

The microstructure and properties of porous alumina/zirconia composites fabricated by a TBA-based freeze casting route

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Porous alumina/zirconia composites with a controlled “designer” pore structure have been prepared by the tertiary-butyl alcohol (TBA)-based freeze casting technique. The porous materials were characterized in terms of their sintered microstructures, physical and mechanical properties. Unidirectional aligned macropore channels with highly dense structured walls were developed by controlling the solidification direction of the TBA solvent. The sintered porosity and pore size generally decreased with increasing solid loading, this leading to higher compressive strength. The resulting porous materials exhibited an average porosity and compressive strength in the range 63.5-28.8% and 48-341 MPa, respectively, depending on the processing conditions applied. With further addition of zirconia to alumina, the compressive strength was enhanced with a decrease in the porosity, presumably due to the relatively high densification of compacts containing zirconia powder.

Key words: Alumina/zirconia, Tertiary-butyl alcohol, Solidification, Pore channels, Compressive strength.

Introduction

Porous ceramics have attracted a great deal of attention because of their wide applications including thermal insulation, liquid/gas filters, bone tissue engineering scaffolds, supports for catalytic agents and electrodes in fuel cells [1-3]. Also, porous ceramics can possess inherent advantages, i.e., high melting points, a high corrosion and wear resistance, a low thermal mass and thermal conductivity, and a high specific strength. In particular, porous ceramics with interconnected pore channels are attractive because they have an excellent permeability and large specific surface area. The characteristics and applications of porous ceramics are mainly governed by the nature of the materials, pore morphology and mechanical properties. The mechanical strength of porous ceramics is closely related to the pore and wall structure which are determined by the processing technique applied; therefore, the relationship between the porous structure and the mechanical behavior must be well understood in designing unique pore microstructures with an improved strength.

Various processing routes have been developed to produce porous ceramics [1]. Compared to dry processing, wet chemical forming routes are widely used for fabricating porous ceramics due to their advantages; in particular, they can give complex-shaped porous bodies with a controlled pore structure and high porosity. Among wet forming techniques, freeze casting is a

promising approach to produce microstructure-controllable porous ceramics since it is flexible in processing and cost-effective, and enables scarcely drying shrinkage [4]. This method involves the preparation of a ceramic slip that is poured into a mold, it is then frozen and the solvent sublimated away. The removal of the frozen solvent by sublimation can lead to a near net shaped porous ceramic with uniquely controlled pore channels (e.g., long-range ordered and/or gradient pore structures), mainly depending on the slurry concentration, freezing solvent, freezing direction and rate, and freeze-drying operation [5-8]. Water, camphene, naphthalene-camphor [9], or tertiary-butyl alcohol (TBA) [10] can be used as a freezing vehicle. Unlike water- and camphene-based freeze castings, which develop a dendritic porous network, TBA-based freeze casting can result in relatively long pore channels parallel to the freezing direction after sublimation, due to the unidirectional solidification characteristic of the TBA solvent [11].

The objective of this study is to explore the application of TBA-based freeze casting to fabricate highly porous alumina/zirconia composites with tailored pore structures and an improved compressive strength and to investigate the effects of processing variables (e.g. the slurry concentration, mixed $\text{Al}_2\text{O}_3/\text{ZrO}_2$ ratio and sintering temperature) on the micro-structure and properties of the resultant porous composites. An alumina/zirconia composite is a potential engineering ceramic because of its good mechanical and thermal properties [12-15].

Experimental Procedure

Al_2O_3 powder (AES-11C, Sumitomo Chemical Co.,

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Japan) was mixed with 5 ('95A5Z') and 15 vol.% ZrO₂ ('85A15Z') (TZ-3YS-E, Tosho Co., Japan). The mean particle size and specific surface area of the Al₂O₃ powder were 0.57 μ m and 9.1 m²/g, and those of the ZrO₂ powder were 0.28 μ m and 7.2 m²/g, respectively.

