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Filter cake forming and hot isostatic pressing for TZP-dispersed hydroxyapatite composite

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The combination of a filter cake forming process and hot isostatic pressing was applied to prepare hydroxyapatite composites containing dispersed tetragonal zirconia polycrystal (TZP) with high strength and toughness. Fine TZP powder was dispersed into as-synthesized hydroxyapatite slurry, formed with the filter cake process and hot isostatically pressed at 800–1150 °C at 100 MPa for 2 h. The temperature needed for densification increased with increasing TZP content; 1100 °C was needed to fully densify the composite with 26.8 wt % TZP. No phase change was found in TZP nor in the hydroxyapatite phase up to the maximum temperature examined in hot isostatic pressing. Significant phase change was found in specimens annealed in air at 1200 °C. The strength and toughness achieved were respectively 190 MPa and 2.3 MPa $m^{1/2}$. These values were approximately 20% and 100% higher than the corresponding values for hydroxyapatite ceramics without TZP particle dispersion.

1. Introduction

Hydroxyapatite is a potential material in dental and biomedical fields [1, 2], and a huge commercial application will be opened if a material with high strength and toughness becomes available. The strengthening of materials is one of the most active research areas in the field of ceramics and various methods are being examined [3]. Among them, the most well-established ones are probably transformation toughening utilizing the tetragonal–monoclinic martensitic transformation of zirconia, and particle dispersion in which the toughness increases through microcrack formation or/and crack deflection by the dispersed particle. A ceramic with dispersed tetragonal zirconia polycrystal (TZP) particles is expected to have excellent mechanical properties, since both transformation toughening and particle dispersion effects contribute to strengthening. However, the development of hydroxyapatite toughened by dispersed TZP particles has been difficult [4, 5]. One major obstacle has been the reaction between the matrix and the dispersed particles during the sintering process. Calcium, which is the major constituent of hydroxyapatite, diffuses into TZP and changes it to a stable cubic phase, for which a transformation toughening mechanism is not expected. To avoid the difficulty associated with the diffusion, the temperature for densification has to be minimized. However, this has been difficult; the composites generally have inferior sintering characteristics and require high temperatures for densification [6].

We have recently reported achieving a considerable reduction of densification temperature in hydroxyapatite ceramics [7]. The process consisted of the combination of colloidal pressing (filter cake method) for forming [8] and hot isostatic pressing for densification. Achievement of transparent hydroxyapatite ceramics at 800 °C was demonstrated, showing a reduction of densification temperature by more than 200 °C compared to the conventional process. This process is very promising for the production of high-density composite at low temperature and is subjected to examination in this study for the processing of composite ceramics containing TZP particles dispersed in hydroxyapatite. The results show that a high-density composite having high strength and toughness can be obtained.

2. Experimental procedure

The starting materials were prepared as in our previous report [9] by adding 2560 ml of an aqueous solution of diammonium hydrogen phosphate (0.188 M) to 1440 ml of an aqueous solution of calcium nitrate (0.556 M) at pH 11. Concentrated ammonium aqueous solution was used for the pH adjustment. The product slurry was aged at 25 °C for 48 h under the constant bubbling of nitrogen. After being concentrated with a centrifugal separator, the slurry was washed four times with distilled water and centrifuged.

Fine commercial TZP powder (TZ-3Y, Toso) was ball-milled for 48 h in a dilute ammonium aqueous solution at pH 12 and was mixed with the above concentrated slurry. After being ball-milled for 96 h, the mixture was formed into pellets (20 mmϕ × 20 mm) by centrifugal colloidal pressing. The pellets were dried in air for several days at room temperature and then heated to 350 °C for 4 h for more complete drying, with a heating rate of 1 °C min^{-1}.

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The composition of the hydroxyapatite phase was determined by wet chemical analysis. The TZP content in the pellet was determined with an X-ray fluorescence spectrometer (System 3080E2, Rigaku). In this measurement, a set of standard specimens were prepared by mixing known amounts of hydroxyapatite and zirconia powders for constructing a calibration curve.

