



ELSEVIER

Journal of Non-Crystalline Solids 285 (2001) 57–63

JOURNAL OF
NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrsol

Synthesis of high porosity, monolithic alumina aerogels

J.F. Poco, J.H. Satcher Jr., L.W. Hrubesh *

Chemistry and Material Science Department, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

Abstract

Many non-silica aerogels are notably weak and fragile in monolithic form. In particular, few monolithic aerogels with densities less than 50 kg/m^3 have any significant strength. It is especially difficult to prepare uncracked monoliths of pure alumina aerogels that are robust and moisture stable. In this paper, we discuss the synthesis of unusually strong, stable, monolithic, high porosity (>98% porous) alumina aerogels, using a two-step sol-gel process. The alumina aerogels have a polycrystalline morphology that results in enhanced physical properties. For an alumina aerogel with a density of 37 kg/m^3 , the specific surface area is $376 \text{ m}^2/\text{g}$, the elastic modulus is 550 kPa, and the thermal conductivities at 30°C, 400°C and 800°C, are 29, 98 and 298 mW/mK, respectively. All of the measured physical properties of the alumina aerogels except the specific surface area are superior to those for silica aerogels for equivalent densities. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 01.30.Cc

1. Introduction

Alumina-based ceramics, in addition to their relatively high strength, are noted for their enhanced thermal and chemical stability. These properties of alumina have been shown to also apply to low-density aerogel materials. To date, the major use for alumina-based aerogels is as high temperature, high surface area catalyst supports. Monolithic alumina aerogels, which have been difficult to produce by current synthetic procedures, would be capable of providing thermal insulation over a larger temperature range than the more common silica aerogels and would be a useful material for many applications. For exam-

ple, monolithic alumina aerogel crucibles could be used for improved high-temperature alloy melt processing. In this paper we report a new synthetic procedure for preparing monolithic, high porosity, alumina aerogels. These aerogels have an unusual polycrystalline microstructure, and a very low thermal conductivity of 98 mW/mK at 800°C and 1 atm.

The sol-gel synthesis of alumina gels has been well studied and it has been found that the complex solution chemistry of aluminum hydroxide complicates the structural formation of the gel. Yoldas [1–5] and Teichner [6] have shown that there are several possible structural variations in the aluminum alkoxide-derived gels. Some of the variables that affect the final structure of the gel include; the type of alkoxide used, the ratio of alkoxide to water, the rate of hydrolysis, the temperature of drying, the type of catalyst used, the pH of the solution, and the temperature at

* Corresponding author. Tel.: +1-925 423 1691; fax: +1-925 423 9242.

E-mail address: hrubeshl@llnl.gov (L.W. Hrubesh).

which the reactions occur. The final form of the aerogel may be monolithic or powder, amorphous or crystalline, or bi-phasic, heterogenous or homogenous.

Considerable work has been published for both pure alumina aerogels [7–11] and composite alumina–silica aerogels [11–17]. The synthesis of monolithic, stable, high porosity alumina aerogels has been found to be especially difficult due to the complex chemical pathways leading to gelation, and the susceptibility to cracking during drying, and the hygroscopic nature of the dried material. Relatively few papers describe the formation of truly monolithic aerogels containing alumina [7,9,10,15,17], and the highest porosity, pure alumina aerogel reported was ~95% porous [9].

Our primary motivation was to develop very high porosity (>98% porous) monolithic alumina aerogels for space applications. Thermal protection is needed for space vehicles and thermal insulation is required for many of the experiment assemblies. Monolithic alumina aerogels could be used separately or they could be added to other thermal protection materials to make composites with superior thermal resistance properties. For space applications, low weight is the most important requirement, thermal resistance is next, and finally robustness and stability. The procedure described here produces monolithic aerogels that exhibit these important features, including robustness, which is inferred from the modulus data and the ease of handling the aerogel.

