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2004

Xu, J., Khor, K. A., Dong, Z. L., Gu, Y. W., Kumar, R., & Cheang, P. (2004). Preparation and Characterization of Nano-sized Hydroxyapatite Powders Produces in a Radio Frequency (rf) Thermal Plasma. *Materials Science and Engineering A*, 374, 101-108.

<https://hdl.handle.net/10356/95567>

<https://doi.org/10.1016/j.msea.2003.12.040>

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Preparation and characterization of nano-sized hydroxyapatite powders produced in a radio frequency (rf) thermal plasma

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ABSTRACT

Nano-sized hydroxyapatite (HA) powders were successfully produced in radio frequency (rf) induction plasma. Fine spray dried (SD) HA powders (average size $\sim 15 \mu\text{m}$) were employed as feedstock. The microstructure, phase composition and thermal stability of SDHA feedstock and the nano-sized HA powders were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD), and differential scanning calorimetry (DSC). Decomposition of powders into other calcium phosphate phases occurred in the high temperature plasma flame. XRD results indicated that an increase in the working power level from 15 to 21 kW led to different trends for SDHA decomposition in the rf plasma flame. At 21 kW, the extreme rf plasma temperature was dominantly responsible for the decomposition of SDHA in the flame. The decomposition at the working plate power of 15 kW was attributed mainly to the relatively lower velocity of the plasma flame. The moderate decomposition of HA feedstock was obtained at a working power level of 20 kW due to mitigating conditions through combined influence of moderate flame temperature and flame velocity. DSC results indicated that amorphous phase content has a positive relation with the recrystallization enthalpy of phase transformation in the nano-sized powders.

Keywords

Nano-sized; Hydroxyapatite; Powder; Radio frequency; Plasma; Thermal decomposition

1. INTRODUCTION

Hydroxyapatite (HA) has attracted a great deal of attention because its chemical composition is similar to that of natural bone tissues [1–5]. It promotes rapid bone growth and bonding between bony tissue and implant surfaces. The stoichiometric HA has an exact Ca:P ratio of 1.67. Thermodynamically, HA is the most stable calcium phosphate compound at the pH, temperature and composition of the physiological fluid [1]. However, the poor mechanical properties of bulk HA ceramics have provided impetus to research in HA coatings on metallic substrates in order to maintain biocompatibility and to improve mechanical properties [6]. Thermal spraying is a widely used coating process to deposit HA powders onto a metallic substrate [3,4,7].

Unfortunately, the HA/substrate interface or HA itself can be fractured even under a relatively low stress because of the low adhesion strength and brittleness of the sprayed layer itself. Additionally, HA lacks sufficient strength and durability for use in load-bearing applications. Therefore, the use of nano-particulate materials to attain more superior mechanical properties has been proposed to solve this problem [5].

As natural bone consists of inorganic/organic composite structure as 20nm in diameter and 50nm in length [8], from a bionics viewpoint, it is expected that HA with similar grain size would be more desirable for the application of implant. Future biomaterials consisting of nano-phase ceramic could be tailored to meet clinical requirements associated with either anatomical differences or patient's age [9]. Nano-crystallized characteristics have proven to be of great biological efficacy [10]. For example, compared with conventionally crystallized HA, nano-crystallized HA can promote osteoblast adhesion and proliferation, osseointegration, and the deposition of calcium-containing minerals on its surface. It is also believed that nano-structured HA can improve the sintering kinetics because of higher surface area and subsequently improve mechanical properties [11]. Thus, the effort is focused on the synthetic routes of nano-sized HA powders.

Many methods have been used to produce nano-sized powders and one of the most efficient physical methods to produce nano-particles is the thermal plasma technique [12–15]. During plasma processing, the raw material is melted or partially melted, and even evaporated instantaneously in a high-temperature flame. The melting or vaporized particles will quench or condense into ultra-fine particles by subsequent rapid cooling.

