Sintering and Ionic Conductivity of CuO-Doped Tetragonal ZrO₂ Prepared by Novel Colloidal Processing

Yoshio SAKKA, Tohru S. SUZUKI, Kiyoshi OZAWA, Tetsuo UCHIKOSHI and Keijiro HIRAGA

National Institute for Materials Science, 1-2-1, Sengen, Tsukuba-shi, Ibaraki 305-0047

新規コロイドプロセスにより作製した CuO 添加正方晶ジルコニアの燃焼とイオン伝導度

目 義雄・鈴木 達・小澤 清・打越哲郎・平賀啓二郎

物質・材料研究機構材料研究所, 305-0047 つくば市千現 1-2-1

Suspensions of Cu²⁺ adsorbed tetragonal ZrO₂ (3Y-TZ: 3 mol% Y₂O₃-doped tetragonal zirconia) powder were prepared and their green bodies consolidated without powdering process by a pressure filtration method. Green bodies with a narrow pore size distribution were obtained after cold isostatic pressing of the pressure filtrated bodies. Small amounts of CuO addition resulted in lower densification temperature by the aid of a liquid phase. Bulk and grain-boundary conductivities were measured by a complex impedance method. Bulk conductivity was nearly independent of CuO addition but grain-boundary conductivity decreased with CuO addition.

[Received July 13, 2001; Accepted September 26, 2001]

Key-words: Colloidal processing, Zirconia, CuO-doped, Sintering, Ionic conductivity

1. Introduction

Yttria-doped tetragonal zirconia (Y-TZ) polycrystalline ceramics have received much attention due to both their ionic conductivity and mechanical property. Recently, considerable attention has been focused on the processing of fine-grained ceramics with controlled density and homogeneous microstructure.^{1,2)} One of the best methods is low temperature sintering of dense and narrow pore sized compact consisting of fine particle.³⁻⁷⁾ To obtain such compact, colloidal processing is suitable.¹⁻⁷⁾ The particle packing is affected by an interparticle force which can be changed from attractive to repulsive by adjusting the pH. High repulsive potential, large zeta potential absolute value, contributes to the dense particle packing with narrow pore size distribution. Utilizing the liquid phase sintering can help low temperature densification.

Liquid-phase sintering of Y-TZ with CuO is known to be effective for densification at low-temperature sintering⁸⁾ and moreover the addition of CuO to Y-TZ can enhance superplasticity.⁹⁻¹¹⁾ As for the CuO addition, milling Y-TZ powder with oxide or acetate of the Cu,⁸⁾ and adsorption of Cu ions on Y-TZ powder as a method of coating the surface¹²⁾ were reported. However, almost methods reported include the conventional powder compaction, which resulting in relatively large pore size distributions.

In the present study, we have consolidated the suspensions of the Cu adsorbed Y-TZ powders directly by a pressure filtration method^{13,14)} without powdering process and obtained narrow pore size distributed bodies. The Cu-doped bodies densified at lower temperatures. Then effects of CuO addition to the Y-TZ on the sintering behavior and ionic conductivity were determined.

2. Experimental procedure

The experimental work was performed using 3 mol% Y₂O₃-doped tetragonal ZrO₂ (3Y-TZ) powder (Tosoh Corp.; mean particle size 70 nm). The impurities of the 3Y-TZ are 0.005 mass% Al₂O₃, 0.004 mass% SiO₂, 0.002 mass% Fe₂O₃ and 0.013 mass% Na₂O. The suspensions of the Cu adsorbed 3Y-TZ powders were prepared as follows. The 3Y-TZ powder was dispersed with an aid of ultrasonic irradiation under 20 kHz and 160 W (Shimadzu; USP-600)

and magnetic stirring in the aqueous solution of ammonium hydroxide and ammonium nitrate keeping the total [NH₃⁺NH₄⁺] equal to 0.1 M at room temperature. Cu²⁺ was added to the solutions by pipetting up to 10 ml of a 2.2 × 10⁻³ M solution of Cu (NO₃)₂. The initial pH was adjusted at 11. To check the suspension stability, the zeta potential was measured by a laser electrophoretic zeta potential analyzer (Otsuka Electronics Co.; LEZA-600). The zeta potential was determined by the Smoluchowski equation¹⁵⁾ from the electrophoretic mobility. The Cu²⁺ added slurry was stirred for 5 h. Concentrated suspension (up to 15 vol% solids) using rotary evaporator was consolidated by a pressure filtration (PF)¹⁶⁾ at 10 MPa. Before the filtration, the suspensions were evacuated in a vacuum desiccator to eliminate air bubbles. The Cu contents of the compacts were determined by chemical analysis.

