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Short communication

Effect of fluoride additive on the mechanical properties of hydroxyapatite/alumina composites

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Abstract

The effect of fluoride additives on the mechanical properties of hydroxyapatite/alumina composites was investigated. When MgF_2 (5 vol%) was added to hydroxyapatite/alumina composites, the decomposition of hydroxyapatite was suppressed due to the substitution of F^- for OH^- in the crystal structure. Comparing two additives, such as MgF_2 and CaF_2, MgF_2 showed much more effective for the suppression of phase decomposition in the hydroxyapatite/alumina composites due to the enhanced substitution of F^- for OH^-. In the case of MgF_2 addition, a relatively high-mechanical properties (flexural strength: ~170 MPa; Vickers hardness: ~7 GPa) was obtained compared to MgF_2-free composites.

Keywords: Hydroxyapatite/alumina composites; Fluoride; Mechanical properties

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is the most promising materials for bone replacement because of its osteoconductive and bio-compatibility properties. However, HAp application is limited at the low-stress region due to a relatively low-mechanical properties and a high-dissolution rate [1–3]. Focusing on the crystal structure modification of HAp, it has been studied that these disadvantages can be eliminated by the ion substitutions of Ca with Mg^{2+}, Sr^{2+}, and Ba^{2+} [4]. Among ion substitutions, Mg^{2+} is known as the most promising dental caries-promoting element due to a high-initial calcification process in the bone formation. The deficiency of Mg^{2+} resulted in the degradation of bone structure, the inhibition of bone growth and also decrease of osteoblast adhesion [5]. If the reinforcing agent such as alumina and zirconia is added, the mechanical properties is reduced due to the phase decomposition from HAp to TCP ($Ca_3(PO_4)_2$) [3]. When we added a fluoride compound, the phase decomposition is reduced because fluoride ions promote the stabilization of HAp crystal structure. The purpose of this study is aimed to evaluate the effect of fluoride ion on the mechanical properties and the inhibition of phase decomposition of HAp. To observe the effect of fluoride ion, we added calcium fluoride and magnesium fluoride into the HAp.

2. Experimental procedure

As a starting powder, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, Samjo Co., Korea) and alumina (AKP50, purity >99.999%, <0.3 μm, Sumitomo, Japan) were used. Fluoride compound was synthesized using the mixing of magnesium nitrate (purity >99%, Aldrich Chemical, USA) and calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$, purity >99.99%, Aldrich Chemical, USA) with fluoric acid. The formation of fluoride compound was confirmed with XRD and EDS. The amount of alumina was fixed to 20 vol% and the addition of fluoride compound was varied (0, 2.5, and 5 vol%). After weighing the powder, the ball-milling with Si_3N_4 ball was carried out for 24 h, and then dried in an oven for 24 h. The composition of powder mixture was indicated in Table 1. Powder mixtures were mold in a die and then cold isostatically pressed at 30,000 psi. The green compact was sintered at various temperatures (1250–1450 °C) for 2 h. Densification behavior was evaluated with dilatometer (DIL 402C, Netzsche, Germany) up to 1450 °C. Phase change was identified with X-ray diffraction pattern and FT-IR (EQUINOX

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Table 1
Specimen notation of HAp with addition of CaF_2 and MgF_2

Notation	Composition
HA	HAp + 20 vol% Al_2O_3
HA-2.5C	HAp + 20 vol% Al_2O_3 + 2.5 vol% CaF_2
HA-5C	HAp + 20 vol% Al_2O_3 + 5 vol% CaF_2
HA-2.5M	HAp + 20 vol% Al_2O_3 + 2.5 vol% MgF_2
HA-5M	HAp + 20 vol% Al_2O_3 + 5 vol% MgF_2

55, Bruker, Germany). Microstructure was observed with Scanning Electron Microscopy (LEO 420, Leo, England). Mechanical properties of specimen were evaluated by four-point flexural strength with a cross head speed of 0.5 mm/min and micro Vickers hardness tester at a load 1.96 N for 10 s. The dimension of mechanical test specimen was 3 mm × 4 mm × 40 mm and the inner span and outer span were 10 and 30 mm, respectively.