2. Experimental procedure

2.1. Aerogel preparation

The monolithic gels are made into two steps; first an alumina sol is generated, followed by induced gelation in the second step. The alumina sol is made following a variation of Yoldas' procedure [2], using less than the stoichiometric amount of water instead of a large water excess. Our protocol is similar to that reported by Himmel et al. [11], with some variations in the chemistry and drying. The chemicals for the preparation are as follows: aluminum tri-sec butoxide 97% from Aldrich,

ethanol-absolute (200 proof) from AAPER, acetic acid (glacial) from EM Sciences, and methanol ACS Grade 99.8% from Aldrich. In the first step, a sol is made by mixing aluminum secondary butoxide, 200 proof ethanol and DI water in a molar ratio of $\{\text{Al}(\text{sec-OBu})_3:\text{EtOH}:\text{H}_2\text{O} = 1:16:0.6\}$, and heating to 60°C while stirring for 45 min. The mixture is initially cloudy but it turns clear after the onset of hydrolysis. The clear sol solution is then cooled to room temperature. In the second step, the gel is made by mixing a portion of the sol solution with methanol, water, and acetic acid. The amounts for this mixture are determined by the targeted porosity of the final aerogel. For example, for a targeted porosity of 98.5%, the weight ratio is $\{\text{Sol}:\text{MeOH}:\text{H}_2\text{O} = 1 \text{ g}:0.2 \text{ g}:0.003 \text{ g}\}$ and the amount of acetic acid is 1 ml for each 30 ml of the mixture. The mixture is stirred for 30 min, then poured into stainless steel molds where the gel typically forms within 120 min. The gels are dried by rapid supercritical extraction (RSCE) of methanol in an autoclave [18].

Typically, the metal mold containing the alcogel is sealed liquid tight, and placed in an autoclave vessel, which is then partially filled with methanol and sealed. The autoclave temperature is raised to 300°C at a rate of 8°C/min while the pressure rises and is controlled at ~12.2 MPa. When the temperature reaches 300°C, the vessel is immediately decompressed at a rate of ~70 kPa/min. The autoclave vessel is evacuated after decompression for about 180 min, while cooling.

2.2. Characterization

Scanning electron micrographs (SEM) were obtained on uncoated specimens using a Hitachi S-800 instrument. The dry aerogel was analyzed with 20 kV beam voltage for a sufficiently short time to limit charging of the sample. High resolution transmission electron micrographs (HRTEM) were obtained on a Philips CM300 FEG instrument, operating at 300 kV. Flecks from the dry sample were dropped onto a holey carbon film and analyzed directly.

The thermal conductivity was measured with a heat flux-meter operating in a temperature range 30–50°C. This non-commercial instrument was

calibrated using NIST traceable standards. The high temperature thermal conductivity measurements were made by Energy Materials Testing Laboratory, Biddeford, ME, USA, using a guarded hot plate apparatus, according to the ASTM C 177 procedure.

Sound velocity measurements were made using a Panametrics Ultrasonic Analyzer Model 5052UA with 180 kHz center frequency transducers. The monolithic aerogel specimens were prepared with flat, parallel surfaces, with 1.5 cm thickness. The elastic modulus of the aerogels was calculated from the densities and the measured longitudinal and shear sound velocities, according to the procedures reported by Gross et al. [19].

Densities are calculated from weight and volume measurements on the aerogels. Surface area measurements were made on a Micromeritics L3000 Analyzer, using the BET nitrogen adsorption/desorption technique.

3. Results

The unusual morphology of the RSCE dried alumina aerogel is shown in the SEM (Fig. 1) and HRTEM (Figs. 2 and 3) micrographs. Electron

diffraction of the aerogel (the inset in Fig. 3) shows distinct ring patterns indicating an ordered structure. The alumina aerogel exhibits a polycrystalline morphology which can be seen as randomly oriented patches of ordered planes in the HRTEM, Fig. 3. The microstructure consists of randomly connected acicular, leaf-like particles, quite different from the typical morphology of colloidal, amorphous aerogel that consists of interconnected spheroidal particles.