Cold isostatic pressing (CIP) treatment at 400 MPa was conducted to improve the packing density. Pore channel size distributions of the PF and CIP treated compacts were determined by mercury porosimetry using standard values for the mercury surface energy (0.48 N/m) and the contact angle (140°). The compacts after PF and CIP treatment were dried overnight at 120°C and sintered at fixed temperatures for 2 h in air, where the heating rate to the sintering temperatures was 5°C/min, and the cooling rate down to 1000°C was 10°C/min and then furnace cooling. Linear shrinkage behavior of the compacts after CIP treatment was observed using a dilatometer (Rigaku; Thermo Plus 2) at a constant heating rate of 5°C/min. The density of the compacts was measured by the Archimedes' method using kerosene or distilled water.

Phase analysis of polished sample was determined at room temperature via X-ray diffractometry (JEOL, JDX-3500). Cu Kα radiation, at 35 kV and 300 mA, was used. The fraction of monoclinic content was evaluated using the method of Toraya et al.¹⁷⁾ The microstructure of the sintered bodies were observed by a high-resolution SEM (JEOL, JSM-840F) and TEM (JEOL, 3000F). The grain size was determined using a linear intercept method.¹⁸⁾ Conductivity measurements were conducted using an impedance analyzer (Hewlett Packard, 4194 A) in air over the frequency range of 100 Hz to 15 MHz. Platinum electrodes

were painted on the samples by applying a conductive platinum paste onto the surface and heated at 1000°C for 1 h.

3. Results and discussion

3.1 Consolidation and sintering

Figure 1 shows the zeta potential vs pH of the 3Y-TZ. Zeta potential of the suspension of Cu-adsorbed 3Y-TZ at pH = 11 is also shown. It is seen that the values are nearly same between with and without Cu ions. Similar results were reported for Al_2O_3 , SiO_2 , TiO_2 and Fe_2O_3 in the presence of Cu, where the values of zeta potential are quite different at low pH but that tend to coincide at higher pH.¹⁹⁾ During the procedure described above, the suspension kept dispersed state due to the relatively large zeta-potential.

The experimental CuO mole percent adsorbed on the 3Y-TZ powder, which was determined from the CuO content of the compact through the pressure filtration, was shown in Fig. 2 as a function of initial concentration of Cu^{2+} solution. The obtained data coincide with the reported data¹²⁾ standardized by BET surface area ($16.0 \text{ m}^2/\text{g}$). It is reported that the adsorption of copper on zirconia occurred by a combination of ion-exchange and ion-dipole interaction, and that the Cu^{2+} adsorption on 3Y-TZ powder obeyed the

Fig. 1. Zeta potential vs pH of TZ3Y (open circle) and CuO adsorbed TZ3Y (closed circle).

Fig. 2. Obtained CuO mol% adsorbed on 3YTZ powder as a function of initial solution $[\text{Cu}^{2+}]$. The solid line was the data reported in Ref.12).

Langmuir type adsorption isotherm.¹²⁾ The Cu is originally adsorbed onto the 3Y-TZ powder as a coordination complex and CuO forms during drying step.²⁰⁾

The green densities of undoped and CuO-doped 3Y-TZ after the PF followed by the CIP treatment are shown in Table 1. The green densities of as-PF is low but increase after CIP treatment. Figure 3 shows pore channel size distributions of the PF and CIP treated compacts. Table 2 compares the mean pore size as-PF and after CIP treatment. CIP treatment is quite effective to increase the density and decrease the mean pore size. The results indicate that a green compact with a narrow pore channel size distribution with small pores could be obtained by PF and CIP treatment.

