

Alkali-Resistant BaO-TiO₂-SiO₂ Glasses

Tadashi KOKUBO and Hiroshi TAKAGI*

Received May 15, 1981

The results of the authors' investigations on alkali resistance of glasses in the system BaO-TiO₂-SiO₂ and those modified with some components are described. Five pieces of glass fibers (250-300 μmφ × 5 mm) of the composition 15SrO·15BaO·40TiO₂·30SiO₂ mol% (S4-15Sr) were immersed in a 100 ml of 2*N*-NaOH aqueous solution held at 95°C for 108 h, together with 2 g of the glass grains (297-500 μmφ) of the same composition. Its diameter reduction was about 1/10 times that of a ZrO₂-containing sodium silicate glass fiber G20 of the composition 1Li₂O·11Na₂O·1Al₂O₃·71SiO₂·16ZrO₂ wt%. Its high alkali resistance was interpreted in terms of the low solubility of the TiO₂ in the NaOH solution and the high capacity of the TiO₂-rich layer formed on the glass surface for adsorbing Sr²⁺ and Ba²⁺ ions. Fifteen pieces of the S4-15Sr glass fibers (15-30 μmφ × 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-TiO₂-SiO₂ 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 SiO₂. The constituent ZrO₂ is much more stable in alkaline solutions than the SiO₂.²⁾

Titanium oxide is not only as stable as the ZrO₂ in alkaline solutions, but also form glasses more easily by the addition of smaller amounts of the SiO₂ than the ZrO₂. The present paper describes the results^{3,4)} of the investigations on alkali resistance of the glasses containing large amounts of TiO₂, especially those in the system BaO-TiO₂-SiO₂ 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-TiO₂-SiO₂, (R_mO_n-BaO)-TiO₂-SiO₂ and BaO-(TiO₂-ZrO₂)-SiO₂, where

* 小久保 正, 鷹木 洋: Laboratory of Ceramic Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

R_mO_n is Li₂O, Na₂O, K₂O, 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 ZrO₂-containing sodium silicate glass, G20, of the composition 1Li₂O·11Na₂O·1Al₂O₃·71SiO₂·16ZrO₂ 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 ethylalcohol and dried. Five pieces of them were immersed in a 100 ml of 2*N*-NaOH aqueous solution (pH 14.3 at 25°C) in a polypropylene flask. The flask was shaken 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 ethylalcohol, 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, 0.1*N*-HCl aqueous solution and ethylalcohol, 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 $\text{Ca}(\text{OH})_2$ in 0.88, 3.45 and 0.48 g, respectively, into a 1 l of water, following the method of Majumder *et al.*¹⁾ 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 Al_2O_3 powder. The longitudinal and shear sound velocities, v_l and v_s , of the glass specimens were measured by a pulse superposition method⁵⁾ with 12 MH quartz transducers. Densities, ρ , of the glass specimens were measured by Archimedeian technique with water. Young's modulus of the specimens E were calculated from v_l , v_s and ρ using the following relation.

$$E = \rho v_s^2 (2v_l^2 - 4v_s^2) / (v_l^2 - v_s^2)$$

III. RESULTS

1. Alkali Resistance of Glasses

The diameter reductions of the glass fibers in the systems $\text{BaO-TiO}_2\text{-SiO}_2$, $(\text{R}_m\text{O}_n\text{-BaO})\text{-TiO}_2\text{-SiO}_2$ and $\text{BaO}-(\text{TiO}_2\text{-ZrO}_2)\text{-SiO}_2$ caused by the NaOH treatment 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 $\text{TiO}_2/\text{SiO}_2$ mole ratio for the system $\text{BaO-TiO}_2\text{-SiO}_2$ and by the partial substitution of the BaO with the SrO. The diameter reduction of the glass fiber of the composition $20\text{SrO}\cdot 10\text{BaO}\cdot 40\text{TiO}_2\cdot 30\text{SiO}_2$ 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 $15\text{SrO}\cdot 15\text{BaO}\cdot 40\text{TiO}_2\cdot 30\text{SiO}_2$ 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

