Capsule Free Hot Isostatic Pressing of Ceria-Doped Tetragonal Zirconia Powder Crystallized in Supercritical Methanol

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Capsule free hot isostatic pressing (HIPing) of 12 mol% CeO_2-88 mo% ZrO_2 ($12CeO_2$-$88ZrO_2$) powder was conducted at 1100~1200°C using the powder crystallized in supercritical methanol followed by supercritical drying. Porous $12CeO_2$-$88ZrO_2$ ceramics with ~35% open porosity, micropore diameter of ~23 nm and a narrow pore size distribution were fabricated by capsule free hot isostatic pressing at 1100°C. The porosity increased with decrease in HIPing temperature and was accompanied by a steady decrease in fracture strength.

Key words : Capsule free het isostatic pressing, porous ceramics, Ceria-doped tetragonal zirconia, Supercritical, methanol

I. Introduction

Porous ceramic materials have received considerable attention for many industrial applications such as heat insulators, catalysts, chemical sensors/transducers and filters because of their excellent heat resistance and chemical stability.[1-3] Several methods such as leaching,[4,5] hydrothermal hot pressing,[6] polymer impregnation[7] and capsule free hot isostatic pressing (capsule free HIPing)[8,9] have been developed for fabricating porous ceramic compacts. The objective of such work is to fabricate porous materials with sufficiently high open porosity, uniform pore size and excellent mechanicl properties.[7-12] Capsule free HIPing, in which pressed powder samples and/or presintered bodies are hot isostatically pressed without encapsulation, is a promising method to achieve this objective. In order to prepare well defined porous ceramics by capsule free HIPing, it is essential to use soft agglomerated powders with a narrow particle size distribution as starting materials. In previous papers,[13-15] it was reported that soft agglomerated fine ceramics powders could be prepared by crystallizing amorphous gel precursors in an organic solvent such as methanol followed by suprecritical drying. In the present study, preparation of porous $12CeO_2$-$88ZrO_2$ ceramic was conducted by capsule free HIPing using $12CeO_2$-$88ZrO_2$ powders crystallized in methanol followed by supercritical drying.

II. Experimental Procedure

High purity $ZrO(NO_3)_2 \cdot 2H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (Kanto Chemical Co. Ltd., Tokyo, Japan) were dissolved in distilled water to produce 0.25 mol dm^{-3} mixed solutions {$[ZrO(NO_3)_2]+[Ce(NO_3)_3]$=0.25 mol dm^{-3}} to yield a $12CeO_2$-$88ZrO_2$ composition. An amorphous gel of the $12CeO_2$-$88ZrO_2$ composition, prepared by slowly adding the mixed solution into vigorously stirred 15 mol dm^{-3} NH_4OH aqueous solution, was successively washed with water, 50 : 50 (vol.-%) water/methanol solution and methanol three times in each case and then suspended in methanol to form 10 wt.-% slurry. The slurry (80 cm^3) was placed into a SUS 314 stainless steel sutoclave of 120 cm^3 internal volume and heated at 250°C for 5 h to crystallize the gel. The crystallized powders were dried by supercritically releasing methanol while keeping the temperature of the autoclave at 250°C and then the powder was calcined at 500°C to remove remaining methanol completely. The powder was designated as SC powder. For comparison, commercial $12CeO_2$-$88ZrO_2$ powder supplied from Tosoh Co. Ltd., Tokyo, Japan (denoted as commercial powder) was also used.

