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Influence of alkali content and alkali mixing on the chemical durability of fluorozirconate glasses

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The corrosion of alkali-containing fluorozirconate glasses in water and acidic and alkaline solutions was studied with glasses of the compositions $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xLiF$ and $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot xLiF \cdot (20 - x)NaF$. The corrosion of the glasses in deionized water and 0.1 N HCl solution is mainly controlled by diffusion with an inductive period due to the passage from reaction-controlled to diffusion-controlled mechanisms, and the weight loss of glass increases with increasing LiF content in the single-alkali glasses. There was no appreciable effect of alkali mixing on the corrosion of glasses in deionized water and 0.1 N HCl solution. The glasses exhibited good stability in alkaline solution. The weight loss due to corrosion of the glasses in acidic buffered solution increased exponentially with increasing LiF content.

1. Introduction

Heavy-metal fluoride glasses containing alkali fluorides, such as ZBLAN and ZBLAL, have much smaller critical cooling rates as to crystallization than those containing no alkali fluorides and are suitable for preparing optical fibres [1]. It has been proposed that there is a proper alkali content to make the most stable fluoride glass [2]. However, there have been very few studies on the chemical durability of alkali-containing fluoride glasses and no paper can be found as to the mixed alkali fluoride glasses so far, in spite of their significance in practical application and from the scientific viewpoint. Mitachi [3] reported that the addition of NaF or LiF to ZrF_4–BaF_2–GdF_3 glasses increases the rate of leaching of fluoride ions in aqueous solutions. Loehr *et al.* [4] reported that a large addition of NaF increases the rate of dissolution of glass. Simmons and Simmons [5] showed that Li, Na and Al elements are extracted at higher rates than other elements such as Zr and Ba. However, no paper can be found on the change of the rate of leaching with the concentration of alkali fluoride in heavy-metal fluoride glasses.

Mixed alkali effects have been found in the electrical conductivity, dielectric loss and elastic moduli of fluoride glasses [6–9], as in oxide glasses. In oxide glasses, a mixed alkali effect was found in the chemical durability; the substitution of an alkali ion by another caused a decrease in the dissolution rate [10, 11]. Accordingly, the mixed alkali effect in the chemical durability of fluoride glasses is very interesting from the scientific viewpoint.

In this paper, the corrosion of alkali-containing fluoride glasses in water and acidic and alkaline solutions will be reported, and the effects of alkali fluoride concentration and alkali mixing on the chemical durability of fluoride glasses will be discussed.

2. Experimental procedure

LiF-containing glasses of the compositions $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xLiF$ and mixed alkali glasses of compositions $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot xLiF \cdot (20 - x)$ NaF were prepared from extra-pure reagents $(NH_4)_2ZrF_6$, AlF_3, BaF_2, LiF and NaF. The mixture of starting materials, together with about 10 wt % of NH_4HF_2, was preheated at about 450 °C for 1 h and then melted at 850–900 °C for 20 min in a platinum crucible under a nitrogen atmosphere in an electrically heating furnace. The melt was cast into a brass mould of about 200 °C to make a glass plate and the glass plate was annealed at about 30–40 °C below the glass transition temperature of the respective glass for 6–8 h.

The chemical durability was measured with rectangular glass samples of which each surface was polished with 2000 grit polishing powder in liquid paraffin. Deionized water (pH 5.8), 0.1 N HCl solution (pH 1), 0.1 N NaOH solution (pH 12.3) and buffered solutions with pH values 4.01, 6.86 and 9.18 (at 40 °C) were used as the test solutions. Samples were immersed in the test solutions at 40 °C for various times. The test solutions were put in sealed polyethylene containers placed in a water bath. The glass sample was placed in a platinum basket suspended in the test solution by a platinum wire. The solution was vibrated constantly at a rate of 120

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strokes min^{-1}. The volume of the test solution was kept as 50 cm^3 for 1 cm^2 of the glass surface area. After a given time of immersion, the glass sample was removed from the test solution, dried in an air bath of about 105 °C and weighed to estimate the weight loss of the glass, ΔW. The test solution was subjected to chemical analysis to estimate the amount of leaching (LW) of the constituent elements.

The analysis of the test solution was carried out by atomic emission spectroscopy for Li, Na and Ba elements and by inductively coupled plasma spectroscopy for Zr, Al and Ba. A fluoride ion-selective electrode was used to analyse the concentration of fluoride anion.

The amount of leaching of an individual element was normalized to unit surface and glass composition by the equation

$$NLW = LW/(S\,wt) \qquad (1)$$

where LW is the amount of leaching of an element in the solution, S the surface area of glass sample and wt the weight fraction of element in the original glass. A comparison between the weight loss of glass and the amount of leaching of an individual element and a comparison among the amounts of leaching of elements can be made by using this parameter, NLW. The NLW for each element would be identical and equal to the weight loss of glass if the dissolution of the glass was not selective.

Observation of the formation of a hydrated surface layer was made with a rectangular glass sample. All the surfaces were polished with 2000 grit polishing powder in liquid paraffin and subsequently optically polished to obtain two parallel surfaces. The sample was held between two polychlorovinyl plates by rubber rings as shown in Fig. 1, immersed in deionized water at 40 °C with the polychlorovinyl plates in the way described above, and removed from solution for observation of surface layer formation in an optical microscope. Thereafter, the sample was again immersed in water to repeat the above procedure. It should be noted that the volume of aqueous solution per cm^2 of surface area of glass was about 200 cm^3 in this case, while it was 50 cm^3 for measurements of the weight loss or amount of leaching of elements.

The composition of the hydrated surface layer was determined with three samples immersed in deionized water. The surface layer was removed after drying at 105 °C, dissolved in 1 N HCl solution and analysed by atomic emission and inductively coupled plasma spectroscopies.

