JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **13** (2002) 307–310

Effect of calcinations of starting powder on mechanical properties of hydroxyapatite–alumina bioceramic composite

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The effect of calcinations of starting powder on the mechanical properties of hydroxyapatite (HA)-based bioceramic composite was investigated. The calcinations of HA powder in air at 900 °C increased the crystallinity as well as the size of the powder. Ball milling after the calcinations was effective in eliminating large agglomerates in the powder. When the powder was mixed with reinforcing Al_2O_3 powder, the mixture became fine and homogeneous. The flexural strength of HA–Al_2O_3 composite was increased by the calcinations processes at all the Al_2O_3 concentration. However, the fracture toughness was not much influenced by the calcinations. These results lead to the conclusion that the calcinations process effectively reduced the critical flaw size in the body by removing the agglomerates in the HA powder.

1. Introduction

Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is potentially very useful as a substitute material for human teeth or bones because of its crystallographical and chemical similarity with them [1, 2]. The biocompatibility of this ceramic is good enough that, when used as an implant material, it forms a direct bonding with the neighboring bones. However, poor mechanical property of this bioceramic is one of the most serious obstacles for wider applications [3]. Accordingly, there has been much effort to improve the mechanical properties of the HA.

The mechanical properties of ceramics have been improved significantly by additions of strong reinforcing agents. To be effective as a reinforcing agent for a ceramic–matrix composite material, the strength and the elastic modulus of the second phase must be higher than those of the matrix [4]. In addition, the reinforcement should be chemically compatible with respect to the matrix. Furthermore, the coefficient of thermal expansion (CTE) of the reinforcing agent should be close to that of the matrix to avoid the formation of microcracks around the second phase during cooling after the densification [5]. To be used as a reinforcing agent for the HA, the biocompatiblity of second phase should be considered most importantly.

Various reinforcing agents have been employed before to improve the mechanical properties of the HA. Among those, alumina is one of the most widely investigated materials as reinforcement. When large alumina platelets were added, the fracture toughness of HA increased [6]. However, the improvement in strength was minimal because of the formation of microcracks around the platelets due to the large difference in the CTE between the Al_2O_3 and the HA. On the other hand, when fine Al_2O_3 powder was used as reinforcement, the strength increased steadily with increasing the amount of Al_2O_3. In this case, however, further improvements in mechanical properties were hindered because of the incomplete mixing and the excessive reaction between HA and Al_2O_3 [7–9].

Therefore, to improve the mechanical properties of HA-based composite, it is necessary to improve the mixing process as well as to suppress the reaction between HA and Al_2O_3. In the present research, we calcined the starting HA powder before mixing with Al_2O_3 powder. By the calcination process, the HA became more stable via complete crystallization and grain growth. Agglomerates in the powder were effectively removed by the ball milling after the calcination. The effect of calcination on the mechanical properties, flexural strength and fracture toughness, of the HA–Al_2O_3 composite was measured and correlated with the changes in composition and morphology of the material.

2. Experimental procedure

Starting materials were commercial $Ca_{10}(PO_4)_6(OH)_2$ (HA: Alfa Aesar Co., Ward Hill, MA, USA) and Al_2O_3 (HP-DBM, Reynolds, Bauxite, AK, USA) powders. The HA powder has a specific surface area of 68 m^2/g by BET measurement. SEM observations showed the

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powder was severely agglomerated. According to inductively coupled-plasma atomic-emission spectroscopy (ICP-AES; ICP Q-1000, Shimadzu, Kyoto, Japan) analyses, the Ca/P ratio of the powder was 1.64, indicating slight deficiency of Ca compared to stoichiometric HA (Ca/P = 1.67). The Al_2O_3 powder has a purity of 99.97% with key impurities of Na_2O ($< 0.018\%$) and Fe_2O_3 ($< 0.012\%$). The Al_2O_3 had an average particle size of 0.35 μm and the surface area of $12\,m^2/g$ by BET measurement.