The radio frequency plasma (rf plasma) has a larger flame than conventional direct current (DC) plasma, and this allows longer residence time for particles injected into plasma jet and makes it suitable for the production of ultrafine particles and coatings [2]. Furthermore, the rf plasma is more homogeneous and it possesses less severe gradients, which results in better control of the material processed in the plasma [13]. Rf suspension plasma has been employed for the ultra-fine powder processing of HA and

HA/ZrO₂ composite [15,16].

The objective of the present study is to produce nano-sized HA powders through an rf induction plasma spraying technique, which employs spray dried HA powders as feedstock. The nano-sized HA powders obtained were characterized using X-ray diffractometry (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to investigate the influence of operating parameters. Furthermore, differential scanning calorimetry (DSC) was used to examine the thermal stability of the synthesized nano-powders. The in vitro behavior of the nano-sized powders was analyzed through the SBF (simulated body fluids) immersion.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Preparation of spray-dried HA

The HA feedstock used for rf plasma process were prepared using a wet chemical approach by reacting 0.6 mol of orthophosphoric acid (H₃PO₄) with 1 mol of calcium hydroxide (Ca(OH)₂). The precipitation reactants were carried out at 40 ± 5 °C in house and terminated when the pH reached 9 through the addition of H₃PO₄. After the complete mixing of the reactants, the precipitate was stirred for two more hours and left overnight to settle. The so-formed HA suspension was then transported into the spray dryer (Ohkawara LT-8, Japan), where the atomization and drying processes took place. The spray-dried HA powders were collected and kept in an oven at 60 °C for 12 h to remove any absorbed moisture. The spray-dried HA powders were sieved and the powders with a particle size larger than 20 μm were sieved out. Powders with a particle size less than 20 μm were heat-treated at 1000 °C for 5 h to increase the thermal stability of the HA feedstock.

2.2. Nano-sized HA powders production

According to Koura et al. [17], when the HA feedstock entered into the plasma flame, its surface began to melt and evaporate, and the powders stayed in the plasma flame for a few milliseconds. The time was not considered to be sufficiently long for melting and the evaporation processes to penetrate into the core of the feedstock powders unless their sizes were sufficiently small. The unmelted solid core, which emerged from the plasma flame becomes a median-sized particle, which is not discussed in the present study. The melting or vaporized particles quenched or condensed into nano-sized powders. In this paper, the primary focus is on the characterization of nano-sized HA powders.

An inductively coupled plasma torch (PL-35, Tekna Plasma System, Canada) was used for the nano-powder production. The carrier gas (argon, 99.99% pure) transported

the feedstock through a narrow pipeline to the torch injector probe. Table 1 gives the experimental condition for the rf plasma process. After plasma processing, the nano-sized HA powders were collected from the chamber for the following investigation.

2.3. Characterization

The spray dried HA feedstock and plasma synthesized nano-HA powders were investigated by various advanced techniques. X-ray diffraction analysis (Philips vertical goniometer; generator: PW1830; Cu- K_{α} radiation) under the operating conditions of 30 kV and 20 mA was performed on the powders to determine the phase compositions. The spray dried HA was characterized at a 2θ -step size of 0.02° and 1 s per step. The nano-sized HA were analyzed at a step size of 0.01° and 2s per step. Thus, the analysis time of nano-sized powders is four times that of spray dried powders. Rietveld analysis was carried out to determine the quantity of amorphous phase in the nano-sized powders obtained. Details of Rietveld analysis can be found in a previous paper [18].

The morphology of samples was investigated in a SEM (JEOL 5600LV, Japan), a field emission (FE) SEM (JEOL 6340F) and a TEM (JEOL JEM 2010, Japan). The SEM samples were coated by gold to increase the conductivity in case of charging under SEM. In TEM analysis, the powders were first immersed in ethanol and ultrasonically agitated for a few minutes. Then, a standard copper grid with a carbon film was used to collect some of the small powders from the ethanol suspension. Finally, after drying at room temperature, the sample was directly observed in the TEM. DSC (Netzsch 404 with TASC 414/3A controller, Germany) was used to determine the phase transition temperature in the nano-sized HA powders. The powders were placed in an alumina (Al_2O_3) pan with cover and subjected to DSC measurements. The protective atmosphere of DSC was nitrogen (flowing rate: 150 ml/min) and the thermal cycle was as follows: heating to $900^{\circ}C$ at $10^{\circ}C/min$ followed by cooling down to room temperature at $20^{\circ}C/min$. The SBF solution used is a modified formulation proposed by Kokubo et al [29]. The in vitro test was conducted in a continuously stirred bath containing purified water with a stable temperature of $37^{\circ}C$.