3. Results

3.1. Corrosion in water

3.1.1. Variation of ΔW and NLW of elements with immersion time

Fig. 2 shows the weight loss of glass (ΔW) and the normalized leaching amounts (NLW) of Li, Na, Ba, Al and Zr in deionized water at 40 °C as a function of the immersion time for the 48 ZrF_4·8AlF_3·24BaF_2·10LiF·10NaF glass. ΔW increases linearly with time in the initial period within 4 h of immersion and then the rate of increase decreases with time. NLW values of elements show a time dependence similar to that of ΔW, except for Ba, which shows an almost constant NLW after 2 h of immersion. It is seen that the rate of leaching of each element expressed by the slope of the NLW curve changes in the order Li > Na > Al > Zr > Ba within 4 h and in the order Li > Al > Na > Zr > Ba after 4 h.

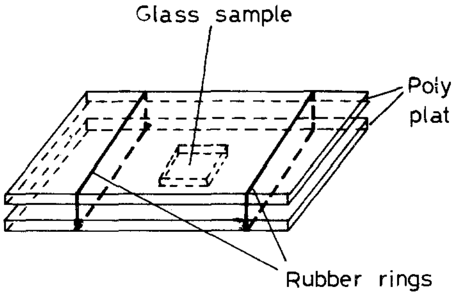

Figure 1 Schematic diagram of sample arrangement for observation of the formation of surface layer.

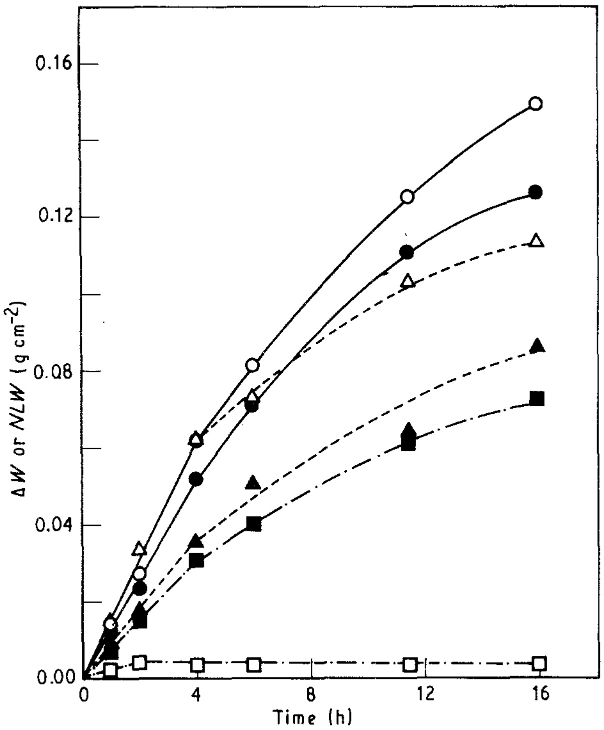

Figure 2 NLW for elements and ΔW of 48ZrF_4·8AlF_3·24BaF_2·10LiF·10NaF glass immersed in deionized water at 40 °C as a function of the immersion time. NLW: (○) Li, (△) Na, (□) Ba, (●) Al, (▲) Zr; (■) ΔW.

Fig. 3 shows ΔW of glass and NLW values of elements plotted against the square root of the immersion time. It is seen that ΔW or NLW of each element except Ba increases linearly with the square root of the immersion time after 4 h.

An attempt was made to measure the amount of leaching of F by using a fluoride ion-selective electrode. In the initial stage, it was five to six times larger than that predicted from the amounts of leaching of metal elements. It decreased as the immersion time increased, and, after 12 h, it became smaller than that predicted from the weight loss of glass.

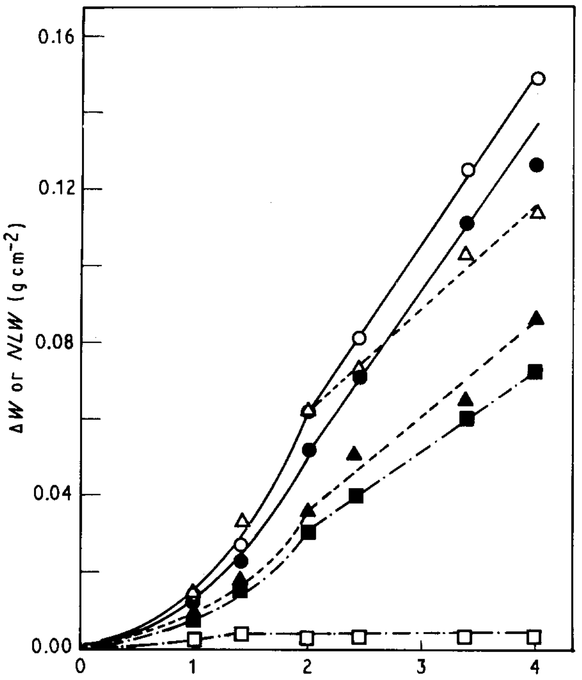

Figure 3 *NLW* for elements and ΔW of $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot 10LiF \cdot 10NaF$ glass in deionized water at 40 °C plotted against the square root of the immersion time. *NLW*: (○) Li, (△) Na, (□) Ba, (●) Al, (▲) Zr; (■) ΔW.