3. Results and discussion

Fig. 1 shows the XRD pattern of HAp composite sintered at 1400 °C. In the HAp composite, the formation $CaAl_2O_4$ and $CaAl_4O_7$ phase was observed due to the reaction between Ca and alumina. Such a new phase formation was related to the phase transition from HAp to β-TCP and α-TCP. In the HA-5M specimen (5 vol% MgF_2), phase transition was fully inhibited and the formation of $MgAl_2O_4$ was observed. In the HA-5C specimen (5 vol% CaF_2), however, phase transition was occurred. In the case of HA-2.5C specimen, the formation of $MgAl_2O_4$ and calcium aluminates compound was observed, simultaneously. Compared to phase analysis between HA-5M and HA-5C, the addition of MgF_2 is more effective for the inhibition of phase transition.

Fig. 2 shows the analysis of FT-IR result, which was carried out for the identification of ion substitution between OH and F. In the HA-5M, Mg–O–Al peak was observed in the vibration range of 600–900 cm^{-1}. In the HA-5C, Ca–O–Al peak was observed in the vibration range of 437–930 cm^{-1}. Both specimens as shown in Fig. 2(a), F–OH bond (3535 cm^{-1}) was observed due to the ion substitution between OH and F. When the temperature was increased up to 1400 °C, however, F–OH bond peak was disappeared in HA-5M specimen, as shown in Fig. 2(b). These results indicate that the F ion substitution content in HA-5M is much higher than HA-5C due to the lower dissociation temperature of MgF_2.

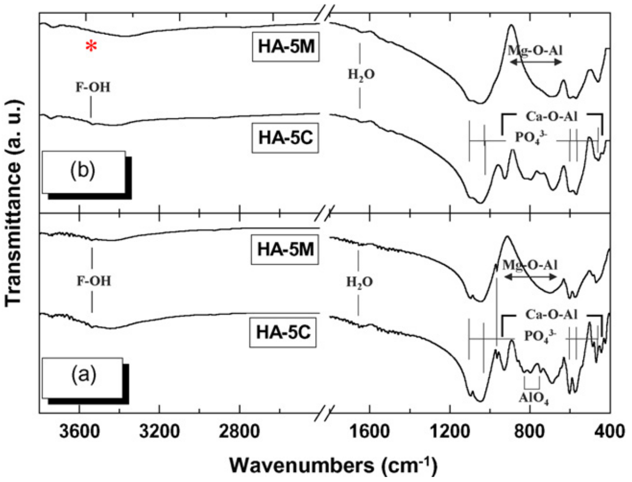

Fig. 2. FTIR analysis of HA composites with sintered at (a) 1300 °C and (b) 1400 °C.

Fig. 3 shows the variation of linear shrinkage of HAp composites up to 1500 °C. With the addition of MgF_2, much higher densification rate was obtained compared to the addition of CaF_2. Both composites showed the first shrinkage behavior at 700 °C due to the crystallization of HAp. In contrast of HA-5C showed normal shrinkage behavior, HA-5M showed rapid shrinkage behavior due to the dissociation of MgF_2. But the shrinkage rate of HA-5C compared to HA-5M from 1250 °C was increased due to the formation of $MgAl_2O_4$ phase near by 1000 °C. However, shrinkage rate at 1457 °C was reversed due

