Journal of Ceramic Processing Research. Vol. 14, No. 3, pp. 279~283 (2013)

J O U R N A L O F
Ceramic Processing Research

Carbon black sintering effects on the composition of multiphase calcium phosphate bioceramics

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The presence of carbonate (CO_3^{2-}) combined with calcium phosphates has been believed to increase the susceptibility of natural bone formation. This study was carried out to investigate the thermal properties of apatite in nano scale precipitates with added carbon black that could act as a sintering inhibitor and a carbonate preserver. In addition, the present study aimed to determine the effects of those additives and analyze their chemical compositions. Ceramics processed at different heating temperatures were compared and characterized. The results showed that a multiphase ceramic of apatite-calcium carbonate ($CaCO_3$)-calcium oxide (CaO) was formed in a temperature range of 600 to 800 °C. By observing the morphologies of the ceramics, the addition of carbon black which acts as a carbonate supplier in the heating processes and further as an inhibitor to prevent the sintering effect of the nano scale particles in sub-micro range efficiently at 1400 °C were established.

Key words: Ceramics, Composite, Chemical synthesis, X-ray diffraction, Phase transactions.

Introduction

To prevent the occurrence of allograft and xenograft and to limit the risk of cross contamination, synthetic bone substitutes are generally proposed for reconstructing bone defects. Calcium-related chemicals have been used extensively in periodontal defects [1] that act as scaffolds or bone fillers for bone reconstruction [2-5]. Hydroxyapatite (HA) is generally recognized as a bioconductive material which has the same mineral composition as bone and enamel. In general, the monophase calcium phosphate bioceramic has several drawbacks which are either due to its poor bioresorbability rates or its extremely high resorbable rates prior to novel *in vivo* bone-structure development [6-8]. The main concern in clinical applications is to determine whether a biomaterial is workable, which might be related to the materials' resorbability rate with developing bone. A strategic mixture of calcium phosphates, such as biphases, could maintain the bioconductive advantages of calcium phosphate ceramics while avoiding their disadvantages due to there unadjustable bioresorbability rate. Biphases, such as the popular biomaterials that are composed of HA and beta-tricalcium phosphate (TCP), are generally prepared as blocks, granules or powders and have already proven their efficiency as bone substitution materials in different human applications [9-12].

The alkaline aqueous chemical wet-synthesis method is suitable for producing fine and evenly distributed nano-particles (below 100 nm) with relatively low amounts of crystalline precipitates of high Ca/P molar ratio. Multiphase materials with high calcium-to-phosphous (Ca/P) ratios enhance bone regeneration and reconstruction by releasing high concentrations of Ca^{2+}, phosphate and CO_3^{2-} ions into the surrounding biological medium. *In vivo*, the formation of carbonatehydroxyapatite (CAP) on the surfaces of calcium phosphate fillers at the bone-particle interface is thought to be a cell-mediated dissolution and precipitation process [13]. In addition, Ca^{2+}, phosphate, Mg^{2+}, and CO_3^{2-} ions from the medium are incorporated into CAP crystals that form an intimate association with an organic component. This process leads to bone formation. Practically, it means that Ca^{2+}, phosphate combined with CO_3^{2-} ions dissolved from the biomaterials could play an important role in the formation of natural new bone. An aqueous chemical synthesis method applicable for high alkaline ions solution has been well established for the preparation of high calcium-to-phosphous (Ca/P) ratio and poorly crystallized precipitates. The present study focuses on characterizing the thermal stability and phase transformations of these precipitates with carbon black during the heating process.

Materials and Methods

The following chemicals were used: calcium acetate ($Ca(C_2H_3OO)_2$) (purity 98%, Showa Chemical Co., Japan), potassium phosphate n-hydrate ($K_3PO_4nH_2O$)

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(98%, Katayama Chemical Co., Japan) and potassium hydroxide (KOH) (85%, Osaka Chemical Co., Japan). To prevent the powders from sintering and evaluate the carbonate preservation ability, carbon black (99%, CSRC, Kaohsiung, Taiwan) with an average diameter of 20 nm was used.