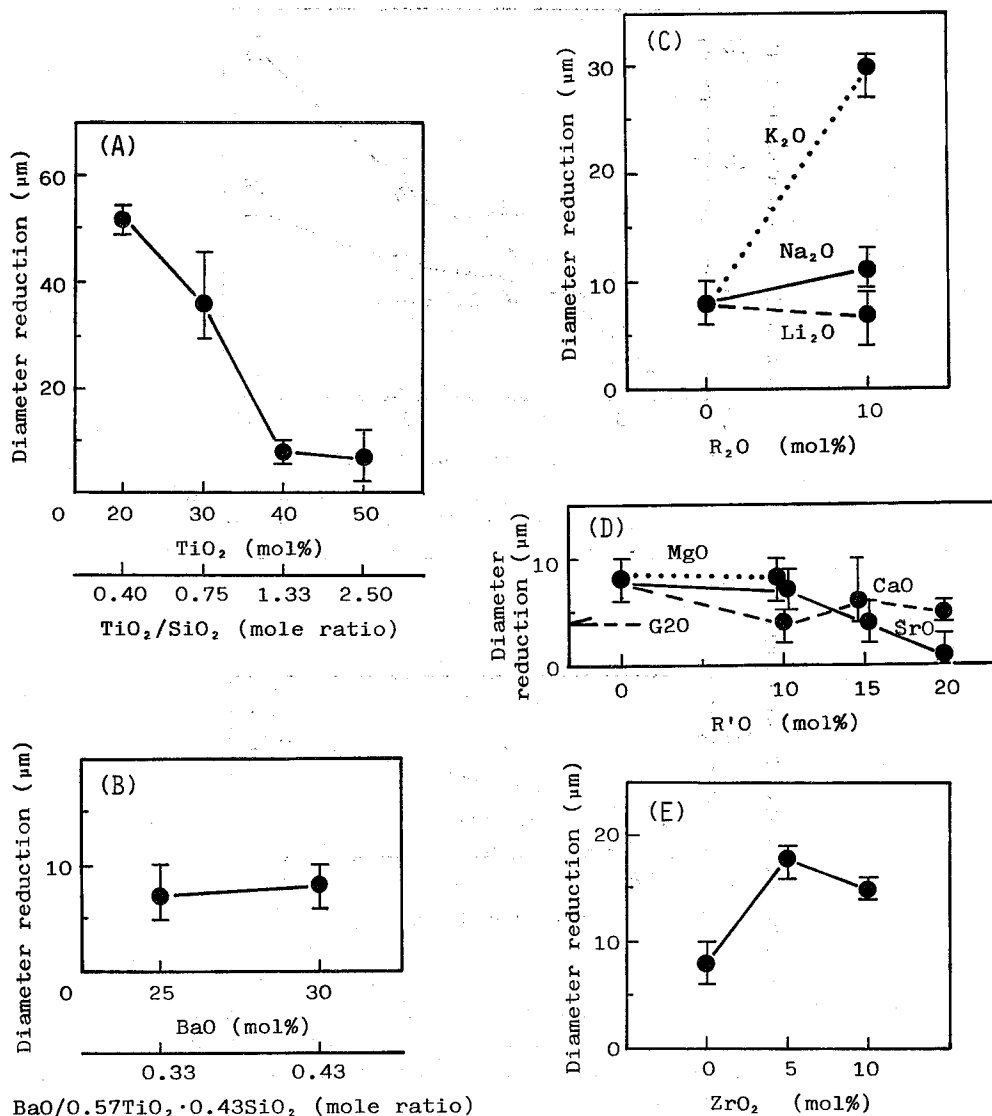


Fig. 1. Diameter reduction of glass fibers caused by the immersion in the NaOH solution of 18 h; (A) $30\text{BaO}\cdot x\text{TiO}_2\cdot(70-x)\text{SiO}_2$, (B) $y\text{BaO}\cdot(100-y)(0.57\text{TiO}_2\cdot 0.43\text{SiO}_2)$, (C) $p\text{R}_2\text{O}\cdot(30-p)\text{BaO}\cdot 40\text{TiO}_2\cdot 30\text{SiO}_2$, (D) $q\text{R}'\text{O}\cdot(30-q)\text{BaO}\cdot 40\text{TiO}_2\cdot 30\text{SiO}_2$ and (E) $30\text{BaO}\cdot(40-r)\text{TiO}_2\cdot r\text{ZrO}_2\cdot 30\text{SiO}_2$ (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

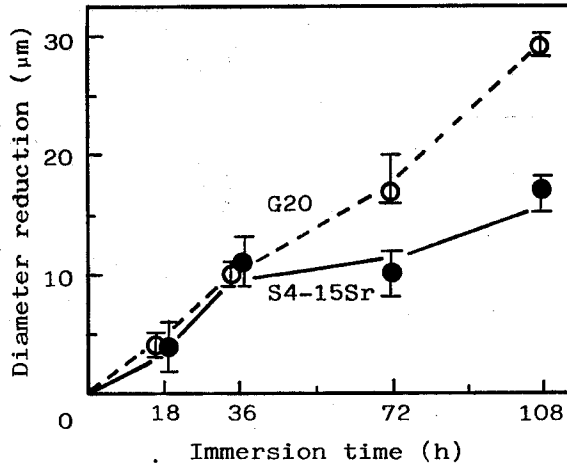


Fig. 2. Effect of immersion time in the NaOH solution on diameter reduction of S4-15Sr and G20 glass fibers. (● or ○) Mean value and (I) maximum and minimum of measured values.

