength under uniaxial compressive loading (figure 10). The results of tests revealed that the sintered structures of pure natural HA had average strength of 13MPa and 17MPa at 1150°C

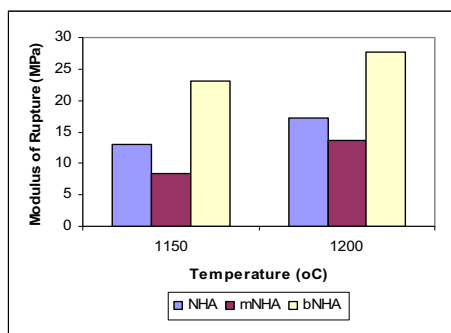


Figure 10: MOR result of specimens at 1150°C and 1200°C

and 1200°C respectively. The average strength of MgO and BaO doped natural HA at 1150°C were found to be 8MPa and 23MPa respectively. However at 1200°C, the strength increased to 14MPa and 28MPa respectively. This result associated with the percentage of density specimen at both temperatures. From the microstructure result, the highest strength value of BaO obtained at 1200°C due to the grains and grain boundaries development which indicates that the sintering is almost completed.

IV. CONCLUSION

In this study, a dense natural HA was developed via sintering process. The strength of specimen increased from 13MPa to 17MPa with increasing temperatures. However, the porosity inversely decreased with temperatures. Subsequently, densification, grain growth and fracture behaviour of natural HA ceramics with BaO and MgO additives, sintered at 1150-1200°C, have been studied. From the results, exaggerated grain growth was observed at 1200°C with BaO additive. Meanwhile, the MgO did not enhance densification of HA whereas BaO improved the densification significantly. The mechanical properties of natural HA enhance with BaO additive to 28MPa at 1200°C. On the other hand, MgO decrease the strength of natural HA. Thus, this project will be extended to study the effect of additive at higher sintering temperature (1250°- 1350°C) to the decomposition and phase properties of natural HA.

ACKNOWLEDGMENT

This work was supported by Science fund grant (9005-00010) from MOSTI.

REFERENCES

- [1] Haberko, K., Bucko, M.M., Brzezinska- Miecznik, J., Haberko, M., Mosgava, W., Panz, T., Pyda, A., Jerzyzarebski. (2006). Natural Hydroxyapatite - Its behaviour during heat treatment. *J. of The European Cer. Soc.* [26], 537-542
- [2] Hiller J. C., Thompson T. J. U., Evison M. P., Chamberlain A. T., Wess T. J. (2003) Bone mineral change during experimental heating: an X-Ray scattering investigation. *Journal Biomaterials* 24. 5091-5097.
- [3] Javidi M., Bahrololoom M. E. and Ma J. (2008) Electrophoretic deposition of natural hydroxyapatite on medical grade 316L stainless steel. *J. Materials Science and Engineering C28.* 1509-1515.
- [4] Jingxian Zhang, Hideaki Tanaka, Feng Ye, Dongliang Jiang, Mikio Iwasa (2007) Colloidal processing and sintering of hydroxyapatite. *J. Materials Chemistry and Physics* 101. 69-76
- [5] Nasser Y. Mostafa (2007) Characterization, thermal stability and sintering of hydroxyapatite powders prepared by different routes. *J. Materials Chemistry and Physics* 94. 333-341
- [6] Suchanek W., Yashima M., Kakihana M. and Yoshimura M. (1997) Materials and Structures Laboratory, Hydroxyapatite ceramics with selected sintering additives *Biomaterials* [18.] 923-933.
- [7] Wei-Jen Shih, Szu-Hao Wang, Wang-Long Li, Min-Hsiung Hon, Moo-Chin Wang (2006) The phase transition of calcium phosphate coatings deposited on a Ti-6Al-4V substrate by an electrolytic method. *Journal of Alloys and Compounds*