The measured thermal conductivity values at 1 atm pressure for the alumina aerogel are 0.029 W/mK at 30°C, 0.058 W/mK at 400°C, and 0.098 at 800°C. These values are compared in Table 1 with values for silica aerogels of the same nominal density, made by two separate methods, base catalyzed (BC) [20] and two step acid/base catalyzed (ABC) [21]. The thermal resistance of the alumina aerogel is clearly superior to the silica aerogels at elevated temperatures.

Unlike the silica aerogels that shrink at temperatures as low as 600°C, the monolithic alumina aerogels do not sinter until >950°C. This was determined by experiments with monoliths of alumina aerogel heated to various temperatures from 600°C to 1050°C for 4 h. The change of linear dimensions measured before and after heat

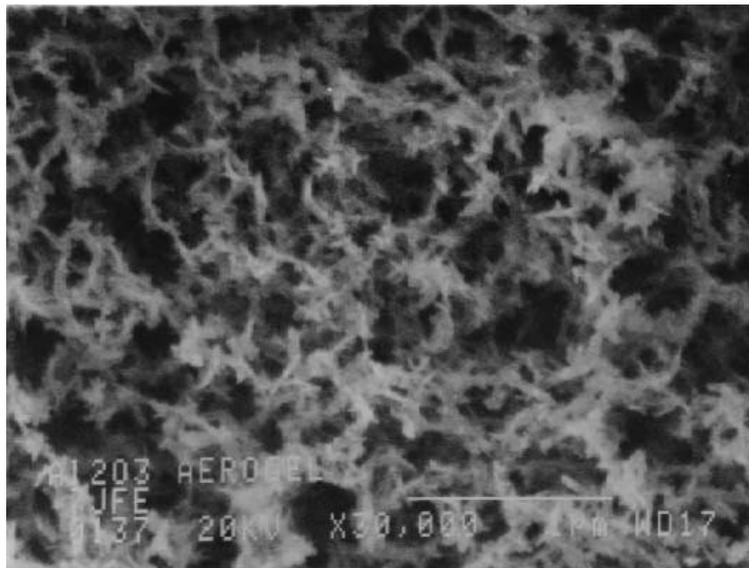


Fig. 1. Scanning electron micrograph of 98.5% porosity alumina aerogel showing acicular morphology.

