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Solid state reaction, sintering and Pb removal activity of hydroxyapatite/zirconia layered composite

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In order to form a layered hydroxyapatite/zirconia ceramic, the solid state reaction and sintering were examined by the three processes of powder mixture, dry-pressing compaction and tape cast. The solid state reaction between hydroxyapatite and zirconia occurred in the thin width of 10–50 μm at interface in a layered composite body. In both sintered layer composites from dry compaction and tape cast, the significant deformation of composite bodies was observed, depending on sintering temperatures. By selecting a sintering temperature of 1200°C, we fabricated a layer ceramic composite of hydroxyapatite/zirconia exhibiting the flat film shape. The tape cast process was useful to form a porous sintered composite of hydroxyapatite and zirconia. The porous composite showed the removal performance of aqueous lead from wastewater.
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1. Introduction

Application of hydroxyapatite, besides its unique role as a clinically used ceramic, have been widely expanded to environmental improvement devices using its high capacity of heavy metal ion-exchange and molecular separation, as well as catalysis [1–8]. The column reactors using powder absorbent have the problem of the movement of powder during use for long period, resulting in the degradation of filtration or reaction efficiency. Therefore, a porous sintered medium is required as an improved reactor for the several separation and removal processes, especially under the extreme conditions. In a heavy metal separation process from wastewater, the fine powder of hydroxyapatite is often subjected to a strong acid solution. Several workers suggested the formation of a crystalline precipitation on a hydroxyapatite medium after a removal test, which is caused by the dissolution phenomenon of hydroxyapatite in the low pH region [1, 3, 4]. In order to stabilize the active medium of hydroxyapatite, a composite or supported ceramic with inert composition is useful. Tetragonal zirconia polycrystal (TZP) is known as a high performance ceramic showing high strength and toughness due to its transforming mechanism, as well as high resistance capability to chemicals such as a strong acid solution [9–11]. Previous references have described that the sintering of starting powder composites produces the reactant phases besides zirconia and hydroxyapatite [12–22]. Therefore, the control of solid state reaction at interface is significant for the practical fabrication of ceramic composite between hydroxyapatite and zirconia.

The aim of this work is to examine several factors for controlling the sintering and solid state reaction of them, then for making a layered hydroxyapatite/zirconia ceramic. We compare the ceramics of hydroxyapatite/zirconia composites, which were made through three processes; powder mixture, dry-pressing compaction and tape cast, regarding with their solid state reaction, forming and sintering. Finally, we demonstrate the removal activity of aqueous lead using a porous layered ceramic of hydroxyapatite/zirconia.

2. Experimental

Starting hydroxyapatite (HA) powder was synthesized by a precipitation process that phosphoric acid was slowly added into an agitated $Ca(OH)_2$ suspension. The precipitate was filtered, dried and heated at 600°C for 3 h in air, then ground. The particle size of the obtained powder was 20 μm in average diameter. 2 mol% Y_2O_3 doped ZrO_2 (2Y-TZP) powder with 2 μm in diameter was supplied from Toso Co. Ltd. (Tokyo, Japan).

Mixing of hydroxyapatite and zirconia in water was performed with a ball-milling apparatus using zirconia balls for 3 h. The powder mixture with a ratio of $HA/ZrO_2 = 10/1$ after drying was pressed to form a 1 mm-thick disk under 60 MPa for 3 min in air using a uniaxial press apparatus.

In the dry-pressing process to make a layered green composite, ZrO_2 powder was first pressed under 10 MPa in a die with the cross section of 4.5×50 mm^2, and then hydroxyapatite was added on the ZrO_2 powder compact in the same die, followed by pressing under 60 MPa for 3 min in air using a uniaxial press apparatus.