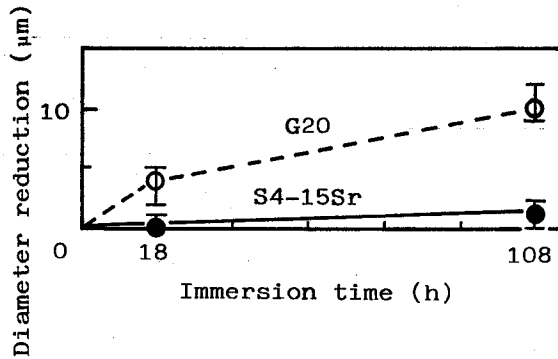


Fig. 3. Diameter reduction of S4-15Sr and G20 glass fibers immersed in the NaOH solution together with glass grains. (● or ○) Mean value and (I) maximum and minimum of measured values.

alone in the NaOH solution.

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.

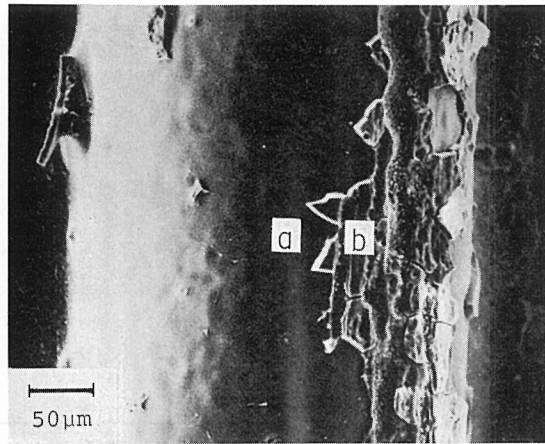
3. EPMA of Glass Surface

The results of EPMA for the S4-15Sr glass fiber treated with the NaOH solution

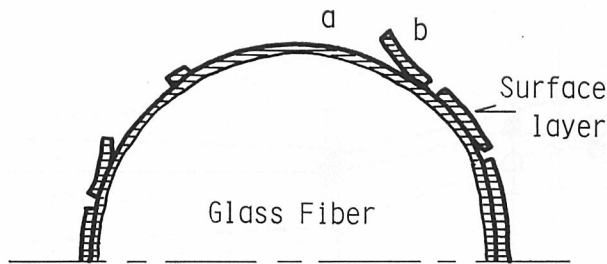
Alkali-Resistant BaO-TiO₂-SiO₂ Glasses

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

Additive chemical		Diameter reduction of glass fiber (μm)
None		4
Sr(OH) ₂ ·8H ₂ O	30.9 mg	0
Ba(OH) ₂ ·8H ₂ O	24.6 mg	0
TiO ₂ ·1.5H ₂ O	16.2 mg	2
SiO ₂ ·0.67H ₂ O	14.4 mg	13