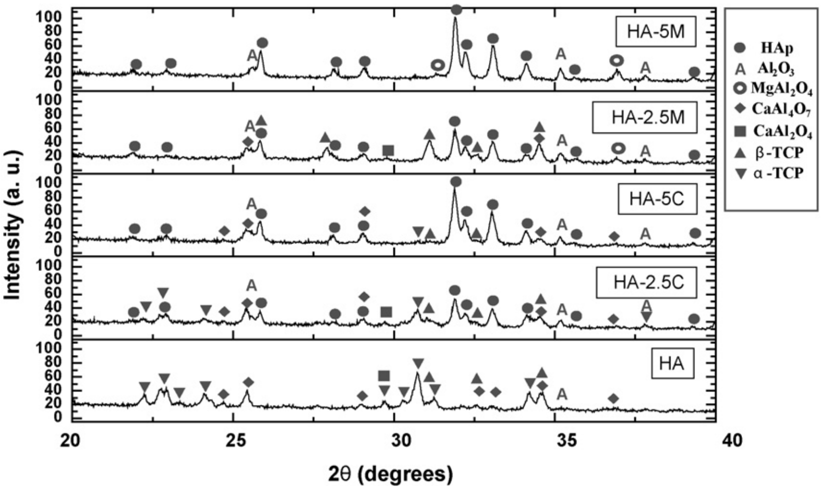

Fig. 1. X-ray diffraction analysis of HA composites sintered at 1400 °C.

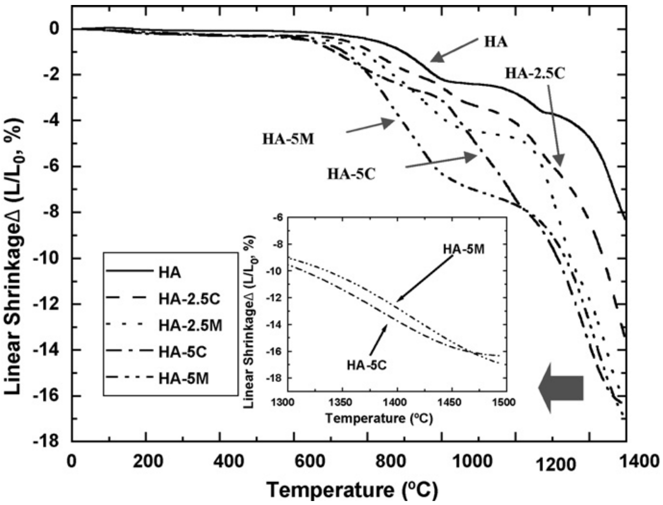

Fig. 3. Variation of linear shrinkage with respect to sintering temperature.

to the high-formation rate of fluoride apatite because of high-liquid-phase content.

Fig. 4 shows microstructures with CaF_2 and MgF_2 sintered at 1400 °C. When MgF_2 was added, a relatively high-densified composite was obtained (Fig. 4(b) and (d)). Sintered microstructures showed a high-densification behavior with increasing the F content (HA-5M > HA-5C > HA-2.5M > HA-2.5C). Fig. 5 shows the mechanical properties of HAp composites. With increasing the sintered temperature, mechanical properties was increased. Compared to the HAp monolith (flexural strength: ~70 MPa; Vickers hardness: ~2 GPa), HAp composites (HA-5M) showed an enhanced mechanical properties (flexural strength: ~170 MPa; Vickers hardness: ~7 GPa). Considering the mechanical properties of tooth enamel (flexural strength: 160–180 MPa; Vickers hard-