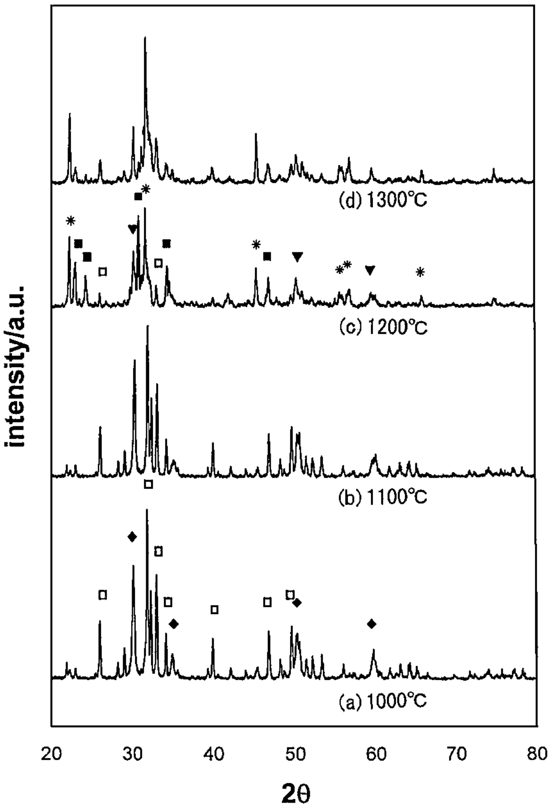

Figure 1 X-ray diffraction patterns of the mixed powder compacts of hydroxyapatite and ZrO$_2$ sintered at (a) 1000°C, (b)1100°C, (c)1200°C, and (d)1300°C for 1 h in air. □: hydroxyapatite, ♦: ZrO$_2$(tetragonal), ■: α-TCP, ∗: CaZrO3, ▼: ZrO$_2$(cubic).

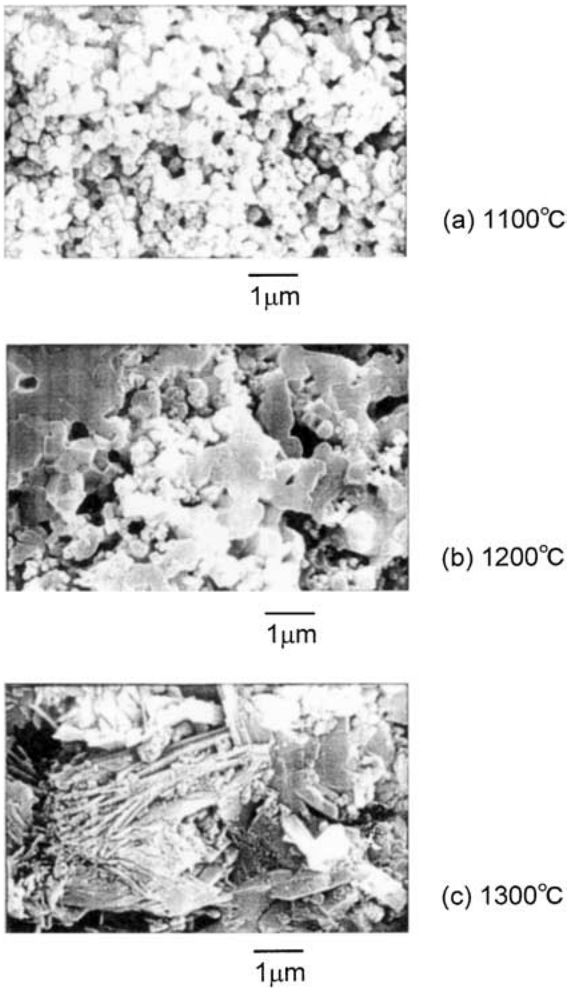

Figure 2 SEM photograph of the mixed powder compacts of hydroxyapatite and ZrO$_2$ sintered at (a) 1100°C, (b) 1200°C, and (c) 1300°C for 1 h in air.

The volume ratio of two powders was selected at that HA/ZrO$_2$ = 1/2.

In the tape cast process of a layered composite, two aqueous suspensions were prepared. The aqueous suspension of 35 mass% of hydroxyapatite powder was prepared by adding 2 mass% polyacrylic ammonium (dispersant), 12.5 mass% polycarbonate ammonium (binder) and 12.5 mass% polyethylene grycol (plasticizer). The residual percent was water. The suspension of 50 mass% of zirconia powder was prepared by adding 1 mass% Polyacrylic ammonium (dispersent), 11 mass% polycarbonate ammonium (binder) and 11 mass% polyethylene grycol (binder). Mixing procedure was performed in a ball milling using the resin balls and a polypropylene jar. The suspensions were consolidated on a polyester sheet using a doctor blade apparatus (Tugawa-seiki Co. Ltd., Tokyo, Japan) at a transfer rate of 25 cm/min. The double layer sheet was made through one-step drawing procedure using two tanks of suspensions. The clearance of a front blade was controlled to form a 0.5 mm-thick upper layer of hydroxyapatite and 1 mm-thick bottom layer of zirconia. The formed sheets were dried at room temperature for 1 day in vacuum after freezing them at 160 K. The obtained green tapes were once burned out at 650°C before sintering.