The particles of stable and homogeneous precipitates with a high Ca/P ratio were prepared according to the modified protocols of the study [14]. Briefly, 0.2 mole $Ca(C_2H_3OO)_2$ and 0.1 mole $K_3PO_4 \cdot nH_2O$ were dissolved in de-ionized water to make 0.67 M Ca^{2+} 300 ml and 0.14 M phosphate 700 ml ions solutions, respectively. Under continuous stirring, the Ca^{2+} solvent was added to the phosphate ion solvent over a 10-minute period. Continuously monitoring pH value of the solution was performed and the pH value was kept at 12.0 and the temperature at 25 °C for 3 h. To stabilize the pH values, the processes were dynamically adjusted by adding 0.1 M KOH. Then, the precipitates were immediately vacuum-filtered, washed with 3 l of de-ionized water and dried. To study the effects of temperature and the carbon black additive on the phases of the resultant ceramics, the precipitate powders were mixed with carbon black before heating at a 1 : 1 weight ratio of carbon black to the precipitate. For carbon black pyrolyzed below 400 °C, a set of heating temperatures of 400, 600, 800 and 1400 °C was chosen and the heating rate was 10 Kminute^{-1}. After the respective temperatures were reached, the samples were immediately quenched to room temperature (25 °C). Ten replicate specimens were prepared and analyzed for each process in this study.

The powder samples from different temperatures were prepared for X-ray diffraction (XRD) characterization that was carried out at 30 kV, 20 mA and 1 °minute^{-1} in a Rigaku D-max IIIV. A Fourier-transform infrared spectroscopy (FTIR) system (Jasco, FT/IR-460 Plus, USA) with a spectral resolution of 2 cm^{-1} was used in transmission absorption mode. In order to study the morphological and Ca/P atomic-ratio changes after different temperature processes, non-dispersed and dispersed powders (produced by ultrasonic treatment in ethanol for 20 minutes) of the samples were examined using a field-emission scanning electron microscope (SEM, Hitachi S-4100, Hitachi, Tokyo, Japan) and a scanning transmission electron microscope (STEM, JEOL JEM-3010, Japan) which was equipped with an energy dispersive spectroscopy (EDS) system. A one-way ANOVA method was used to evaluate the statistical significance. Results were considered statistically significant if $p < 0.05$.

Results and Discussion

The mixed phases of high Ca/P atomic-ratio precipitates were obtained from reactions of ions in solution. The end products of the reactions of ions in solution used in this study were powders of precipitates with a high Ca/P ratio of 1.93 ± 0.10 (mean ± S.D., n = 10). The sizes of the precipitates were generally in the range of below 100 nm and were globular biphase particles. The precipitate of $CaCO_3$ (approximately 17 molar percent) combined with apatite was clarified through XRD and FTIR. Such a high solubility of the precipitate which resulted in high ion concentrations within aqueous solutions would be expected to play an important role in the process of natural new bone regeneration [13]. Comparing with the commercial product of Norian® SRS, the powder is composed of TCP, $CaCO_3$ and monocalcium phosphate monohydrate (MCPM), of which the highly resorbable $CaCO_3$ and MCPM phases comprise about 15%. The precipitates in this study had the near composition of the highly resorbable phases and had the potential as restorative fillers. However, the experimental results showed that these high Ca/P atomic-ratio precipitates had elevated reactivity with moisture and could not be sterilized through the steam method with an autoclave. That was why we needed to evaluate the thermal stability of this aqueous chemical synthesis precipitates which would be applied in a sterilization process for further applications. Figure 1 shows the dominant broad diffraction peaks of apatite (2θ) at 25.9 ° and 31.8 ° due to the presence of the precipitates. The crystallization of the apatite increased gradually as the processing temperature increased up to 800 °C. Beyond 800 °C, the apatite was completely transformed into a monophase ceramic of TTCP at 1400 °C. It was observed that a multiphase ceramic of $CaCO_3$ (104)/(2θ = 29.4 °) and CaO (111)/(2θ = 32.3 °) with apatite was formed at a transition temperature of 600 °C. According to the patterns shown in Fig. 1, an

