Alkali-Resistant BaO–TiO$_2$–SiO$_2$ Glasses

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The results of the authors' investigations on alkali resistance of glasses in the system BaO–TiO$_2$–SiO$_2$ and those modified with some components are described. Five pieces of glass fibers (250–300 μm × 5 mm) of the composition 15SrO·15BaO·40TiO$_2$·30SiO$_2$ mol% (S4–15Sr) were immersed in a 100 ml of 2N NaOH aqueous solution held at 95°C for 108 h, together with 2 g of the glass grains (297–500 μm3) of the same composition. Its diameter reduction was about 1/10 times that of a ZrO$_2$-containing sodium silicate glass fiber G20 of the composition 1Li$_2$O·11Na$_2$O·1Al$_2$O$_3$·71SiO$_2$·16ZrO$_2$ wt%. Its high alkali resistance was interpreted in terms of the low solubility of the TiO$_2$ in the NaOH solution and the high capacity of the TiO$_2$-rich layer formed on the glass surface for adsorbing Sr$^{2+}$ and Ba$^{2+}$ ions. Fifteen pieces of the S4–15Sr glass fibers (15–30 μm × 40 mm) were immersed in a 250 ml of a Portland cement aqueous phase solution held at 95°C for 108 h, together with 5 g of the glass grains of the same composition. Its tensile strength was about 2 times that of the G20 glass fiber after the immersion.

KEY WORDS: Glass fiber-reinforced cement/ Alkaline durability/ Glass fiber/ Tensile strength/ Young’s modulus/ BaO–TiO$_2$–SiO$_2$ glass/

I. INTRODUCTION

Zirconium-containing sodium silicate glasses are known as alkali-resistant glasses used as fibers for reinforcing cement materials. In a long period, however, these glasses are still liable to be corroded by alkaline solutions, and their strengths gradually decrease.$^{1)}$ The corrosion by alkaline solutions is generally considered to be caused mainly by preferential dissolution of the SiO$_2$. The constituent ZrO$_2$ is much more stable in alkaline solutions than the SiO$_2$.$^{2)}$

Titanium oxide is not only as stable as the ZrO$_2$ in alkaline solutions, but also form glasses more easily by the addition of smaller amounts of the SiO$_2$ than the ZrO$_2$. The present paper describes the results$^{3,4)}$ of the investigations on alkali resistance of the glasses containing large amounts of TiO$_2$, especially those in the system BaO–TiO$_2$–SiO$_2$ and those modified with other components.

II. EXPERIMENTAL PROCEDURE

1. Preparation of Glasses

About 50 g of batch mixtures yielding various oxide compositions in the systems BaO–TiO$_2$–SiO$_2$, (R$_m$O$_a$–BaO)–TiO$_2$–SiO$_2$ and BaO–(TiO$_2$–ZrO$_2$)–SiO$_2$, where

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R$_m$O$_n$ is Li$_2$O, Na$_2$O, K$_2$O, MgO, CaO or SrO, were prepared from optical silica sand and reagent grade chemicals of oxides and carbonates. The batches were put into a 50 ml Pt10Rh crucible with a Pt lid and melted in a SiC furnace at 1500°C for 1 h. The crucible was then taken out of the furnace and filaments 15 to 300 μm in diameter were drawn by hand from the melts during cooling. The melts left in the crucible were reheated at 1500°C for 1 h, poured on to a stainless steel plate and pressed into plates 1 to 10 mm thick. A part of the glass plates was annealed from their transition temperatures. Another part of the glass plates was crushed by WC Mixer Mill (Spex Industries, Inc. Model 8000) and their grains passing through sieve 32 mesh (500 μm opening) and retained by 48 mesh (297 μm opening) were collected.

For comparison, a ZrO$_2$-containing sodium silicate glass, G20, of the composition 1Li$_2$O·11Na$_2$O·1Al$_2$O$_3$·7SiO$_2$·16ZrO$_2$ wt% was prepared in the form of fibers, plates and grains by the same method as described above.