3. RESULTS AND DISCUSSION

3.1. HA feedstock

The morphology of spray dried (SD) HA feedstock is shown in Fig. 1. It can be observed that the particle size of the powders is below $20\ \mu m$ ($\sim 15\ \mu m$) and the powders were predominantly spherical. Rough surface texture with a porous internal structure is formed in the SDHA due to the agglomeration of finer particles. The high level of porosity could be attributed to the extensive evaporation of liquid from HA agglomerate during the spray drying process.

XRD analysis proves that the feedstock is made up of HA phase. After heat treatment at 1000 °C for 5 h, the peaks of HT powders are sharper and stronger than those of spray dried powders (Fig. 2). No new phases are observed after heat treatment, which indicates that the SD HA feedstock is quite stable before entering the rf plasma flame. A typical TEM image of the raw powder is presented in Fig. 3, which shows that the powder consists of fine particles. The selected area diffraction (SAD) of these particles from the 'A' region (Fig. 3b) represents discrete rings showing that the diffraction consists of a large number of ultra-fine crystalline powder particles.

3.2. Rf plasma sprayed nano-sized HA powders

3.2.1. SEM morphology

In the rf plasma synthesis process, the HA feedstock was fed by Ar carrier gas, and injected into the high temperature plasma flame. As the powders entered the high temperature flame and accelerated towards the collection chamber, various phenomena occurred. First, there was the melting and evaporation of the surface of the feedstock. This was followed by the condensation of the evaporated materials into nano-particles. Fig. 4 shows a typical SEM micrograph of nano-sized HA powders obtained from rf plasma process. The powders are self-agglomerated into micrometer-sized clusters due to the size effect. It is difficult to clearly observe individual particles without using a high resolution SEM. The self-agglomerated powders are not very dense. There is an apparent lack of cohesion between the individual particles within the agglomerates and between different agglomerates. The result from SEM has shown that the rf plasma process can be used to produce nano-structured HA powders.

3.2.2. Phase analysis

As can be observed from the XRD pattern (Fig. 5), HA is preferentially dominated in the nano-sized powders. Apart from the HA phase, alpha-tricalcium phosphate (α -TCP) and calcium oxide (CaO) are also found in the powders, which confirm the decomposition of HA feedstock due to the high temperature of rf plasma flame. Two other peaks at about 38.4 ° and 44.7 ° (2θ) belong to aluminum (Al), which is the sample holder material.

A broad hump centered at about $2\theta = 29^\circ$ in the XRD pattern is attributed to an amorphous phase in the nano-sized HA powders. The amorphous phase is formed through the rapid solidification during rf plasma processing. Such amorphous phase that exists in the as-synthesized powders can be effectively transformed into the crystalline HA phase through post-spray heat treatment [12].

The decomposition of the HA during the plasma heat treatment can be described by

the following reaction:

α -TCP and CaO are the high temperature metastable phases. The formation of different phases in nano-sized powders is the main result of extremely high temperature and highly reactive atmospheres that favor non-equilibrium or metastable structures [19]. This is not uncommon particularly with non-equilibrium processes like thermal spraying. However, the consequences are more severe and less tolerable in biomedical application where such additional phases can induce unfavorable tissue response.

Referring to the XRD results (the main peak intensity of CaO) in Fig. 5, it can be seen that the nano-powders experiences significant decomposition at working plate power levels of 15 and 21 kW, respectively (with other working parameters kept constant), whereas there is no significant decomposition at 20kW.

The enthalpy of plasma flame is the primary driving force for the decomposition of HA. An increase in the working plate power adds to the energy of the plasma and in turn generates a higher flame temperature, leading to an increase in the extent of decomposition of HA powders in the plasma flame. However, it is important to emphasize that the plasma power level is related to the particle velocity. An increase in working plate power will also increase the plasma velocity, which in turn will increase particle velocity [20]. An increase in the particle velocity will decrease the resident time of HA feedstock in the flame, and as a result, the decomposition of the HA powders will decrease.