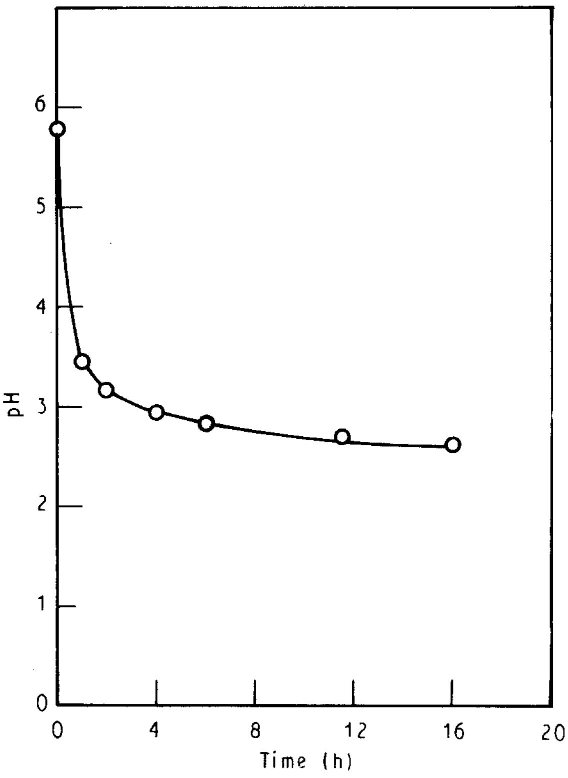

Figure 4 pH of the water solution at 40 °C in which $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot 10LiF \cdot 10NaF$ glass was immersed as a function of the immersion time.

3.1.2. Change of pH of the water solution with time

The pH values of the water solutions in which a glass of the composition $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot 10LiF \cdot 10NaF$ was immersed are shown in Fig. 4 as a function of the immersion time. The pH value decreases continuously with the immersion time.

3.1.3. Change of ΔW and NLW of Li with LiF content

Fig. 5 shows ΔW values of glasses and *NLW* of Li for LiF-containing glasses immersed in deionized water at 40 °C for 16 h as a function of the LiF content. ΔW increases and *NLW* for Li decreases with increasing LiF content of the glass. The addition of 10 mol % LiF to the alkali-free glass increases ΔW by about six times, but the increase due to further addition of LiF is very slight.

3.1.4. Effect of alkali mixing on the corrosion in water

Fig. 6 shows ΔW of glass and *NLW* values of Li and Na after immersion in deionized water at 40 °C for 16 h as a function of the alkali ratio Na/(Li + Na) for $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot xLiF \cdot (20 - x)$ NaF glasses. ΔW of glass shows a non-linear change with alkali ratio, i.e. a slight upward deviation from additivity. *NLW* for Li first increases and then decreases with the substitution of Na for Li. On the other hand, *NLW* for Na increases continuously with the substitution of Li for Na.

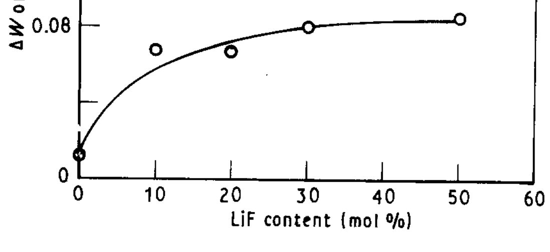

Figure 5 (●) *NLW* for Li and (○) ΔW for immersion in deionized water at 40 °C for 16 h as a function of the LiF content for $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot x$LiF glasses.

3.1.5. Formation of a hydrated surface layer

Fig. 7 shows optical micrographs of the hydrated surface layer of $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot 20NaF$ glass after immersion in deionized water at 40 °C for various times. It is seen that at 30 min a hydrated surface layer, about 0.1 mm thick, is formed on the glass. The thickness of the layer remains almost constant up to 2 h and then increases with immersion time. After 10 h, a part of the hydrated surface layer comes off the surface.

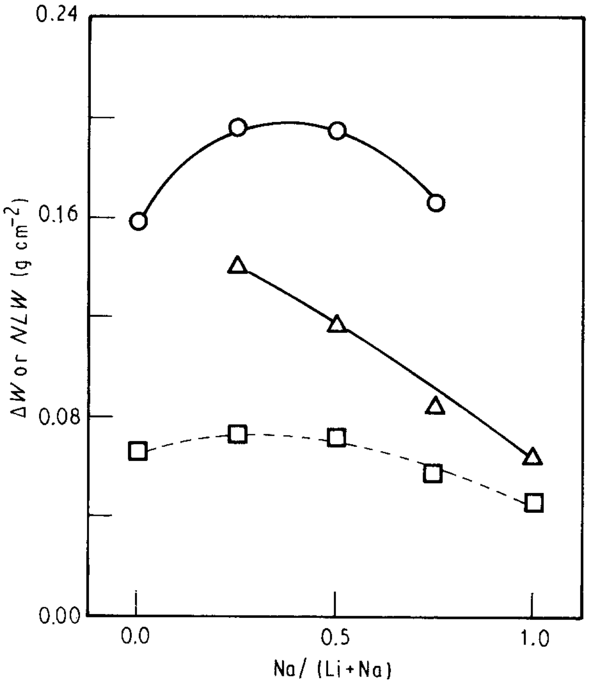

Figure 6 NLW values for (○) Li and (△) Na, and (□) ΔW, for immersion in deionized water at 40 °C for 16 h as a function of the alkali ratio for $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot xLiF \cdot (20 - x)$ NaF glasses.

3.1.6. *Composition of the surface layer*

The compositions of the dried surface layer of three samples immersed in deionized water at 40 °C are shown in Table I together with that of the original glass. It is found that the concentrations of Ba are much larger than those in the original glass. Concentrations of all the other elements are smaller than those in the original glass.

3.2. Corrosion in acidic solution

3.2.1. *Change of ΔW and NLW values of elements with immersion time*

ΔW of glass and NLW values of Zr, Al, Ba, Li and Na elements in 0.1 N HCl solution at 40 °C are plotted against the square root of the immersion time in Fig. 8 for the $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot 15LiF \cdot 5NaF$ glass. ΔW of glass and NLW values of the elements except Ba increase linearly with the square root of the immersion time. However, these straight lines do not go through the origin of the coordinates. NLW for Ba first increases and then decreases slowly with the square root of time. It is also seen that the rate of leaching of an element changes in the order Li > Al > Na > Zr > Ba.

3.2.2. *Change of ΔW and NLW of Li with the LiF content of glass*

Fig. 9 shows the ΔW and NLW of Li in LiF-containing glasses immersed in 0.1 N HCl solution at 40 °C for 16 h as a function of the LiF content of glass. ΔW increases and NLW for Li decreases with increasing LiF content. This behaviour is in coincidence with the case of corrosion in water.

