Development of Silica Aerogel with Any Density

M. Tabata, I. Adachi, T. Fukushima, H. Kawai, H. Kishimoto, A. Kuratani, H. Nakayama, S. Nishida, T. Noguchi, K. Okudaira, Y. Tajima, H. Yano, H. Yokogawa, H. Yoshida

***Abstract*–New production methods of silica aerogel with high and low refractive indices have been developed. A very slow shrinkage of alcogel at room temperature has made possible producing aerogel with high refractive indices of up to 1.265 without cracks. Even higher refractive indices than 1.08, the transmission length of the aerogel obtained from this technique has been measured to be about 10 to 20 mm at 400 nm wave length. A mold made of alcogel which endures shrinkage in the supercritical drying process has provided aerogel with the extremely low density of 0.009g/cm^3, which corresponds to the refractive index of 1.002. We have succeeded producing aerogel with a wide range of densities.**

I. Introduction

Silica aerogel has been widely used as Cherenkov radiators in high energy experiments. The method for producing aerogel with refractive indices of 1.01 to 1.07 was developed in the previous studies [1], [2]. To obtain more transparent aerogel with the above range of refractive indices, a new solvent has been introduced in the sol-gel step [3], [4].

However, it was difficult to produce aerogel with higher and lower refractive indices and a certain amount of volume for the following reasons:

1. *for higher refractive index*
   Compared to methylalkoxide oligomer, solvent is small in amount. The sol-gel process dose not appear to progress.
2. *for lower refractive index*
   In the supercritical drying process, alcogel with extremely low *target* refractive indices heavily shrinks by nature. The resultant aerogel had higher refractive indices than desired.

Manuscript received November 11, 2005.

M. Tabata, T. Fukushima and A. Kuratani are with the Graduate School of Science and Technology, Chiba University, Chiba, 263-8522 Japan (e-mail: makoto@hepburn.s.chiba-u.ac.jp, tomokazu@hepburn.s.chiba-u.ac.jp and kuratani@hepburn.s.chiba-u.ac.jp).

I. Adachi and S. Nishida are with IPNS, the High Energy Accelerator Research Organization (KEK), Tsukuba, 305-0801 Japan (e-mail: ichiro.adachi@kek.jp and shohei.nishida@kek.jp)

H. Kawai and H. Nakayama are with the Faculty of Science, Chiba University, Chiba, 263-8522 Japan (e-mail: kawai@hepburn.s.chiba-u.ac.jp and hiron@office.chiba-u.jp).

H. Kishimoto and H. Yokogawa are with the New Business Planning Office, the Matsushita Electric Works, Ltd., Osaka, 571-8686 Japan (e-mail: hkishi@rda.mew.co.jp and yokogawa@mewaa.mew.co.jp).

T. Noguchi is with the Faculty of Science, Ibaraki University, Mito, 310-8512 Japan (e-mail: tngc@mx.ibaraki.ac.jp).

K. Okudaira and H. Yano are with ISAS, the Japan Aerospace Exploration Agency (JAXA), Sagamihara, 229-8510 Japan (e-mail: okudaira@planeta.sci.isas.jaxa.jp and yano.hajime@jaxa.jp).

Y. Tajima and H. Yoshida are with the Faculty of Science, Yamagata University, Yamagata, 990-8560 Japan (e-mail: tajima@sci.kj.yamagata-u.ac.jp and yoshida@ksquark.kj.yamagata-u.ac.jp).

It is important to mention here that there is the following relationship between the refractive index n and the density ρ of silica aerogel: $n = 1 + \alpha\rho$, where $\alpha \sim 0.25\text{cm}^3/\text{g}$ is the constant. Since the transparency of aerogel with extremely low refractive indices is too low for the refractive index to be measured, not n but ρ is useful for the discussion as to aerogel with low refractive indices.

