Fabrication of fibrous $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}/\text{HAp-(t-ZrO}_2\text{)}$ core/shell composites with elongated grain formation

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Fibrous $\text{Al}_2\text{O}_3\text{-(monoclinic-ZrO}_2\text{)}/\text{HAp-(tetragonal-ZrO}_2\text{)}$ composites were fabricated with a core/shell microstructure by the multi-pass extrusion process depending on the volume fraction of $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ core and $\text{HAp-(t-ZrO}_2\text{)}$ shell. In the sample sintered at 1200°C , the $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ core was composed of porous, equiaxed grains, independent of core/shell volume fraction. However, after sintering at 1500°C , the core phase was changed with elongated grains of a reaction phase $\text{CaAl}_{12}\text{O}_{19}$. Formation of elongated grain increased as the core diameter decreased. A significantly improved value of fracture toughness ($4.3 \text{ MPa}\cdot\text{m}^{1/2}$) was obtained in the $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}/\text{HAp-(t-ZrO}_2\text{)}$ composites with $50_{\text{core}}/50_{\text{shell}}$ composition sintered at 1500°C .

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1. Introduction

Hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has been recognized as an important bioceramic because of its excellent biocompatibility due to similar chemical composition to human bone.⁽¹⁾ However, HAp cannot be used as implant in heavy load bearing parts like artificial teeth or hip joints due to its inherent low mechanical properties, particularly low fracture toughness ($1 \text{ MPa}\cdot\text{m}^{1/2}$) compared to human bone ($2\text{--}12 \text{ MPa}\cdot\text{m}^{1/2}$).⁽²⁻⁴⁾ Many studies have been reported on the improvement of fracture toughness of HAp ceramic by the addition of a second phase including particles,^(5,6) whiskers or fibers^(7,8) and metallic coating or dispersion⁽⁹⁾ etc. One important point is to improve the mechanical property without dispensing the excellent biocompatibility of HAp. This fact limits the choice of a second phase to modify HAp ceramic matrix. Al_2O_3 and ZrO_2 are two common ceramics with good biocompatibility and better mechanical properties although bio-inert in nature. A combination of the strengthening effect of Al_2O_3 and ZrO_2 with the bioactivity of HAp can give a better balance between these two systems, as already have been reported previously.^(10,11) These studies mainly focused on the composites made by mixing powders and morphological characterization and biocompatibility was investigated. However, microstructural modification of the composites to modify the mechanical properties of the composites system was not attempted in detail. Recently, the fibrous monolithic process has been investigated with different material systems to improve the mechanical properties, specially the fracture toughness.^(12,13) The unidirectionally aligned fibrous microstructure with either hard or soft interface was reported to be the reason for the improved fracture toughness. Multi-toughening mechanisms were introduced by selecting material combination. The fibrous micro-

structure was also described to be a reason to improve the mechanical property.

In our previous work we fabricated fibrous $\text{HAp-(20 vol\% t-ZrO}_2\text{)}/\text{Al}_2\text{O}_3\text{-(25 vol\% m-ZrO}_2\text{)}$ composites with core/shell microstructure.⁽¹⁴⁾ But in this system due to the encapsulation of the bioactive HAp phase with the bio-inert $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ network, the overall cell response for the system is deemed to be analogous with the bio-inert Al_2O_3 or ZrO_2 ceramics. To take account the superior cell response for the HAp phase an interconnected rather than encapsulated HAp phase is desirable. Moreover, it was reported that the formation of elongated Al_2O_3 grain was observed in the presence of CaO , SiO_2 ,⁽¹⁵⁾ SrO ,⁽¹⁶⁾ La_2O_3 ⁽¹⁷⁾ etc. This elongated grain improved the mechanical properties specially the fracture toughness. The HAp phase dissociates to produce CaO while sintered at high temperature, which can induce the grain elongation of the Al_2O_3 phase. In this context the development of the elongated grains in the $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}/\text{HAp-(t-ZrO}_2\text{)}$ fibrous composites system is desirable for the improvement of fracture toughness.