The dried pellet was coated with boron nitride powder and placed in a glass capsule. After evacuation at 600 °C for 1 h, the capsule was sealed. Commercial equipment (QIH-9, NKK-ASEA) was used for the hot isostatic pressing. The capsule was heated to 700 °C in a vacuum at 10 °C min^{-1} and pressurized to 100 MPa at this temperature. After the pressure reached the specified value, the capsule was heated again to the final temperature (800–1150 °C) at the same heating rate as above. After being held for 2 h at this temperature, the capsule was cooled to room temperature. The capsule was then cut with a diamond saw to take out the specimen. The density after hot isostatic pressing was measured by the Archimedes method.

Values of toughness by indentation method and micro-Vickers hardness were determined with a micro-Vickers hardness tester (Type M, Shimazu). The loading conditions were the applied loads 1.92 N for 30 s and 0.147 N for 5 s for the measurement of toughness and hardness, respectively. Niihara's equation [10, 11] was used for the calculation of toughness. The strength was measured by three-point bending on small specimens (3 mm x 3 mm x 10 mm) with span length 5.5 mm and crosshead speed 0.5 mm min^{-1}, using standard test equipment (DSS-500, Shimazu). The surface of the specimen was ground with a fine grinding wheel (No. 3000) and finished by lapping with 0.25 μm diamond powders. The phases were examined with a powder X-ray diffractometer (Type 2038, Rigaku).

3. Results

Fig. 1 shows the effect of hot isostatic pressing temperature on the relative densities of various specimens. The relative density increased with increasing temperature and with decreasing TZP powder content. The specimen without TZP powder reached the full density at 800 °C and became transparent. With further increasing temperature, the density was approximately constant, but the transparency decreased. In the densification of composites, the relative density increased more sharply with temperature in the specimens with higher TZP content. To achieve near-full density, 1000 °C was needed for specimen with a low TZP content (10.1 wt %), but 1100 °C was required for specimens with a high TZP content (26.8 wt %). The density tended to decrease at the maximum temperature examined, 1150 °C.

Fig. 2 shows the microstructures of specimens hot isostatically pressed at 1150 °C. The microstructures of composites are uniform and have uniformly dispersed small TZP particles. The grain size of the hydroxyapatite matrix phase was very small and of the order of 1 μm. No sign of abnormal grain growth was found in this phase. The size of the dispersed zirconia phase was still smaller, and was in the sub-micrometre region. The microstructure of the specimen without TZP was uniform and consisted of grains with a size of approximately 10 μm. Abnormal grain growth was not found in this specimen, but significant grain growth was noted.

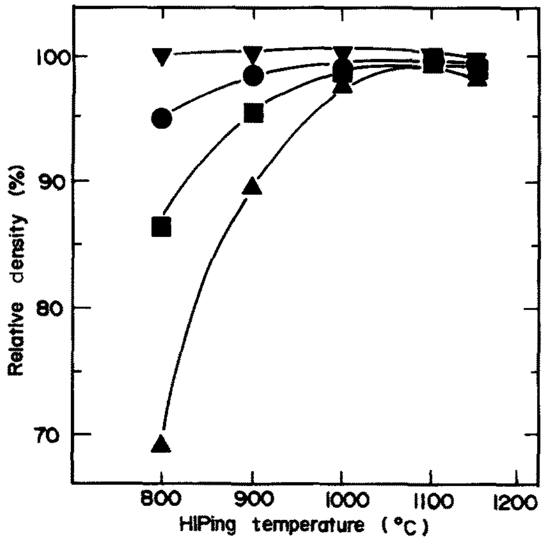

Figure 1 Effect of hot isostatic pressing temperature on the relative density: (▼) 0 wt % TZP (SHAp), (●) 10.1 wt %, (■) 16.3 wt %, (▲) 26.8 wt %.