Compacts of dimensions 25 mm × 25 mm × 5 mm were prepared by uniaxial pressing at 20 MPa before cold isostatic pressing (CIPing) at 200 MPa. The compacts were hot isostatically pressed (HIPed) without encapsulation at 1100~1200°C and 200 MPa for 5 h in an 80 vol.-% argon-20 vol.-% oxygen gas atmosphere (Kobe Steel, Ltd. Dr-O_2-HIP). Before heating, samples were pressurized to 70 MPa, then heated at a rate of 2 $Kmin^{-1}$ to a desired temperature and held at the temperature for 1 h. They were cut into rectangular bars, 2 mm × 4 mm × 12 mm and polished to a mirrorlike finish. The phase constitution of powders and sintered compacts was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using Ni filtered CuKα radiation. Powder crystallinity was determined by XRD, thermogravimetry and differential thermal analysis (TG-DTA, Rigaku TAS-200). The specific surface area was determined by measuring the amount of nitrogen

adsorption at 77 K (BET, Sibata, SA-1000). Microstructures of powders and sintered compacts were observed by scanning electron microscopy (SEM, Hitachi S-900) and the grain sizes of compacts were measured by the intercept method.[18] Sintered density was determined by the Archimedes technique and open porosity was determined by the water immersion method at room temperature. The theoretical density of 12CeO$_2$-88ZrO$_2$ was calculated as being 6.25 g cm^{-3} using lattice constants determined by XRD analysis. Fracture strength was measured by three point bend tests with a crosshead speed of 0.5 mm min^{-1} and a span width of 10 mm. Pore size distributions were determined by nitrogen desorption isotherms (Micrometritics ASAP 2010, Shimadzu) by BJH method.[17]

III. Results and Discussion

The scanning electron micrographs of (a) SC-powder and (b) commercial powders are shown in Fig. 1. Both powders consisted of the tetragonal phase. It may be seen that SC powder consisted of soft agglomerates and the agglomerated particle size of SC powder was much smaller than that of commercial powder.

BET specific surface areas and BET particle diameters of commercial and SC powders are summarised in Table 1. The SC 500 powder possessed a much larger BET specific surface area and smaller BET particle diameter

Table 1. BET Specific Surfaces Areas and BET Particles Diameter of 12CeO$_2$-88ZrO$_2$ Powders Prepared by Different Methods

	BET specific surface area (m^2 g^{-1})	BET particle diameter (nm)
SC powder	130	7.4
Commercial	19.5	49.3

than those of the commercial powder.

As was previously reported, SC powders possessed excellent sinterability and densified to almost full theoretical density by normal sintering at a low temperature such as 1,100°C. However, porous compacts with 13~52% porosity were obtained by capsule free HIPing of SC powders at 1100~1200°C (Fig. 2(a)). The increase of the porosity by capsule free HIPing compared with normal sintering is thought to be due to the penetration of highly pressurized gas which prevents shrinkage of pores and enhances bridging of particles.[8,9] On the other hand, sintering of commercial powder did not effectively occur to high density even by normal sintering in the present temperature range. Therefore, the porosities of compacts fabricated by
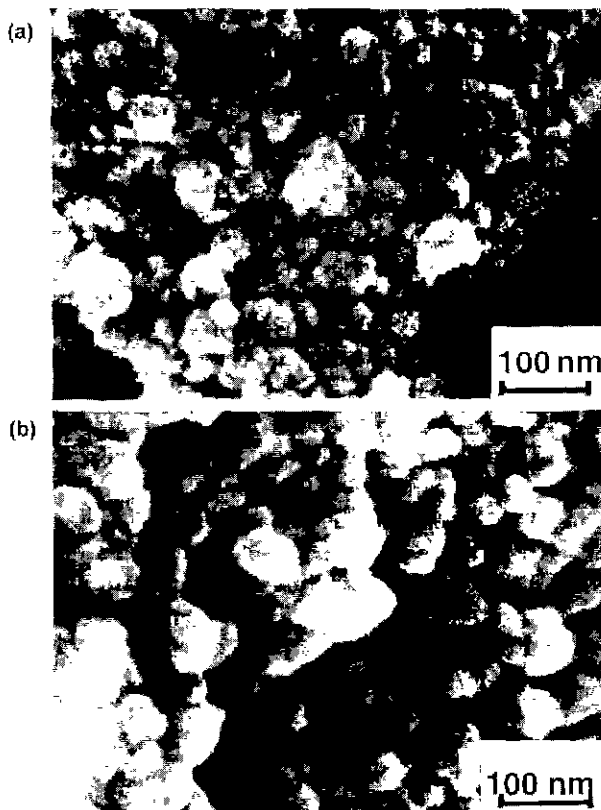