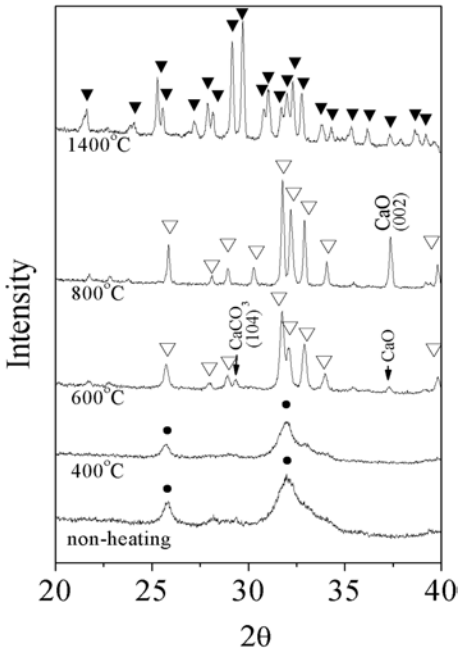

Fig. 1. Variation in XRD patterns at different heating temperatures. ● : apatite; ▽ : HA; ▼ : TTCP.

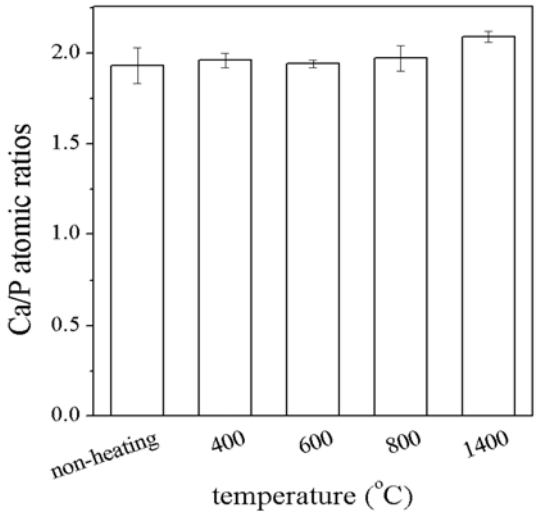

Fig. 2. Ca/P molar ratios of powders with heat treatment. (n = 10; $p > 0.05$).

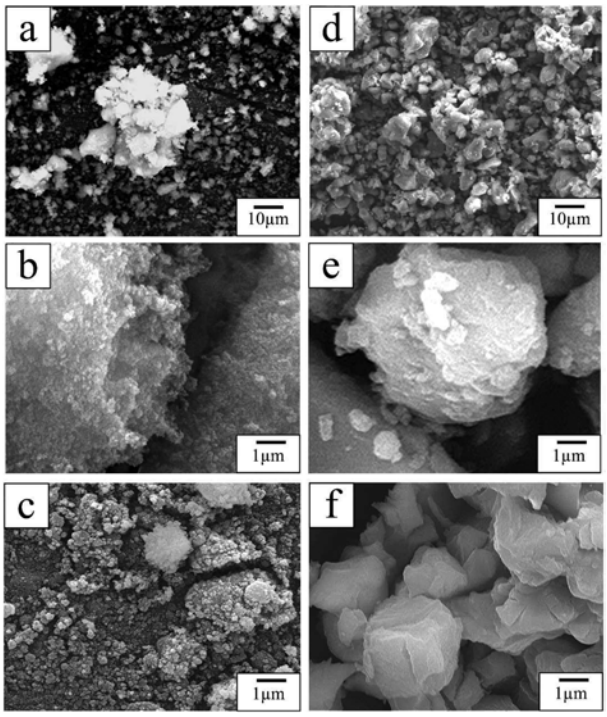

Fig. 3. Variation in morphologies of precipitates mixed with carbon black (a), (b) and (c); after 1400 °C sintering temperature of (d), (e) and (f). (b), (e): non-dispersed; (c), (f): dispersed powders.

apatite-CaO biphase without $CaCO_3$ was formed at 800 °C.

The Ca/P atomic ratios of the ceramics formed by heating at 1400 °C were 2.09 ± 0.03 (Fig. 2). There were no statistically significant differences ($p > 0.05$) between the Ca/P atomic ratios of particles subjected to different heating temperatures. This result suggested that phase transformations of the heating processes had no Ca or P atoms bonded directly to carbon black which was vaporized through heat generation.