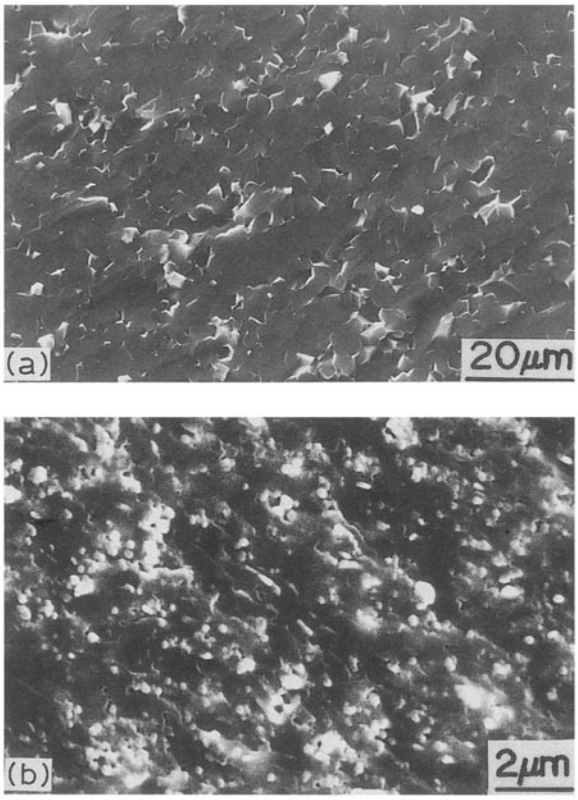

Figure 2 SEM micrographs of specimens hot isostatically pressed at 1100 °C: (a) specimen without TZP, (b) composite with 26.8 wt % TZP.

Fig. 3 shows the powder X-ray diffraction patterns of composites with 26.8 wt % TZP which were hot isostatically pressed at various temperatures. All specimens showed only the diffraction peaks of tetragonal

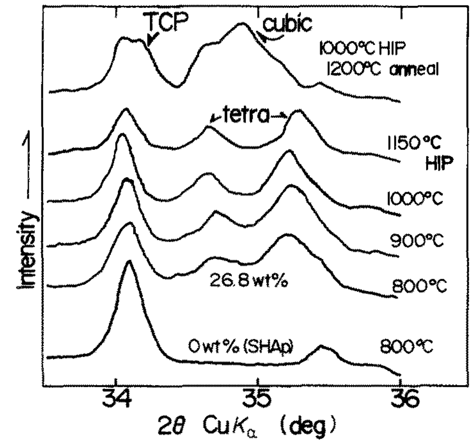

Figure 3 Effect of hot isostatic pressing temperature on the powder X-ray diffraction pattern of composite with 26.8 wt % TZP.

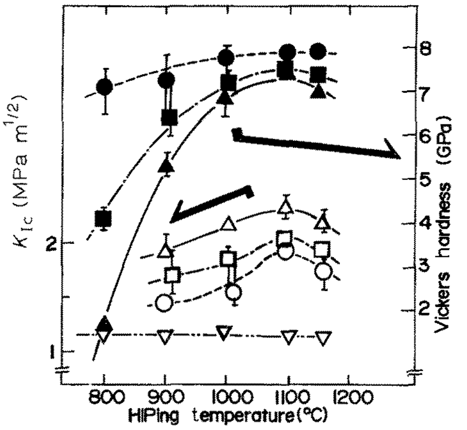

Figure 4 Effect of hot isostatic pressing temperature on the fracture toughness (open symbols) and micro-Vickers hardness (closed symbols): (▽) 0 wt % TZP (SHAp); (○, ●) 10.1 wt %; (□, ■) 16.3 wt %; (△, ▲) 26.8 wt %.

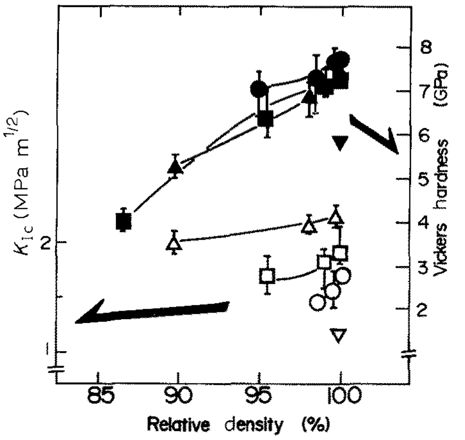

Figure 5 Changes of fracture toughness (open symbol) and micro-Vickers hardness (closed symbol) with relative density: (▽, ▼) 0 wt % TZP (SHAp); (○, ●) 10.1 wt %; (□, ■) 16.3 wt %; (△, ▲) 26.8 wt %.