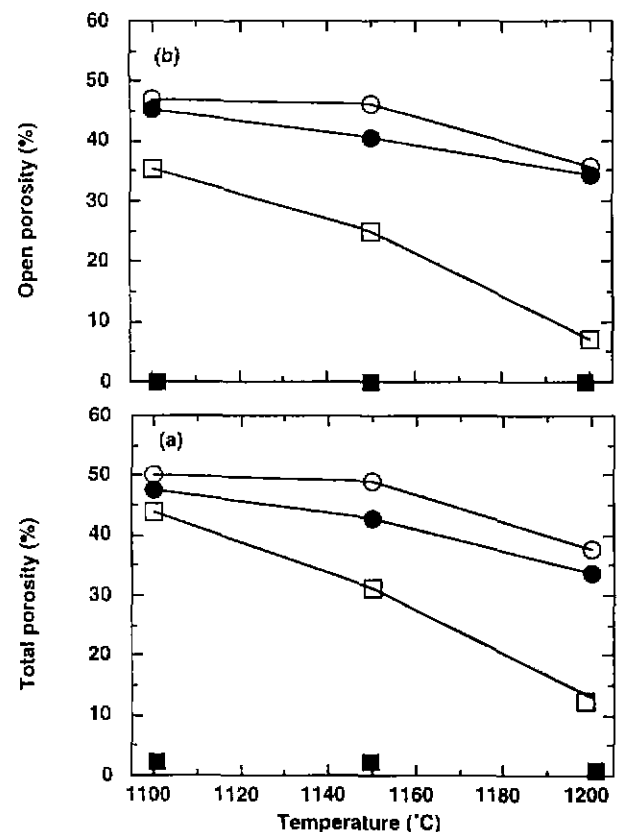**Fig. 1.** Scanning electron micrographs of (a) SC-powder and (b) commercial powder.

Fig. 2. Temperature dependence of (a) total porosity and (b) open porosity of compacts fabricated by capsule free HIPing of (□) SC and (○) commercial powders and normal sintering of (■) SC and (●) commercial powders.

both normal sintering and capsule free HIPing using commercial powder were almost identical falling from 50 to 34% with increase in temperature. The porosities of compacts fabricated at 1100°C using both powders were similar as 40~50%, but those at 1200°C changed significantly depending on the starting powder; the porosities of the compacts fabricated with commercial powders were much larger than those with SC powders. It may be attributed to the difference in the sinterability of the powder. It was also seen that the pores were mainly open state when the total porosity was more than 25%, however, the ratio of open pores/total pores decreased with decreasing total porosity (Fig. 2(b)). Usually, commercially sintered ceramic filters possess 25~50% open porosity. It was found that in order to obtain porous $12CeO_2$-$88ZrO_2$ compacts with more than 25% open porosity, capsule-free HIPing of SC powders should be carried out below 1150°C, whereas the open porosity in the sample fabricated using commercial powder was 34% even at 1200°C.

The scanning electron micrographs of the fracture surfaces of compacts possessing ~35% open porosity fabricated by capsule free HIPing of (a) SC powder at 1100°C and (b) commercial powder at 1200°C are shown in Fig. 3. The microstructures of SC compacts and the commercial compact were quite different. The grain size of SC compacts were ~30 nm, whereas that of the commercial compact were 150 nm. Consequently, the pore sizes in SC compacts seemed to be much smaller than that of the commercial compact.