In this work, we fabricated the fibrous $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}/\text{HAp-(t-ZrO}_2\text{)}$ composites with an aim to improve the material properties and biocompatibility with a suitable microstructure design. Especially, the characteristics of fibrous microstructure with different core/shell volume fraction and the resulting variation of the elongated grain morphology of the $(\text{Al}_2\text{O}_3\text{-m-ZrO}_2)$ phase were investigated in details. Furthermore, material properties for all of the composites were evaluated and compared depending on the volume fraction of the core and shell phases.

2. Experimental procedure

The starting powders used were HAp (about $10 \mu\text{m}$, Strem Chemical, USA), Al_2O_3 (about $0.3 \mu\text{m}$, AKP-50, Sumitomo, Japan), t-ZrO_2 (about 80 nm , m- ZrO_2 , Tosho Co., Inc., Japan), and m- ZrO_2 (about 80 nm , m- ZrO_2 , Tosho Co., Inc., Japan. Eth-

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ylene vinyl acetate (EVA) (ELVAX 210 and 250, Dupont, USA) and stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, Daejung Chemicals & Metals Co., Korea) were used as binder and lubricant, respectively to make extrudable plastic lump. HAp/t-ZrO₂ (volume fraction 80:20) and Al₂O₃/m-ZrO₂ (volume fraction 75:25) mixture powders were homogeneously mixed separately in ethanol by ball milling using Al₂O₃ balls. The (Al₂O₃/m-ZrO₂)/EVA/stearic acid (volume fraction 60:30:10) were homogeneously mixed using a shear mixer (Shina Platec. Co., Korea) making a thermoplastic mixture. Similarly (HAp/t-ZrO₂)/EVA/stearic acid (volume fraction 50:40:10) were mixed in the shear mixer. The (HAp/t-ZrO₂)/EVA/stearic acid mixture was warm press in an aluminum die to make tube shape preform. On the other hand the (Al₂O₃/m-ZrO₂)/EVA/stearic acid mixture was extruded to make rods with pre-designed diameters. Then the Al₂O₃/m-ZrO₂/EVA rod and HAp/t-ZrO₂/EVA tube were assembled to make a feed roll with 29.5 mm diameter and extruded in a heated (120°C) die to make the 1st passed filaments about 3.5 mm in diameter. The tube thickness and rod diameter were varied so that the volume ratios of the (Al₂O₃/m-ZrO₂)/EVA and (HAp/t-ZrO₂)/EVA becomes 50/50, 40/60, 30/70 and 20/80 when assembled as a feed roll. The 1st passed filaments were cut 8 cm in length and reloaded in the same extrusion die and extruded at 120°C to make the 2nd passed filaments. The 3rd passed filaments were produced in the same way subsequently. To remove the EVA binder, burn-out process was carried out at 700°C for 2 h in a N₂ atmosphere and then at 1000°C in air atmosphere. Finally, the pressureless sintering process was carried out at 1200°C and 1500°C for 2 h in air.

The microstructures were examined using a scanning electron microscope (SEM, JEOL-JSM 5410). The crystal phases were analyzed by X-ray diffraction (XRD, D/MAX-250, Rigaku Co., Japan). The relative density was measured by the Archimedes method in an immersion medium of water. The average Vickers hardness was measured by randomly indenting with a load of 2.5 kg (10 points/sample) in core and shell regions. Fracture toughness was measured by indentation technique using Evans equation. Four point bending strength measurement was carried out

using a UTM (Unitech™, R & B, Korea).

