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Low temperature synthesis of a monolithic silica glass by the pyrolysis of a silica gel

MASAYUKI YAMANE, SHINJI ASO,* SEITARŌ OKANO, TERUO SAKAINO
Department of Inorganic Materials, Faculty of Engineering,
Tokyo Institute of Technology, 12-1, O-okayama 2 chome, Meguro-ku,
Tokyo 152, Japan

The reaction process in the pyrolysis of silica gel has been investigated as the basic study on the low temperature synthesis of monolithic glass from a metal alkoxide. A large volume change which may cause stress-induced fracture of a gel occurred in the following process stages: (a) the decompostion of residual organic compounds into carbon dioxide (300 to 500° C); (b) small pore collapse (400 to 500° C); (c) larger pore collapse (700 to 900° C). A fracture-free monolithic silica glass was successfully prepared from a dry silica gel formed by the hydrolysis of silicon methoxide by careful heat-treatment. The properties of the synthetic silica glass were similar to those of commercial vitreous silica.

1. Introduction

In a previous paper, we reported the preparation of a monolithic gel from metal alkoxide, and its properties as a precursor of oxide glass [1]. A silica gel formed by the hydrolysis of silicon methoxide was found to be porous having a porosity of 30% to 40%. The dehydration polymerization of a dry gel at room temperature proceeded to 60% to 70%, but this also contained a residual organic compound due to incomplete hydrolysis of the alkoxide.

When such a gel is subjected to pyrolysis to form an oxide glass, some reactions due to structure and properties of the gel will occur as well as further dehydration polymerization. The reactions are as follows: (1) the carbonization of residual organic groups; (2) the formation of micropores resulting from the oxidizing of formed carbon into carbon dioxide; (3) micropore collapse; (4) the possible desorption of absorbed water from the micropore walls. Any one of these reactions can yield either thermal or mechanical stress in a gel resulting in the onset of fracture. To prepare a monolithic glass by a low temperature process, it is therefore necessary to know the temperature ranges where respective reactions occur, in order that the gel may be heated slowly or maintained at a temperature until the reactions are completed.

During the above reactions, information on the development of Si–O–Si dehydration polymerization bonding can be obtained by infra-red spectroscopy. This bonding is known to be almost completed at 700° C [2]. The desorption from the micropore walls of physically absorbed water is detected by DTA, and is supposed to occur in the temperature range 150 to 200° C [3]. The information on temperature ranges for other reactions relevant to micropore formation and collapse has not yet been obtained. This information is, however, essential for the preparation of monolithic glass.

The present study was conducted to clarify these reaction processes with respect to temperature, in order that a heating schedule for the pyrolysis of a silica gel into a monolithic glass could be established. By careful heat-treatment we were able to prepare directly a disc of monolithic silica glass from a porous gel without hot-pressing.

2. Experimental details

2.1. Heat-treatment of a gel

Two kinds of dry silica gel prepared in the previous study [1] (A: hydrolysis of $Si(OCH_3)_4$ with distilled water and, B: with $8.54 \times 10^{-3}\%$

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*Present address: Hirohata Seitetsu-Sho, Shin-Nippon Seitetsu-Co, 1. Fuji-chō, Hirohata-ku, Himeji-shi, Hyogo-ken, 671-11 Japan.

ammonia water) were heat-treated at the following temperatures below 1000° C; 100, 300, 500, 700, 900° C. A gel settled in a platinum basket was heated at a rate of 2° C min^{-1} up to the predetermined temperature, and maintained at that temperature for 18 h to allow the gel to attain any temperature-dependent equilibrium structures. To promote the decomposition of residual organic compounds into carbon dioxide, oxygen gas was fed into the fused quartz reaction tube throughout the pyrolysis at a rate of 300 ml min^{-1}.

2.2. Measurements of gel properties after pyrolysis

True density, specific surface area, hydrogen and carbon content, Vickers hardness and refractive index were measured on the gels after pyrolysis. The method and apparatus employed for the first three properties were the same as in the previous study on a dry gel [1]. Vickers hardness was measured by applying a load of 100 g to the polished specimen surface for 15 sec with a Shimazu M-6 microhardness tester. The refractive index was determined under a polarizing microscope using the Becke-Line method on a pulverized specimen.

3. Results and discussion

3.1. Change in gel appearance by pyrolysis

The initial appearance of a disc of untreated dry gel was monolithic, colourless and translucent at room temperature. This remained unchanged after soaking for 18 h at 100° C. Gel heated to 300° C, however, turned yellow, and cracked into a few pieces although basically maintaining its original shape. Sample B contained more unreacted methoxy group than sample A, and for B the yellow colour was deeper than A. The origin of this yellow colour was thus considered to be due to the carbonization of residual organic compounds in the gel.