2. Test of Alkali Resistance

The glass fibers 250–300 μm in diameter were cut into 5 mm in length, washed with a ethylalchol and dried. Five pieces of them were immersed in a 100 ml of 2N·NaOH aqueous solution (pH 14.3 at 25°C) in a polypropylene flask. The flask was shaked at a rate of 120 strokes/min by a stroke length of 30 mm for 18–108 h in an oil bath held at 95°C. After the treatment, the glass fibers were washed with distilled water, and with ethylalchol, and then dried. Their diameter reductions were measured with an optical microscope and the data for five pieces were averaged.

Two grammes of the glass grains, 297–500 μm in diameter, after washed with distilled water and alcohol, and then dried, were immersed in the NaOH solution in the same manner as in the case of the glass fibers. After the immersion, they were separated from the solution by a Teflon filter with average pore diameter of 2–5 μm, washed successively with distilled water, 0.1N-HCl aqueous solution and ethylalchol, and then dried. Their weight losses were measured and the data for three runs were averaged.

3. EPMA of Glass Surface

The surfaces of the glass fibers were coated with a thin carbon film and analyzed with a electron probe microanalyzer (Shimadzu Seisakusho Ltd. Model ARL–EMX–SM), before and after the NaOH treatment.

Intensities of characteristic X-rays radiated from various spots on the surface of the glass fibers were integrated for 10 sec and the five measurements for one spot were averaged. The electron acceleration voltage, the specimen current and the electron beam diameter were 15 kV, 0.01 μA and 5 μm, respectively.

4. Measurement of Mechanical Properties

Fifteen pieces of the glass fibers 15–35 μm in diameter and 40 mm in length were mounted on a polypropylene frame, washed and dried in the same manner as in the alkali resistance test. They were immersed in a 250 ml of a Portland cement aqueous phase solution contained in a polypropylene bottle, together with 5 g of the glass grains
of the same composition as that of the glass fibers. The addition of the glass grains to
the solutions was to increase the ratio of the glass surface area to the solution volume so
as to bring the experimental condition as near as possible to the actual condition for
the production of fiber-reinforced cement materials. The Portland cement aqueous
phase solution was prepared by dissolving chemicals of NaOH, KOH and Ca(OH)₂
in 0.88, 3.45 and 0.48 g, respectively, into a 1 l of water, following the method of
Majumder et al. Its pH was 12.9 at room temperature. The polypropylene bottle
was placed in the oil bath held at 95°C and shaken for 3–108 h in the same manner
as in the alkali resistance test. The methods for washing and drying the glass fibers
were also the same as in the alkali resistance test. The glass fibers thus treated, as
well as those untreated, were subjected to the measurement of tensile strength. For the
measurement, both ends of the glass fiber samples were stuck on two pieces of square
drafting paper (5.0 by 5.0 by 0.2 mm) with polyvinyl acetate adhesive, respectively, and
the papers were clamped in the jaws of the Instron-type testing machine (Shimadzu
Seisakusho Ltd. Autograph Model DSS–500). The gage length of the fiber was 25 mm
and the strain rate was 0.8 cm/cm·sec. The measured tensile strengths for 10 pieces
were averaged.

Rectangular glass specimens (10 by 10 by 8 mm) were cut from the annealed
glass plates described in the section I and abraded with #2000 Al₂O₃ powder. The
longitudinal and shear sound velocities, v₁ and v₂, of the glass specimens were measured
by a pulse superposition method with 12 MH quarts transducers. Densities, ρ, of
the glass specimens were measured by Archimedean technique with water. Young’s
modulus of the specimens E were calculated from v₁, v₂ and ρ using the following relation.

\[ E = \rho v_2^2(2v_1^2 - 4v_2^2)/(v_1^2 - v_2^2) \]

III. RESULTS

1. Alkali Resistance of Glasses

The diameter reductions of the glass fibers in the systems BaO–TiO₂–SiO₂,
(R₉O₉–BaO)–TiO₂–SiO₂ and BaO–(TiO₂–ZrO₂)–SiO₂ caused by the NaOH treat-
ment of 18 h are given in Fig. 1 (A)–(E). The result for G20 glass fiber is also given
for comparison in Fig. 1 (D). It can be seen from Fig. 1 that the diameter reduction
is suppressed by the increase in TiO₂/SiO₂ mole ratio for the system BaO–TiO₂–SiO₂
and by the partial substitution of the BaO with the SrO. The diameter reduction of
the glass fiber of the composition 20SrO·10BaO·40TiO₂·30SiO₂ mol% was lower than
that of G20 glass fiber.

