## Preparation of hydroxyapatite powder by a spray dry method

Presented in The 2<sup>nd</sup> Progress in Advanced Materials: Micro/Nano Meterials and Applications

N. Monmaturapoj, C. Yathongchai and W. Soodsawang

# Abstract

Hydroxyapatite (HA) powder was prepared by solid-state reaction method. HA powder was divided into two parts. The first is used as a control and the second was calcined at 900°C for 1h used for spray drying. As-prepared HA and calcined HA powders were characterized by XRD and SEM. The ratios of HA powder to water content were varied then spray dried at  $150^{\circ}$ C and  $200^{\circ}$ C to investigate the morphology. Spray dried powders were compacted under uniaxial a stress of 2 MPa and sintered at  $1250^{\circ}$ C for 2h. The density of sintered compacts was determined using Archimedes's technique. The flexural strength of sintered specimens was measured in a three-point bending using a universal testing machine. From the results, spherical HA granules of  $2-35 \,\mu$ m were obtained by spray drying the calcined HA. The morphology of spray dried granules varied with the concentration of slurries. Solid spheres and doughnut shapes were produced at slurry concentrations of 15-20%HA and 30%HA, respectively. The physical and mechanical properties of HA ceramics were improved by spray drying technique. The maximum density and fracture strength of spray dried calcined HA of 90.90 % theoretical and 117 MPa could be obtained from 30%HA spray dried at  $200^{\circ}$ C.

Keywords: Hydroxyapatite, Spray dry, Microstructure, Characterization, Mechanical Properties

## 1. Introduction

Over the past decades, one of the most investigated bioceramics for bone substitution is hydroxyapatite  $(Ca_{10}(PO_4)_6(OH)_2, HA)$  because of its chemical similarity with the mineral component of natural bones and excellent in bonding to bone onto its surfaces (P.Penggsha et al., 2007; S.ramesh et al., 2007). Several forms of HA such as in the compacts, porous and granules can be applied for various applications especially as bioactive implant materials and extensively used in many medical, orthopaedic and dental applications (S.Ramesh et al., 2007). HA can also be used as biological chromatography supports in protein purification and DNA isolation (M. Jarcho et al.,1976). However, its mechanical properties have been found to be unsuitable for major load-bearing applications, but it is regularly applied as a coating on materials such as titanium and titanium alloys for dental and orthopaedic implants (P. Luo and T.G. Nieh, 1996; T.Kokubo,1993). The changing the morphology of the granules is therefore required to improvement

National Metal and Materials Technology Center, 114 Thailand Science Park, Paholyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand

in mechanical properties, physical and chemical stability of dense HA (P. Luo and T.G. Nieh, 1995). Incidentally, several HA synthesizing methods have been reported, such as wet chemical precipitation (M.Jarcho et al., 1976), solid-state reaction (W.Kim, 2000) and hydrothermal methods (X.Zang and K.S. Vecchio, 2007), etc. A solid-state reaction method is uncomplicated, low cost and high productive, which makes it a helpful route for industry to produce HA powders. Therefore, in this study, the powder synthesized by a solid-state reaction route was produced as slurry with various concentrations prepared to spray dry and heated under a proper sintering schedule then its microstructure, mechanical and physical properties were discussed and compared.

#### 2. Experimental procedures

#### 2.1. Samples preparation

Nano-size hydroxyapatite powder was produced through a solid-state reaction method. The reaction for this method is as follows:

 $6CaHPO_{4} + 4CaCO_{3} \rightarrow Ca_{10}(PO_{4})_{6}(OH)_{2} + 6H_{2}O$  $+ 4CO_{9}$ 

HA powder was divided into two parts. The first was used as a control (uncalcined powder) and the second was calcined at 900°C for 1h. Slurry was made up by varying amount of HA powder during 15-30%wt. in deionised water then milling for 12h for deagglomerating HA powders. The mixture of polyvinyl alcohol (PVA) and polyethylene glycol (PEG), 3%wt, as a binder and plasticizer respectively were added. Then, HA slurry was spray dried by using BUCHI Mini spray dryer 290 at temperature of 150°C and 200°C. Spray dried powders were compacted under uniaxial a stress of 2 MPa. The green compacted were sintered at temperatures of  $1250^{\circ}$ C for 2h in air in a furnace. All the sintered specimens were then polished to a 3  $\mu$ m prior to evaluation.