It is known that aerogel with higher refractive indices than 1.07 is obtained by annealing aerogel with temperature higher than 900°C. The resultant aerogel have the uneven refractive indices and the low transparencies. In contrast, aerogel with refractive indices of 1.01 to *1.005* has produced by using a glass mold and a thin glass plate put on the alcogel in the supercritical drying process. The electrical force of attraction between alcogel and glass would decrease shrinkage. The aerogels with refractive index of 1.007 were used in the KEK proton synchrotron E248 experiment [5] and the SPring-8 LEPS experiment [6].

These arguments point to a need for controlling shrinkage of alcogel in order to develop aerogel with higher and extremely low refractive indices. The present paper will report on the first result from our attempts to control the refractive index or the density of aerogel.

II. Production Methods

A. Pinhole Drying Method

In general, to control the refractive index of aerogel, the molar ratio of each solution is adjusted before being mixed. A relative decrease in solvent produces higher refractive index.

In the pinhole drying method, which is our new technique for producing aerogel with higher refractive index, the mixing ratio for higher is not employed. An alcogel with target refractive index of ~1.05 where aerogel has lower refractive index and higher transparency than desired now is produced in a polystyrene mold by using methyl alcohol as a solvent. The alcogel is extracted from the mold and moved into a container which has some pinholes or minute gaps and is filled with ethyl alcohol vapor at room temperature (Fig. 1). Since the ethyl alcohol vapor is very slowly replaced by air, the dry alcogel shrinks and its density increases, which will lead to an increase in its refractive index. Natural dryness in air causes the fine structure of aerogel to be easily destroyed. In contrast, the pinhole drying method makes possible the shrinkage without cracks (Fig. 2). The velocity of shrinkage strongly depends on the form of a container, the size and position of gaps and temperature, in addition, it should influence the shape of an alcogel after shrinkage. A strain-free alcogel ideally costs about 1 to 2 months, in fact, it can be produced in about 2 weeks. Maintaining the pinhole drying until obtaining the alcogel with desired density produces the aerogel with any refractive index which is higher than initial. After the pinhole drying, the alcogel is sunk in ethyl alcohol and dealt with by the usual means. The shrunk alcogel does not expand again.

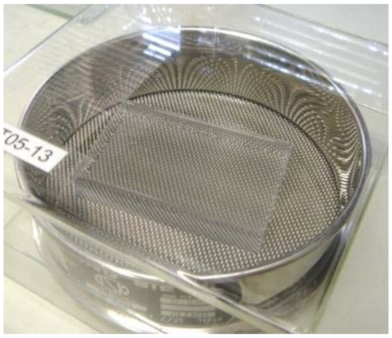

Fig. 1. Photograph of alcogel (95mm×60mm×15mm) before shrinkage.

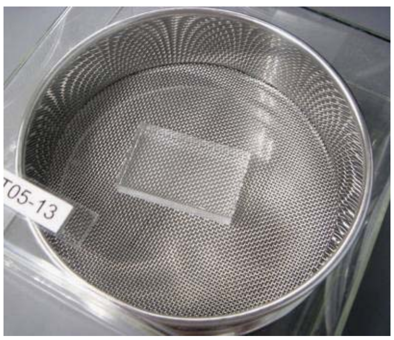

Fig. 2. Photograph of alcogel without cracks after 3 weeks.

B. *Frame Structure Method*

A monolithic aerogel block consisted of multiple layers with different refractive indices has been developed as the radiator of a ring imaging Cherenkov (RICH) counter [3], and it is not broken away after the supercritical drying process. The technique combined with the method of using a glass mold and a thin glass plate can be applied to development of aerogel with extremely low density. An alcogel which does not shrink in the supercritical drying process due to having somewhat higher density (refractive index $n > 1.01$) is formed in a glass mold, and then another alcogel mixed for extremely low density by using ethyl alcohol as solvent is put on the first alcogel. A chemical force of attraction on the boundary between alcogels should almost completely prevent the upper alcogel from horizontal shrinkage.

