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

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1. Introduction

Hydroxyapatite (HAp, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) has been recognized as an important bioceramic because of its excellent biocompatibility due to similar chemical composition to human bone. 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 MPa·m$^{-1/2}$) compared to human bone (2–12 MPa·m$^{-1/2}$). Many studies have been reported on the improvement of fracture toughness of HAp ceramic by the addition of a second phase including particles, whiskers or fibers and metallic coating or dispersion 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$_2$O$_3$ 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$_2$O$_3$ and ZrO$_2$ with the bioactivity of HAp can give a better balance between these two systems, as already have been reported previously. 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. 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 HAp-(20 vol% t-ZrO$_2$)/Al$_2$O$_3$-(25 vol% m-ZrO$_2$) composites with core/shell microstructure. But in this system due to the encapsulation of the bioactive HAp phase with the bio-inert Al$_2$O$_3$-(m-ZrO$_2$) network, the overall cell response for the system is deemed to be analogous with the bio-inert Al$_2$O$_3$ 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$_2$O$_3$ grain was observed in the presence of CaO, SiO$_2$, SrO, La$_2$O$_3$ 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$_2$O$_3$ phase. In this context the development of the elongated grains in the Al$_2$O$_3$-(m-ZrO$_2$)/HAp-(t-ZrO$_2$) fibrous composites system is desirable for the improvement of fracture toughness.

In this work, we fabricated the fibrous Al$_2$O$_3$-(m-ZrO$_2$)/HAp-(t-ZrO$_2$) 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 (Al$_2$O$_3$-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 μm, Strem Chemical, USA), Al$_2$O$_3$ (about 0.3 μm, AKP–50, Sumitomo, Japan), t-ZrO$_2$ (about 80 nm, m-ZrO$_2$), Toho Co., Inc., Japan), and m-ZrO$_2$ (about 80 nm, m-ZrO$_2$), Toho Co., Inc., Japan. Eth-

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1200°C in air atmosphere. Finally, the pressureless sintering was performed at 1000°C. The 1st passed filaments were cut 8 cm in length and reloaded in the 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 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).

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 50core/50shell composites to about 22 μm for the 20core/80shell composites. For 40core/60shell and 30core/70shell 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 50core/50shell to 18 μm, 23 μm and 30 μm for 40core/60shell, 30core/70shell and 20core/80shell 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 50core/50shell 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 material.
material. The temperature was chosen as it was near the sintering temperature of Al$_2$O$_3$ and ZrO$_2$ ceramics.

Figure 2 showed the cross sectional SEM micrographs of the fibrous Al$_2$O$_3$-(m-ZrO$_2$)/HAp-(t-ZrO$_2$) 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 50core/50shell 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 50core/50shell 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 30core/70shell and 20core/80shell 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$_2$O$_3$, ZrO$_2$, HAp and $\beta$-TCP are different. This leads to generation of residual stress in the core and shell phase during sintering process. The CTE of Al$_2$O$_3$ is lower compared to HAp and ZrO$_2$. So the Al$_2$O$_3$-(m-ZrO$_2$) core undergoes with compressive and the HAp-(t-ZrO$_2$) 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 SiO$_2$ can trigger the elongation of Al$_2$O$_3$ grains while sintering. The Al$_2$O$_3$ 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. 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$_2$O$_3$ reacts with basic oxide like CaO. The formation of reaction product CaAl$_2$O$_{19}$ is further confirmed from the XRD profile in Fig.
4. The reactions are given below,

\[ \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow 3\text{Ca}_3 (\text{PO}_4)_2 + \text{CaO} + \text{H}_2 \text{O} \]
\[ 6\text{Al}_2\text{O}_3 + \text{CaO} \rightarrow \text{CaAl}_{12}\text{O}_{19} \]

Figure 4 shows the XRD profiles of fibrous \( \text{Al}_2\text{O}_3-(\text{m-ZrO}_2)/\text{HAp-(t-ZrO}_2) \) 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-ZrO\(_2\), Al\(_2\)O\(_3\) and m-ZrO\(_2\) 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 \( \alpha \) and \( \beta \)-TCP phases. In addition, the intensity of Al\(_2\)O\(_3\) peak decreased as evident from the minor peaks and narrowing of the primary peak’s width which coincides with the t-ZrO\(_2\) peak. Formation of CaAl\(_{12}\)O\(_{19}\) as a reaction phase was observed but weak compared to the very high intensity of t-ZrO\(_2\).

In Fig. 5(a), the enlarged SEM image of the 50\(_{\text{core}}$/50\(_{\text{shell}}\) 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 ZrO\(_2\) phase and the stretched dark contrasts are the elongated grains of reaction phase CaAl\(_{12}\)O\(_{19}\). The length of the elongated grains is about 5 \( \mu \)m and the width is less than 1 \( \mu \)m. However, despite this high temperature the \( \beta \)-TCP grain growth was not significant and the average grain size of the \( \beta \)-TCP was around 1 \( \mu \)m. The t-ZrO\(_2\) 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\(_2\)O\(_3\)-(m-ZrO\(_2\)) 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 Al\(_2\)O\(_3\) and m-ZrO\(_2\) 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\(_2\)O\(_3\)-(m-ZrO\(_2\)) 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\(_2\)O\(_3\)-(m-ZrO\(_2\)) 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\(_2\)O\(_3\)-(m-ZrO\(_2\)) core volume fraction, the mechanical properties increased and the highest values of Vickers hardness, bending strength and fracture toughness were obtained in the 50\(_{\text{core}}$/50\(_{\text{shell}}\) composites. Fracture toughness was considerably higher in the composites sintered at 1500°C for the composites. This high value is attributed to the
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$_2$O$_3$-(m-ZrO$_2$) core volume fraction increased. The improvements in strength and toughness of t-zirconia polycrystal/Al$_2$O$_3$ have been achieved by the incorporation of platelet grains of hexaluminate phases namely LaAl$_{11}$O$_{18}$ and SrAl$_2$O$_{19}$. However, in the TCP-Al$_2$O$_3$-ZrO$_2$ 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$_2$O$_3$-(m-ZrO$_2$)/HAp-(t-ZrO$_2$) 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$_2$O$_3$-(m-ZrO$_2$) core most of Al$_2$O$_3$ grains were appeared with elongated grains of CaAl$_2$O$_4$ in all the compositions. However, as decreasing the Al$_2$O$_3$-(m-ZrO$_2$) core diameter the amount of elongated grains were remarkably increased and in the sample with 20core/80shell volume fraction, the most regions of Al$_2$O$_3$-(m-ZrO$_2$) cores were found with elongated grains. The elongated grains improved the fracture toughness significantly. With only 20 vol% of Al$_2$O$_3$-(m-ZrO$_2$) as the core, the fracture toughness was as high as 4.2 MPa·m$^{1/2}$. The highest value was 4.3 MPa·m$^{1/2}$ in the 50core/50shell composites sintered at 1500°C.

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References