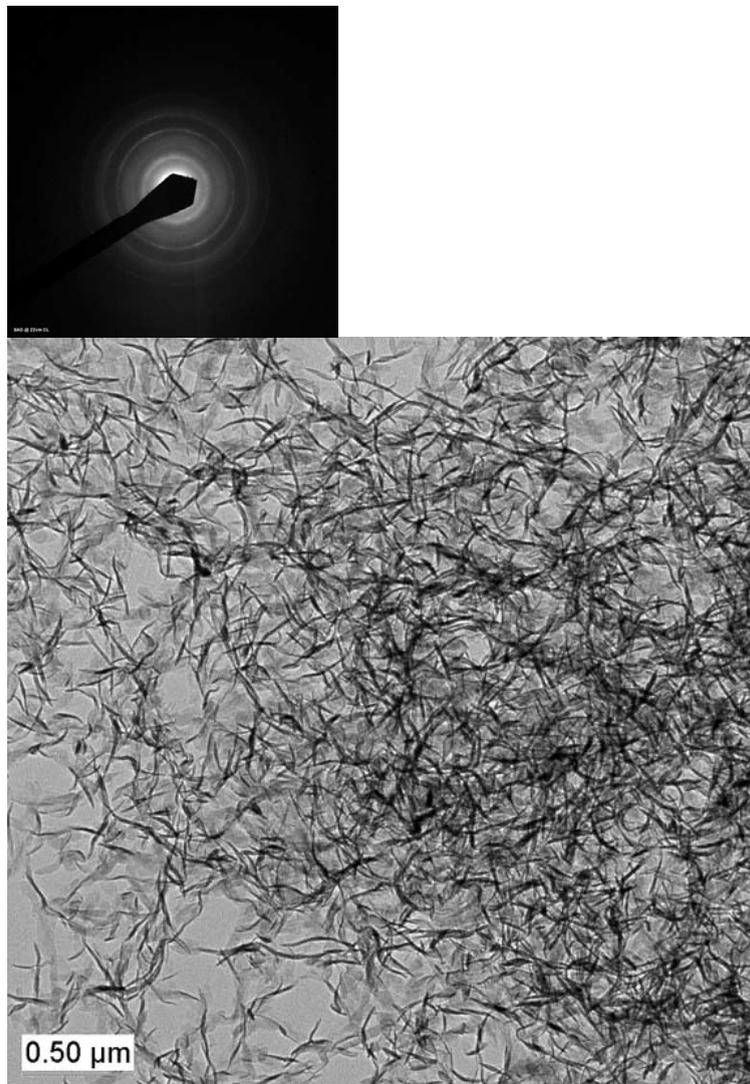


Fig. 2. High resolution transmission electron micrograph of the alumina aerogel showing the acicular, leaf-like nature of the morphology. The inset is the electron diffraction pattern that verifies the existence of an ordered microstructure in the alumina aerogel.

treatment was less than the experimental error (i.e., <1.5%) for all samples treated at temperatures below 950°C; the dimensional change was approximately 2% for the samples treated at 1050°C. This result is consistent with similar results for aluminum–silicate aerogel compositions that have high alumina content [16].

The isotherm plot for nitrogen adsorption/desorption on the alumina aerogel is a Type II. The specific surface area determined from the desorp-

tion curve is 376 m²/g. The specific surface areas of several types of aerogels are compared in Table 1. The relatively low value for alumina aerogel is attributed to the leaf-like morphology, compared with the colloidal morphology for high porosity silica aerogels.

The elastic modulus of the alumina aerogel (550 kPa) is determined from the measured longitudinal (158 m/s) and shear (87 m/s) sound velocities. As can be seen in Table 1, the elastic modulus of the

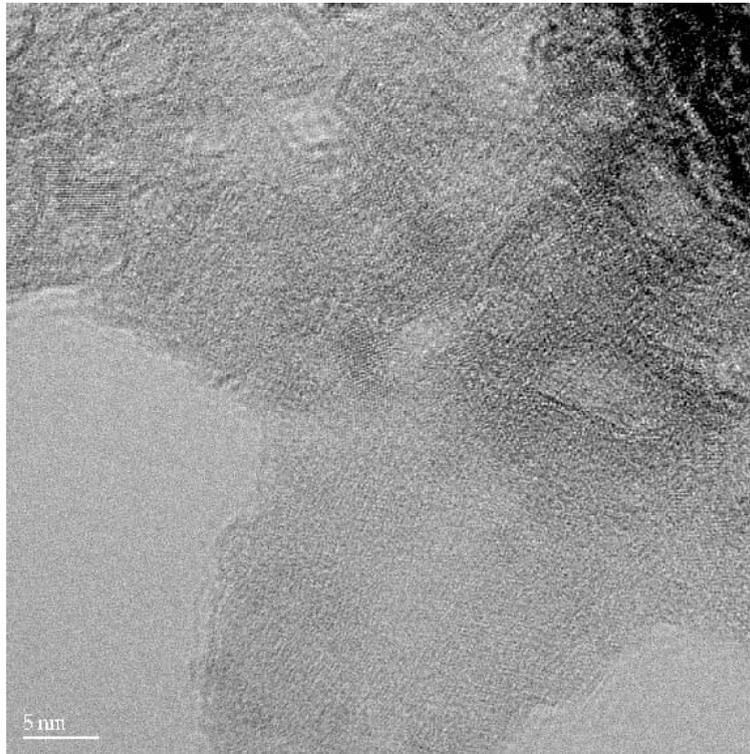


Fig. 3. HRTEM of the alumina aerogel in which randomly oriented crystal lattices can be identified.