TABLE I Weight fractions of elements in the surface layer for $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot 10LiF \cdot 10NaF$ glass after corrosion in deionized water at 40 °C for various times compared with those in the original glass

Immersion time (h)	Zr	Al	Ba	Li	Na
0	0.322	0.010	0.243	0.005	0.017
2	0.258	0.010	0.371	0.001	0.002
11.5	0.258	0.008	0.404	0.000	0.004
16	0.254	0.008	0.393	0.000	0.005

3.2.3. *Effect of alkali mixing on corrosion*

The ΔW and NLW values of Li and Na of $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot xLiF \cdot (20 - x)$ NaF glasses immersed in 0.1 N HCl solution at 40 °C for 16 h are given in Fig. 10 as a function of the alkali ratio. The NLW values for Li and Na change with the alkali ratio in a way similar to those observed in corrosion in water. However, the ΔW of glass changes with the alkali ratio in a different way; that is, in the case of 0.1 N HCl solution, ΔW shows a slight downward deviation from the additivity expected from the values of the two end members.

3.3. Corrosion in alkaline solution

Table II gives ΔW values of the mixed alkali glasses immersed in 0.1 N NaOH solution at 40 °C for 2 and 16 h. These glasses show a high resistance to corrosion by alkaline solution. For the corrosion for 2 h, weight loss cannot be detected within the limit of experimental error. For the corrosion for 16 h, the ΔW values are also very small. An attempt was made to analyse the amount of leaching of Li using atomic emission spectroscopy. However, it was too small to be detected.

3.4. Corrosion in buffered solutions

Fig. 11 shows NLW values of Li and ΔW for $(100 - x)(0.6ZrF_4 \cdot 0.1AlF_3 \cdot 0.3BaF_2) \cdot xLiF$ glasses in a buffered solution with pH = 4.01 as a function of the LiF content. Both NLW for Li and ΔW increase with increasing LiF content of glass. This behaviour is in contrast with corrosion in deionized water and 0.1 N HCl solution. Further, in the glasses of LiF contents smaller than 30 mol %, ΔW and NLW for Li in the buffered solution are much smaller than those in deionized water and 0.1 N HCl solution. In the glass with 50 mol % LiF, however, ΔW in the buffered solution is larger than in deionized water, but smaller than in 0.1 N HCl solution. The glass with 50 mol % LiF gives also a larger NLW for Li in the buffered solution than in both deionized water and 0.1 N HCl solution.

NLW for Li and ΔW values of $48ZrF_4 \cdot 8AlF_3 \cdot 24BaF_2 \cdot xLiF \cdot (20 - x)$ NaF glasses immersed in the buffered solution of pH = 4.01 at 40 °C for 16 h are shown in Fig. 12 as a function of the alkali ratio. ΔW changes almost linearly with the alkali ratio; that is,