The HA powder was calcined in air at 900 °C for 4 h. Changes in size and morphology of the powder were monitored with a scanning electron microscopy (SEM, XL-20, Philips, Nijmegen, Netherlands) and a transmission electron microscopy (TEM, JEM-200CX, JEOL, Tokyo, Japan). The crystallinity and the size of the powder were characterized by X-ray diffraction analysis (XRD, M18XHF22, Mac Science Co., Yokohama, Japan) and BET measurement.

Up to 40 vol % of Al_2O_3 were added to HA powder and mixed by ball milling in ethanol for 36 h using alumina ball as media. The slurry was dried by evaporating the ethanol on a hot plate. Mixed powders were hot pressed in a graphite mold at 1200 °C for 2 h in Ar atmosphere with an applied load of 30 MPa.

The hot-pressed discs were sliced with a diamond saw to produce flexure bars with dimensions of $25 \times 4 \times 3\,mm^3$. The prospective tensile surface was polished with 1 μm diamond paste and edges were chamfered to eliminate machining flaws that could act as fracture origins. Flexural strengths were measured at room temperature in air by four-point flexure configuration with inner and outer spans of 10 and 20 mm, respectively. The fracture toughness was determined by measuring the crack length generated when the polished surface was indented with a Vickers indentor with an applied load of 49 N [10].

3. Results and discussion

Specific surface area of as-received HA powder measured by the BET method was $68\,m^2/g$, implying the powder is very fine. When calcined at 900 °C for 4 h in air, the surface area was reduced to $16\,m^2/g$. The change in particle size is well observed in the TEM micrographs in Fig. 1(A) and (B). Before the calcination, the primary particle of HA was extremely small and agglomerated, as shown in Fig. 1(A). Such agglomerates are known to be very difficult to disperse due to its extremely small particle size. When the powder was calcined in air, the particles became larger but still agglomerated, as shown in Fig. 1(B). However, such agglomerates (composed of large particles) are relatively easily separated by subsequent ball milling processes.

The effect of calcination was also observed in XRD patterns in Fig. 2. Before the calcination, the peaks of the powder were broad as seen in Fig. 2(A), implying that the powder was extremely small and/or incompletely crystallized. After calcination, the peaks became sharp and narrow, Fig. 2(B), indicating that the powder was completely crystallized with appreciable size.

The calcination effect on the mechanical properties of the HA–Al_2O_3 composite is shown in Figs 3 and 4. With addition of Al_2O_3, the strength of HA increased steadily regardless of the calcination process as shown in Fig. 3. Increases in strength by the addition of Al_2O_3 powder have also been observed previously. However, the strength was further improved whenever the calcined HA powder was used for the composite. Such an improvement was attributed to the homogeneous mixing of the Al_2O_3 with the HA powder via eliminating the large agglomerates in the matrix. Reduction in surface area of HA is deemed to have a positive effect on the strength by suppressing the reaction between HA and Al_2O_3.

The fracture toughness of the HA was also increased by the addition of the Al_2O_3 particles, as shown in Fig. 4. However, different from the case of strength, the calcination had negligible effects on the fracture toughness. The strength (σ_f) and fracture toughness (K_{IC}) of a material have following relationship:

$$\sigma_f = \frac{K_{IC}}{Yc^{1/2}}$$

where Y is the geometric factor and c is the length of most severe crack in the material. Observed increases in strength and negligible changes in fracture toughness, in Figs 3 and 4, respectively, indicate that the calcination process actually reduced the crack size in the system.

SEM micrographs of the specimen support this interpretation. The fracture surface of the specimen fabricated with HA powder without the calcination process is shown in Fig. 5(A). As clearly shown in this