Accordingly, at a higher working plate power of 21 kW, significant decomposition of HA is obtained, due predominantly to the higher temperature of the rf plasma flame. However, a working plate power of 15 kW also causes significant decomposition, which is mainly attributed to the increased resident time of powders due to the low plasma velocity. Slight decomposition is achieved at a power level of 20 kW due to a combined influence of flame temperature and plasma velocity.

3.2.3. TEM morphology

Fig. 6 presents a TEM image of nano-sized HA powders. The network of ultrafine particles is actually composed of agglomerated nano-sized spherical particles. The particle size of nano-sized powders ranges from 10 to 100 nm. Some of the near-100 nm particles result from coagulation and coalescence of smaller ones prior to complete solidification. Particle coalescence occurs by concomitant solidification, the main driving force being the presence of adequate liquid phase and rapid quenching conditions [21].

High-resolution transmission electron microscopy (HRTEM) image in Fig. 7 shows the nano-sized particles contain a mixture of amorphous and crystalline phases. The lattice spacing in the crystalline phase is about 3.85 Å corresponding to the d-value of (111) plane in HA structure, which is referred in JCPDS 9-432. Fig. 8 presents morphology of boundary between the nano-crystallites and the amorphous phase in HRTEM view, and the crystallites constitute a transition step between the amorphous matrix and the well-ordered crystals. The unit cells show that the crystalline HA was oriented along <001> direction, which is the c-axis of HA structure. The formation of a large amount of interfaces between the nano-crystallites and amorphous phase has a significant influence on the transformation thermodynamics.

There are two hypotheses on the formation of crystalline HA phase. Firstly, due to the fluctuation of rf plasma temperature, the liquid or evaporated particle under-cools to the nucleation temperature before solidification initiated [22]. Then during rapid solidification, the nucleation of the under-cooled liquid grows to well-oriented nano-crystals with grain boundaries. These grains cannot nucleate near the melting point because there is insufficient driving force to overcome the solid–liquid surface energy barrier, and it also cannot grow at low temperatures because there is insufficient thermal energy to drive atomic diffusion [22].

Another possibility is that some of the crystalline HA is retained in the nano-sized powders due to the short duration of the feedstock in the plasma flame. From exactly the same orientation (Fig. 7), which indicates epitaxial crystallization [23,24], it seems more probable that the former is the main reason for the crystalline HA formation.

3.2.4. Analysis of phase changes by DSC

The DSC results of nano-sized HA powders at working power levels of 15, 20, and 21 kW are shown in Fig. 9. A slow exothermic tendency prevails from 200 to 640 °C and this is partially attributed to the difference in heat capacity between the amorphous phases and the Al₂O₃ reference [25]. At a working power of 15 kW, two exothermic peaks positioned at about 656.4 and 679 °C can be observed. These peaks at working power levels of 20 and 21 kW are positioned at 642.4 and 647.9 °C, respectively. All peaks lie on a slow exothermic rise and these peaks represent the crystallization of the amorphous calcium phosphate [26] arising from the uptake of the hydroxyl ions into the lattice of HA. Crystallization is such a transformation during which an amorphous phase crystallizes into one or more metastable crystalline phases. The driving force for the crystallization is the difference in Gibbs free energy between the amorphous and the crystalline states. The amorphous phase is in thermodynamical metastable state and it will transform into a more stable state under appropriate circumstances [27].

At a working power of 15 kW, the two exothermic peaks are partially overlapped. The first peak at a lower temperature of 656.4 °C contributes to a crystallization of hydroxyl-

rich amorphous region [25]. As subsequent crystallization occurs, the second peak at a higher temperature of 679 °C presents the diffusion of hydroxyl ions into hydroxyl-depleted regions. Gross et al. [25] have reported this phenomenon in transformation of amorphous phases in HA coatings. In plasma processing, the fast heating and high temperature attained in this process would cause hydroxyl removal and in turn would induce different regions, one is a hydroxyl-rich region and the other is hydroxyl-depleted or even oxy-rich region.