Sintering of green bodies was performed at 1000°, 1100°, 1200° and 1300°C for 1 h in air at heating rate of 5 K/min using an electric furnace.

The crystal phase was analyzed using a powder X-ray diffraction apparatus (XRD; Rigaku Rint2000, Tokyo, Japan). A scanning electron microscopy (SEM; JM6100, Tokyo, Japan), attached with an energy dispersion X-ray spectrometer (EDX), was applied to investigate the microstructure and chemical composition in the cross section area of layered sintered bodies.

The lead (Pb) removal test was performed using a cut piece from a tape-casting layer composite after sintering. An aqueous lead nitrate solution of 0.3 dm^3 with 2.5×10^{-4} mol/dm^3 (0.25 mM) were passed slowly through a filter film of 2×2 cm^2 cross section at a rate of 0.12 dm^3/h. The same permeation procedure was repeated several times with the same piece. The concentration of Pb in a filtrated solution was analyzed using an inductively coupled plasma atomic emission spectrometer (ICP; SPS7800, Seico Instruments Inc., Tokyo, Japan).

3. Results and discussion

3.1. Solid state reaction

Fig. 1 shows the XRD patterns of the sintered bodies from the powder mixtures, which were heated at 1000°, 1100°, 1200° and 1300°C. The starting phases of hydroxyapatite and tetragonal zirconia were kept below 1100°C. In a sample heated at 1200–1300°C, hydroxyapatite, tetragonal ZrO$_2$, CaZrO$_3$ and α-type tricalucium