3. Results and discussion

Figure 1 showed the SEM micrographs of the fibrous Al₂O₃-(m-ZrO₂)/HAp-(t-ZrO₂) composites sintered at 1200°C. The change in microstructure with the variation in core/shell volume fraction is clearly evident in Fig. 1(a) and (b), which consisted of core/shell volume fraction of 50/50 and 20/80, respectively. The Al₂O₃-(m-ZrO₂) core diameter of the composites decreased gradually from about 35 μm for the 50_{core}/50_{shell} composites to about 22 μm for the 20_{core}/80_{shell} composites. For 40_{core}/60_{shell} and 30_{core}/70_{shell} composites, their diameters were 27 μm and 31 μm , respectively. The HAp-(t-ZrO₂) shell thickness of the composites increased from 14 μm for the 50_{core}/50_{shell} to 18 μm , 23 μm and 30 μm for 40_{core}/60_{shell}, 30_{core}/70_{shell} and 20_{core}/80_{shell} composites, respectively. The core/shell microstructure was well controlled in all the composites without any large deviation from the core/shell geometry. A homogeneous microstructure was observed in both of the composites. Figure 1(c) showed the longitudinal section image of the 50_{core}/50_{shell} composites. The microstructure was very well controlled with unidirectionally aligned fiber like phase as shown in the SEM image. The enlarged SEM images (d, e) from the Al₂O₃-(m-ZrO₂) core and HAp-(t-ZrO₂) shell, respectively, confirmed that the core and shell had a porous structure which indicates a low densification due to low sintering temperature (1200°C). In the Al₂O₃-(m-ZrO₂) core (d), the average grain size was less than 0.25 μm while in the HAp-(t-ZrO₂) shell region (e), the average grain size of t-ZrO₂ was about 0.3 μm which was homogeneously embedded in the large sized HAp grains. This observation indicates that the HAp phase has undergone significant grain coarsening. In general, monolithic HAp is densified at 1200°C temperature and further increase of sintering temperature causes the phase transformation of HAp into β -TCP. The Al₂O₃-ZrO₂ system is usually sintered at around 1500°C. So to achieve higher density and consequently better material properties, sintering was performed at 1500°C, despite the transformation of HAp into β -TCP. This doesn't hamper the biocompatibility as the β -TCP phase is also a highly biocompatible

Fig. 1. Cross sectional (a, b) and longitudinal (c) SEM images of 3rd passed Al₂O₃-(m-ZrO₂)/HAp-(t-ZrO₂) composites (sintered at 1200°C) depending on volume fraction of core/shell: (a) 50/50, (b) 20/80, (c) 50/50 and (d) enlarged Al₂O₃-(m-ZrO₂) core and (e) enlarged HAp-(t-ZrO₂) shell.

material. The temperature was chosen as it was near the sintering temperature of Al_2O_3 and ZrO_2 ceramics.

Figure 2 showed the cross sectional SEM micrographs of the fibrous Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) composites depending on the core/shell volume fractions with successive compositions (a) 50/50, (b) 40/60, (c) 30/70 and (d) 20/80 sintered at 1500°C. But in this case, the cores of the composites in all the configurations showed a slightly different morphology. Even though most of the core geometry still remained round with the 50_{core}/50_{shell} composite, but with the decrease of the core volume fraction, the core morphology was significantly changed. The distinction between the core and shell near the interface became progressively faded away with the decrease in core volume fraction. Elongated grains were observed in the core phase. In the 50_{core}/50_{shell} composites all the cores did not incorporate the same level of elongated grain growth as well as the degree of grain elongation was not that much high. With increasing shell phase, the degree of grain elongation increased and in the 30_{core}/70_{shell} and 20_{core}/80_{shell} composites the whole core region was converted with elongated grains.

The enlarged image of the core/shell in **Fig. 3** depicted this phenomenon more clearly. The co-efficient of thermal expansion (CTE) of the core and shell phases are different as the CTE of Al_2O_3 , ZrO_2 , HAp and β -TCP are different. This leads to gener-

ation of residual stress in the core and shell phase during sintering process. The CTE of Al_2O_3 is lower compared to HAp and ZrO_2 . So the Al_2O_3 -(m-ZrO₂) core undergoes with compressive and the HAp-(t-ZrO₂) shell undergoes with tensile residual stress. With the higher volume fraction of core phase the stress distribution is different than that with lower volume fraction core. This variation of compressive and tensile residual stress in the core and shell regions may influence the development of grains. The variation of the extent of reacted phase in the core with the variation of the core volume fraction might be due to this reason. With higher shell volume fractions some microcracks were observed as shown in **Fig. 3(b)**. This indicates that in this case the tensile residual stress is greater compared with that of lower shell volume fraction composites.

