Preparation of Glass Fibers of the $\text{ZrO}_2\text{-SiO}_2$ System from Metal Alcoholates

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金属アルコレートを原料とする $\text{ZrO}_2\text{-SiO}_2$ 系ガラス繊維の製造

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Glass fibers containing ZrO_2 have been paid attention to as alkali-resistant fibers for reinforcing cement. It has been confirmed that the ZrO_2 component provides the fibers with alkali-resistance^{(1),(2)}. It has been known, however, that the highest possible ZrO_2 content in silicate glasses is limited to about 20% in weight, and the melting of glasses with more ZrO_2 content is difficult to achieve.

The present study was undertaken with the purpose of preparing glass fibers containing much more ZrO_2 than achieved with the conventional glass-melting technique. Metal alcoholates were employed as starting materials for this purpose. Preparation of glass fibers in the present study consists of (1) fiber drawing from the spinnable, viscous liquid formed in the course of hydrolysis of starting alcoholate mixtures and (2) heating of the drawn fibrous materials to about 500°C into oxide glass fibers⁽³⁾. Accordingly, this is different from preparation of glass powders or their agglomerate or films⁽⁴⁾ from alcoholates in that success of fiber drawing depends largely on whether the liquid becomes spinnable or not.

The experiment will be illustrated with the alcoholate mixture which would give 43 $\text{ZrO}_2\cdot 57 \text{SiO}_2$ (in weight) glass if no loss of any particular metal ion. Zirconium tetrapropoxide dissolved in propanol $\text{Zr}(\text{OC}_3\text{H}_7)_4\cdot 2\text{C}_3\text{H}_7\text{OH}$ provided by Alfa-Inorganics Inc. and silicon tetraethoxide $\text{Si}(\text{OC}_2\text{H}_5)_4$ provided by Wako Chemicals Company were used as the materials for ZrO_2 and SiO_2 , respectively. Both these were liquids. 22.8 g $\text{Zr}(\text{OC}_3\text{H}_7)_4\cdot 2 \text{C}_3\text{H}_7\text{OH}$, 28.3 g $\text{Si}(\text{OC}_2\text{H}_5)_4$ and 50 ml absolute ethanol* were stirred and mixed in a flask at 80°C for 3 h under

refluxing. The liquid mixture of low viscosity was then transferred to a 300 cc beaker and held open in air. During holding in air the temperature of the liquid mixture was constant at 30°C and the ambient temperature was $20\pm 1^\circ\text{C}$. The viscosity of the liquid increased gradually as hydrolysis progressed due to moisture and carbon dioxide in the atmosphere. After about 40 h it was viscous and sticky, although it was still transparent with no white precipitate indicating inhomogeneous partial hydrolysis. Fibers could be drawn from the resultant viscous liquid by inserting a glass stab of 6 mm in diameter and pulling it up manually. Adjustment of the speed of pulling up provided fibers with various diameters, for example, 20 μm or more and with varying lengths, for example, 50 cm or more. The liquid remained viscous and spinnable for more than 5 h before solidifying to a solid mass. This would indicate that use of an appropriate fiber drawing apparatus makes it possible to obtain endless fibers with vary-

Fig. 1. Photograph of the fibers drawn from the alcoholate solution containing zirconium and silicon. 1 cm

* ethanol dehydrated by using metallic magnesium.

ing diameters. The drawn fibers did not shrink and fracture spontaneously, but they were set immediately after drawing. A photograph of the drawn fibers is shown in **Fig. 1**. These fibrous materials changed to oxide glass fibers on heating them to about 500°C. The fibers thus obtained showed a black appearance probably due to a slight amount of remaining carbonaceous substance.

The viscous liquid used for fiber drawing solidified to a mass finally, which became a glass powder or agglomerates of powder on heating at 500°C. Micellaneous measurements were made on this powder instead of the fiber. Chemical composition determined by X-ray fluorescence spectrometry was $26 \text{ ZrO}_2 \cdot 74 \text{ SiO}_2$ in weight, showing that the glass fibers which contain as much as 26% ZrO_2 can be obtained, although a portion of ZrO_2 is lost during preparation of the glass. X-ray diffraction of the specimens heated at various temperatures for 3 h showed a

slight indication of precipitation of a crystal after heating at 800°C.

Besides the glass fiber mentioned above, the fibers with varying ZrO_2 contents such as 18, 11, 7 and 3% in weight by chemical analysis were obtained in the present procedure. The measurements of the properties of these fibers are being made at present.

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