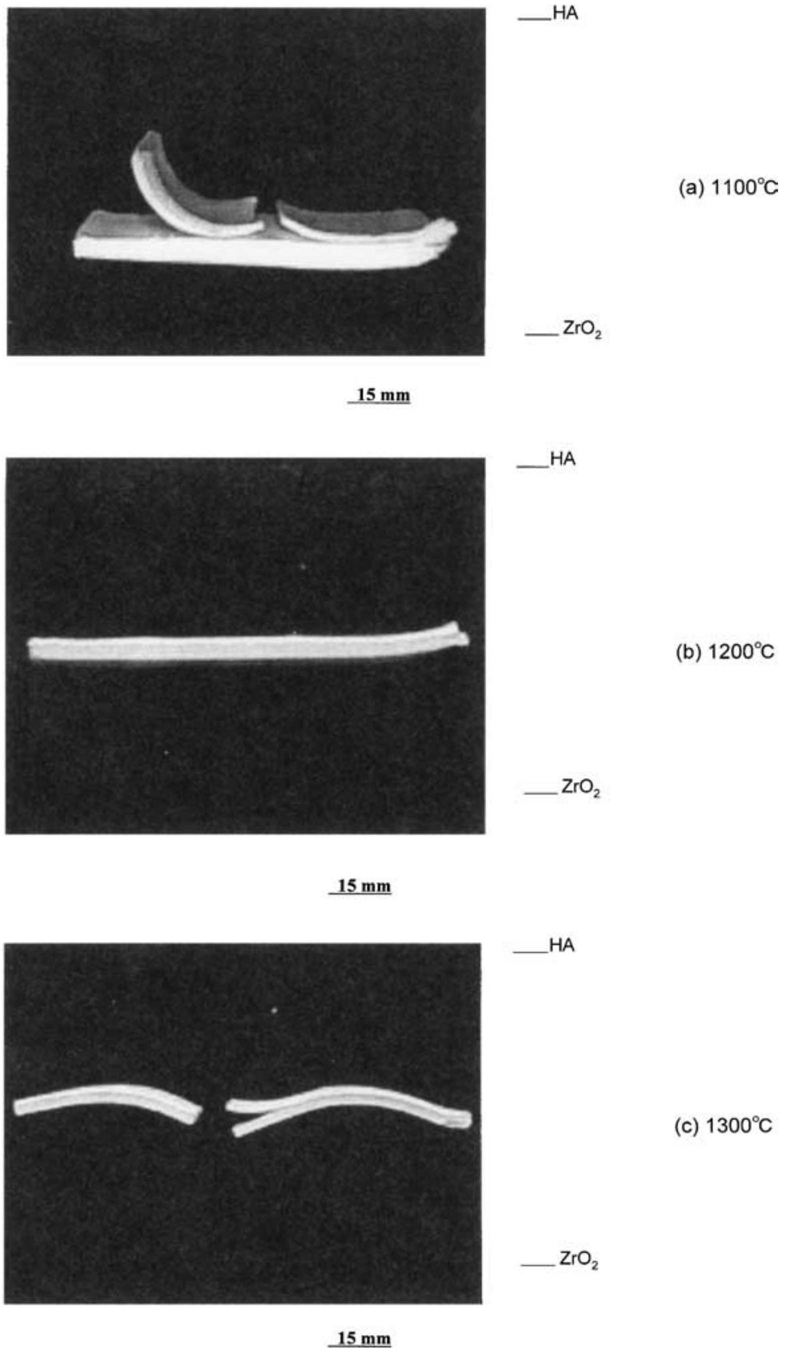

Figure 3 Whole side view of three composite ceramic plates from two-step powder pressing process, sintered at (a)1100°C, (b)1200°C and (c)1300°C for 1 h in air.

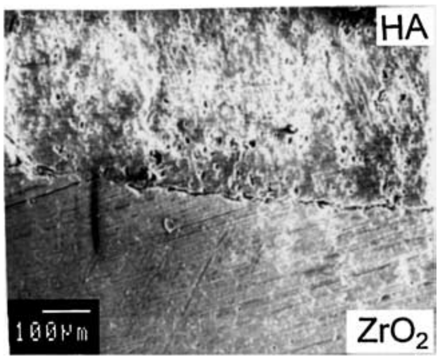

Figure 4 Cross sectional SEM view near interface in a layered composite from two-step powder pressing process, followed by sintering at 1200°C for 1 h.

phosphate (TCP) were detected. Thus, the solid state reaction at 1200°C was as follows.

$$\begin{aligned}Ca_{10}(PO_4)_6(OH)_2 + ZrO_2 \\ = CaZrO_3 + 3Ca_3(PO_4)_2 + H_2O \qquad (1)\end{aligned}$$

Here, small amount of Y_2O_3 in 2Y-TZP powder is assumed to be in $CaZrO_3$ phase. The XRD of a sample heated at 1300°C indicated the structural changes, such as the grain growth of $CaZrO_3$ (from peak sharpness) and the formation of cubic ZrO_2, with the reservation of hydroxyapatite phase.

Fig. 2 shows the microstructure of a power mixture compact heated at 1000°, 1100° and 1200°C. At 1200°C, the grain growth of sintered hydroxyapatite was observed, however zirconia remained as a