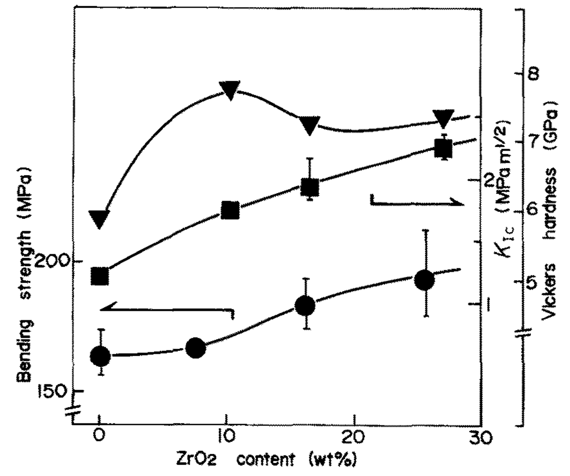

Figure 6 Effect of TZP content on the fracture strength (●), toughness (■), and micro-Vickers hardness (▼).

zirconia and of hydroxyapatite up to 1150 °C. No sign of phase change was found either in the TZP dispersed particles or the hydroxyapatite matrix phase. The specimen annealed at 1200 °C for 2 h in air shows strong diffraction peaks of cubic zirconia and weak peaks of tricalcium phosphate (TCP), which is the decomposition product of hydroxyapatite.

Fig. 4 shows the effect of hot isostatic pressing temperature on the fracture toughness and the micro-Vickers hardness for various specimens. Note that specimens prepared at the same temperature have different densities. For composites, both toughness and hardness increased with increasing temperature up to 1100 °C, and tended to decrease at higher temperature. The toughness of the specimen without TZP was much lower than that of the composites and was approximately constant for all temperatures.

Fig. 5 shows the toughness and hardness as a function of relative density. Both hardness and toughness increased with increasing relative density. The toughness increased significantly with increasing TZP content; the composite with 26.8 wt % TZP had almost twice as high a toughness as hydroxyapatite without TZP addition. The hardness of composites was almost the same for all compositions, and approximately 7.5 GPa at full density. This value is significantly higher than that for hydroxyapatite without TZP.

Fig. 6 shows the effect of TZP content on the fracture strength, toughness and hardness for the approximately fully dense materials. Both strength and toughness increased approximately linearly with increasing TZP content, whereas hardness was approximately constant except for the specimen without TZP. Strength and toughness were significantly lower for the specimen without TZP addition than for composites.

4. Discussion

High-density TZP particle-dispersed hydroxyapatite composite was successfully produced in this study through the combined application of a colloidal pressing technique and densification by hot isostatic pressing. The strength and toughness achieved in the composite both exceeded the respective values required for practical application.

The maximum strength and toughness of the composites of this study are 190 MPa and 2.3 MPa m$^{1/2}$, respectively. Compared to the reported values of Tamari *et al.* [5] for similar material, the toughness is approximately 1.6 times higher and the strength is approximately the same. Still higher strength is believed to be possible at higher TZP contents as in the study of Tamari *et al.*, but was not examined in this study. The approximately linear changes of hardness and strength suggest that the increased strength is due to the increased toughness of the composite. The size of the fracture origin must be approximately the same in all specimens. In the preparation of these high strength and toughness materials, the critical point is the successful dispersion of the TZP phase in the hydroxyapatite matrix. In past studies, the TZP phase changed into cubic phase during processing.

The application of hot isostatic pressing is critical for the preparation of high-density materials, even for the very active slurry of this study. In a preliminary experiment with normal sintering, the relative density reached was under 60% for the specimen with 23.5 wt % TZP at 1000–1200 °C. This result is consistent with that of past studies of composites [4, 5]. Increased difficulty of densification with increasing fraction of dispersed second phase is commonly found in the composite ceramics of many systems [6].