Effect of prolonged NaOH treatment on the diameter reduction is given in Fig. 2
for the glass fibers of the composition 15SrO·15BaO·40TiO₂·30SiO₂ mol% (S4–15Sr)
and G20. Figure 2 indicates that the diameter reduction of the former glass fiber is
about 1/2 times that of the latter after the 108 h treatment, although their diameter
reductions are almost equal at the 18 h treatment.

In the case when 2 g of the glass grains of the same compositions as those of the
Fig. 1. Diameter reduction of glass fibers caused by the immersion in the NaOH solution of 18 h; (A) 30BaO·xTiO₂·(70—x)SiO₂, (B) yBaO·(100—y)(0.57TiO₂·0.43SiO₂), (C) pR₂O·(30—p)BaO·40TiO₂·30SiO₂, (D) qR'₀·(30—q)BaO·40TiO₂·30SiO₂ and (E) 30BaO·(40—r)TiO₂·rZrO₂·30SiO₂ (mol%) glasses. (●) Mean value and (I) maximum and minimum of measured values.

fibers were placed together with the fiber samples in the NaOH solution, the diameter reductions of the S4—15Sr glass fibers after 18 h and 108 h were both about 1/10 times that of the G20 glass fibers, as shown in Fig. 3. The weight losses of the glass grains caused by the NaOH treatment of 18 h were 0.17 and 1.93 wt% for the S4—15Sr and G20 glasses, respectively, i.e. the weight loss of the former was about 1/10 times that of the latter, when 2 g of them were immersed
2. Effects of Additives on Alkali Resistance

The diameter reductions of the S4-15Sr glass fibers after immersed for 18 h in the various NaOH solutions, to which small amounts of powdered chemicals of Sr, Ba, Ti or Si hydrates were added, are shown in Table I. The addition of the Sr, Ba and Ti hydrates markedly suppressed the diameter reduction of the fibers whereas that of the Si hydrate enhanced.

3. EPMA of Glass Surface

The results of EPMA for the S4-15Sr glass fiber treated with the NaOH solution
Table I. Diameter reduction of S4–15Sr glass fibers immersed in the NaOH solution added with some chemicals for 18 h

<table>
<thead>
<tr>
<th>Additive chemical</th>
<th>Diameter reduction of glass fiber (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>4</td>
</tr>
<tr>
<td>Sr(OH)₂·8H₂O</td>
<td>30.9 mg</td>
</tr>
<tr>
<td>Ba(OH)₂·8H₂O</td>
<td>24.6 mg</td>
</tr>
<tr>
<td>TiO₂·1.5H₂O</td>
<td>16.2 mg</td>
</tr>
<tr>
<td>SiO₂·0.67H₂O</td>
<td>14.4 mg</td>
</tr>
</tbody>
</table>

Fig. 4. (A) Secondary electron micrograph of surface of S4–15Sr glass fiber immersed in the NaOH solution for 72 h and (B) its schematic cross section.

for 72 h and those untreated are given in Table II. The analyzed spots on the treated glass fiber are shown on Fig. 4. It can be seen from Table II that a thin TiO₂-rich layer forms on the glass surface after the NaOH treatment.
Table II. Intensity ratios of SrLa/TiKa, BaLa/TiKa or SiKa/TiKa for S4-15Sr glass fibers measured before and after immersed in the NaOH solution for 72 h

<table>
<thead>
<tr>
<th>Intensity ratio</th>
<th>SrLa/TiKa</th>
<th>BaLa/TiKa</th>
<th>SiKa/TiKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before immersed</td>
<td>0.37</td>
<td>0.15</td>
<td>0.81</td>
</tr>
<tr>
<td>After immersed</td>
<td>0.21</td>
<td>0.07</td>
<td>0.52</td>
</tr>
<tr>
<td>(a)*</td>
<td>0.08</td>
<td>0.04</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Intensity ratios at (a) and (b) spots on Fig. 4.