### 2.2. Characterization

Specific surface areas of HA powders were determined by nitrogen absorption analysis (BET: Autosorb-1C, Quantachrome instrument). Phase analysis was carried out on all specimens using X-ray diffraction XRD (JEOL JDX 3530) operating from  $10^{\circ}-70^{\circ} 2\theta$  at a scan speed of  $2^{\circ} 2\theta$ /min. and a step size of  $0.02^{\circ} 2\theta$  with Cu<sub>Ka</sub> radiation ( $\lambda_{cu} = 0.1540562$  nm) at 50 kV and 30 mA. The spectra were analyzed using JADE software and JCPDS cards. The microstructure evolution of samples were investigated by scanning electron microscopy (SEM: JEOL 6301F).

The density of sintered compacts was determined using Archimedes's technique. The result is the average of five measurements then the relative density was calculated by using the theoretical density of hydroxyapatite as 3.156 g/cm<sup>3</sup>. The flexural strength of sintered specimens was measured in a three-point bending using a universal testing machine (Instron 55R4502) at a crosshead speed of 0.5 mm/min on polished specimens. Five specimens were prepared for each condition and the average value of flexural strength was taken.

### **3. Results and discussion**

#### 3.1. Powder characteristics

The specific surface areas of as-synthesized (uncalciend) and calcined HA were 46.98  $m^2/g$  and 10.26  $m^2/g$ , respectively. The significantly drop

of specific surface area of both powders is owing to the effect of calcinations. After spray drying, the specific surface areas were increasing to  $84.71 \text{ m}^2/\text{g}$ g and  $14.88 \text{ m}^2/\text{g}$ , in uncalcined and calcined powders respectively, in associated to the finer in particle size which trend to form more undesirable agglomerate.

XRD patterns of powders before and after spray drying show in Figure 1. It is clear that XRD patterns can be indexed only peak corresponding to hydroxyapatite, JCPDS no. 09–0432 as the dominant phase of powders without the observation of the secondary phase for instance tricalcium phosphate (TCP) or calcium oxide. There is no considerable change in either crystalline structure or phase impurity even though granules were prepared at 150°C. The SEM micrographs of the powders in Figure 2 present the spray drying granules produced by uncalcined powders under different processing conditions. According to their shapes, spherical and doughnut of hydroxyapatite granules were produced in which prepared by using slurry concentration of 15%wt HA and 30%wt HA, respectively. No significant different in size and size distribution observed between spray drying temperature 150°C and 200°C.

Figure 3 illustrates the morphology of spray drying granules prepared by calcined powders under different processing conditions. Spherical and doughnut shapes can be observed at low concentration and high concentration in the similar trend to the spray dried uncalcined powders shown in Figure 2. Spray drying temperature also has no important role in changing the morphology of the granules.



Figure 1. XRD pattern of uncalcined and calcined HA powders before and after spray drying,  $\blacktriangle$ : HA, $\bullet$ :  $\beta$ -TCP.



Figure 2. SEM images of a) Uncalcined HA15%wt. spray dried at 150°C, b) Uncalcined HA15%wt. spray dried at 200°C, c) Uncalcined HA30%wt. spray dried at 150°C and d) Uncalcined HA30%wt. spray dried at 200°C.



Figure 3. The morphology of a) Calcined HA15%wt. spray dried at 150°C, b) Calcined HA20%wt. spray dried at 200°C, c) Calcined HA30%wt. spray dried at150°C and d) Calcined HA30%wt. spray dried at 200°C.



Figure 4. SEM images of sintered samples a) Uncalcined HA b) Uncalcined HA15%wt spray dried at 150°C,
c) Uncalcined HA15%wt. spray dried at 200°C, d) Uncalcined HA30%wt spray dried at 150°C and d) Uncalcined HA30%wt. spray dried at 200°C.



Figure 5. SEM images of sintered samples a) Calcined HA b) Uncalcined HA15%wt. spray dried at 150°C,
c) Calcined HA15%wt. spray dried at 200°C, d) Calcined HA30%wt. spray dried at 150°C and
d) Calcined HA30%wt. spray dried at 200°C.