Through the determination of the area under the exothermic peak, the enthalpy of the phase changes can be ascertained. The calculated recrystallization energies of the nano-sized HA powders prepared at 15, 20 and 21 kW are 58.42, 52.77, and 60.16 J/g, respectively. It is expected that the enthalpy is positively related to the magnitude of the amorphous phase. The higher the melting enthalpy, the more will be the amorphous phase in the nano-powders [28]. The amorphous content in the nano-sized powders was indirectly calculated using crystalline alumina as an internal standard through Rietveld analysis, pattern fitting was performed and good result was obtained. The data at 20–70° fit well, and deviation from the calculated pattern was very small. The amorphous phase content of powders obtained at working power of 15, 20, and 21 kW were about 72, 68 and 75, respectively. These data indicate directly that amorphous phase content has a positively relation with the recrystallization enthalpy of phase transformation in the nano-sized powders, and the amount of amorphous phase formed can be modified by the working conditions of rf plasma flame.

3.2.5. In vitro behavior

The as-formed nano-powders were compacted through a hydrometric press at room temperature. After immersion in SBF for about 40 days, the sample was removed from the solution, cleaned in distilled water and dried in air. The surface morphology was examined via FE-SEM. As shown in Fig. 10a, the nano-particles were about 100 nm which is coincident with the results obtained from TEM. Before immersion, the nano-particles were only compacted together (Fig. 10b). On the surface of the compacted sample, fine apatite crystals were found to grow after immersion in SBF (Fig. 10c). Under higher magnification, it was found that the nano-structured network was in fact made up of finer (about 20nm) new apatite granules (Fig. 10d). The formation of new apatite crystal is mainly attributed to the high solubility of amorphous phase in the nano-particles. The presence of TCP also contributed to the growth of new apatite layer. The fast dissolution of amorphous phase and TCP would increase the Ca^{2+} and PO_4^{3-} in the SBF solution and thus result in the reprecipitate of calcium phosphate crystals. The formation of a layer of biologically active bone-like apatite on the surface of the nano-sized HA powders is an essential requirement for an artificial material to bond to living bone. It is expected that these nano-sized HA powders could be used in the following study with higher mechanical and higher bioactive properties.

4. Conclusions

Radio frequency plasma spray process, a new technique to produce nano-sized HA powders has been developed. Agglomeration of the nano-powders was found and the particle size of the nano-sized HA powder was in the range of 10–100 nm. Decomposition of HA phase into α -TCP and CaO was found. An increase in the working power led to different decomposition trends of HA feedstock, which was due to the combined influence of the rf plasma flame temperature and flame velocity. The high cooling rate resulted in the formation of amorphous phase in the synthesized nano-powders. DSC results showed that the exothermic enthalpies of the amorphous phase were positively related to the amorphous phase content in different nano-HA powders. Nano-structured networks was detected on the surface of nano-sized HA compacts after immersion in SBF.

ACKNOWLEDGEMENTS

Financial assistance in the form of research grant no. 012 101 034 from Agency of Science, Technology & Research (A*STAR), Singapore is appreciated.