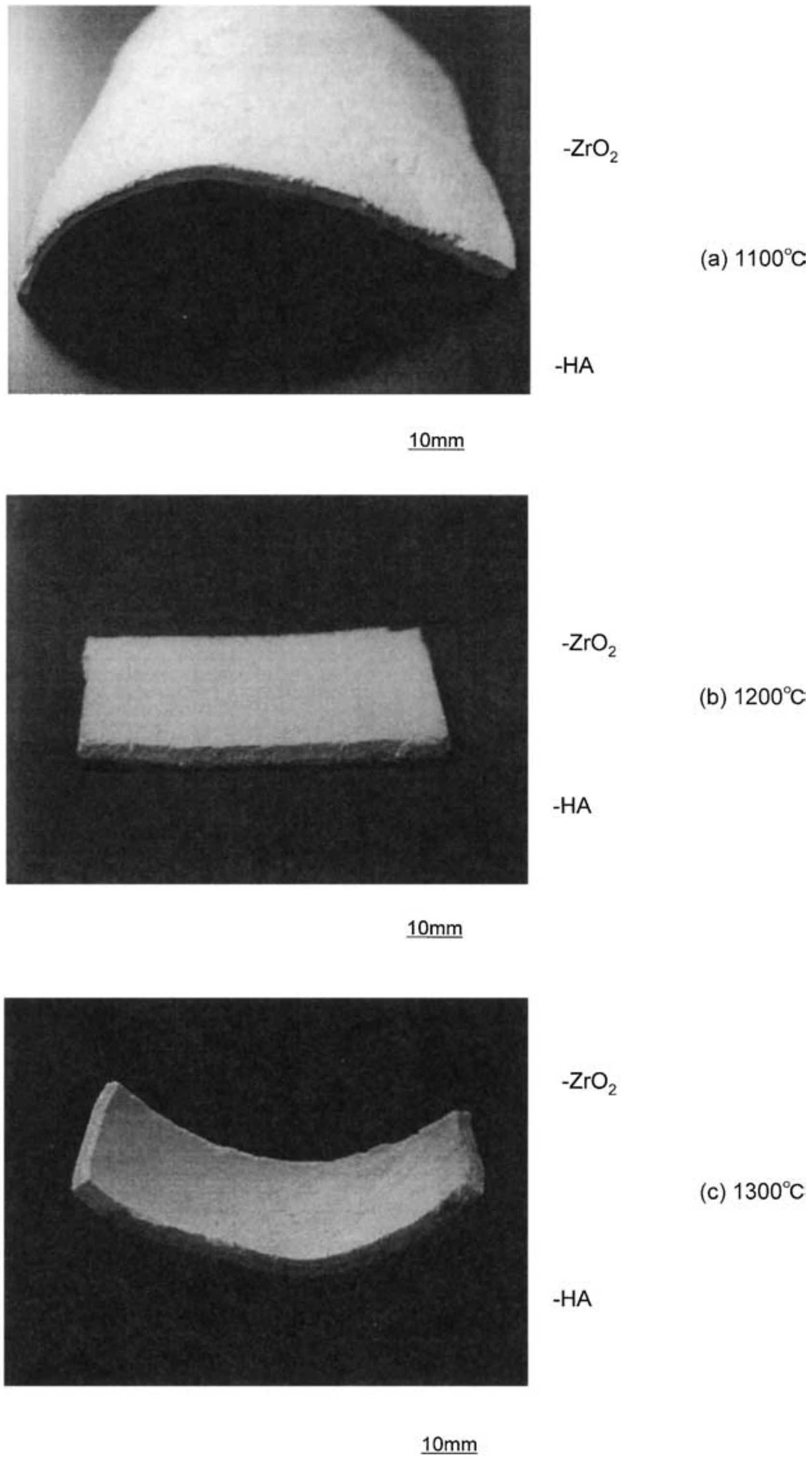

Figure 5 Whole view of three composite ceramic plates from tape cast process, followed by sintering at (a)1100°C, (b)1200°C, and (c)1300°C for 1 h in air.

partially sintered porous body. At 1300°C, the solid state reaction between them produced $CaZrO_3$ grains.

3.2. A layer composite from pressing compact

Fig. 3 shows the whole side view for three layered composites from press forming, followed by sintering at 1100°, 1200°, and 1300°C for 1 h in air, respectively. A relatively flat plane was obtained under the condition of sintering at 1200°C (Fig. 3b), however the other composites sintered at 1100° and 1300°C showed strongly a curving feature and fracture (Fig. 3a and c). The curvature was in a different sense, depending on whether sintering was done at 1100° or 1300°C. A hydroxyapatite compact showed a sintering behavior and start to its shrinkage at around 1100°C. On the other hand, ZrO_2 seemed to sinter at higher temperatures. The curving phenomenon was explained by the difference of the amount of shrinkage between hydroxyapatite and zirconia during sintering at selected temperatures of 1100–1300°C. Thus, by selecting a temperature of

1200°C, we can fabricate a layer composite plate of hydroxyapatite and zirconia.