Moreover, in order to avoid vertical shrinkage, all or except the top sides of the upper alcogel is surrounded by an alcogel with higher density: a frame made of alcogel is used as a mold for aerogel with extremely low density (Fig. 3)

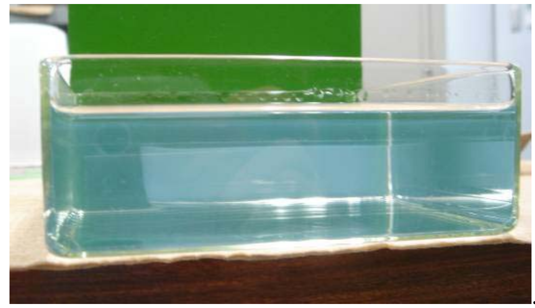

Fig. 3. Photograph of alcogel with the frame structure. Trapped alcogel looks white.

III. Results

A. *High Refractive Index*

Aerogels in good condition has produced by using glass cases and stainless-steel sand strainers. The application of the pinhole drying method to aerogels with the initial refractive indices of 1.024 to 1.060 has produced aerogels with refractive indices of 1.034 to 1.265. The measurement of the refractive index was done using the Fraunhofer method with a 405 nm laser. Fig. 4 indicates that shrunk aerogel almost maintain its initial transparency. It is our expectation that aerogel produced in the pinhole drying method should have higher transparency than that produced directly.

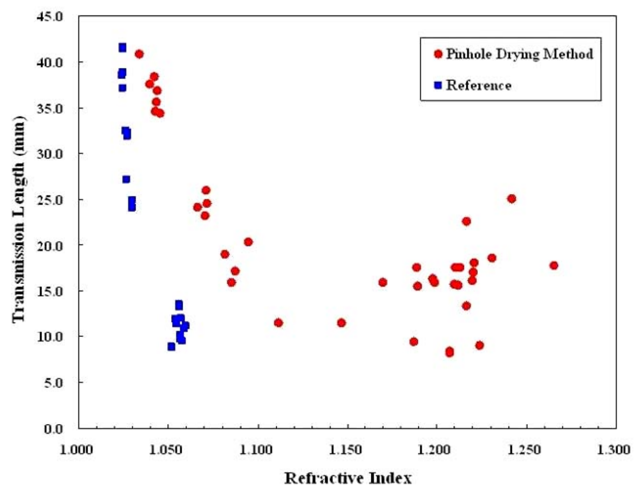

Fig. 4. Transmission length at 400 nm wave length as a function of refractive index for pinhole drying method samples. "Reference" is not used the pinhole method. The aerogels produced at the same time as references with the refractive index of ~1.05 obtain refractive indices of 1.10 to 1.265 in the method.

Fig. 5 shows a high refractive index sample produced in the pinhole drying method. Practically, there are some aerogels with crack, but the sample has not any crack.

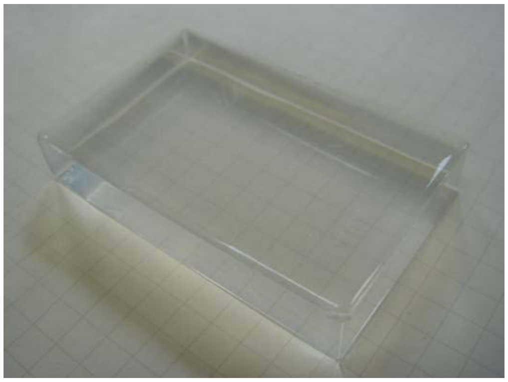

Fig. 5. Photograph of high refractive index sample.
Refractive Index : 1.2206±0.0009
Transmission Length @ 400 nm : 18.1±0.5mm
Size : 57×36×9mm
Shrinkage : 86ml → 18ml (21%)
Initial Refractive Index (reference) : 1.057

As can be seen in Fig. 6, the densities of an aerogel broken to pieces have been measured. There is no measurable difference in the density of each part.