After pyrolysis at 500° C, the gel became transparent and colourless, but cracked more extensively. At this temperature, the disc shape was still maintained. The shape was lost at the 700° C pyrolysis and the gel disintegrated into particles 2 to 5 mm in diameter. When heated to 900° C, the gel shattered into smaller pieces and had a glossy surface typical of glass which contains a cloudy central core. Since X-ray analysis showed no particular diffraction peak, the white cloud in the sample gel was considered to be bubbles trapped inside due to the collapse of small pores near the surface.

3.2. Properties of gel after heat-treatment

3.2.1. True density

The densities of gels after the heating for 18 h at various temperatures are shown in Fig. 1 for those prepared by hydrolysis with distilled water (sample A) and 8.54×10^{-3} wt% ammonia water (sample B). The density, which increased according to the development of dehydration polymerization, reached a value comparable to that of fused silica (2.20 g cm^{-3}) at a temperature around 700° C, showing that the formation of glass is substantially completed at this temperature. This agrees with the result obtained by infra-red spectroscopy [2].

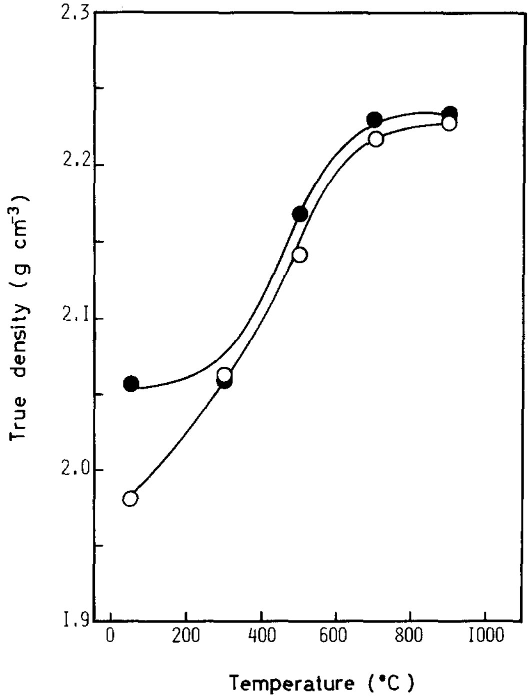

Figure 1 True densities of gels after pyrolysis at various temperatures, (○) sample A, (●) sample B.

3.2.2. Specific surface area

The specific surface area of a gel first increased up to a temperature around 300° C, and then decreased as shown in Fig. 2. The increase at the low temperature is considered to indicate the formation of new micropores resulting from oxidation of carbonized organic compounds into carbon dioxide. The decrease in the specific surface area above 500° C is the result of the collapse of micropores. This is responsible for the

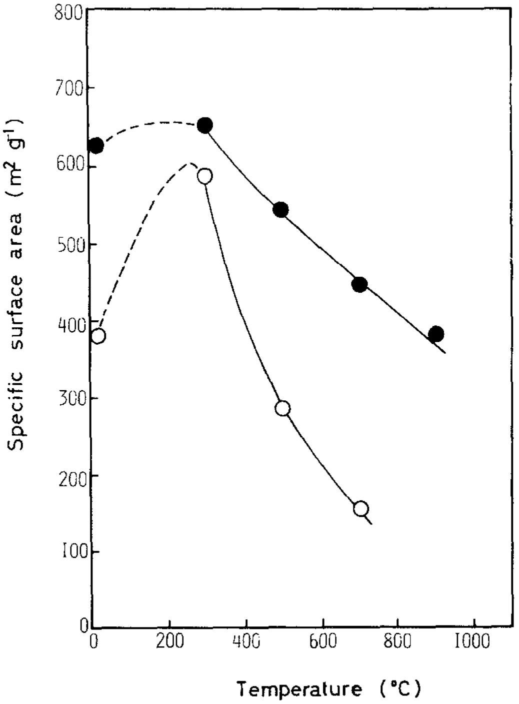

Figure 2 Change in the specific surface area of a gel with temperature, (○) sample A, (●) sample B.

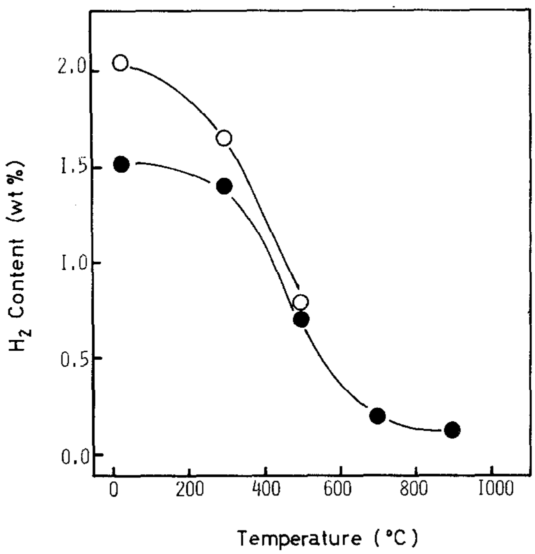

Figure 3 Decrease in hydrogen content in a gel with pyrolysis, (○) sample A, (●) sample B.