Table 1
Some measured properties of high porosity alumina and silica aerogels

Aerogel type	Density (kg/m ³)	Elastic modulus (kPa)	Thermal conductivity (mW/mK) @P = 1 atm			Specific surface area (m ² /g)
			30°C	400°C	800°C	
Alumina	37 ± 2	550 ± 57	29 ± 3	98 ± 9	298 ± 18	376 ± 28
Silica (BC)	40 ± 2	434 ± 45	31 ± 3	122 ± 19	–	574 ± 46
Silica (ABC)	39 ± 2	489 ± 51	33 ± 3	106 ± 16	–	649 ± 53

very high porosity alumina aerogel is higher than for silica aerogels having the same nominal density.

4. Discussion

The alumina aerogels produced by this procedure are mostly crystalline, in contrast with most common aerogels, which are mostly amorphous. Some crystallinity of the alumina aerogel is ex-

pected based on the observation by others of the sol–gel formation in aluminum alkoxide systems. Yoldas' method to make sols at elevated temperatures is known to produce particles with the boehmite phase [2]. Also, it is known that supercritically drying the gels at high temperature can convert the gels to the boehmite phase and the degree of conversion of the pseudoboehmite phase depends on the time held at temperature in the autoclave [7]. Mizushima and Hori observed the formation of boehmite 'fibrils' in aerogels that

were dried at 270°C in an autoclave [9]. This crystalline form prevented sintering until higher temperatures and caused strengthening of the alumina aerogels. The degree of crystallinity of the aerogel produced by our procedure is very high; estimated from the HRTEM images to be >90%. We believe that this is due to a combination of effects, including the fact that we carry out the supercritical extraction in an autoclave at elevated temperature and pressure.

As pointed out earlier, a number of variables affect the final structure of the gel. For example, it has been reported that the degree of crystallinity in pure alumina aerogels depends on the alcohol used as a solvent [7,14]. In our procedure we use a substoichiometric amount of water and no acid is added in the first step. Acetic acid was chosen for the second step because its reactions liberate water in alcohol solutions, thus offering a means to control hydrolysis–condensation reaction rates [11,22]. Reaction rates are especially critical for the formation of homogeneous gels from highly reactive or partially hydrolyzed alkoxides. These processing conditions may contribute to the ultimate formation of the highly crystalline nature of the materials we are producing.

The transmission electron diffraction data from the alumina aerogel shows peaks that do not match either the boehmite or bayerite phase for alumina. We have not made measurements to determine the crystal composition. It is possible that the crystal structure matches that of $\text{Al}(\text{OEt}_3)$ as was proposed by Himmel et al. [11] for gel preparations similar to ours. They also observed flat, disc-like regions in their alumina aerogels, which appear to be similar to the leaf-like character for our alumina aerogels.

While the very low density aerogels are all quite fragile materials, the high degree of crystallinity of the structure may lead to increased strength of the alumina aerogel. The modulus of the alumina aerogel is 12–26% higher than silica aerogels having similar density. The crystalline structure and the highly connected, leaf-like morphology may also be responsible for the enhanced mechanical properties. Yoldas [5] points out that the physical properties, such as melting point, viscosity, mechanical behavior and capability of the network to

remain monolithic (during drying or consolidation) of the dried gels, depends on high connectivity in the network.

Our attempts to make low density, monolithic alumina gels using Yoldas' method with large excess water were not successful, either by supercritical drying in CO_2 or by autoclave drying. The gels were either not monolithic as removed from the dryer, or they converted to powder after exposure to atmospheric moisture. The apparent conversion of the gels to bayerite phase could cause the instability to atmospheric moisture [1].

5. Conclusions

Very strong, very low density alumina aerogel monoliths can be prepared using a two-step sol-gel process. Our method of preparing pure alumina aerogel, modifies the Yoldas sol method by combining the use of substoichiometric water for hydrolysis, the use of acetic acid to control hydrolysis/condensation, and high temperature supercritical drying. All of these procedures contribute to the formation of a polycrystalline aerogel microstructure. This structure is responsible for the exceptional mechanical properties of the alumina aerogel, as well as the enhanced thermal resistance and high temperature stability. The monoliths exhibit excellent insulating and refractory behavior, having low thermal conductivity up to 800°C and they do not undergo significant structural changes up to 1050°C.