It was reported that the addition of CaO or SiO₂ can trigger the elongation of Al_2O_3 grains while sintering. The Al_2O_3 phase reacts with the CaO, liberated from the HAp dissociation and forms a very thin liquid phase which in turn causes a directional growth of the grains.¹⁸⁾ Due to the high temperature sintering at 1500°C, the HAp phase undergoes a decomposition reaction yielding CaO. Moreover, due to its amphoteric nature Al_2O_3 reacts with basic oxide like CaO. The formation of reaction product CaAl_2O_9 is further confirmed from the XRD profile in **Fig.**

Fig. 2. Cross sectional SEM images of 3rd passed Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) composites (sintered at 1500°C) depending on volume fraction of core/shell: (a) 50/50, (b) 40/60, (c) 30/70 and (d) 20/80.

Fig. 3. SEM images of Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) composites sintered at 1500°C, (a) 50/50, (b) 20/80 core/shell composites.

4. The reactions are given bellow,

Figure 4 shows the XRD profiles of fibrous Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) composites which were sintered at 1200°C (a) and 1500°C (b). At the 1200°C, it is confirmed that the peaks of HAp, t-ZrO₂, Al₂O₃ and m-ZrO₂ phases were clearly detected without the formation of any reaction compounds. However, in the sample sintered at 1500°C, the HAp peaks were not detected due to the phase transformation of HAp to α and β -TCP phases. In addition, the intensity of Al₂O₃ peak decreased as evident from the minor peaks and narrowing of the primary peak's width which coincides with the t-ZrO₂ peak. Formation of CaAl₁₂O₁₉ as a reaction phase was observed but weak compared to the very high intensity of t-ZrO₂.

In Fig. 5(a), the enlarged SEM image of the 50_{core}/50_{shell} composite was clearly shown with the elongated microstructure along with the core and shell phase at bottom left and top right part marked as Q P and R, respectively. The In the enlarged SEM image 5(b), the bright contrasts are the ZrO₂ phase and

Fig. 4. XRD profiles of Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) bodies depending on the sintering temperatures: (a) 1200°C, (b) 1500°C.

stretched dark contrasts are the elongated grains of reaction phase CaAl₁₂O₁₉. The length of the elongated grains is about 5 μm and the width is less than 1 μm . However, inside the core the Al_2O_3 -(m-ZrO₂) core was unchanged except the conventional equiaxed grain growth as shown in Fig 5(c). The average grain size of the m-ZrO₂ was about 500 nm in diameter, while that of the Al₂O₃ grains was about 700 nm in diameter. In the shell region as shown in the enlarged SEM image 5(d), the grains seen with bright and dark contrasts were t-ZrO₂ and β -TCP phases, respectively. However, despite this high temperature the β -TCP grain growth was not significant and the average grain size of the β -TCP was around 1 μm . The t-ZrO₂ did not undergo any phase change as confirmed by the XRD profile in Fig. 4, except a usual grain growth.

To examine the reason of elongated grain formation a separate experiment was conducted with and without addition of HAp with the Al_2O_3 -(m-ZrO₂) composites with the same 75/25 volume composition and sintered at 1500°C. The resultant microstructure is shown in Fig. 6. In Fig. 6(a) equiaxed Al₂O₃ and m-ZrO₂ was observed and there was no sign of elongated grain formation. However, in Fig. 6(b) with 10% addition of HAp elongated grain was frequently observed and the grain size and morphology is consistent with that of the previous system. The EDS profiles were taken from both of them. In case of HAp added Al_2O_3 -(m-ZrO₂) EDS profile taken from the elongated grain as marked by box in Fig. 6(b) showed that the elongated grain had a trace of Ca, where as in the EDS profile taken for Al_2O_3 -(m-ZrO₂) composites with out HAp addition as marked on Fig. 6(a) did not show any sign of Ca and the microstructural configuration was unchanged.