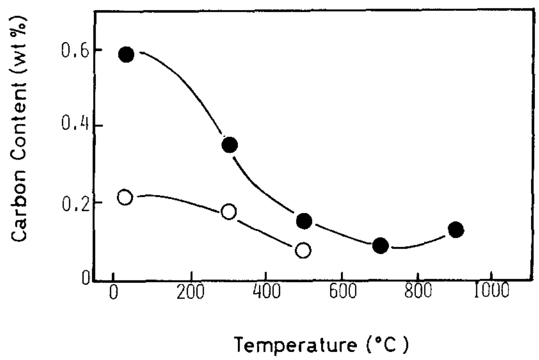

Figure 4 Decrease in carbon content in a gel with pyrolysis, (○) sample A, (●) sample B.

onset of extensive cracking. From consideration of the pore size distribution in a dry gel [1], the micropores determining the specific surface area of the gel after pyrolysis at 700° C are thought to be those having a diameter larger than 50 Å, i.e. serious disintegration occurs most probably when about 80% of the micropores had disappeared.

3.2.3. Hydrogen and carbon content

The monotonic decrease in hydrogen content with temperature shown in Fig. 3 corresponds to the development of dehydration polymerization which is reflected in the increase in density. It is uncertain whether or not the small amount of water still remaining in the gel heated to 900° C should be ascribed to the residual OH group due to incomplete dehydration polymerization. However, this water must be expelled before complete collapse of the micropores in order to avoid the formation of small bubbles trapped inside.

Fig. 4 shows that the carbon content decreases with temperature in the range above 300° C, with a corresponding colour change. That is, although part of the residual organic compounds is already decomposed into carbon dioxide, the remainder is in a carbonized state giving a brown colour at 300° C. The carbon is then oxidized into carbon dioxide which escapes from the gel on heating to a higher temperature. Fig. 4 shows that the decomposition reaction is almost completed at 700° C.

3.2.4. Refractive index

The refractive index of the gel first decreased with heating and then increased until it reached a value comparable to that of fused silica, i.e., $n_d = 1.4584$ (see, for example, [4]), as shown in Fig. 5. When the monotonic increase in density (Fig. 1) and the existence of a maximum specific surface area (Fig. 2) are taken into consideration, this decrease in refractive index is supposed to be caused by experimental error due to the existence of very fine pores in the gel. That is, the newly formed pores resulting from the oxidation of carbon into carbon dioxide are too small to be filled with

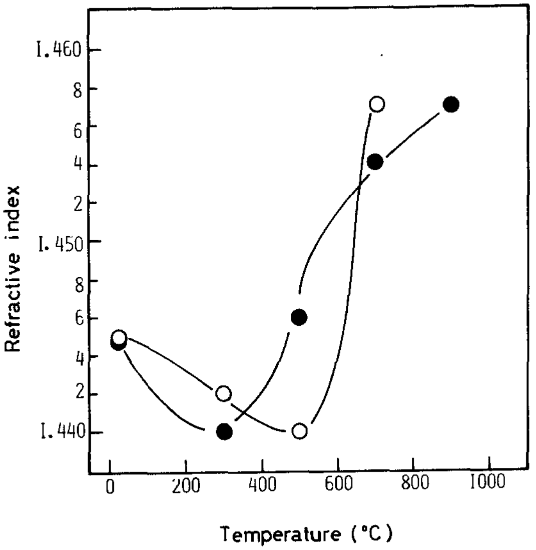

Figure 5 Refractive indicies of gels after pyrolysis at various temperatures, (○) sample A, (●) sample B.

immersion liquid for index measurement, thus the measured value is an apparent one which includes the effect of air trapped in the pores.

3.2.5. Vickers hardness

The Vickers hardness of the gel increased with temperature, as shown in Fig. 6. The hardness of the gel heated to 700° C, however, is much lower than that of fused silica, i.e. $H_V \approx 700\,\mathrm{kg\,mm^{-2}}$ (see, for example, [5]), although the true densities are comparable with each other.

This low value of Vickers hardness is attributed to micropores which still exist at 700 to 900° C, because the indentation hardness is determined from the area of specimen directly supporting an applied load [6], and it is dependent on porosity in the case of porous material. This is also understood from the fact that sample B, which has larger pores and porosity than A, always has a lower hardness despite the fact that its true density is higher than that of A.

