VITRIFICATION OF SILICA GEL

By

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Abstract

Transformation of pure silica gel at high temperature was reexamined. Finely divided silica gel (I) was prepared from tetraethyl ortho silicate and then pressed to a disc. It was found to vitrify into translucent mass by heating at about 1150°C in a vessel made of silica glass. In platinum vessel, it was liable to convert into cristobalite. Silica gel (II) was prepared by the hydrolysis of silicon tetrachloride with water and dried to a lump. It became transparent at somewhat lower temperature of 1050°C, then began to pop at about 1100°C owing to the release of minor component, probably water confined therein.

I. Introduction

Vitrified silica bodies are commonly fabricated by melting of high purity quartzite, but they are able to be prepared by sintering of finely divided silica as reported by Vasilos1) and by Hearny2).

Vasilos described a hot pressing by which powdered fused silica was converted into vitrified silica shape of high density at temperature ranging from 1100°C to 1200°C. In Hearny’s process finely divided silica, produced by decomposition of silicon compounds such as silico-chloroform and ethyl silicate in gaseous state, is used to form shape by conventional fabrication techniques. This material is then consolidated into translucent and nonporous body by firing at a temperature above 1200°C, but below the fusion point of silica.

On the other hand, when silica gels made from sodium silicate solution by neutralizing with acid or made from ethyl silicate by hydrolysis are heated at a temperature above 1000°C, they become in general cristobalite3), 4) and do not form glass at temperatures ranging from 1000°C to 1400°C.

The present study was performed to reexamine that which form of silica, crystalline or glassy,

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would appear on heating of the high purity silica gels which had been prepared from ethyl silicate and silicon tetrachloride.

II. Materials and their preparation

Starting materials were silica gel (I) and (II). Silica gel (I) was "High Purity Grade" silica gel powder supplied from Tama Kagaku Kogyo K.K., which was prepared by hydrolysis of ethyl silicate using ammonia as catalyster and semidrying to moisture-content of about fifty percent by weight of the powder. It contained a small amount of residual ammonia which, however, could easily be expelled by heating it to a temperature of 250°C for few hours. Silica gel (II) was prepared by hydrolysis of semiconductor grade silicon tetrachloride supplied by SHIN NIPPON CHISSO HIRYO Co. Ltd. About 100 grams of the silicon tetrachloride was dropped into 1000 ml of distilled pure water under rapid stirring and ice-cooling. Apparatus for distillation of water, a reaction vessel and a stirring rod used are all made of quartz glass. The addition of silicon tetrachloride was completed within about thirty minutes, then the mixture was allowed to set. The time of setting was about five hours at room temperature. When the gel formed was heated for four days at a temperature of about 105°C, it shrank to a volume of about one thirtyth that of original gel and there remained no smell of hydrochloride vapour. The moisture contents of both silica gels and the impurities therein estimated from qualitative emission spectroanalysis are shown in Table 1.

III. Experimental procedure

To reexamine the thermal transformation of the silica gel (I) and (II) in air they were heated in the electric resistance rectangular furnace (15×15×25 cm) using silicon carbide as a heating element. Silica gel (I) was always used in the form of disc (diameter 2 cm, thickness about 4 mm), which was shaped in the hardened steel die under various pressure and then shaved the surface to get rid of any dirt stuck to during pressing operation. The samples of silica gel (I) in the form of disc and silica gel (II) in the form of lump as prepared

| Table 1. General qualitative spectrochemical analysis of source materials. |
|-----------------------------|----------------|-------------|-------------|-------------|-------------|
| Form                        | H₂O            | Na          | Mg          | Ca          | Al          | Fe          |
| Fine powder                 |                |             |             |             |             |             |
| 0.5~1.0 micron in size      | 5.0, wt%       | T           |             |             |             | T           |
| Translucent lump            |                | V            | W           |             |             |             |
| 1~10 mm in size             | 5.77 wt%       | VW          |             |             |             |             |
| Bulk density being          | 0.71 g/cm³     |             |             |             |             |             |
| Note : In general the following concentration range are indicated by the symbols: VW, 0.001~0.01%; T, less than 0.0005%; -, not detected |

Firing temperature, 1350°C

a) Figure of line a) shows pressure in kg/cm², exerted to at forming step.
b) Figure of line b) shows holding time in hour at firing temperature.

Fig. 1. Transparency of the compressed disc of silica gel (I), after firing under various conditions.
IV. Result and Discussion

Silica gel (I) was found to vitrify into a transparent or translucent material at a temperature of 1150°C or higher. The degree of vitrification or transparency of the resulting specimen was depending on the pressure for shaping, temperature and time of holding as they are shown in Fig. 1, in which it may be roughly estimated from the clearness of the letter underlaying the fired specimens.

At a temperature of 1100°C, the specimen was opaque even when the highest pressure had been exerted on, but it became translucent at 1150°C and became almost transparent at 1200°C when the pressure for shaping of 8000 kg per sq. cm, temperature ranging from 1000°C to 1400°C, and holding time up to 24 hours were used in this study. The properties such as transparency, refractive indices and densities of resulting specimens were measured.

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The true density of transparent specimen was found to be 2.208 g. per cubic cm, and its refractive index was 1.458±0.001. These values are comparable with those of ordinary fused silica.

The linear shrinkage of silica gel (I) in the course of heating was measured by extension rod dilatometer. The specimen used was a rectangular bar approximately 3×10 mm in cross section and 15 mm in length and was heated at a steady rate of 5°C/min until the maximum temperature of 1200°C. The curve obtained is shown in Fig. 2, in which shrinkage starts gradually from 200°C and becomes serious above 1000°C.

The over-all linear shrinkage of the green specimen disclosed after vitrification was depending app

![Fig. 2. Thermal contraction of silica gel (I) compressed to a rectangular bar under various pressures.](image_url)
Thus the silica gel (II) was found to become clear and transparent at around 1050°C and then it began to pop into such a expanded material as poped pearlite at 1100°C or above.

The true density of 2.204 g. per cubic cm and refractive index of 1.458±0.001 were obtained for this transparent specimen which are coincident with those of ordinary fused silica.

From the difference in weight between the transparent specimen prepared by heating for 2 hours at 1150°C and the expanded one obtained by reheating the same for two hours at 1400°C, it was indicated that some minor component, probably being a combined water but not identified, weighing about 0.15% of the transparent specimen vaporized away during popping. In addition to the presence of such a volatile component, there must be needed of some what viscous state for enabling the specimen to expand at popping point, and such viscous state may probably be attained already at the minimum temperature of 1050°C for allowing silica gel(II) to become transparent.

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