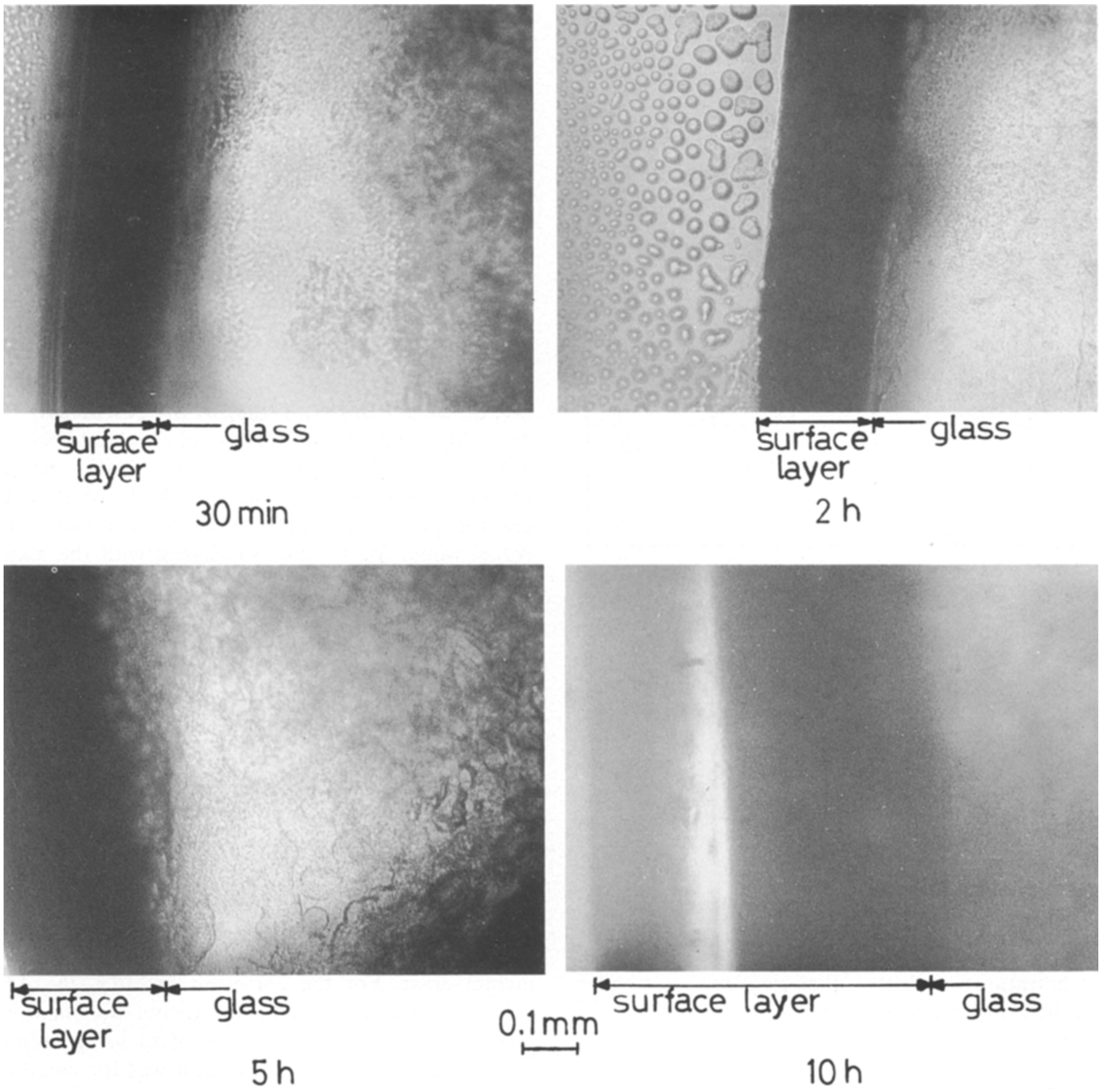

Figure 7 Optical micrographs of the surface layer formed on $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}20NaF$ glass immersed in deionized water at 40 °C for various times.

no appreciable mixed alkali effect is found in the weight loss of glass. *NLW* for Li shows a minimum in the curve in contrast with the corrosion in deionized water and HCl solution.

In the corrosion in buffered solutions with pH values of 6.86 and 9.18 at 40 °C for 16 h, ΔW values of glasses and *NLW* for Li cannot be detected in the present experiments.

4. Discussion

4.1. Mechanism of corrosion

It was found that the weight loss of glass, ΔW, and the normalized amounts of leaching of elements, *NLW*, in deionized water increase linearly with immersion time in the initial stage (Fig. 2) and then linearly with the square root of the immersion time (Fig. 3). This indicates that the corrosion of glass in deionized water is reaction-controlled in the initial period and diffusion-controlled in the later period.

Taking into account the decrease in pH value of the water solution by the dissolution of glass as shown in Fig. 4, Simmons *et al.* [12] and Frischat and Overbeck [13] have suggested a simple anion exchange between the F^- ions at the glass surface and OH^- ions from the water solution as a mechanism of corrosion of heavy-metal fluoride glasses:

$$H_2O + F^-(\text{glass}) \rightarrow OH^-(\text{glass}) + H^+(\text{aq.}) + F^-(\text{aq.}) \tag{2}$$

OH^- ions can be transported into the interior of the bulk glass by interdiffusion with the mobile F^- ions and some of the OH^- ions will produce molecular water H_2O:

$$2OH^-(\text{glass}) \rightarrow H_2O(\text{glass}) + O^{2-}(\text{glass}) \tag{3}$$

The rest of the OH^- ions and resulting O^{2-} ions will be bonded to metal cations in glass.

Simmons and Simmons [5] have indicated, however, that the reaction given by Equation 2 is not

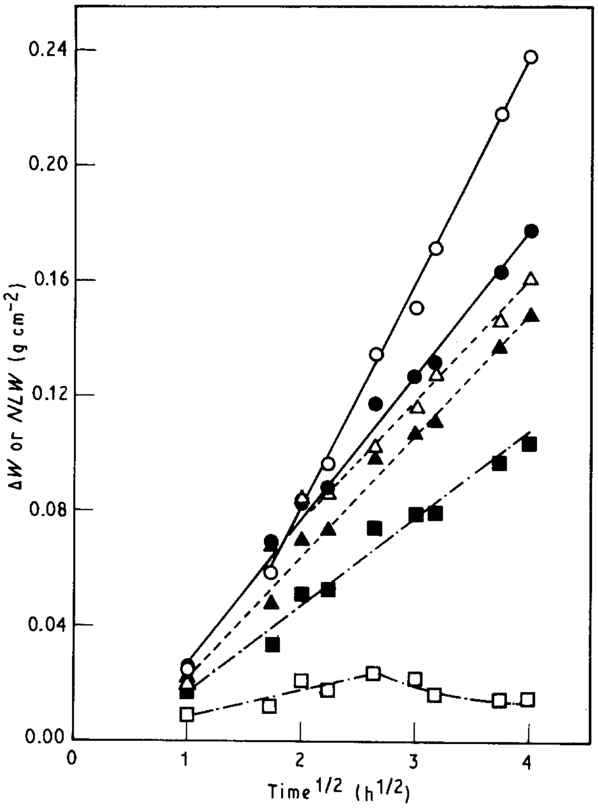

Figure 8 *NLW* for elements and ΔW of $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}15LiF{\cdot}5NaF$ glass in 0.1 N HCl solution at 40 °C as a function of the square root of the immersion time. *NLW*: (○) Li, (△) Na, (□) Ba, (●) Al, (▲) Zr; (■) ΔW.

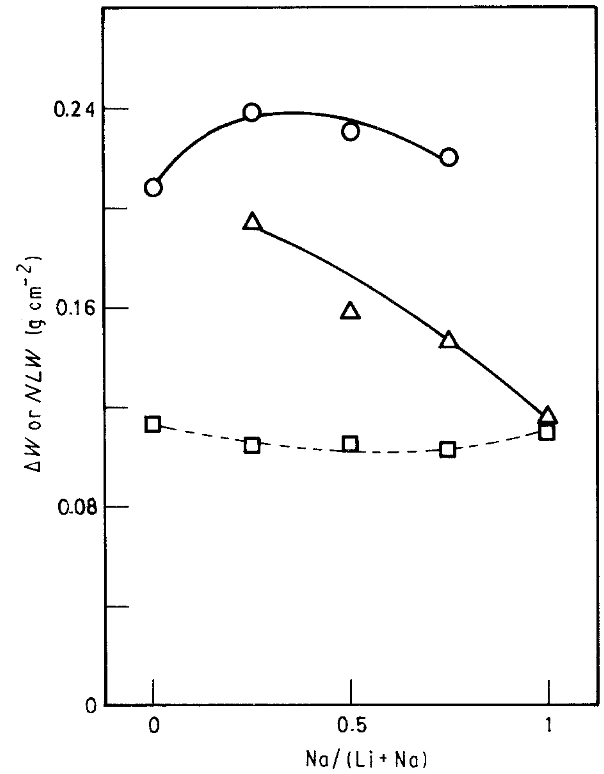

Figure 10 *NLW* values for (○) Li and (△) Na, and (□) ΔW, for immersion in 0.1 N HCl solution at 40 °C for 16 h as a function of the alkali ratio for $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}xLiF{\cdot}(20-x)$ NaF glasses.