4. Mechanical Properties of Glasses

Tensile strength of the fibers of the S4–15Sr glass and its modified glass, 7.00Na2O·5.75CaO·5.75SrO·11.50BaO·33.00TiO2·7.00ZrO2·30.00SiO2 mol% (S4–134), both treated with the cement aqueous phase solution for various times, as well as those of the fibers untreated, are shown in Fig. 5. The S4–134 glass is one of the glasses which can be drawn continuously by an automatic machine into fibers. The results for the G20 glass fibers are also shown for comparison in Fig. 5. It can be seen from Fig. 5 that the fibers of the S4–15Sr and S4–134 glasses show tensile strengths about 2 times that of the G20 glass, even after the 108 h treatment. No diameter reduction was observed for all of the glass fibers even after the 108 h treatment.

![Fig. 5. Tensile strength of S4–15Sr, S4–134 and G20 glass fibers immersed in Portland cement aqueous phase solution together with glass grains. (●, ○ or □) Mean value and (I) 95% confidential limits.](230)
The Young's moduli of the S4-15Sr and S4-134 glasses were 1032 and 1067 kbar, respectively, which were about 1.25 times that of the G20 glass, 820 kbar.

IV. DISCUSSION

Experimental results described in section III. 1 showed that fibers of SrO–BaO–TiO2–SiO2 glasses represented by the S4–15Sr glass have high alkali resistance, especially in the case when the glass fiber samples were immersed in the NaOH solution together with 2 g of the glass grains of the same composition as that of the fiber samples.

Table I indicates that Sr2+, Ba2+ and Ti4+ ions dissolved in the NaOH solution have a strong effect of suppressing the corrosion of the S4–15Sr glass. The fact that the co-immersion of the glass grains of the same composition as that of the S4–15Sr glass fiber in the NaOH solution suppresses the corrosion of the S4–15Sr glass fibers (Fig. 3) can be explained by the dissolution of the constituent Sr2+, Ba2+ and Ti4+ ions of the S4–15Sr glass fibers into the NaOH solution. The high ratio of the surface area of the glass sample to the volume of the NaOH solution would facilitate the rapid rise of the concentrations of Sr2+, Ba2+ and Ti4+ ions in the NaOH solution. The concentrations of these ions in the NaOH solution necessary to suppress the corrosion of the mother glass would not be high, since amount of these ions actually added to the NaOH solution were extremely low (Table I).

The followings are the detailed explanations of the effects of the Sr2+, Ba2+ and Ti4+ ions in suppressing the corrosion of the S4–15Sr glass fibers. Figure 6 shows the stabilities of the TiO2 and SiO2 in aqueous solution at various pH (25°C). Their activities were calculated from thermodynamic data after Paul. It is apparent from Fig. 6 that the solubility of the TiO2 in the alkaline solution is extremely low compared with that of the SiO2. Therefore, when the S4–15Sr glass fibers are immersed in the NaOH solution, the saturation concentration of the TiO2 in the NaOH solution will soon be approached by the dissolution of the TiO2 from the mother glass fibers, and consequently the rate of dissolution of the TiO2 from the mother glass fibers will fall down.

Solubilities of the SrO and BaO in alkaline solutions, however, are not so low as that of the TiO2. Therefore, the dissolution of these components, as well as that of the SiO2, will continue for a while even after the TiO2 stops dissolving. As the results, a TiO2-rich layer will form on the surface of the mother glass fibers. The presence of such surface layer was confirmed by the EPMA of the S4–15Sr glass fiber treated with the NaOH solution for 72 h (Table II). It is well known that the hydrated TiO2 bears negative charge in alkaline solutions and readily adsorbs alkaline earth cations. Therefore, once the TiO2-rich layer is formed, Sr2+ and Ba2+ ions having dissolved into the NaOH solution will be adsorbed on the TiO2-rich surface layer. If the Sr2+ and Ba2+ ions are adsorbed on the surface layer of the glass, not only their concentrations at the surface increase, but also the surface structure consisting of disconnected hydrated TiO2 will be compacted since the negative charges of the hydrated TiO2 are neutralized. As the results, the diffusions of the SrO and BaO, as well as that of the SiO2, through the TiO2-rich surface layer, will be suppressed.
Fig. 6. Stability of the (A) TiO₂ and (B) SiO₂ in aqueous solution at different pH (25°C).

and consequently the rate of corrosion of the glass will fall down.

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