The XRD indicated each phase of hydroxyapatite and zirconia on the two surfaces of composites. No solid state reaction reached the free surface of the sintered body. Fig. 4 shows the SEM photograph at the interface of hydroxyapatite and zirconia heated at 1200°C. The EDX on some grains in the interface region revealed the coexistence of Ca and Zr with the molar ratio of 1:1, indicating the formation of $CaZrO_3$. The solid state reaction at an interface of this composite seems to be essentially the same as in a sintered powder mixture. However, the reaction area was limited within ca. 10 μm-width. Also, the SEM revealed the cracks at an interface of hydroxyapatite and zirconia after cross-sectional polishing procedure. As seen in Fig. 4, the local stress seems to induce the cracks along the interface. This fact suggests that it would be difficult to form a stable dense composite with high strength. However, a porous medium for an absorbent bed should be formed if the solid state reaction would produce an intermediate phase, where the stress can be relaxed with a certain gradient, between two layers. The result suggests that co-sintering of a plate-shaped hydroxyapatite/zirconia layer ceramic is not so easy because of shrinkage mismatch and solid state reaction. However, it is found that a flat sintered body is obtained when a sintering temperature of 1200°C is selected. Therefore, the fabrication of a porous composite, in which strain is partially relaxed, will be possible. Since the solid state reaction is very limited near the interface, the desired original property of hydroxyapatite will remain. In the following section, a porous composite is fabricated to make a column reactor.

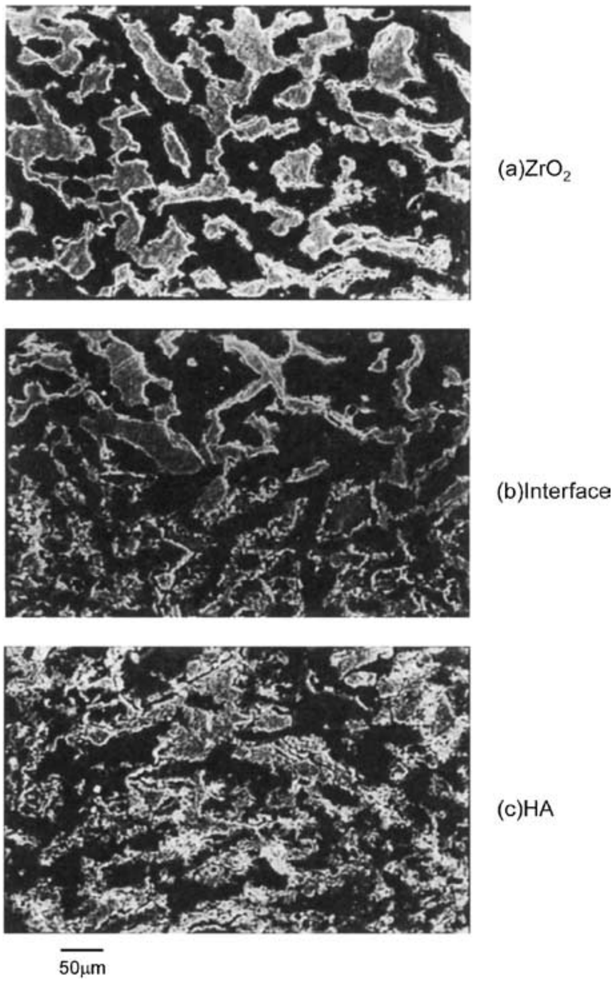

Figure 6 SEM photograph of cross sectional view on zirconia (a), near interface (b), and on hydroxyapatite (c) in a layered composite from tape cast process, followed by sintering at 1200°C for 1 h.

3.3. A layer composite from tape cast

In general, difficulty of forming via a tape cast process is caused by the phenomenon that the green sheet is often accompanied by heterogeneous shrinkage and cracking during drying. In this work, since we applied the freeze-drying process to forming, the green tapes hardly exhibited shrinkage and curving before sintering.

Fig. 5 shows the whole view of sintered layered tapes, heated at 1100°, 1200°, and 1300°C for 1 h in air, respectively. Although they should be porous bodies, the curving phenomenon with the same curvature direction as in the sintered compact bodies were observed. The layer composites heated at 1100° and 1300°C have the opposite curvature each other, whereas the body sintered at 1200°C was flat. This result indicates the importance of careful selection of the sintering temperature in order to make a porous layered composites by tape casting.