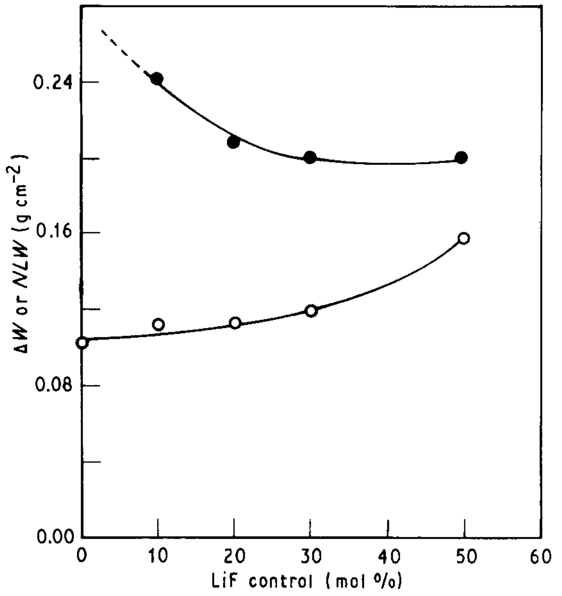

Figure 9 (●) *NLW* for Li and (○) ΔW, for immersion in 0.1 N HCl solution at 40 °C for 16 h as a function of the LiF content for $(100-x)\,(0.6ZrF_4{\cdot}0.1AlF_3{\cdot}0.3BaF_2){\cdot}xLiF$ glasses.

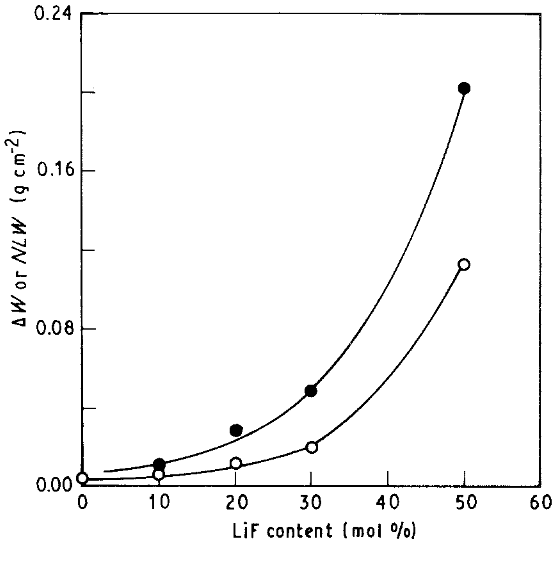

Figure 11 (●) *NLW* for Li and (○) ΔW, for immersion in buffered solution with pH = 4.01 at 40 °C for 16 h as a function of the LiF content for $(100-x)\,(0.6ZrF_4{\cdot}0.1AlF_3{\cdot}0.3BaF_2){\cdot}xLiF$ glasses.

necessary for the change of pH value in fluorozirconate glasses by showing that the dissolution of a small amount of ZrF_4 in water causes a large pH decrease of the solution as a result of the formation of H_3O^+ ions.

In order to know whether ion exchange between F^- ions in glass and OH^- ions in solution occurs or not in the present case, it is necessary to know the amount of leaching of F. The result that the amount of leaching of F is five to six times as large as that predicted from the amounts of leaching of metal elements indicates that anion exchange has occurred in the initial stage.

Assuming that the dissolution of a metal atom causes a dissolution of *n* fluorine atoms, e.g. the dissolution of a Zr atom produces a dissolution of four F atoms, the amount of leaching of F is calculated and then the amounts of leaching of all the elements are

TABLE II Weight losses (ΔW) of $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}20RF$ (RF = LiF–NaF) glasses immersed in 0.1 N NaOH solution at 40 °C for 2 and 16 h

RF	Weight loss (g/cm^{-2})	
	2 h	16 h
20LiF	0.0002 ± 0.0003	0.0012 ± 0.0003
15LiF·5NaF	0.0000 ± 0.0003	0.0001 ± 0.0003
10LiF·10NaF	0.0002 ± 0.0003	0.0002 ± 0.0003
5LiF·15NaF	0.0002 ± 0.0003	0.0003 ± 0.0003
20NaF	0.0000 ± 0.0003	0.0005 ± 0.0003

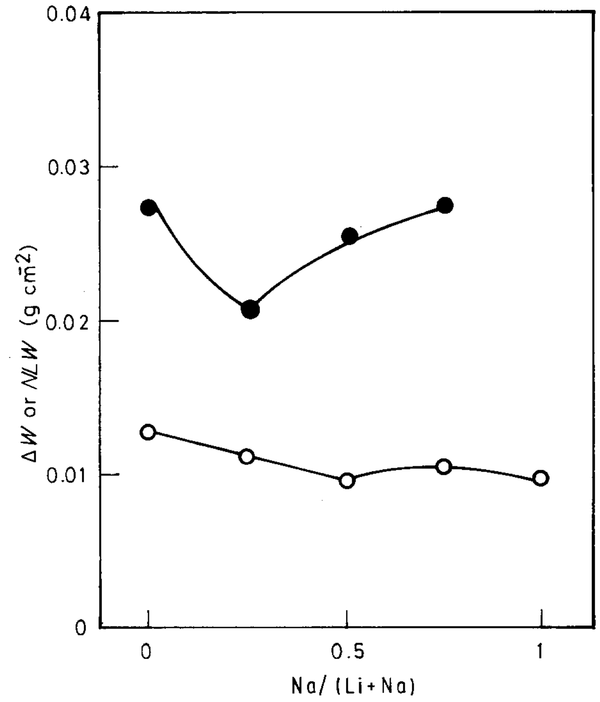

Figure 12 (●) *NLW* for Li and (○) ΔW, for immersion in buffered solution with pH = 4.01 at 40 °C for 16 h as a function of the alkali ratio for $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}xLiF{\cdot}(20-x)NaF$ glasses.

