JOURNAL OF MATERIALS SCIENCE **39** (2004) 4367–4369 LETTERS

Preparation of porous alumina using CO_2 laser firing of amorphous powder synthesized by chemical solution deposition

S. ONO, Y. MASUO
Nagoya Municipal Industrial Research Institute, 3-4-41, Rokuban, Atsuta, Nagoya 456-0058, Japan
E-mail: ono.satomi@nmiri.city.nagoya.jp

A new method of fabricating porous alumina using powder synthesis by chemical solution deposition followed by fast laser firing is proposed. Although there are many reports of alumina films synthesized using chemical solution deposition [1–6], heat treatment above 1000 °C is needed to crystallize the aluminum hydroxide gel, which is prepared by the hydrolysis of aluminum alkoxide precursor, to α-alumina [1]. Laser firing is an excellent method for rapid heat treatment at temperatures above 1000 °C. Fast laser firing of sol–gel coating films, such as alumina, silica, titania and SnO_2:Sb, is now established [6–10], but the sintering of pressed sol–gel derived powder using laser firing has not yet been reported. A problem with the synthesis of a sol–gel derived monolithic body is breakage due to shrinkage of the gel body during the drying process, and due to weight loss with burnout of organic residues in the heating process. Here, to prepare a porous alumina disk without breakage, fast laser firing is applied to crystallize a pressed powder disk, which is a compact of amorphous alumina powder that has been preheat-treated at a temperature that prevents weight loss.

Fig. 1 shows the procedure for preparing porous alumina. Amorphous alumina powder is prepared by a modified sol–gel method using aluminum alkoxide as a starting material. For each mole of aluminum tri-sec-butoxide, which is dissolved in ethyl acetate, 2 moles of acetic acid are added into ethanol and the two are mixed at around 80 °C to prepare a homogeneous precursor solution. Homogeneous gel powder is prepared by evaporating the solvent of ethyl acetate and ethanol at this temperature.

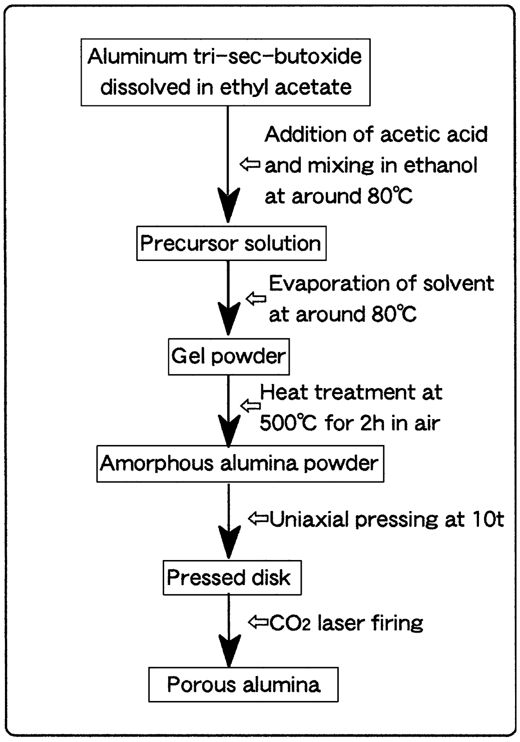

Figure 1 Procedure for preparing porous alumina.

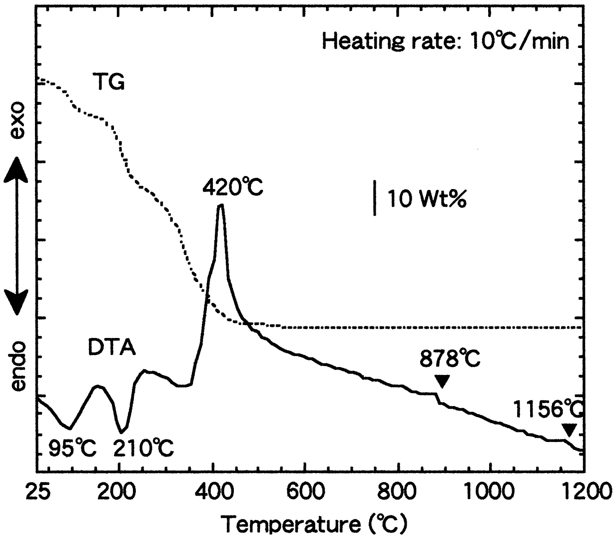

Figure 2 Thermal analyses of gel powder.