(A)



(B)

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 $SrL\alpha/TiK\alpha$, $BaL\alpha/TiK\alpha$ or $SiK\alpha/TiK\alpha$ for S4-15Sr glass fibers measured before and after immersed in the NaOH solution for 72 h

	Intensity ratio		
	$SrL\alpha/TiK\alpha$	$BaL\alpha/TiK\alpha$	$SiK\alpha/TiK\alpha$
Before immersed	0.37	0.15	0.81
After immersed (a)*	0.21	0.07	0.52
(b)*	0.08	0.04	0.08

* 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, $7.00Na_2O \cdot 5.75CaO \cdot 5.75SrO \cdot 11.50BaO \cdot 33.00TiO_2 \cdot 7.00ZrO_2 \cdot 30.00SiO_2$ 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.

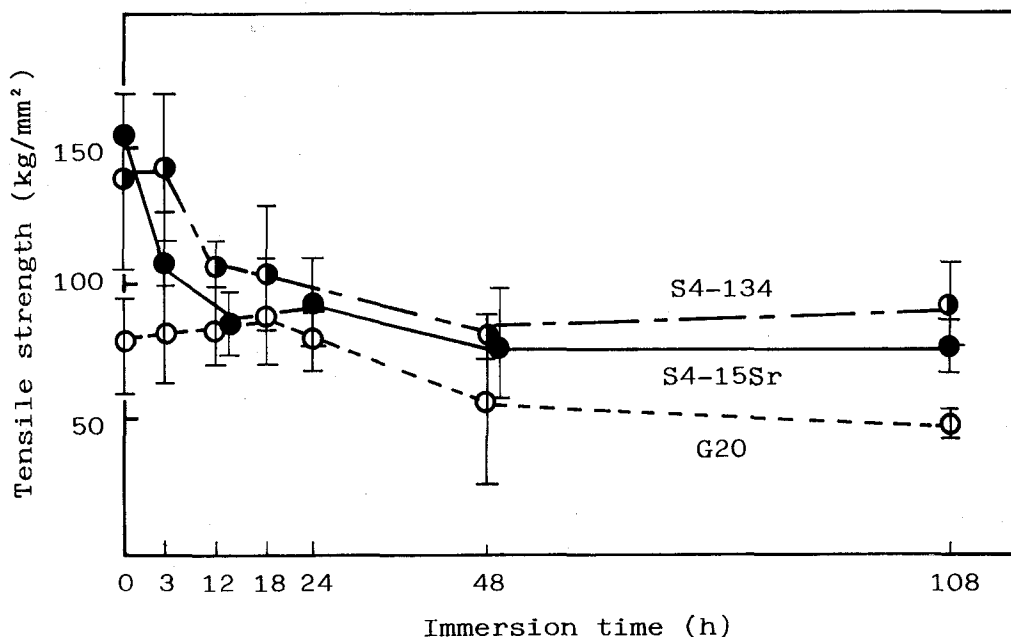


Fig. 5. Tensile strength of S4-15Sr, S4-134 and G20 glass fibers immersed in Portland cement aqueous phase solution together with glass grains. (●, ● or ○) Mean value and (I) 95% confidential limits.