added together. The results are shown in Figs 13 and 14 as a function of the square root of the immersion time for the corrosion of $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}10LiF{\cdot}10NaF$ glass in deionized water and the corrosion of $48AlF_3{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}15LiF{\cdot}5NaF$ glass in 0.1 N HCl solution, respectively. The weight losses calculated from the amounts of leaching of elements are very close to those measured for both cases. This shows that the corrosion of glass both in deionized water and in 0.1 N HCl solution is mainly controlled by the selective dissolution of metal ions following a dissolution of n fluorine atoms.

The composition of the dried surface layer shown in Table I indicates that the hydrated surface layer is constructed mainly by Zr^{4+}, Ba^{2+} and OH^- ions and molecular water H_2O. Some of the residual F^- ions may be present in the surface layer. These results also support the concept that the corrosion of fluorozirconate glasses in deionized water or acidic solution in the present study is controlled by the selective

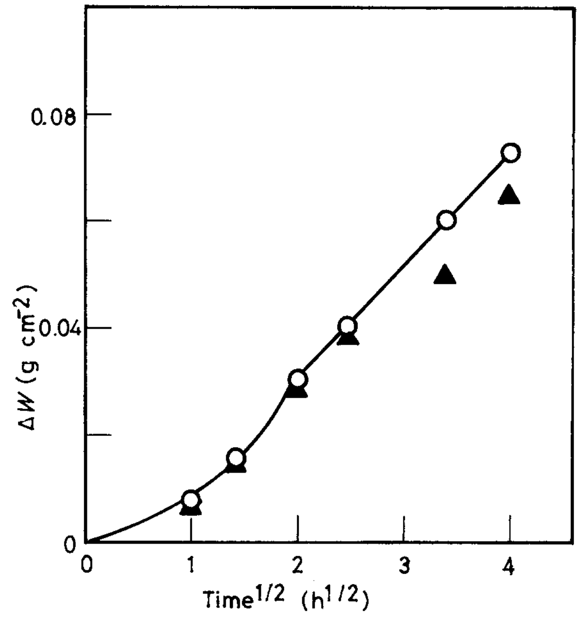

Figure 13 (○) Measured and (▲) calculated ΔW of $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}10LiF{\cdot}10NaF$ glass immersed in deionized water at 40°C for various times.

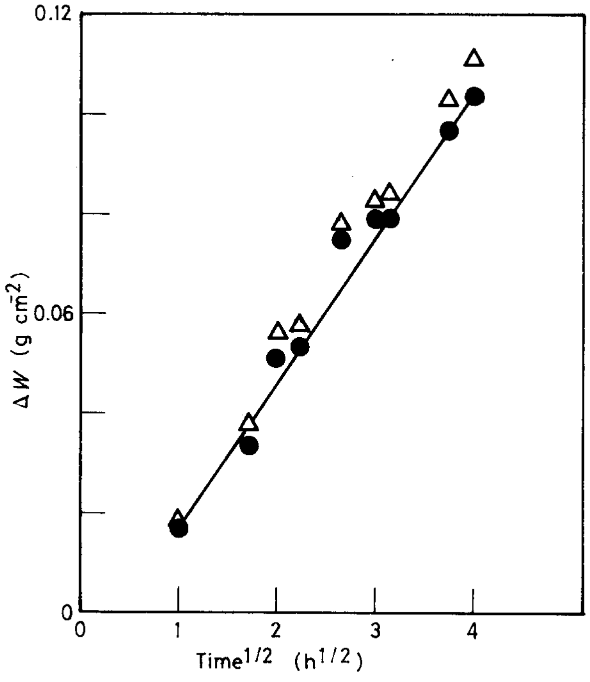

Figure 14 (●) Measured and (△) calculated ΔW of $48ZrF_4{\cdot}8AlF_3{\cdot}24BaF_2{\cdot}15LiF{\cdot}5NaF$ glass immersed in 0.1 N HCl solution at 40 °C for various times.

dissolution of metal ions following a dissolution of n F^- ions.

It should be noted that the reaction based on Equation 3 may not occur in the present case, since the hydrated surface layer contains almost no O^{2-} ions if the anion concentrations are calculated from the concentrations of metal cations.

Loehr *et al.* [4], Houser and Pantano [14] and the present authors have shown from the infrared spectroscopy [4], SIMS [14] and direct observation of the surface layer (this study, Fig. 7) that on immersing a fluorozirconate glass in water a hydrated surface layer forms and increases in thickness with the immersion time. Fig. 7 indicates that the thickness of the hydrated surface layer remains almost constant from 30 min to 2 h. After 2 h, the surface layer increases in thickness.

According to the above discussion, a corrosion process of the present fluorozirconate glasses in water can be proposed as follows:

1. Firstly, the ion-exchange reaction as shown by Equation 2 occurs and the pH of water solution decreases. As the solution becomes acidic, the dissolution of the most dissolvable metal ions such as Li, Na and Al ions will become appreciable. At this stage, the corrosion of glass is mainly controlled by the ion-exchange reaction since the surface layer is not thick enough to protect the dissolution of these ions during this period.
2. As the immersion time increases, the surface layer constructed by Zr^{4+}, Ba^{2+} and OH^- ions increases in thickness and the dissolution of glass changes from reaction-controlled to diffusion-controlled. The diffusion process may correspond to the diffusion of molecular water into the unreacted glass through the surface layer and the counterdiffusion of dissolved species such as Li^+, Na^+, Al^{3+} and F^- ions into solution.
3. When the hydrated surface layer becomes enough thick the outside of the surface layer starts to peel off, entering the solution as shown in the micrograph of Fig. 7.