Properties of the gel powder were determined using differential thermal analysis and thermogravimetry (TG/DTA 2000, MAC Science Co. Ltd., Tokyo, Japan). Fig. 2 shows DTA and TG data for the gel powder. Two broad endothermic peaks are seen at 95 and 210 °C, and a single broad exothermic peak around 420 °C, associated with the weight loss in TG. With DTA, two further weak exothermic peaks are visible at 878 and 1156 °C, without weight loss. The endothermic peak at 95 °C is due to evaporation of ethyl acetate and ethanol solvent remained in the gel powder. The endothermic peak at 210 °C is due to dehydration. The exothermic peak with weight loss at 420 °C is the result of burnout of organic residues. Weight loss virtually ceases at around 500 °C. The two exothermic peaks without weight loss are due to phase transitions of alumina. The peak at 878 °C is tentatively identified as η-alumina to θ-alumina, and the peak at 1156 °C as θ-alumina to α-alumina, based on powder XRD analysis. Amorphous alumina powder was prepared by heat treatment of the gel powder for 2 h at 500 °C in a furnace (10 °C/min, in air).

0022–2461

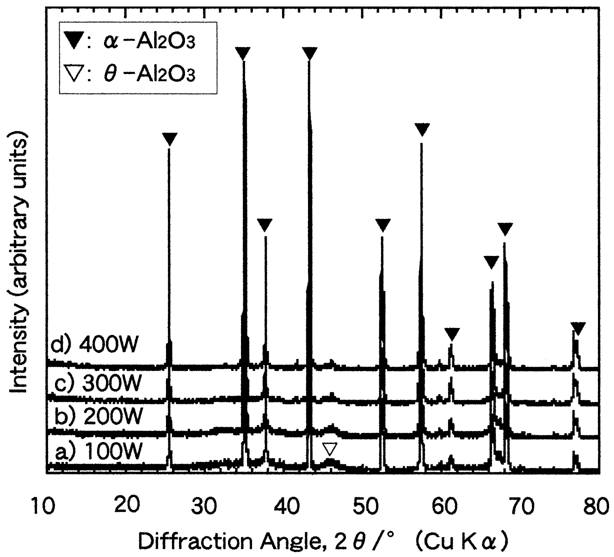

Figure 3 XRD profile of uniaxially pressed disks fired by CO_2 laser firing with a kaleidoscope at 100–400 W for 30 s (1.5–6.1 kJ/cm^2).

Alumina disks were prepared by pressing the amorphous powder uniaxially at 10t, followed by firing using a CO_2 laser (ML15S2-6X, Mitsubishi Electric) with a kaleidoscope, at 100–400 W for 30 s (1.5–6.1 kJ/cm^2) or 200 W for 60 s (6.1 kJ/cm^2). The kaleidoscope is used to ensure uniform heat-treatment over all the area irradiated by the laser.

Crystallization of the alumina disks was examined by X-ray diffraction (XRD) (Rint 2000, Rigaku, Tokyo, Japan). Fig. 3 shows the XRD profile of pressed disks prepared by CO_2 laser firing with the kaleidoscope at 100–400 W for 30 s (1.5–6.1 kJ/cm^2). The crystalline phase of the disks is α-alumina. A trace of θ-alumina remains in disks irradiated at 100 W (1.5 kJ/cm^2) and 200 W (3.1 kJ/cm^2). These results indicate that CO_2 laser firing, even at 100 W (1.5 kJ/cm^2), involves heating to a temperature greater than 1200 °C, which is sufficient to crystallize α-alumina.