The batch powder slurries with a solid loading of 10–25 vol.% were homogenized by ball milling in TBA (Junsei Chemical Co., Japan) for 24 h at 40 °C using a polyethylene bottle with alumina ball media; 1 wt.% citric acid (Aldrich Chemical Co., USA) dispersant and 0.5–4 wt.% polyvinyl butyral (PVB, Aldrich Chemical Co., USA) binder, based on powder content, and 0.25 wt.% ethoxylated acetylenic diol (Dynol 604, Air Products and Chemicals, Inc., USA) surfactant, based on TBA solvent were used. After de-airing under vacuum for 3 minutes, the warm 95A5Z and 85A15Z slurries were poured into a cylindrical epoxy mold (diameter 25 mm) protected by a heat insulating layer in which the bottom face of the mold was tightly capped. Subsequently, the mold was placed on a stainless steel plate which was temperature-controlled at < 0 °C using liquid nitrogen; in such a condition, controlled freezing of the TBA gradually occurs from the bottom to top of the specimen, possibly resulting in unidirectional pore channels through the whole cast body after evaporation. The frozen samples were carefully removed from the mold and then the suspension medium was sublimated in a freeze drier (Labconco 77540, Western Medics, USA). After calcining the green bodies at 600 °C for 1 h in air with a heating rate of 2 °C minute⁻¹ to remove organic materials, sintering was carried out at 1400 and 1500 °C for 2 h.

Sintered porosity was measured by the water immersion method based on Archimedes' principle. Crystalline phases were identified by X-ray diffractometry (XRD, D/max-IIA, Rigaku, Japan). The linear shrinkage in the direction perpendicular to the freezing direction was determined by the following equation: shrinkage (%) = $[(l_g - l_s)/l_g \times 100]$, where l_g and l_s are the diameter of samples before and after firing, respectively. The pore and wall morphologies were observed using a scanning electron microscope (SEM, JSA-840A, Jeol, Japan). The pore size and wall thickness were determined for 15–20 pores and walls, arbitrarily selected in each sintered specimen. The compressive strength in the direction parallel to the freezing direction was measured for five sintered specimens with dimensions of 19 mm diameter $\times$ 10 mm height using a universal testing machine (model 6025, Instron, USA) with a crosshead speed of 0.5 mm minute⁻¹ and a load cell of 1 kN.

Results and Discussion

XRD patterns of Al₂O₃-ZrO₂ materials sintered at 1400 °C for 2 h are shown in Fig. 1. Nearly all characteristic peaks corresponding to α -Al₂O₃ (JCPDS

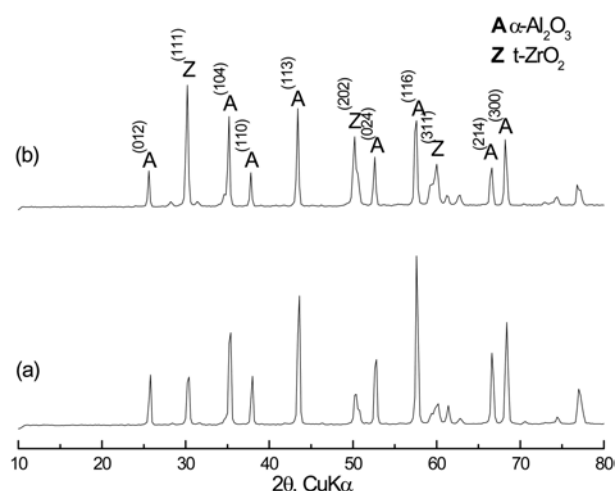


Fig. 1. XRD patterns of (a) 95A5Z and (b) 85A15Z composites sintered at 1400 °C for 2 h.

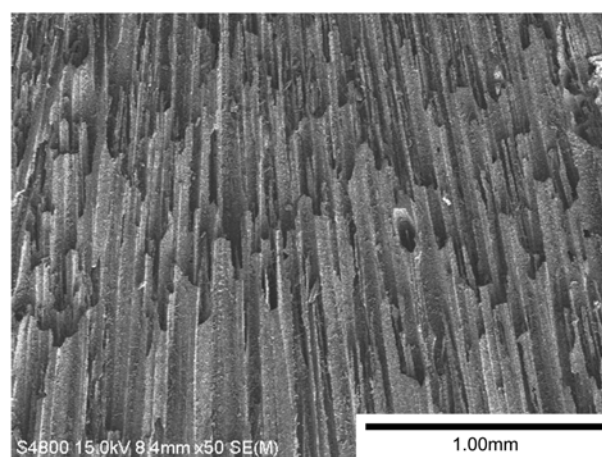


Fig. 2. SEM micrograph of a cross-section parallel to the macroscopic TBA solid growth direction, showing unidirectional pore channels; 95A5Z specimen sintered at 1400 °C with 10 vol.% solid loading.