Pore size distributions of the compacts are shown in Fig. 4. Although they all possessed similar open porosity of ~35%, the pore size distribution curves were significantly different. The compacts fabricated by capsule free HIPing of SC powder showed a narrow pore size distribution with a peak around 23 nm, indicating the mesopore structure of the compact. On the other hand, only a small amount of mesopores were found in compacts fabricated by commercial powders, indicating that the compacts con-
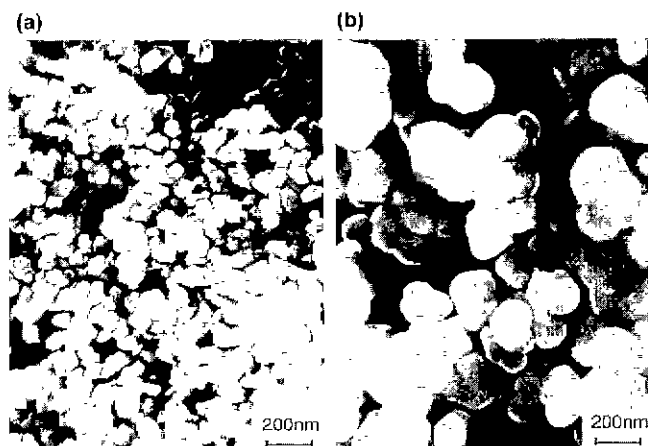

Fig. 4. Pore size distribution curves of compacts fabricated by capsule free HIPing (a) at 1100°C of SC powder and (b) at 1200°C of commercial powder.

sisted of macropores. These difference may be attributed to the difference in crystallite size, agglomerated particle size and the strength of agglomerates of the starting powders.

The sintering behavior for the two types of powders is schematically shown in Fig. 5. Since the HIPing was carried out at low temperature (1100~1200°C) and the sintering between agglomerated particles is inhibited by penetrated highly pressurized gas, sintering seems to proceed mainly between the crystals in the agglomerated particles and the sintering between agglomerated particles does not effectively proceed. As shown in Fig. 1 and Table 1, the crystallite size and agglomerated particle size of SC powder were much smaller than those of the commercial powder. Therefore, the crystals in the agglomerated particles in SC powder may be fully sintered, while the pores remain between the agglomerated particles as shown in Fig. 5(a). On the other hand, the larger crystals in the commercial powder might lead the formation of large agglomerated particles and for pores to remain both in the agglomerated particles and between them as shown in Fig. 5(b). Consequently, compacts fabricated

Fig. 3. Scanning electron micrographs of fracture surfaces of the compacts fabricated by capsule free HIPing (a) at 1100°C of SC powder and (b) at 1200°C of commercial powder.
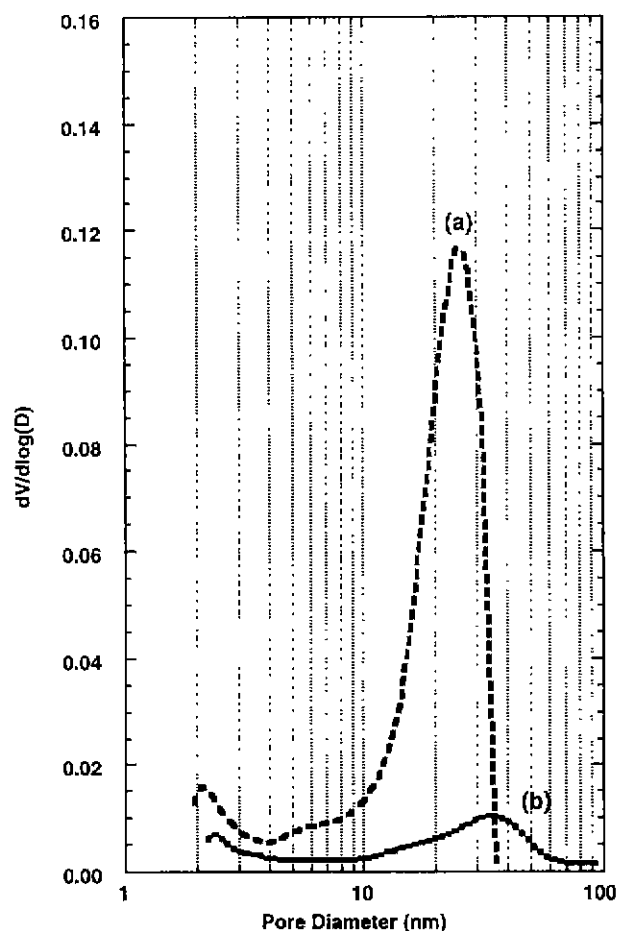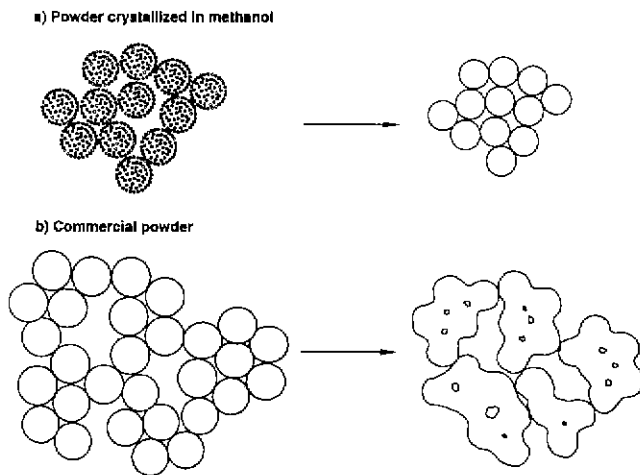
a) Powder crystallized in methanol