Acknowledgements

We wish to acknowledge the excellent TEM and BET analysis done by Mark Wall and Alexander Gash, respectively. We also thank Thomas Tillotson for his critique of this work. This work was performed under the auspices of the US Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References

- [1] B.E. Yoldas, *J. Appl. Chem. Biotechnol.* 23 (1973) 803.
- [2] B.E. Yoldas, *Am. Ceram. Soc. Bull.* 54 (3) (1975) 286.
- [3] B.E. Yoldas, *Am. Ceram. Soc. Bull.* 54 (3) (1975) 289.
- [4] D.P. Partlow, B.E. Yoldas, *J. Non-Cryst. Solids* 46 (1981) 153.
- [5] B.E. Yoldas, in: L. Hench, J.K. West (Eds.), *Chemical Processing of Advanced Materials*, Wiley, New York, 1992, p. 60.
- [6] S.J. Teichner, *Rev. Phys. Appl. Colloque C4, Suppl.* 4 (Apr. 1989) 22.
- [7] Y. Mizushima, M. Hori, *J. Mater. Res.* 8 (1993) 2993.
- [8] Y. Mizushima, M. Hori, M. Sasaki, *J. Mater. Res.* 8 (1993) 2109.
- [9] Y. Mizushima, M. Hori, *J. Non-Cryst. Solids* 167 (1994) 1.
- [10] T. Horiuchi, T. Osaki, T. Sugiyama, H. Masuda, M. Horio, K. Suzuki, T. Mori, T. Sago, *J. Chem. Soc. Faraday Trans.* 90 (1994) 2573.
- [11] B. Himmel, Th. Gerber, H. Burger, G. Holzhter, A. Olbertz, *J. Non-Cryst. Solids* 186 (1995) 149.
- [12] F. Chaput, A. Lecomte, A. Dauger, J.P. Boilot, *Rev. Phys. Appl. Colloque C4, Suppl.* 4 (Apr. 1989) 137.
- [13] C. Hoang-Van, B. Pommier, R. Harivololona, P. Pichat, *J. Non-Cryst. Solids* 145 (1992) 250.
- [14] M.A. Aegerter, D. Bozano, in: L. Hench, J.K. West (Eds.), *Chemical Processing of Advanced Materials*, Wiley, New York, 1992, p. 175.
- [15] S. Komarneni, R. Roy, U. Selvaray, P.B. Malla, E. Breval, *J. Mater. Res.* 8 (1993) 3163.
- [16] R. Saliger, T. Heinrich, T. Gleissner, J. Fricke, *J. Non-Cryst. Solids* 186 (1995) 113.
- [17] T. Osaki, T. Horiuchi, T. Sugiyama, K. Susuki, T. Mori, *J. Non-Cryst. Solids* (1998) 111.
- [18] J.F. Poco, P.R. Coronado, R.W. Pekala, L.W. Hrubesh, in: R.F. Lobo, J.S. Beck, S.L. Suib, D.R. Corbin, M.E. Davis, L.E. Iton, S.I. Zones (Eds.), *Microporous and Macroporous Materials, Mater. Res. Soc. Symp. Proc.*, vol. 431, Materials Research Society, Pittsburgh, PA, 1996, p. 297.
- [19] J. Gross, G. Reichenauer, J. Fricke, *J. Phys. D* 21 (1988) 1447.
- [20] G.A. Nicolaon, S.J. Teichner, *Bull. Soc. Chim. F.* (1968) 1906.
- [21] T.M. Tillotson, L.W. Hrubesh, *J. Non-Cryst. Solids* 145 (1992) 44.
- [22] J. Livage, C. Sanchez, *J. Non-Cryst. Solids* 145 (1992) 11.