Sample ID	Bulk density	Relative Density	MOR (MPa)
	(g/cm <sup>3</sup> )	(%)	
Uncalcined HA	1.923	60.933	40.34 10.01
HA 15%SP150	2.601	82.414	47.34 12.74
HA 30%SP150	2.694	85.361	56.33 10.56
HA 15%SP200	2.592	82.129	45.58 2.39
HA 30%SP200	2.609	82.668	56.60 8.50
Calcined HA	2.731	86.535	79.36 15.70
Calcined HA15%SP200	2.787	88.308	65.34 13.53
Calcined HA20%SP200	2.897	91.793	116.20 2.54
Calcined HA30%SP150	2.830	89.676	108.74 11.62
Calcined HA30%SP200	2.869	90.900	117.88 6.65

 Table 1
 Physical and mechanical properties of sintered samples.

#### 3.2. Compacted sample characterizations

After sintering, XRD patterns can be indexed hydroxyapatite as a major phase with a minor phase of tricalcium phosphate (TCP: JCPDS no. 09–0169) due to the partial thermal decomposition of HA into TCP and/or tetracalcium phosphate at 1250°C.

Figure 4 present SEM images of spray dried uncalcined powders with various concentrations after sintering at 1250°C for 2h reveals a decreasing in porosity of sintered samples. The best improvement was observed in 30%wt. HA and spray dried at 200°C, the relative density of samples after sintering was increasing to 85% as a result of rising in mechanical strength of sintered samples to 56 MPa (see Table 1) compared to samples produced from uncalcined powder without spray drying in consistent very well to SEM images. The superior improvement in mechanical strength of sintered samples could be the resulting of the doughnut shapes of spray dried granules due to the more contacting surface areas and bonding capacity compared to spherical shapes.

In the similar manner, the porosity of the sintered samples prepared by spray dried calcined granules was decreasing as reviewed by SEM images in Figure 5. These show a much more improvement of relative density and mechanical properties of HA ceramics which increased to 90% and 117 MPa (Table 1), respectively in sample produced from 30%wt. calcined HA powder and spray drying at 200°C because of effect of doughnut shapes. The relative density and mechanical strength of sintered samples produced by using spray dried calcined granules were three times higher compare to the as-synthesized HA powder

## 4. Conclusions

The spray drying technique might be an important method to control the morphology of HA granules to spherical or doughnut shapes. However, the calcinations step must be undertaken before spray drying process in order to produce powder with high crystallinity and highly dense morphology. The spherical and doughnut granule shapes can be prepared by spray drying HA powders at low (15%wt HA) and high (30%wt. HA) concentration, respectively with temperature either 150 °C or 200 °C. With the combination of calcinations and spray drying method, therefore, slurry contain 30%wt calcined HA powder spray dried at 200 °C induced the doughnut shape granules in which provided a bonding capacity and contacting surface area as a result of reducing in porosity and increasing in mechanical strength of HA ceramics after sintering at 1250°C for 2h.

## Acknowledgement

This work was performed under the support of National Metal and Materials Technology Center, the Ministry of Science and Technology of Thailand, under Project No. MT-B-50-BMD-07-131.

#### References

Jarcho, M., Bolen, C. H., Thomas, M. B., bobick, J., Kay, J. F. and Doremus, R. H. 1976. Hydroxylapatite synthesis and characterization in dense polycrystalline form, J. Mater. Sci. 11: 2027-2035.

- Kim, W., Zhang Q. and Saito, F. 2000. Mechanochemical synthesis of hydroxyapatite from Ca(OH)<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> and CaO-Ca(OH)<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> mixtures, J. Mater. Sci., 35: 5401-5405.
- Kokubo, T. 1993. A-W glass-ceramic: processing and properties in "An Introduction to Bioceramics", Edited by L. L. Hench and J. Wilson, World Scientific, London, pp 75–88.
- Luo P. and Nieh, T.G. 1995. Synthesis of ultrafine hydroxyapatite particles by a spray dry method, Mater. Sci. Eng. C3: 75–78.
- Luo P. and Nieh, T.G. 1996.Preparing hydroxyapatite powders with controlled morphology, Biomater. 17: 1959–1964.
- Pengsha, P., Wei L. and Ying, L. 2007. Effect of ball mill process on the microstructure of titanium-nanohydroxyapatite composite powder. Rare Metal. 26: 118-123.
- Ramesh, S., Tan, C. Y., Sopyan, I., Hamdi M. and Teng, W.D. 2007.Consolidation of nanocrystalline hydroxyapatite powder. Sci. Tech. Adv. Mater. 8: 124–130.
- Zhang X. and Vecchio, K.S. 2007.Hydrothermal synthesis of hydroxyapatite rods. J. Cryt. Growth. 308: 133-140.

##