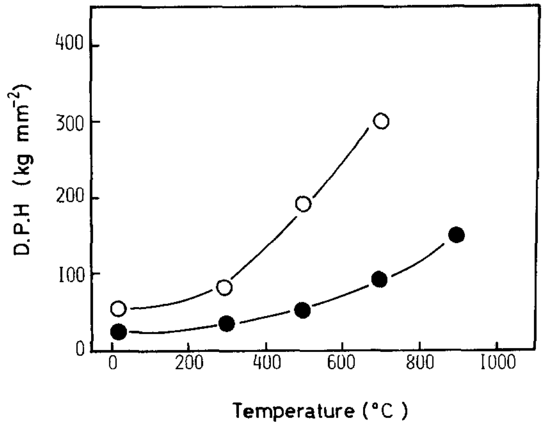

Figure 6 Increase in Vickers hardness of a gel with pyrolysis, (○) sample A, (●) sample B.

3.3. Discussion of the reaction process

From the above results and discussion, the reaction process which occurs in the pyrolysis of a silica gel can be described with respect to temperature as follows: in the temperature range from room temperature to 100° C, only dehydration polymerization occurs if the gel is completely free from alcohol. Between 100 and 200° C, the desorption from the micropore walls of physically adsorbed water is the main process; dehydration polymerization, which proceeds up to about 700° C, also occurring.

Above 200° C, the carbonization of residual organic compounds is pronounced up to 300° C. The carbon is then oxidized into carbon dioxide, resulting in the formation of micropores in the temperature range 300 to 500° C. The newly formed micropores, as well as small pores originally existing in a dry gel, begin to collapse at a temperature near 500° C.

The collapse of larger pores is pronounced at higher temperature, say 700 to 900° C, until it is finally completed at a temperature near 1000° C.

4. Preparation of a monolithic silica glass and its properties

Since stress to induce the onset of fracture is developed when a large volume change is required in a gel, crack formation may occur in the following process stages: (a) the decomposition of organic compounds into carbon dioxide (300 to 500° C); (b) the collapse of small pores (400 to 500° C; (c) the collapse of larger pores (700 to 900° C). Therefore, care should be taken when heating the gel in these temperature ranges that enough time is allowed for the respective processes to be completed. The collapse of pores before the completion of dehydration polymerization, in particular, must be avoided in order to allow the water to evaporate from the gel.

Taking these results into consideration, a fracture-free monolithic silica glass was successfully prepared by the pyrolysis of a gel up to 1070° C. The appearance of the glass is shown in

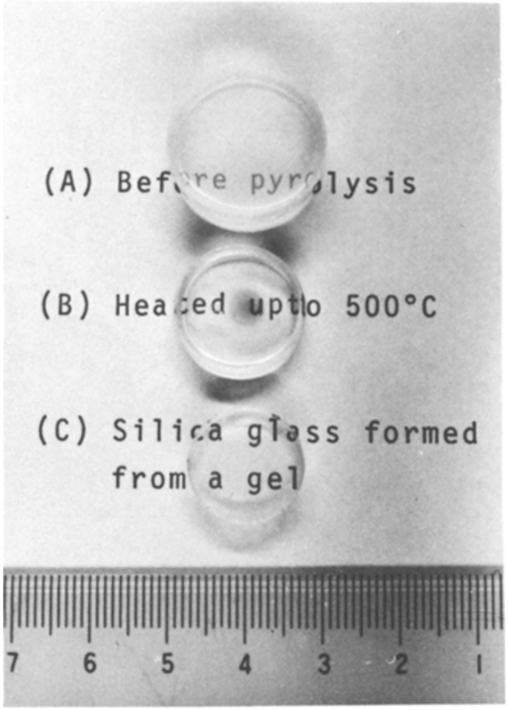

Figure 7 Silica glass formed by the pyrolysis of a gel up to 1070° C.

Fig. 7 along with an untreated dry gel and one heated to 500° C.

Some properties of the glass are compared with those of commercial vitreous silica in Table I. The Young's and shear moduli were determined from the density and longitudinal and shear wave velocities measured by the pulse propagation technique on a sample 15 mm diameter and 4.4 mm thick. The thermal expansion coefficient was determined by the optical lever method on a rod 3 mm diameter and 10 mm long which was cut from a disc. It is obvious from the table that the properties of synthesized silica glass in this study are similar to those of commercial vitreous silica.

TABLE I Some properties of a monolithic silica glass prepared in the present study

	SiO_2 glass prepared in the present study	Commercial silica glass
Density ($g\,cm^{-3}$)	2.20	2.21
Refractive index (n_d)	1.457	1.4584 [4]
Vickers hardness ($kg\,mm^{-2}$)	680 ± 20	680–700 [5]
Thermal expansion coefficient ($°C^{-1}$) (–500° C)	5.5×10^{-7}	5.5×10^{-7}
Young's modulus (kbar)	710 ± 10	730 [7]
Shear modulus (kbar)	310 ± 5	314 [7]

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