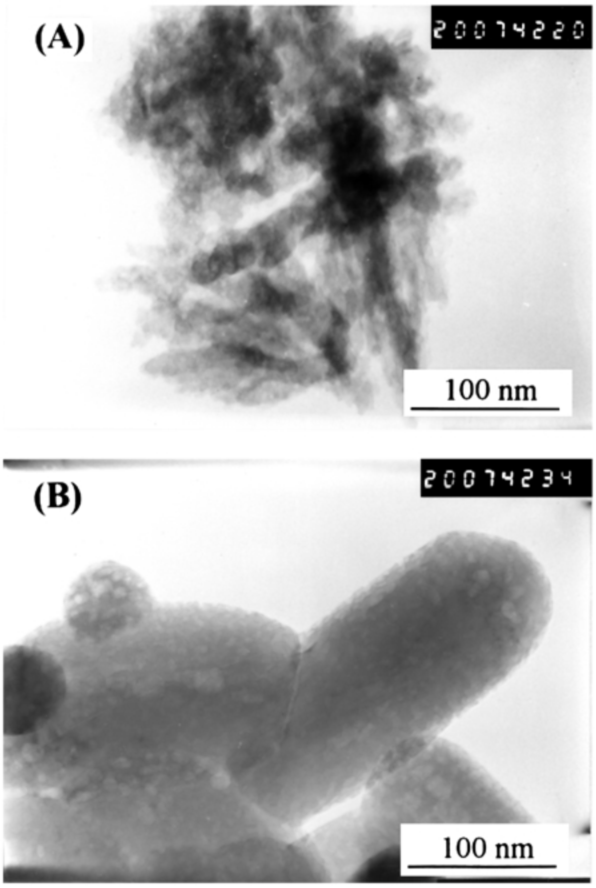

Figure 1 TEM micrograph of HA powder; (A) before calcination, (B) after calcination at 900 °C in air for 4 h.

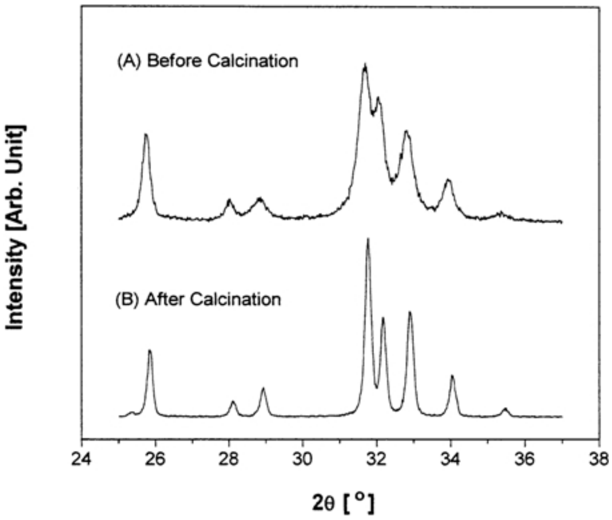

Figure 2 XRD patterns of HA powder; (A) before calcination, (B) after calcination at 900 °C in air for 4 h.

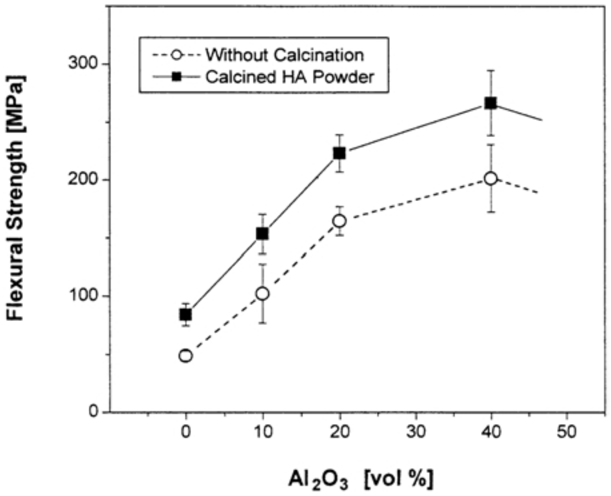

Figure 3 Effect of calcination on the flexural strength of HA–Al_2O_3 containing different amounts of Al_2O_3. Error bars represent ± 1 standard deviations.

micrograph, the fracture surface is rough and corrugated, indicating non-uniform composition in the body because of the agglomerates in the HA powder. On the other hand, when the specimen was fabricated using the calcined HA powder, the fracture surface was relatively flat as shown in Fig. 5(B). Generally, when the microstructure of a material is fine and homogeneous without residual stress, the chance for crack generation is low, so that the strength of the material becomes high. On the other hand, when the microstructure is non-uniform, the fracture toughness is enhanced because of the inhibition of crack propagation by the microstructural non-uniformity. In the present system, the observed identical fracture toughness of the specimens regardless of the calcination process, therefore, is deemed to be a consequence of combined effects of compositional and the microstructural factors.