The original dispersed sizes of these globular-like particles were placed in ethanol under ultrasonic

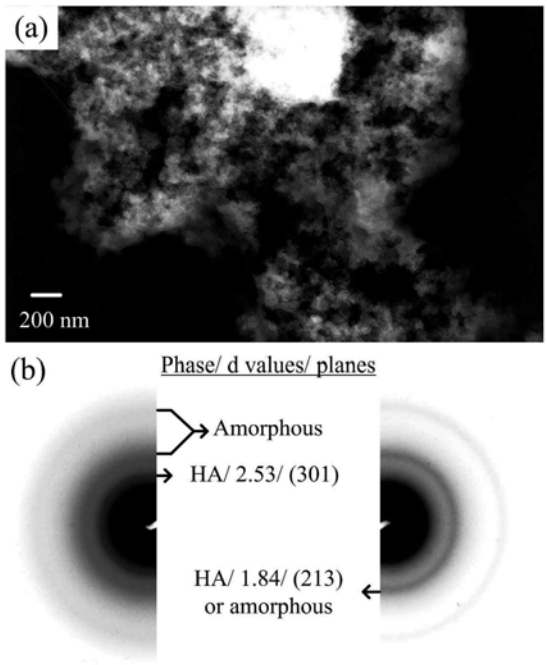

Fig. 4. Bright field (BF) image of precipitates mixed with carbon black (a) and respective SAD patterns with indices (b).

treatment for 30 minutes and then evenly distributed below 100 nm (Fig. 3a-c). The morphologies of the mixtures with carbon black sintered at 1400 °C were revealed, as shown in Fig. 3d-f. A cluster of granular-like particles was formed, and the granular sizes were in the range of sub-micro to about one micro after sintering.

Figure 4 shows the typical morphology and electron diffraction pattern of an as-fabricated, mixture of precipitates and carbon black. As shown in the bright field (BF) image, clustered nanoparticles were observed. The selected-area diffraction (SAD) pattern and its indices (Fig. 4b) clearly show that the typical SAD patterns in different zones showed nanoparticles having either crystalline of apatite-dominant or an amorphous phase of carbon black. The particle sizes through the sintering processes had made larger particles (sub-micro scales) to the non-sintering precipitates (nano scales).

The width at half height of the XRD peaks is related to the dimensions of the perfect crystalline domains and/or strain. The broadened XRD peaks of apatite (25.9 ° and 31.8 °) at high temperature indicated a poor crystallinity level of apatite. The band at approximately 890 cm^{-1} of the FTIR spectrum was attributed to the HPO_4^{2-} groups of apatite at heating temperatures less than 400 °C [18]. The phases other than apatite, i.e., $CaCO_3$ and CaO, made the Ca/P ratios of the elemental analyses appear to be larger than the value of 1.67 of stoichiometric HA (s-HA). The potential rate of such a high Ca/P ratio materials in the initial precipitates excluded from s-HA was about 16% molar percentage. Although the diffraction pattern of $CaCO_3$ was not

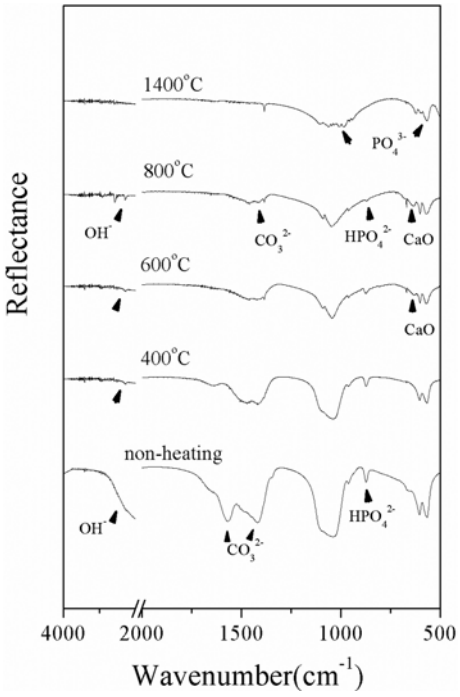

Fig. 5. FTIR absorption spectra of different heating temperatures.

clearly observed by XRD (Fig. 1), the FTIR absorption bands of CO_3^{2-} clearly appeared, as shown in Fig. 5, with the exception of the sample treated at 1400 °C. The presence of CO_3^{2-} at heating temperatures less than 400 °C indicated that these powders could be a mixture of $CaCO_3$ with apatite or that a CAP was present.