In acidic solution, Fig. 8 indicates that the corrosion is controlled mainly by a diffusion process similar to that for corrosion in water.

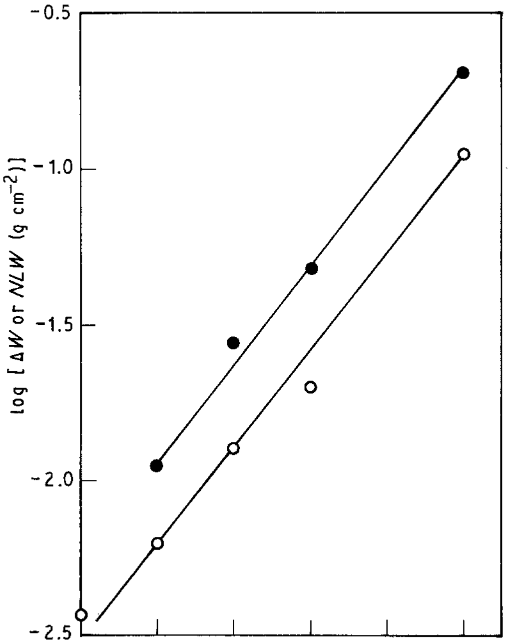

Figure 15 Logarithms of (○) ΔW and (●) *NLW* for Li as a function of the LiF content for (100-x) ($0.6ZrF_4$·$0.1AlF_3$·$0.3BaF_2$)·xLiF glasses immersed in buffered solution with pH = 4.01 at 40 °C for 16 h.

4.2. Effect of LiF content on the corrosion of glass

In the corrosion in water, the addition of 10 mol % LiF to the alkali-free glass causes a weight loss about six times that of the alkali-free glass, but a further addition of LiF does not increase the weight loss so much. In 0.1 N HCl solution, however, the weight loss of glass containing LiF of less than 30 mol % remains almost constant (Fig. 9). In the buffered solution of pH = 4.01, both the weight loss of glass and *NLW* for Li increase with increasing LiF content, but the rate of increase in the weight loss of glass is very small when the LiF content is less than 30 mol %. These results indicate that the alkali fluoride content of glass should be limited to less than 30 mol % from the viewpoint of the practical uses of fluorozirconate glasses. It should be noted that, as shown in Fig. 15, both *NLW* for Li and the weight loss of glass in the buffered solution of pH = 4.01 at 40 °C for 16 h increase exponentially with increasing LiF content. The reason for this behaviour should be sought in further study.

4.3. Effect of alkali mixing on the corrosion of glass

It was found that alkali mixing has little effect on the corrosion of glass in all the test solutions. This results probably from the fact that the main diffusing species are not H_3O^+ ions but molecular water, different from those in common oxide glasses. The *NLW* of an alkali increases with the substitution of another alkali in deionized water and in 0.1 N HCl solution. This tendency is opposite to that observed in oxide glasses [10, 11]. These results may mean that the interdiffusion between cations is not important in the corrosion of fluorozirconate glasses.

5. Conclusions

The corrosion of single-alkali and mixed-alkali fluorozirconate glasses in water and acidic and alkaline solutions has been studied. The corrosion in water is controlled by the anion-exchange reaction in an inductive period and thereafter by the diffusion of molecular water and the counterdiffusion of dissolved species such as Li^+, Na^+, Al^{3+} and F^- ions. In acidic solution, the corrosion mechanism is similar to that in water, but the inductive period is much shorter. In alkaline solution, the glasses exhibited good stability.

The weight loss of glass due to corrosion in water and 0.1 N HCl solution increases with increasing LiF content. In the buffered solution with pH = 4.01, the weight loss of glass increases exponentially with increasing LiF content.

No appreciable mixed alkali effect was found in the corrosion of the studied glasses in all the solutions.

References

1. T. KANAMORI, *Mater. Sci. Forum* **19/20** (1987) 363.
2. XIUJIAN ZHAO and S. SAKKA, *J. Non-Cryst. Solids* **95/96** (1987) 487.

3. S. MITACHI, *Phys. Chem. Glasses* **24** (1983) 146.
4. S. R. LOEHR, A. J. BRUCE, R. MOSSADEGH, R. H. DOREMUS and C. T. MOYNIHAN, *Mater. Sci. Forum* **5** (1985) 311.
5. C. J. SIMMONS and J. H. SIMMONS, *J. Amer. Ceram. Soc.* **69** (1986) 661.
6. N. L. PERAZZO, R. MOSSADEGH and C. T. MOYNIHAN, *Mater. Sci. Forum* **6** (1985) 775.
7. XIUJIAN ZHAO, T. KOKUBO and S. SAKKA, *J. Mater. Sci. Lett.* **6** (1987) 143.
8. XIUJIAN ZHAO and S. SAKKA, *J. Non-Cryst. Solids* **103** (1988) 93.
9. XIUJIAN ZHAO, H. KOZUKA and S. SAKKA, *J. Mater. Sci.* **22** (1987) 4103.
10. J. O. ISARD, *J. Non-Cryst. Solids* **1** (1969) 235.
11. D. E. DAY, *ibid.* **21** (1976) 343.
12. C. J. SIMMONS, H. SUTTER, J. H. SIMMONS and D. C. TRAN, *Mater. Res. Bull.* **17** (1982) 1203.
13. G. H. FRISCHAT and I. OVERBECK, *J. Amer. Ceram. Soc.* **67** (1984) C238.
14. C. A. HOUSER and C. A. PANTANO, in Extended Abstracts, 2nd International Symposium on Halide Glasses, Troy, New York, 1983, Paper No. 15.

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