In the CuO-doped 3Y-TZ, following reaction is suggested.²⁰⁾ CuO transforms to Cu_2O at 1031°C and consequently melts at 1134°C in air. Then an endothermic reaction takes place around 1200°C, which might be a reaction between the CuO and 3Y-TZ. This phase initially $\text{Y}_2\text{Cu}_4\text{O}_5$,

Table 1. Green Densities after Pressure Filtration and CIP Treatment

Sample	Green density as PF (%)	Green density after CIP (%)
undoped	38.5	51.9
0.16% CuO doped	37.7	51.8
0.45% CuO doped	40.0	51.4
0.96% CuO doped	34.1	49.6

Fig. 3. Pore channel size distributions of the pressure filtrated and CIPed compacts.

Table 2. Mean Pore Size after Pressure Filtration and CIP Treatment

Sample	Mean pore size as PF (nm)	Mean pore size after CIP (nm)
undoped	50.2	27.7
0.16% CuO doped	44.8	25.3
0.45% CuO doped	52.0	27.3
0.96% CuO doped	51.7	25.2

Fig. 4. Lineal shrinkage curves of CuO-doped and undoped TZ3Y compacts at a constant heating rate of 5°C/min.

Fig. 5. Relative sintered density after heating at fixed temperatures for 2h in air.

Fig. 6. SEM micrographs of the polished and thermal etched surfaces of (a) 0.16 mol% CuO-doped 3Y-TZ sintered at 1300°C, (b) 0.4 mol% CuO-doped 3Y-TZ sintered at 1200°C, and (c) 0.96 mol% CuO-doped 3Y-TZ sintered at 1300°C.

but after extended holding at high temperatures, equilibrates to the Y₂Cu₂O₅ composition that has a melting point of 1110°C.

Figure 4 compares shrinkage curves of 0.16 and 0.96 mol% CuO doped and undoped 3Y-TZ. It is seen that CuO doping decreases the initial shrinkage temperature and that CuO-doped compact densifies at lower temperatures in comparison with the undoped one. However, higher CuO addition (0.96% CuO) depresses the densification, and dense bodies cannot be obtained (Fig. 5). Figure 6 shows SEM micrographs of polished and thermally etched. The mean grain size of the 0.16% CuO-doped 3Y-TZ sintered at 1300°C was 0.24 μm and the grain size was nearly same as that of undoped 3Y-TZ sintered at the same temperature (0.23 μm). However, significant grain growth of 0.40% CuO-doped 3Y-TZ was observed as is shown in Fig. 6(b), where the sintering temperature was 100°C lower (1200°C) than that of 0.16% CuO-doped one but the grain size is larger. In case of more large amount of CuO-doped sample, the depression of sintering was observed as described above. Similar decrease in sintered density was reported if amount of CuO-doped exceed 0.8 mol% to TZ.¹¹ This can be interpreted as follows; the higher CuO-doped sample shrinks at lower temperature and closed the pore channel before the gas evolution temperature (transformation of CuO to Cu₂O), which resulting in remaining large pores as is shown

Fig. 7. Complex impedance spectra of the 0.16 mol% CuO-doped and undoped TZ3Y at 400°C.

in Fig. 6(c). The stability of tetragonal phase was decreased with CuO addition. The monoclinic volume fraction of 0.96% CuO-doped TZ3Y after sintering at 1300°C was 67.3%, but those of 0.16 and 0.40% CuO-doped samples were negligible small as was the case of undoped 3Y-TZ.

3.2. Ionic conductivity and microstructure

Figure 7 shows complex impedance spectra (Cole-Cole

Fig. 8. Arrhenius plot of the total bulk conductivity.

Fig. 9. Arrhenius plot of the total grain boundary conductivity.

Table 3. Activation Energies of Bulk and Grain Boundary Conductivities of Undoped and CuO-doped Y-ZrO₂ Systems