Fig. 4a is a photograph of a porous α-alumina disk (diameter: 11.3 mm, thickness: 2.7 mm) prepared by CO_2 laser firing at 200 W for 60 s (6.1 kJ/cm^2). The density of the disk is 2.1 g/cm^3, and its porosity is 0.47. The surface area and the average pore diameter were calculated by the BET (Brunauer-Emmett-Teller) method using nitrogen gas absorption (Autosorb-1, Yuasa Ionics, Tokyo, Japan). The surface area of the disk is 5.0 m^2/g, and the mean pore diameter is about 19 nm. Results of measurement of the adsorption and desorption isotherms indicate that the porous alumina has macropores ($\geq$50 nm) with open ends. The small surface area of 5.0 m^2/g is due to the macropores which do not

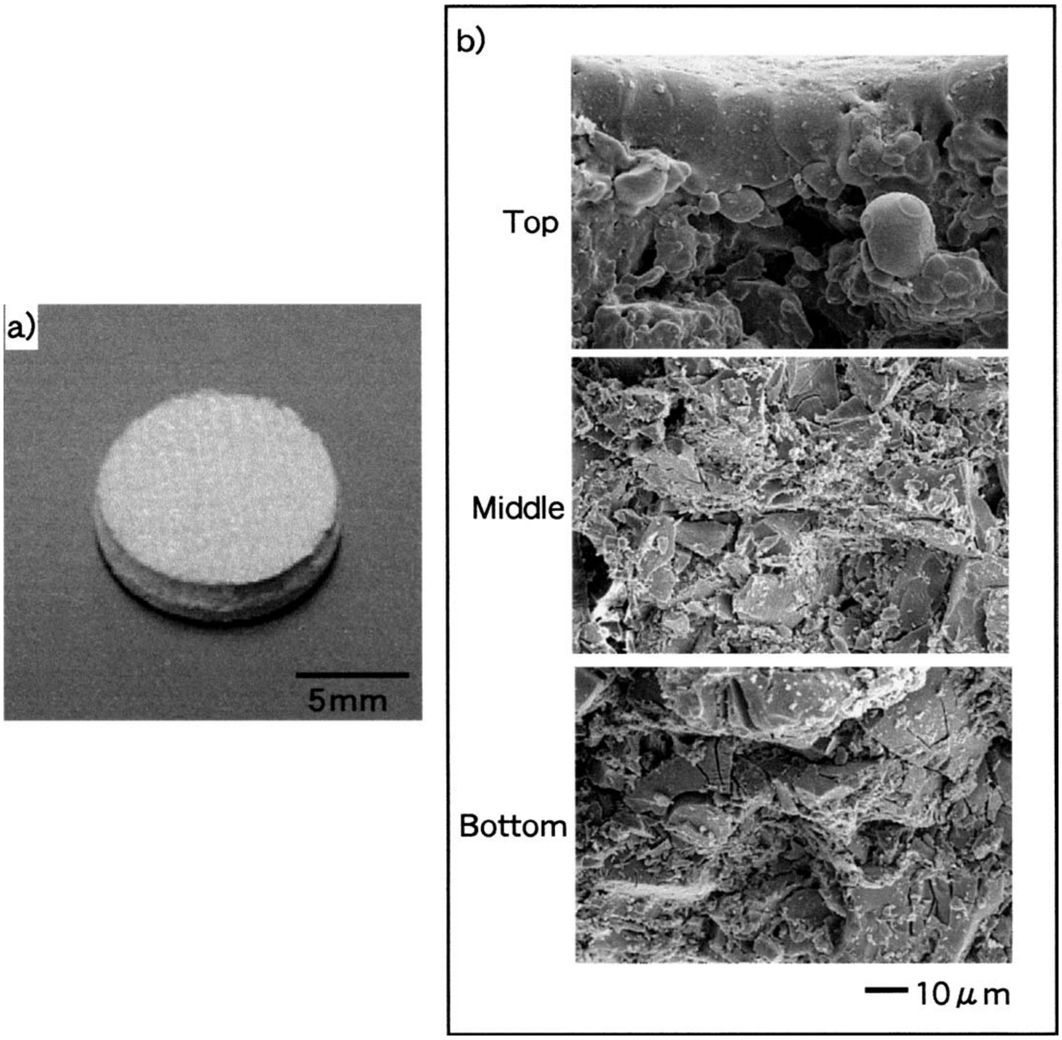

Figure 4 (a) Photograph of a α-alumina disk prepared by CO_2 laser firing at 200 W for 60 s (6.1 kJ/cm^2) and (b) Microstructure of a cross section of the disk; top (laser irradiated side), middle and bottom.

contribute to the surface area and the total pore volume. The small surface area and the nanometer-size mean pore diameter suggest that alumina nanoparticles form the disk, which has mesopores (2–50 nm) and macropores.