4. Conclusions

The flexural strength of HA–Al_2O_3 composite was improved by the calcination of HA powder before mixing with reinforcing Al_2O_3 powder. Calcination in air and subsequent ball milling were effective in eliminating the agglomerates in the HA powder. As the agglomerates were removed from the HA powder, the microstructure of the HA–Al_2O_3 composite became more uniform and homogeneous. The strength of the composite was enhanced at all the Al_2O_3 concentration as a result of this improvement in microstructure and composition.

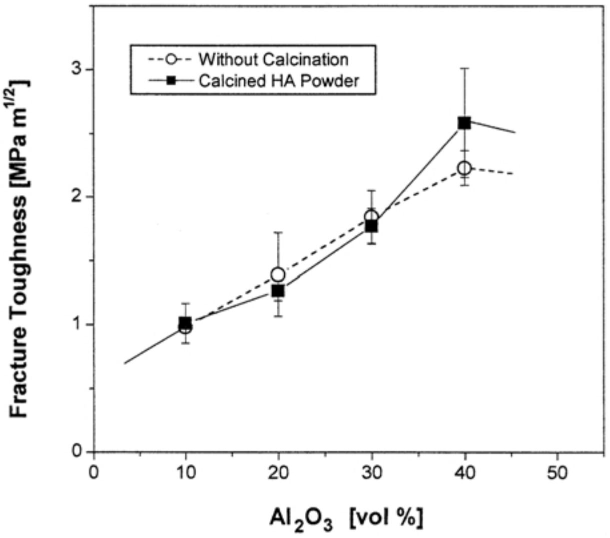

Figure 4 Effect of calcination on the fracture toughness of HA–Al_2O_3 containing different amounts of Al_2O_3. Error bars represent ± 1 standard deviations.

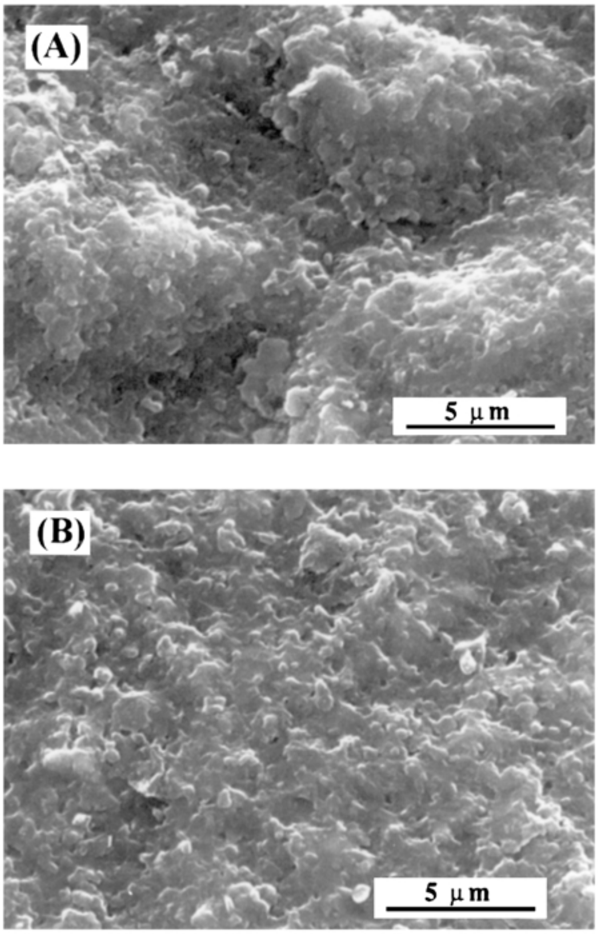

Figure 5 SEM micrographs of HA–40 vol % Al_2O_3 composite hot pressed at 1200 °C using HA powder of (A) before calcination, (B) after calcination at 900 °C in air for 4 h.

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Received 24 April 2000
and accepted 29 June 2001