The material properties of the fabricated composites in relation to the core/shell volume fraction sintered at 1200°C and 1500°C are shown in Table 1. It is seen that after sintering at higher temperature all of the property values were increased. Moreover, with the increase of the Al_2O_3 -(m-ZrO₂) core volume fraction, the mechanical properties increased and the highest values of Vickers hardness, bending strength and fracture toughness were obtained in the 50_{core}/50_{shell} composites. Fracture toughness was considerably higher in the composites sintered at 1500°C for the composites. This high value is attributed to the

Fig. 5. Enlarged SEM images of the core and shell region of the 50/50 Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) bodies sintered at 1500°C: (a, b) interface of the core/shell, (c) inside the core and (d) shell.

Fig. 6. SEM images of Al_2O_3 -(m-ZrO₂) sintered composites without addition of HAp (a) and with addition of 10% HAp. Both of the samples were sintered at 1500°C. EDS profiles (c) and (d) are taken from the marked regions of figure (a) and (b) respectively.

Table 1. Material Properties of the Fibrous Core/Shell Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) Composites

Composition (%)	Sintering temperature (°C)	Vickers hardness (Hv)	Bending strength (MPa)	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
Core/Shell 20/80	1200°C	58 ± 18	32 ± 8	1.83 ± 0.1
	1500°C	602 ± 20	175 ± 14	4.22 ± 0.2
Core/Shell 50/50	1200°C	114 ± 12	64 ± 8	2.2 ± 0.1
	1500°C	662 ± 21	397 ± 8	4.32 ± 0.2

increased densification and formation of the elongated grain. The elongated microstructure can act as active crack deflector and may take part in crack bridging. The bending strength of the composites increased as the Al_2O_3 -(m-ZrO₂) core volume fraction increased. The improvements in strength and toughness of t-zirconia polycrystal/ Al_2O_3 have been achieved by the incorporation of platelet grains of hexaluminate phases namely $\text{LaAl}_{11}\text{O}_{18}$ and $\text{SrAl}_{12}\text{O}_{19}$.¹⁷⁾ However, in the TCP- Al_2O_3 -ZrO₂ system this kind of elongated grain formation was rarely reported. Although the primary goal of this work was to make unidirectionally aligned fibrous microstructure to tailor the composite, the elongated grain formation further enriched the design characteristics. The fine and homogeneous fibrous microstructure along with the formation of elongated grain can be seen as a potential improvement to design a bio-ceramic material with improved mechanical characteristic, especially the fracture toughness.

4. Conclusion

The fibrous core/shell Al_2O_3 -(m-ZrO₂)/HAp-(t-ZrO₂) composites were fabricated by the multi-pass extrusion process. Investigation was carried out for the microstructural variation depending on core/shell volume fraction and the resulting effect on the mechanical properties of the composites. Unidirectionally aligned fibrous microstructure was fabricated with the material system. At lower sintering temperature of 1200°C, the fibrous core/shell microstructure was comprised with low densification. But at higher sintering temperature of 1500°C, the densification increased and in the Al_2O_3 -(m-ZrO₂) core most of Al_2O_3 grains were appeared with elongated grains of $\text{CaAl}_{12}\text{O}_{19}$ in all the compositions. However, as decreasing the Al_2O_3 -(m-ZrO₂) core diameter the amount of elongated grains were remarkably increased and in the sample with 20_{core}/80_{shell} volume fraction, the most regions of Al_2O_3 -(m-ZrO₂) cores were found with elon-

gated grains. The elongated grains improved the fracture toughness significantly. With only 20 vol% of Al_2O_3 -(m-ZrO₂) as the core, the fracture toughness was as high as $4.2 \text{ MPa}\cdot\text{m}^{1/2}$. The highest value was $4.3 \text{ MPa}\cdot\text{m}^{1/2}$ in the 50_{core}/50_{shell} composites sintered at 1500°C.

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