Colloidal pressing is important in the achievement of high density. In our previous study of monolithic hydroxyapatite ceramics, transparent materials could not be obtained if the slurry was once dried before compaction [7]. Considerable loss of sintering activity or/and introduction of processing defects are expected to have occurred in drying, and are believed to be responsible for the formation of opaque ceramics. The same adverse effect of drying should also be important in the processing of composite ceramics. The importance of the forming process needs more studies. With the present method, it is difficult to form large uniform bodies. If possible, development of a less complicated forming process is desirable.

No significant reaction was found between the dispersed TZP particles and the matrix phase up to 1150 °C in hot isostatically pressed specimens, whereas the normally sintered specimen showed significant reaction between matrix and dispersed TZP particles even at 1100 °C. Recalling that reaction in the solid phase is topochemical and requires good contact [12], it is surprising to find that the reaction is less in hot isostatic pressing than in normal sintering. More reaction should be expected in the hot isostatically pressed specimen, since the contact between the matrix and TZP particle should be better in this specimen than in the normally sintered specimen.

Thermodynamics may explain this high stability of TZP particles during the hot isostatic pressing. High pressure is known to affect the equilibrium of a reaction which is accompanied by a large volume change. If calcium is lost from hydroxyapatite to diffuse into the TZP phase, a corresponding amount of hydroxide groups have to be decomposed into water to compensate the charge neutrality of the material: one mole of water vapour for each calcium oxide. A very large volume change accompanies this evolution of water vapour, and the decomposition reaction may not be allowed to occur thermodynamically under the conditions of the present hot isostatic pressing.

We calculated the differences of Gibbs free energy change for reactions at atmospheric pressure and 100 MPa. The assumptions made in the calculation are (i) two hydroxide groups have to be removed for each calcium ion lost to keep charge neutrality, creating one water molecule; (ii) the water vapour follows the ideal gas law; and (iii) water vapour is confined in the glass capsule. The energy gained in the dissolution of calcium into TZP particles is neglected in the calculation, since it involves only a small volume change and the energy change due to the pressure difference should be small. The free energy of the vapour is given by the term $RT\ln P$, and is found to be approximately 82 kJ mol^{-1} higher at the pressure of hot isostatic pressing than at atmospheric pressure. In hot isostatic pressing, the net driving force for the decomposition is then reduced by this amount compared to the reaction at atmospheric pressure. This reduction of energy is believed to be large enough to inhibit the decomposition of hydroxyapatite, since the free energy change associated with the formation of a solid solution is generally not excessively large except for a very dilute system. The good contact between the matrix and the TZP particle should allow the specimen to react if the pressure is removed; this is consistent with the result. When the specimen was annealed at a slightly higher temperature in air, the decomposition occurred as found in Fig. 3.

The significance of this result is that the capsule of this study has, in addition to its normal role as a pressure-transmitting medium, another important role in the successful formation of TZP particle-dispersed hydroxyapatite ceramics. It governs the chemical reaction which involves a large volume change. In the densification of materials, the hot pressing technique provides more or less the same effect as the present method. However, water vapour can escape from the system freely due to the large dead volume of the equipment. Significant reaction should already have occurred before the partial pressure of water vapour rises high enough in the hot-pressing equipment to suppress the decomposition reaction of hydroxyapatite (and formation of cubic zirconia).

The composite has a higher strength and twice as high a toughness as the current monolithic hydroxyapatite ceramics. Two explanations are possible for the improved properties. For the increased toughness, at least two mechanisms are known to be operative in TZP-dispersed materials, microcracking and transformation toughening. The difference of thermal expansion coefficients can create microcracking in the hydroxyapatite matrix. The thermal expansion coefficients of hydroxyapatite and zirconia are 13.8×10^{-6} and 10.5×10^{-6} °C^{-1}, respectively. Tensile stress is induced in the matrix for this case. The presence of the tetragonal zirconia phase is apparent in the powder X-ray diffraction analysis. In both mechanisms, the increase of toughness is proportional to the volume fraction of dispersed particles, which is in agreement to the results shown in Fig. 6.

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