REFERENCES

- [1] R.N. Correia, M.C.F. Magalhaes, P.A.A.P. Marques, A.M.R. Senos, *J. Mater. Sci. Mater. Med.* 7 (1996) 501–505.
- [2] M.C. Chang, J. Tanaka, *Biomaterials* 23 (2002) 3879–3885.
- [3] K.A. Khor, Z.L. Dong, C.H. Quek, P. Cheang, *Mater. Sci. Eng.* 281 (2000) 221–228.
- [4] K.A. Khor, P. Cheang, Y. Wang, *J. Therm. Spray Technol.* 7 (2) (1998) 254–260.
- [5] P.K. Chu, J.Y. Chen, L.P. Wang, N. Huang, *Mater. Sci. Eng.* R36 (2002) 143–206.
- [6] M.C. Kuo, S.K. Yen, *Mater. Sci. Eng.* C20 (2002) 153–160.
- [7] S.W.K. Kweh, K.A. Khor, P. Cheang, *Biomaterials* 23 (2002) 775–785.
- [8] Y. Han, K. Xu, G. Montay, T. Fu, J. Lu, *J. Biomed. Mater. Res.* 60 (2002) 511–516.
- [9] T.J. Webster, R.W. Siegel, R. Bizios, *Nanostruct. Mater.* 12 (1999) 983–986.
- [10] T.J. Webster, C. Ergun, R.H. Doremus, R.W. Siegel, R. Bizios, *Biomaterials* 21 (2001) 1803–1810.
- [11] S. Bose, S.K. Saha, *J. Am. Ceram. Soc.* 86 (6) (2003) 1055–1057.
- [12] P. Buchner, H. Schubert, J. Uhlenbusch, M. Weiss, *J. Therm. Spray Technol.* 10 (4) (2001) 666–672.
- [13] E. Bouyer, F. Gitzhofer, M.I. Boulos, *IEEE Trans. Plasma Sci.* 25 (1997) 1066–1072.
- [14] J. He, J.M. Schoenung, *Mater. Sci. Eng.* A336 (2002) 274–319.
- [15] R. Kumar, P. Cheang, K.A. Khor, *J. Mater. Process. Technol.* 113 (2001) 456–462.
- [16] R. Kumar, P. Cheang, K.A. Khor, *Biomaterials* 24 (2003) 2611–2621.
- [17] S. Koura, H. Tanizaki, M. Niiyama, K. Iwasaki, *Mater. Sci. Eng. A* 208 (1996) 69–75.
- [18] P. Cheang, R. Kumar, K.A. Khor, in: C.C. Berndt, K.A. Khor, E. Cugscheider (Eds.), *Thermal Spray 2001, New Surfaces for a New Millenium*, ASM International, Materials Park, OH, (2001) 28–30.
- [19] K.A. Khor, P. Cheang, *J. Therm. Spray Technol.* 3 (1) (1994) 45–50.
- [20] R. Ramasamy, V. Selvarajan, *Eur. Phys. J. D15* (2001) 229–235.
- [21] E. Bouyer, M. Muller, R.H. Henne, G. Schiller, *J. Nanopart. Res.* 3 (2001) 373–378.
- [22] B. Cantor, in: A.R. Dinesen, et al. (Eds.), *Proceedings of the Twenty Second Risø International Symposium on Materials Science*, Denmark, 2001.
- [23] H.J. Kleebe, E.F. Bres, D.B. Assolant, G. Ziegler, *J. Am. Ceram. Soc.* 80 (1)

- (1997) 37–44.
- [24] R. Baranwal, M.P. Villar, R. Garcia, R.M. Laine, J. Am. Ceram. Soc. 84 (5) (2001) 951–961.
 - [25] K.A. Gross, V. Gross, C.C. Berndt, J. Am. Ceram Soc. 81 (1) (1998) 106–112.
 - [26] C.F. Feng, K.A. Khor, Y.W. Gu, P. Cheang, Mater. Lett. 51 (2001) 88–93.
 - [27] K. Lu, Mater. Sci. Eng. R16 (1996) 161–221.
 - [28] H.J. Chung, E.J. Lee, S.T. Lim, Carbohydr. Polymers 48 (2002) 287–298.
 - [29] T. Kokubo, in: T. Yamamuro, L.L. Hench, J. Wilson (Eds.), CRC Handbook of Bioactive Ceramics, Vol. 1, CRC, Boca Raton, FL, 1990, pp. 41–49.

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Table 1 Experimental conditions for the rf production of nano-HA powders

(a)

(b)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

(a)

(b)

(c)

(d)

Figure 10

Parameters	Experimental
Central gas flow rate (slpm)	20
Sheath gas flow rate (slpm)	50
Carrier gas flow rate (slpm)	4.5
Plate voltage (kV)	4–6
Plate current (A)	1.8–3.5
Power (kW)	15, 20, 21
Feeder rotary speed (rpm)	10
Powders feed rate(g/min)	5.4
Chamber pressure (torr)	400
Probe distance (mm)	35

Table 1