#46-1212) and t-ZrO₂ (JCPDS #17-923) phases were confirmed; m-ZrO₂ phase could be scarcely detected. It is considered that the t-ZrO₂ particles in this study could be effectively controlled by the matrix Al₂O₃ at a given firing temperature below a certain critical grain size (typically < 1 μ m in a 3 mol.% Y₂O₃-ZrO₂ [16]) for spontaneous t $\rightarrow$ m transformation during cooling. Similar diffraction patterns were also obtained in samples sintered at 1500 °C.

Processing variables (e.g. solid loading, sintering temperature, and Al₂O₃/ZrO₂ ratio) can play a great role in determining the microstructures of the sintered materials. The effects of solid loading (10–25 vol.%), firing temperature (1400 and 1500 °C), and the addition of zirconia (5 and 15 vol.%) on the sintered microstructures have been examined. Similar porous structures were obtained. A typical SEM micrograph of the cross-section parallel to the macroscopic growth direction of TBA solid is given Fig. 2. The morphology showed unidirectional, interconnected pore channels

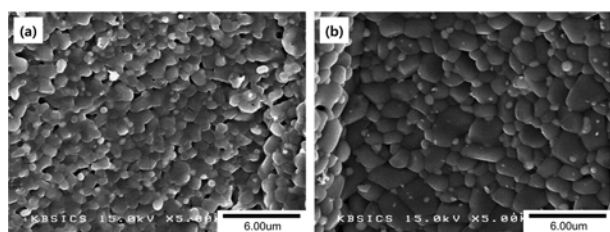


Fig. 3. SEM micrographs of the walls of pore channels in 95A15Z specimens; sintered at (a) 1400 °C with 10 vol.% solid loading and (b) 1500 °C with 25 vol.% solid loading.

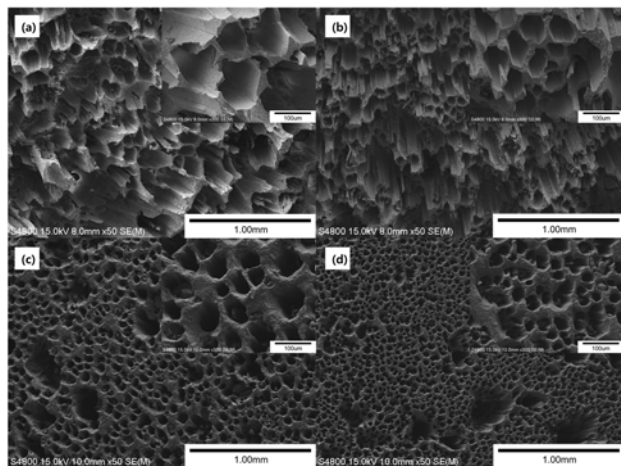


Fig. 4. SEM micrographs of cross-sections perpendicular to the macroscopic TBA solid growth direction; 95A5Z specimens sintered at 1500 °C with (a) 10, (b) 15, (c) 20, and (d) 25 vol.% solid loading.

aligned regularly over a long range along the TBA solid growth direction. This columnar morphology with unidirectional pore channels was clearly different from the lamellar structure with dendrite-like pores obtained mainly in water- or camphene-based freeze castings [17-19]. The growth of the TBA solid in a straight direction over a considerable length during freezing may more easily provide pore channels for improved gas/liquid fluidity and a high specific surface area. Microstructures of walls of long pore channels were examined in detail at higher magnifications and are given in Fig. 3. The walls showed a relatively dense porous structure, which consisted of small polygonal ($< 3.8 \mu\text{m}$) Al_2O_3 grains and fine spherical ZrO_2 inclusions ($< 0.7 \mu\text{m}$) mainly located at the grain boundaries of the matrix. At a higher solid loading (25 versus 10 vol.%), the wall structure became more dense by grain growth through the coalescence process of the initial Al_2O_3 particles. Two types of pores in the TBA-based freeze cast materials formed, i.e., large long interconnected pore channels outside and a few isolated fine pores inside the walls were observed. It is considered that the longitudinal pore channels are determined by the spacing and morphology of the TBA solid structure formed on freezing and removed during sublimation, whereas the fine pores in the walls of the