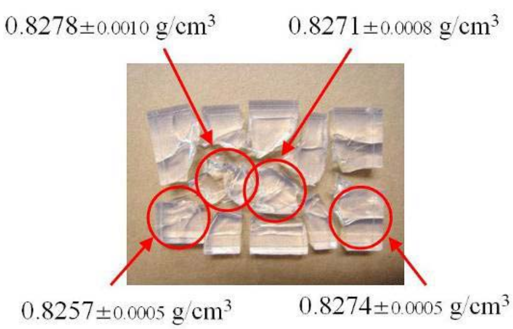

Fig. 6. Photograph of an broken aerogel. The density of each part has measured.

B. Low Refractive Index

In the samples more than 20, the frame structure method has been useful for avoiding shrinkage of alcogel. Two samples are shown in Fig. 7, 8.

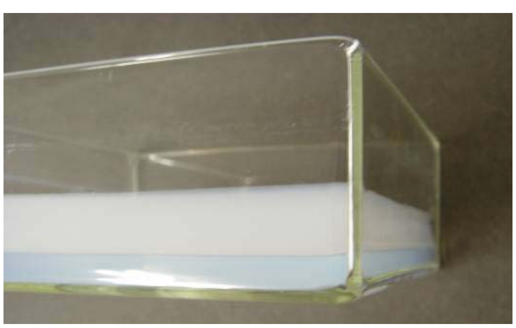

Fig. 7. Photograph of an aerogel consisted of multiple layers with different refractive indices. This is low refractive index sample.
Density : 0.0123±0.0011g/cm^3 (upper aerogel)

Fig. 8. Photograph of an aerogel with the frame structure. The aerogel with extremely low density looks white in the center.
Density : 0.0088±0.0008g/cm^3
Corresponding Refractive Index : 1.002
Size : 7×7×1cm

Through these aerogel samples with low density, we can easily read a newspaper.

IV. Conclusion

The production methods of aerogel with any densities between liquid and gas materials have been demonstrated.

A Cherenkov counter used this aerogel with the refractive index of around 1.20 may be applied as a new gamma detector of positron emission tomography (PET) [7]. An attempt to introduce heavy metal such as Pb into aerogel without decreasing the transparency is under way.

The aerogel with extremely low density will be employed as a cosmic dust collector [8]. To catch cosmic dusts softly, aerogel with as low density as possible is required. An aerogel with the density of ~0.005g/cm^3 would be produced soon.

Acknowledgment

We thank Y. Tanaka at Chiba University for cooperating in the measurements of density.

References

[1] I. Adachi *et al.*, "Study of threshold Cherenkov counter based on silica aerogels with low refractive indices," *Nucl. Instr. and Meth. in Phys. Res. A*, 355 (1995) 390-398.

[2] T. Sumiyoshi *et al.*, "Silica aerogels in high energy physics," *J. Non-Cryst. Soliods*, 225 (1998) 369-374.

[3] I. Adachi *et al.*, "Study of highly transparent silica aerogel as a RICH radiator," *Nucl. Instr. and Meth. in Phys. Res. A*, 553 (2005) 146-151.

[4] M. Konishi *et al.*, "Development of new silica aerogel for the RICH radiator of the Super Belle detector," *IEEE Nucl. Sci. Symp. and Med. Conf.,* Conference Record, Rome, Italy, Oct. 2004.

[5] H. Kawai *et al.*, Proceedings of the Workshop on Hadron Physics at e^+e^- Collider, IHEP, Beijing, Oct. 1994, p. 38

[6] T. Nakano *et al.*, "Multi-GeV laser-electron photon project at SPring-8," *Nucl. Phys. A*, 684 (2001) 71-79.

[7] T. Ooba *et al.*, "Proposal of Cherenkov TOFPET with silica aerogel," *IEEE Nucl. Sci. Symp. and Med. Conf.,* Conference Record, Rome, Italy, Oct. 2004.

[8] K. Okudaira *et al.*, "Evaluation of mineralogical alteration of micrometeoroid analog materials captured in aerogel," *Advances in Space Research*, 34 (2004) 2299-2304.