b) Commercial powder

Fig. 5. Schematic illustration of sintering behaviour.

using SC powder possessed smaller grain and pore size, and a narrower pore size distribution than compacts fabricated using commercial powders.

The bend strengths of compacts fabricated by normal sintering and capsule free HIPing using SC powders are shown in Fig. 6 as a function of total porosity. The bend strength of both compacts steadily decreased with increasing total porosity, however, at the same porosity the bend strength of HIPed compact was higher than that of normal sintered compact. It is known that the fracture strength, σ, of ceramics can be described by Eq. (1).

$$\sigma = (2E\gamma)^{1/2}/Yc^{1/2} \tag{1}$$

when E, γ, c and Y are Young's modulus, fracture energy, crack length and a constant depending on the crack shape, respectively. Since γ, E, and c are considered to remain constant at the same porosity, the difference in fracture strength may be due to the change in the values of Y. It was reported[3] that the pore shape of HIPed body
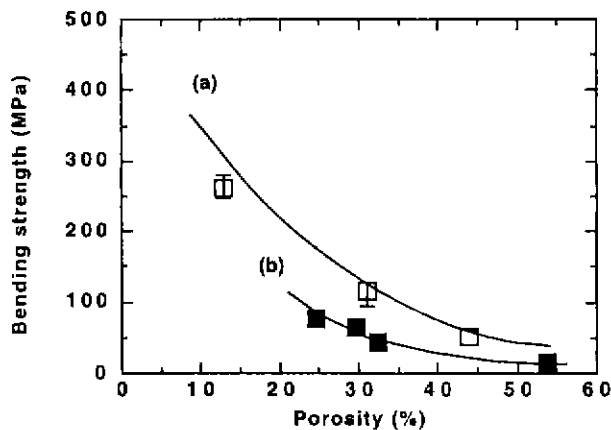

Fig. 6. Relationship between porosity and three point bend strengths of compacts fabricated by (□) capsule free HIPing and (■) normal sintering using SC powders.

is more round than that of normally sintered one due to the enhanced surface diffusion which leads to the well-grown bridges. Namely, the round pore formed by HIPing might resulted in the increase in the fracture strength.

IV. Conclusions

1) Porous $12CeO_2$-$88ZrO_2$ ceramics with 25~35% open porosity, micropre diameters of ~20 nm and a narrow pore size distribution were fabricated by capsule free HIPing at a low temperature (1100~1150°C) using powders crystallized in methanol followed by supercritical drying.

2) The porosity of compacts increased with decrease in HIPing temperature, accompanied with a steady decrease in fracture strength.

3) The bend strength of HIPed compact was higher than that of normal sintered compact at the same porosity.

Acknowledgment

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