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 data⁶⁾ after Paul.²⁾ 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 SrO⁷⁾ and BaO⁸⁾ 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.⁹⁾ 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 probably 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

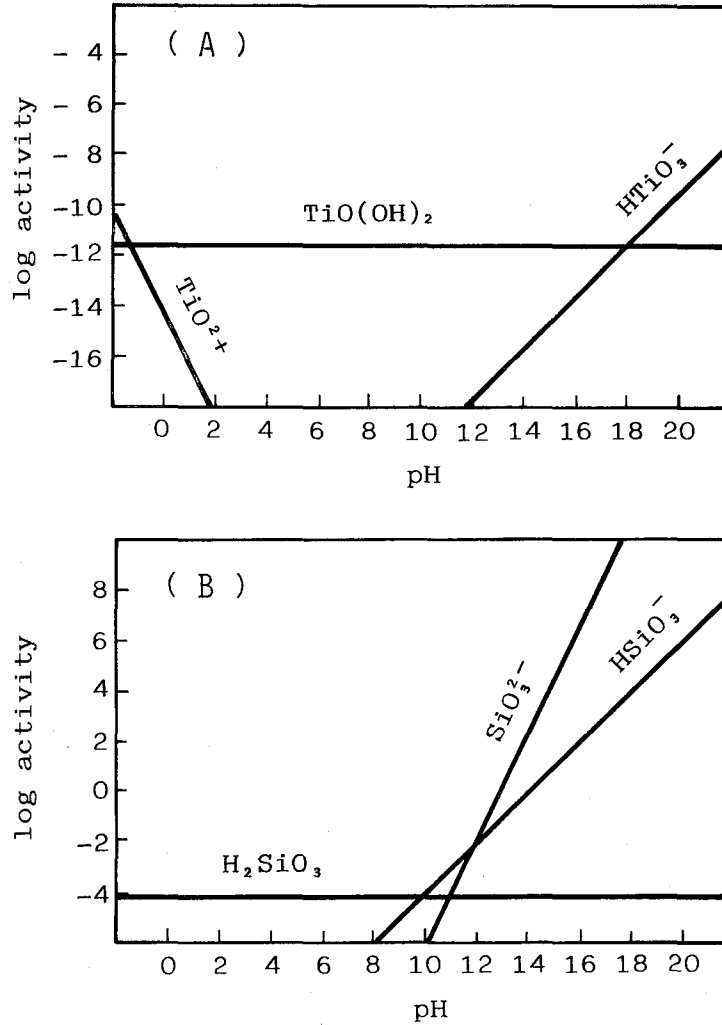


Fig. 6. Stability of the (A) TiO_2 and (B) SiO_2 in aqueous solution at different pH (25°C).

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

ACKNOWLEDGMENT

The authors wish to thank Professor M. Tashiro for his suggestion and helpful discussion in this study.

REFERENCES

- (1) A. J. Majumder and J. E. Ryder, *Glass Technol.*, **9**, 78 (1968).
- (2) A. Paul, *J. Mater. Science*, **12**, 2246 (1977).

Alkali-Resistant BaO-TiO₂-SiO₂ Glasses

- (3) H. Takagi, T. Kokubo, and M. Tashiro, to be published in *Yogyo-Kyokai-Shi*.
- (4) H. Takagi, T. Kokubo, and M. Tashiro, unpublished work.
- (5) N. Soga, *J. Appl. Phys.*, **40**, 3382 (1969).
- (6) M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", Pergamon Press, London, 1966, p. 214.
- (7) V. Rothmund, *Z. physik. Chem.*, **69**, 523 (1910), cited in W. F. Linke, "Solubilities of Inorganic and Metal-Organic Compounds", Vol. 2, 4th ed., Am. Chem. Soc., Washington D. C., 1965, p. 1515.
- (8) R. Scholder and R. Pättsch, *Z. Anorg. Chem.*, **222**, 135 (1935), cited in W. F. Linke, "Solubilities of Inorganic and Metal-Organic Compounds", Vol. 1, 4th ed., Am. Chem. Soc., Washington D. C., 1965, pp. 378-379.
- (9) M. A. Malati and Ann E. Smith, *Powder Technol.*, **22**, 279 (1979).