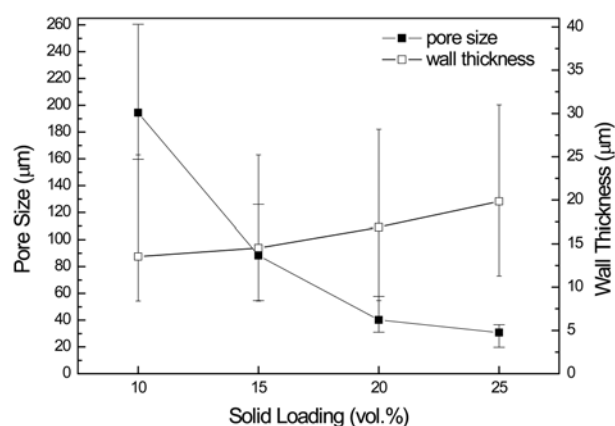


Fig. 5. Pore size and wall thickness of porous alumina/zirconia composites containing 5 vol.% ZrO_2 sintered at 1500 °C as a function of solid loading.

channel are due to the porosity resulting from the sintering stage of the green body of powder, usually leaving the residual voids, some of which are too large to sinter out. After sintering at 1500 °C with 25 vol.% solid loading, it is suggested that the removal of these remaining pores are nearly completed (Fig. 3(b)).

SEM micrographs of the cross-sections perpendicular to the macroscopic growth direction of the TBA solid for freeze cast 95A5Z bodies sintered at 1500 °C with 10-25 vol.% solid loadings are shown in Fig. 4. The presence of a few very large-sized ($\sim 0.2 \text{ mm}$ in diameter) pore channels was locally observed, especially in higher solid loading suspensions ($\geq 20 \text{ vol.}\%$). Higher solid loadings are favorable for producing sintered freeze cast materials with good mechanical strength since they can give a high particle packing density and low porosity; in this case, however, it is not easy to prepare a well dispersed suspension of solid particles due to the increased viscosity, often resulting in partially inhomogeneous porous structures. With increasing solid loading, the average pore size (195-40 μm) decreased and conversely the average wall thickness (13.5-19.8 μm) increased (Fig. 5). Higher solid loading suspensions contain a small volume fraction of solvent and thus relatively narrow spaces are occupied by the solvent, compared with lower solid loadings. As a result in this study, a porous structure with the smallest pore size using a 25 vol.% solid loading suspension could be formed after the sublimation of TBA solvent.

The linear shrinkage, porosity and compressive strength of porous materials fabricated with different solid loadings and sintering temperatures are shown in Table 1. With increasing solid loading, the shrinkage decreased; also, it increased with increasing sintering temperature and zirconia content at a given solid loading. Consequently, the highest shrinkage ($\sim 28.1\%$) was obtained in the relatively porous 85A15Z green bodies containing 15 vol.% zirconia sintered at 1500 °C with 10 vol.% solid loading. The compressive strength

Table 1. Porosity, shrinkage and compressive strength of porous alumina/zirconia composites obtained by sintering at 1400 and 1500 °C with 10-25 vol.% solid loading.

Sintering temperature (°C)	Solid loading (vol.%)	Porosity (%)		Shrinkage (%)		Compressive strength (MPa)	
		95A5Z	85A15Z	95A5Z	85A15Z	95A5Z	85A15Z
1400	10	63.5 ± 1.2	61.1 ± 1.8	25.3 ± 1.4	28.1 ± 0.9	48.2 ± 5.4	48.5 ± 5.7
	15	50.8 ± 2.3	49.4 ± 2.1	20.4 ± 1.2	22.9 ± 0.8	86.4 ± 6.7	113.3 ± 11.2
	20	42.2 ± 1.7	40.9 ± 2.3	19.4 ± 1.1	22.4 ± 1.8	206.2 ± 14.1	237.8 ± 15.7
	25	33.1 ± 1.5	31.6 ± 1.5	14 ± 1.3	18.4 ± 1.4	308.1 ± 20.4	320.9 ± 17.1
1500	10	58 ± 2.4	57.8 ± 1.7	27.8 ± 0.9	30.4 ± 1.1	70.4 ± 5.5	77.6 ± 6.1
	15	49.1 ± 2.2	48.1 ± 1.5	24.2 ± 2	26.7 ± 2.3	100.1 ± 9.8	128.2 ± 10.7
	20	38.9 ± 1.3	38.4 ± 1.5	23.3 ± 2.2	25.2 ± 1.5	211 ± 14.1	312.5 ± 16.3
	25	29.4 ± 0.9	28.8 ± 0.8	22.3 ± 2.6	24.5 ± 2.1	314.1 ± 18.2	341.3 ± 18.8