Sample	Activation energy of bulk conductivity (kJ/mol)	Activation energy of grain boundary conductivity (kJ/mol)	Reference
3Y-TZ	86.3	98.3	this work
0.16 mol%CuO doped 3Y-TZ	90.7	107	this work
0.45 mol%CuO doped 3Y-TZ	92.0	110	this work
2.5Y-TZ	102	110	(26)
0.09mol%CuO doped 2.5Y-TZ	102	110	(26)
0.3 mol%CuO doped 2.5Y-TZ	103	113	(26)
3Y-TZ	88.8	105	(27)
4.7Y-TZ	103	111	(27)
6Y-SZ	103	108	(27)
4Y-TZ	90.7	116	(28)

plots) of the samples at 400°C, where clear two semicircles are seen. The first semicircle at higher frequency and the second semicircle at lower frequency are attributed to the bulk and the grain boundary contributions, respectively.^{21),22)} The intersections of the extrapolated lines of the semicircles with Z' axis give resistivities originated from the bulk and the grain boundary of the sample. The Z' and Z'' value in Fig. 7 is normalized by the division of l/s , where l is the thickness and s the electrode area. Therefore, the bulk and the grain boundary resistivity obtained from the intersection of the arcs with Z' axis is the total bulk and grain boundary resistivity. Figures 8 and 9 show the Arrhenius plots of the total bulk and grain boundary conductivities, respectively. The undoped data are similar to the reported ones.^{23),24)} The activation energies calculated from the Arrhenius plots are summarized in Table 3. The activation energies for bulk and grain boundary conductivities showed a small increase with increasing CuO additions. The activation energies of grain boundary conductivities are higher than those of the bulk conductivities. These results are in agreement with those reported for Y-TZ.²⁶⁾ The absolute values of the total bulk conductivities are nearly independent of the CuO addition for all the samples but that of total grain boundary conductivities decrease with CuO addition (Fig. 10). These results correspond to the recent TEM observation²⁵⁾ that Cu

Fig. 10. Effect of CuO addition on the total bulk (open marks) and grain boundary conductivities (closed marks).

ion is hardly dissolved in the grain but that segregated at grain boundary and triple points as amorphous Y-Cu-O

Fig. 11. HR-TEM micrographs. (a) grain boundary with no extra phase, and (b) grain boundary with a thin layer of amorphous phase.

compound. Figure 11 shows examples of HR-TEM images of grain boundaries. In Fig. 11(a), the lattice fringes of the two grain meet at the grain boundary leaving no grain boundary phase nor no grain junction phase. In Fig. 11(b), however, extra phase in a finite thickness is observed and the thickness is estimated to be ~ 2 nm. Most of the grain boundaries observed at high magnification have no extra phase as is seen in Fig. 11 (a). EDS analyses of Y, Cu and Zr revealed that Y and Cu were enriched at grain boundaries.

Table 3 also compares the activation energies reported.^{26)–28)} The discrepancy in results could be attribut-

ed to the differences in processing conditions; dopant content, sintering and cooling conditions and the resultant grain and grain boundary structure. The activation energy of conductivity in YTZ is the sum of the migration energy and the defect formation energy such as association energy, cluster formation, phase transformation, etc.,^{26),29),30)} which vary with doping concentration, heating history and microstructure. In the present case, it is interpreted that the addition of CuO in 3Y-TZ didn't cause further lattice defects in the YTZ lattice but rather alter the grain boundary microstructure where more resistant Y-Cu compound was formed as is observed by TEM.

4. Conclusion

Dense and homogeneous CuO-doped Y-TZ compacts were fabricated directly from Y-TZ slurry with Cu²⁺ by pressure filtration and CIP treatment without powdering process. The compacts with narrow pore size distribution densified fully at low-temperature sintering by the appearance of liquid phase. Bulk conductivity was independent on CuO addition but grain-boundary conductivity decreased with CuO addition.

Acknowledgements We are grateful to Dr. S. Kuroda at NRIM for help on measurements of pore size distribution and Mr. S. Akutsu and Prof. S. Ito at Science Univ. of Tokyo for help on CIP treatment.