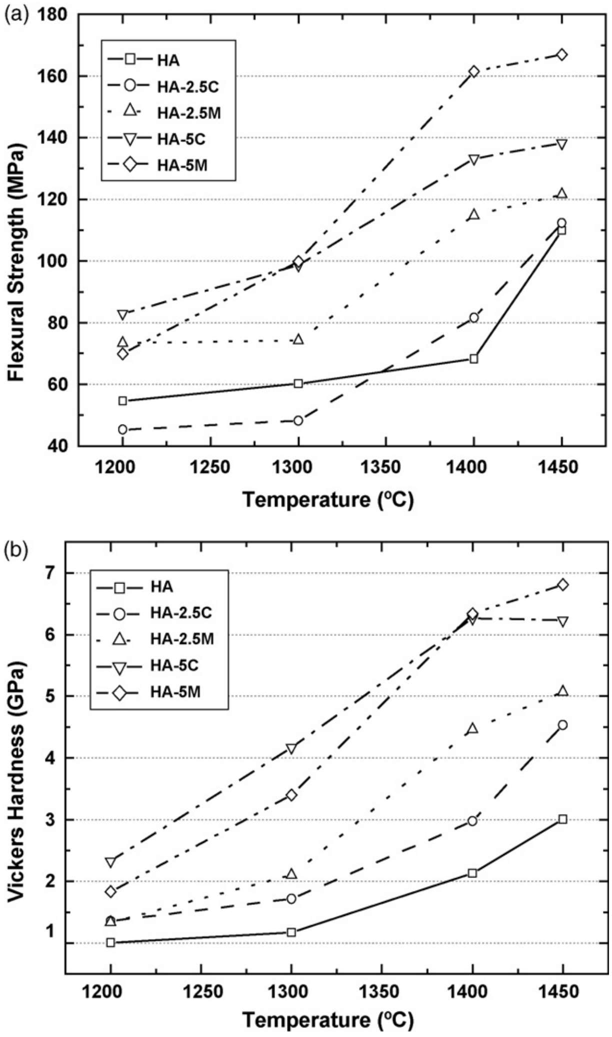

Fig. 5. Variation of mechanical properties of specimens with respect to sintering temperature: (a) flexural strength and (b) Vickers hardness.

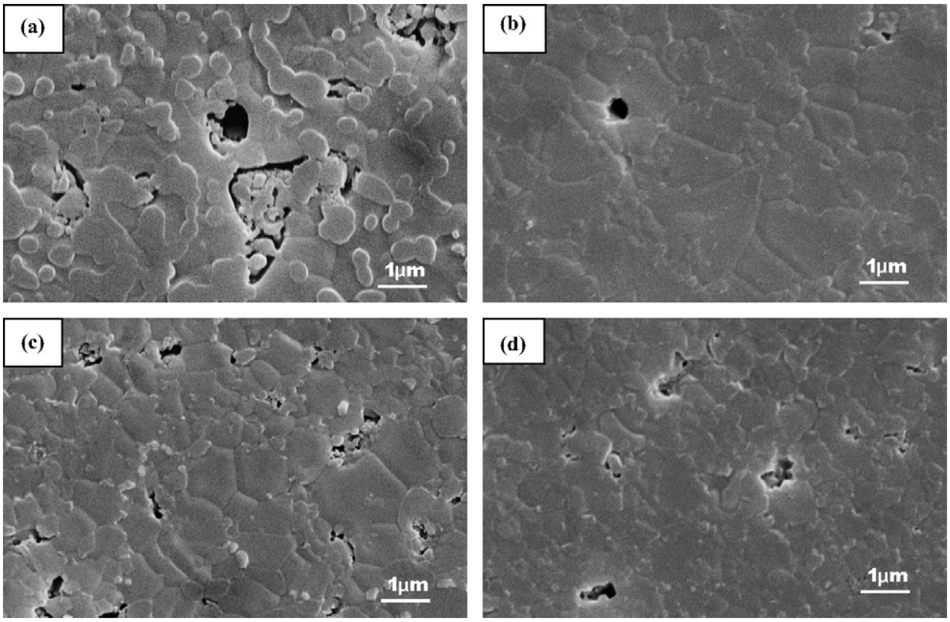

Fig. 4. SEM microstructures of HA composites sintered at 1400 °C with additives: (a) HA-2.5C, (b) HA-5C, (c) HA-2.5M, and (d) HA-5M.

ness: 4–5 GPa), these results is believed to obtain a promising result for the application of artificial teeth [5,6].

4. Conclusions

When we added 5 vol% of MgF_2 into hydroxyapatite–20 vol% alumina composites, the dissociation of hydroxyapatite was fully inhibited below 1400 °C sintered temperature. Also, the addition of MgF_2 was more effective compared to the addition of CaF_2. This result indicates that a high content of F^- ion in CaF_2 was contributed the stabilization of HAp crystal structure. With increasing the F content (HA-5M > HA-5C > HA-2.5M > HA-2.5C), the densification rate of HAp composite was increased. Also, the addition of fluoride compound was effective for the enhancement of mechanical properties (flexural strength: $\sim$170 MPa; Vickers hardness: $\sim$7 GPa).

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