The morphology of the alumina disk was observed by scanning electron microscopy (SEM) (JSM-6300F, Jeol, Tokyo, Japan). Fig. 4b shows SEM images of the microstructure of a cross section, from the top of the disk (laser irradiated side) to the bottom. A surface layer of the disk approximately 20 μm thick is sintered, and micrometer-size pores are visible under the densified region. The microstructures of the middle region and bottom region also indicate that the disk has micrometer-size pores.

The thermal conductivity was determined by measuring the thermal diffusivity of the alumina disk using the laser flash method (TC3000H-NC, Shinkuriko, Tokyo, Japan). The surface of the sample was coated with carbon to improve the emissivity. The thermal conductivity of the disk is 2.17 W/(m·K), which is about 15 times less than the reported value of sintered α-alumina, of 33 W/(m·K) [11], and is comparable to the value of 6.8–0.7 W/(m·K) reported when the porosity is 0.538–0.894 in gelcast alumina foams [12].

In conclusion, it has been shown that porous α-alumina disks can be prepared without breakage. To achieve this, the disk for the CO_2 laser treatment was prepared from an amorphous powder, heat-treated at 500 °C. The combination of powder synthesis by chemical solution deposition followed by CO_2 laser firing is therefore a highly promising method for preparing porous alumina with good thermal resistance.

References

1. R. NASS and H. SCHMIDT, *J. Non-Cryst. Solids* **121** (1990) 329.
2. L. SHAW and R. ABBASCHIAN, *J. Amer. Ceram. Soc.* **78** (1995) 3376.
3. K. TADANAGA, N. KATATA and T. MINAMI, *ibid.* **80** (1997) 1040.
4. E. DRABAREK, K. S. FINNIE, J. R. BARTLETT, J. L. WOOLFREY and D. MITCHELL, in "Ceramic Transactions," Vol. 81, Sol-Gel Processing of Advanced Materials '96, edited by Lisa C. Klein, Edward J. A. Pope, Sumio Sakka and James L. Woolfrey (American Ceramic Society, Westerville, OH, 1998) p.119.
5. J. MASALSKI, J. GLUSZEK, J. ZABRZESKI, K. NITSCH and P. GLUSZEK, *Thin Solid Films* **349** (1999) 186.
6. S. TAKEDA, Y. IKUTA, M. HIRANO and H. HOSONO, *J. Mater. Res.* **16** (2001) 1003.
7. D. J. TAYLOR, B. D. FABES and M. G. STEINTHAL, in Materials Research Society Symposium Proceedings, Vol. 180, Better Ceramics through Chemistry IV, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich and B. J. Zelinsky (Materials Research Society, Pittsburgh, PA, 1990) p. 1047.
8. N. ARFSTEN, B. LINTNER, M. HERNING, O. ANDERSON and C. R. OTTERMANN, in Materials Research Society Symposium Proceedings, Vol. 271, Better Ceramics through Chemistry V, edited by M. J. Hampden-Smith, W. G. Klemperer and C. J. Brinker (Materials Research Society, Pittsburgh, PA, 1992) p. 449.
9. D. GANZ, G. GASPARRO, J. OTTO, A. REICH, N. J. ARFSTEN and M. A. AEGERTER, *J. Mater. Sci. Lett.* **16** (1997) 1223.
10. J. T. M. DE HOSSON and M. DE HAAS, *Suf. Engng.* **14** (1998) 395.
11. R. G. MUNRO, *J. Amer. Ceram. Soc.* **80** (1997) 1919.
12. P. SEPULVEDA, W. N. DOS SANTOS, V. C. PANDOLFELLI, J. C. BRESSIANI and R. TAYLOR, *Amer. Ceram. Soc. Bull.* **78** (1999) 61.

Received 17 September
and accepted 30 December 2003