of porous materials are influenced by many other parameters with interdependency, including porosity, pore morphology, wall thickness and wall density, through the medium of the sintered microstructure, which are mainly determined by fabrication processes. Among these parameters, generally, the compressive strength of porous materials is greatly influenced by the degree of porosity. The compressive strength was found to be inversely proportional to the porosity, i.e., a low porosity gave a high compressive strength possibly due to the increased wall thickness and the decreased pore size of the sintered materials (Fig. 5). The 85A15Z specimens containing 15 vol.% zirconia sintered at 1500 °C with 25 vol.% solid loading exhibited the greatest compressive strength (~341.3 MPa) with the lowest porosity, ~28.8%; on the other hand, the lowest compressive strength (~48.2 MPa) was obtained in the 95A5Z specimens with ~63.5% porosity, sintered at 1400 °C with 10 vol.% solid loading.

Several studies on the compressive strength of freeze cast porous ceramics containing alumina and/or zirconia have been reported. However, it is not reasonable to compare simply the compressive strength of the porous ceramics obtained, mainly due to their different pore morphology. For example, Zuo et al. [7] fabricated water-based freeze cast yttria-stabilized zirconia (YSZ) ceramics with interconnected lamellar porous structures; after sintering at 1300-1400 °C with 75 wt.% initial solid loading, the compressive strength of the porous materials was in the range 23.6-63.9 MPa (66-35% in open porosity). After sintering at 1350-1550 °C, porous YSZ ceramics fabricated by TBA-based gel casting exhibited a porosity of 77-65% and compressive strength of 3-27 MPa [20]. Liu et al. [21] prepared porous alumina/zirconia composites ($\text{Al}_2\text{O}_3/\text{ZrO}_2 = 20/80$, wt.%) by the freeze casting of aqueous suspensions with solid loadings of 40-70 wt.%; the compressive strength and porosity of the bodies sintered at 1550 °C were 15-81 MPa and 74-35%, respectively. Hong et al. [22] obtained highly porous

zirconia ceramics with dendritic pore structures by camphene-based freeze casting of 10-20 vol.% solid loadings; the specimens sintered at 1450 °C for 3 h exhibited a porosity of 81.5-66.5% and a compressive strength of 19-58 MPa. Yoon et al. [23] produced highly-aligned porous alumina ceramics with a compressive strength of 11-95 MPa and a porosity of 82-59% using a room-temperature (3-35 °C) camphene-based freeze casting.

Clearly, the physical and mechanical properties of sintered porous alumina/zirconia composites processed using a TBA-based freeze casting were affected by the processing variables (i.e., solid loading, sintering temperature and zirconia content), especially the level of solid loading. It is considered that the porous materials require a high porosity (macro) with interconnected porous structure for effective fluid permeability, as well as a high wall density (micro) for good mechanical strength. Therefore, the optimum processing conditions corresponding to a specific industrial and/or environmental application can be selected and produced in the form of designer microstructures.

Conclusions

Sintered porous alumina/zirconia composites with a unique pore structure and a good compressive strength can be produced by a controlled TBA-based freeze casting process. The microstructure of the sintered materials was characterized by the presence of large pore channels regularly grown parallel to the solidification direction of the TBA solvent and a few isolated, small sized pores irregularly distributed. The former seemed to be located among the walls and the latter mainly within the walls. With increasing solid loading from 10 to 25 vol.%, the sintered compressive strength (48-341 MPa) increased, in which it behaved in the opposite manner to the porosity (63.5-28.8%). Consequently, since macroporous alumina/zirconia composites with a relatively long tube structure obtained

by the TBA-based freeze casting exhibit a wide-range of physical and mechanical properties depending on the processing variables (i.e., solid loading, sintering temperature and zirconia content added), it should be possible to select the optimum fabrication conditions corresponding to a specific requirement for a particular application.

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