Fig. 6 shows the SEM photograph of a layered porous composite sintered at 1200°C for 1 h in air. Open pores, which were interconnected, with an average size of 17 μm (distribution; 6–30 μm) can be seen in the zirconia (in Fig. 6a), whereas the pore size was as small as 11 μm (distribution; 3–30 μm) in hydroxyapatite (in Fig. 6c). In the region of the interface, a graded feature with different pore diameters is observed as in (b) in Fig. 6. Since the connected pore is structured exists throughout the whole of the thick sintered plate, this ceramic will be useful for a filter or a reactor of porous ceramic.

Fig. 7 shows the XRD, which was measured on both sides of this porous composite. On the surfaces, tetragonal ZrO_2 and hydroxyapatite were observed. Since both the layers are thick, the solid state reaction does not reach the free surfaces. Around the interface, the

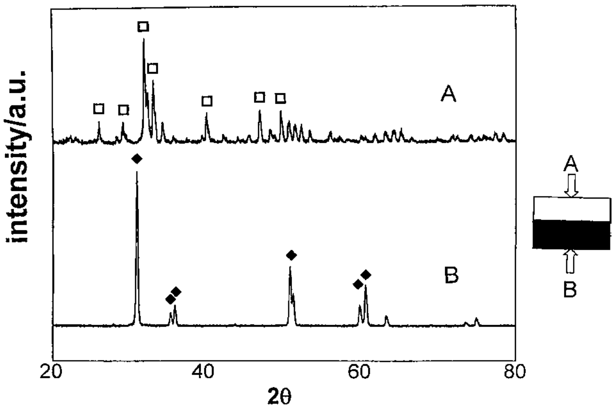

Figure 7 X-ray diffraction patterns of the layered composite of hydroxyapatite and ZrO_2 sintered at 1200°C for 1 h in air (A: hydroxyapatite side, B:ZrO_2 side). □: hydroxyapatite, ♦: ZrO_2(tetragonal).

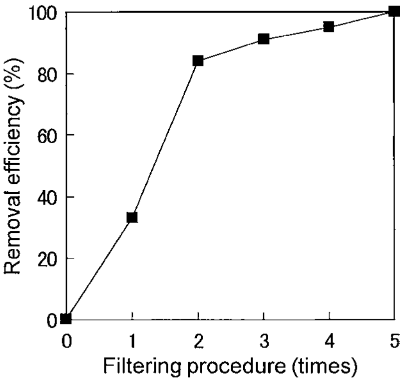

Figure 8 Removal percent of aqueous Pb (0.25 mM) in water as a function of repeated filtering runs using a piece of a layer composite from tape cast process, followed by sintering at 1200°C for 1 h in air.

XRD detected the phases of $CaZrO_3$ and cubic ZrO_2. The XRD measurement was performed on the interface area after carefully polishing a hydroxyapatite side of a composite. Also, the EDX analysis revealed the graded composition of Ca and Zr near interface with a width of ca.50 μm. Although the solid state reaction also occurred in the interface region, the tape cast ceramic plate has sufficient strength for handling and continuous pore structure suitable for a composite filter medium.

3.4. Removal of aqueous lead

Fig. 8 shows the removal efficiency as a function of the repeated runs in a lead immobilization test. The efficiency of Pb removal was 32% in the first run, however it soon reached 92% after three times in repeated runs for the 0.25 mM Pb solution. After the removal test, the shape of a layer composite piece remained without cracks, deformation and deposits. The result suggests that porous zirconia-supported hydroxyapatite layer composite is expected to be effective as a filter for use even in strong acid solutions. A tape cast process is practical to produce this layered composite medium of hydroxyapatite and zirconia.

4. Conclusion

The solid state reaction and sintering in composites, which were formed by powder mixture, dry-pressing compaction and a tape cast process, were examined for the purpose of producing a layered hydroxyapatite/zirconia ceramic. The solid state reaction between hydroxyapatite and zirconia occurred in a limited region at the interface in a layered composite body. After sintering of the layer composites from powder pressing and slip casting, the significant deformation of composite bodies was observed, the extent of which depended on the sintering temperature. By selecting a sintering temperature of 1200°C, we formed a layer ceramic composite of hydroxyapatite/zirconia that was flat. The tape cast process was useful for making a porous sintered composite of hydroxyapatite and zirconia. The porous composite showed good removal of aqueous lead from wastewater without deformation and dissolution.

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