References

- 1) Lange, F. F., *J. Am. Ceram. Soc.*, **72**, 3–15 (1989).
- 2) Aksay, I. A., *Ceramics International*, **17**, 267–74 (1991).
- 3) Sakka, Y. and Hiraga, K., *Nippon Kagaku Kaishi*, 1999[8], 497–508 (1999).
- 4) Uchikoshi, T., Sakka, Y., Ozawa, K. and Hiraga, K., *J. Mater. Res.*, **13**, 840–43 (1998).
- 5) Vasyilkiv, O. and Sakka, Y., *J. Ceram. Soc. Japan*, **109**, 500–05 (2001).
- 6) Vasyilkiv, O. and Sakka, Y., *Scripta Mater.*, **44**, 2219–23 (2001).
- 7) Vasyilkiv, O. and Sakka, Y., *J. Am. Ceram. Soc.*, **84**, 2484–88 (2001).
- 8) Kimura, N., Okamura, H. and Morishita, J., "Advances in Ceramics," Vol. 24A, Science and Technology of Zirconia III, Ed by Sōmiya, S., Yamamoto, N. and Yanagida, H., The American Ceramic Society, Columbus, Ohio (1988) pp. 183–91.
- 9) Chen, I.-W. and Xue, L. A., *J. Am. Ceram. Soc.*, **73**, 2585–609 (1990).
- 10) Hwang, C.-M. J. and Chen, I.-W., *J. Am. Ceram. Soc.*, **73**, 1626–32 (1990).
- 11) Hendrix, W., Kuypers, S., Vangrunderbeek, J., Luyten, J. and Vandermeulen, V., *Mater. Sci. Eng.*, **A168**, 45–47 (1993).
- 12) Seidensticker, J. R., Mayo, M. J. and Osseo-Asare, K., *J. Am. Ceram. Soc.*, **76**, 1844–48 (1993).
- 13) Uchikoshi, T., Sakka, Y., Ozawa, K. and Hiraga, K., *J. Eur. Ceram. Soc.*, **18**, 669–74 (1998).
- 14) Sakka, Y., Ozawa, K., Uchikoshi, T. and Hiraga, K., *J. Am. Ceram. Soc.*, **84**, 2129–31 (2001).
- 15) Ross, T. S. and Morrión, I. D., "Colloidal Systems and Interfaces," Wiley, New York (1988) pp. 205–63.
- 16) Ozawa, K., Sakka, Y., Uchikoshi, T. and Hiraga, K., *J. Ceram. Soc. Japan*, **106**, 234–36 (1998).
- 17) Toraya, H., Yoshimura, M. and Sōmiya, S., *J. Am. Ceram. Soc.*, **67**, C119–21 (1984).
- 18) Mendelson, M. I., *J. Am. Ceram. Soc.*, **52**, 443–46 (1969).
- 19) Fuerstenau, D. W. and Osseo-Asare, K., *J. Colloid Inter. Sci.*, **118**[2], 524–41 (1987).
- 20) Seidensticker, J. R. and Mayo, M. J., *J. Am. Ceram. Soc.*, **79**, 401–06 (1996).
- 21) Bauerle, J. E., *J. Phys. Chem. Solids*, **30**, 2657–70 (1969).
- 22) Rajendran, S., Drennan, J. and Badwal, S. P. S., *J. Mater. Sci. Lett.*, **6**, 1431 (1987).

-
- 23) Gödickemeier, M., Michel, B., Orliukas, A., Bohac, P., Sasaki, K., Gauckler, L., Heinrich, H., Schwander, P., Kostorz, G., Hofmann, H. and Frei, O., *J. Mater. Res.*, **9**, 1228-40 (1994).
- 24) Uchikoshi, T., Sakka, Y. and Hiraga, K., *J. Electroceram.*, **4**: S1, 113-20 (1999).
- 25) Oda, T., Llod, S. J., Suematsu, H., Yamaguchi, H., Greer, A. L., Kurashima, K., Bando, Y. and Hayakawa, M., *Mater. Trans.*, **42**, 145-50 (2001).
- 26) Bowen, C., Ramesh, S., Gill, C. and Lawson, S., *J. Mater. Sci.*, **33**, 5103 (1998).
- 27) Bonanos, N., Slotwinski, R. K., Steele, B.C.H. and Bulter, E. P., *J. Mater. Sci. Lett.*, **3**, 245 (1984).
- 28) Jiang, S., Schulze, W. A., Amarakoon, V. R. W. and Stangle, G. C., *J. Mater. Res.*, **12**, 2374-80 (1997).
- 29) Simkovich, G. and Stubican, V. S. (Ed.), "Nonstoichiometric Compound," Oishi, Y. and Ando, K. (Trans.), Plenum Press (1985) pp. 182-202 [in Japanese].
- 30) Ando, K., Oishi, Y., Koizumi, H. and Sakka, Y., *J. Mater. Sci. Lett.*, **4**, 176-80 (1985).