The XRD patterns of samples subjected to heating temperatures between 600-800 °C had clear distinct shapes, indicating that a higher degree of crystallinity was present in the phases. The peak corresponding to $CaCO_3$ of (104)/(2θ = 29.4 °) had disappeared and the CaO of (111)/(2θ =32.3 °) increased for the 800 °C XRD pattern. This phenomenon suggested that the existing phase of CaO at 600-800 °C was caused by the thermal decomposition of $CaCO_3$ in the heating process and lost the CO_3^{2-} preservation ability at temperature higher than 800 °C. For carbon black pyrolyzed below 400 °C, the phenomenon preserves the carbonate de-participation from the ceramics at a temperature range not higher than 800 °C.

In order to enhance the bioresorbability rate of the ceramics, a fine particle size distribution is necessary [19]. Fine particles are known to be very sensitive to heat, especially at nano scales. High temperatures can cause the grains to sinter and grow which typically cause material diffusion [20]. Addition of carbon black not only inhibited grain growth within the fine particles by atomic diffusion but also provided an atmosphere full of CO_2 to prevent the pyrolysis of $CaCO_3$. As shown in Fig. 3, this effect was clearly seen at 1400 °C. A biphase or multiphase product phase of the calcium relationships, in which one phase were composed of $CaCO_3$ or CaO was derived from such a simple wet and sintering synthetic process. There was easy absorption by the natural tissue versus the opposite bone resorption rate for the sintered natural bone mineral of a bovine origin with basic phases, such as an HA or an HA/TCP [21].

The crystallization properties, mixed phases and powder size distributions of restorative fillers all determine whether such biomaterials can be used in clinical applications. For example, if the solubility of the filler for dental restoration is too low, diffusion of ions such as Ca^{2+}, PO_4^{3-}, HPO_4^{2-} and CO_3^{2-} into the deeper regions of the lesion would be prevented, thus thwarting the full bonding or remineralization to the natural tissues of the alveolus bone or tooth. High Ca^{2+} concentration compounds, such as CaO, $Ca(OH)_2$ and $CaCO_3$ have high bioresorbability rates and create high concentrations of Ca^{2+} that can enhance new bone regeneration as they release largely Ca^{2+} ions into the biological medium [22]. Besides, high calcium atomic chemicals such as CaO and derived $Ca(OH)_2$ are currently used in dentistry for endodontic treatment where their main advantage consists of their antibacterial and anti-inflammatory potency. However, they also have some drawbacks such as pulp necrosis and retraction on drying [23]. The presence of calcium hydroxide a priori confers antibacterial properties to this multiphase bioceramics. The study showed the restorative material could enhance the bacterial growth inhibition which was observed for materials with higher Ca/P atomic ratios (≥ 2.0) against the other materials with lower Ca/P ratios [23]. Thus, this effect makes our recent development of the apatite-$CaCO_3$-CaO multiphase ceramic very practical and is therefore a potential candidate for pulp capping and cavity lining. According to the implant position in clinical trials, those skilled in the art may adjust the ratio of the product phase of the invention to improve the restorative fillers.

Conclusions

A multiphase ceramic of apatite-$CaCO_3$-CaO by thermal treatments at temperatures between 600-800 °C was developed that was derived by a wet chemical synthesis. This newly developed and easily manufactured bio-ceramic material could replace the fillers currently used in restorative dentistry and orthopaedic clinical practice. To preserve the particle dimensions in the heating process, we added carbon black which was effective in preventing sintering among particles.

Acknowledgments

The authors acknowledge, with appreciation, support for this research from the National Science Council of the Executive Yuan, Taiwan. (97-2221-E-037-006; 99-2314-B-037-051-MY3).

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