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Effect of MnO, CaO and nitrogen on the alkaline durability of soda–lime silicate glasses

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MnO containing soda–lime silicate glasses were vitrified and nitrogen was introduced into them. The prepared glasses were subject to density measurement and alkaline durability tests. MnO addition caused poorer alkaline durability in 2N NaOH solution at 82 °C. Needle-like precipitations were observed on the MnO containing glass surface after 96 h durability tests. Glass components were found to dissolve selectively in the alkaline solution in the order $SiO_2 > CaO > MnO$. The density of the obtained glasses increased linearly with increasing amount of nitrogen content in the glasses. A considerable improvement in alkaline durability of the glasses by nitrogen addition was observed, and its effect was larger for the MnO-free glasses.

1. Introduction

Glass fibres, such as optical fibres, reinforcing fibres, chemical filters, glass wool, etc., have been widely used as essential materials. However, most of them require higher chemical durability and mechanical strength. Glass fibre-reinforced cement (GRC), which provides higher mechanical strength, has been developed [1–3]. Nevertheless, basicity in such cements is usually so high that the embedded glass fibre is likely to be attacked by alkalis in the cements. Recently, Na_2O–ZrO_2–SiO_2 glasses, such as G20, have been selected to minimize the attack by alkalis [2, 4–10]. However, such glasses require high-temperature melting and easily devitrify due to the considerable content of ZrO_2 [11].

Paul and Youssefi [12] reported that molar substitution of FeO, and particularly MnO, for CaO in CaO–Na_2O–SiO_2 glasses increased the alkaline durability. The improvement in alkaline durability of SiO_2–Al_2O_3–TiO_2–La_2O_3–Y_2O_3 glasses with the addition of MnO has been reported [13]. Soda–lime glasses have a much lower melting point compared with Na_2O–ZrO_2–SiO_2 glasses and higher stability as a glassy state. In addition, nitrogen addition to glasses is known to provide higher chemical durabilities [14–19].

In this study, MnO was substituted for CaO and nitrogen was introduced into Na_2O–CaO–SiO_2 glasses, and their effect on alkaline durability was investigated.

2. Experimental procedure

A 20 g batch was prepared by mixing reagent-grade chemicals, such as Na_2CO_3, $CaCO_3$, MnO_2 and SiO_2. All chemicals were purchased from Kanto Chemical Co. Inc. The batch was placed in an alumina crucible and was melted in an SiC electric furnace at 1500 °C for 2 h, followed by quenching on to a brass plate. After nitrogen had been added, the obtained glass was ground and mixed with Si_3N_4 powder, and then melted at 1500 °C for 2 h under a nitrogen atmosphere.

Four series of samples, as given in Table I, were prepared. For series A and B, CaO was substituted by MnO at $5Na_2O \cdot 25(CaO + MnO) \cdot 70SiO_2$ and $10Na_2O \cdot 20(CaO + MnO) \cdot 70SiO_2$, respectively, while for the series C and D, SiO_2 was substituted by $SiN_{4/3}$ at $10Na_2O \cdot 20CaO \cdot 70(SiO_2 + SiN_{4/3})$ and $10Na_2O \cdot 10CaO \cdot 10MnO \cdot 70(SiO_2 + SiN_{4/3})$, respectively. In this paper, all compositions are expressed in mole per cent except for the nitrogen content.

The nitrogen content of the obtained samples was determined by LECO EF-400 TN-334 oxygen nitrogen analyser. Glass formation was confirmed by X-ray diffraction analysis (Mac Science MXP18). The density of the samples was measured by Archimedes' method with kerosin. In order to confirm nitrogen introduction into glass series D, infrared absorption spectra were recorded in the range 400–2000 cm^{-1} with an Nippon Denshi Kagaku JIR100 Fourier transform interferometer using KBr pellets.

Each sample was subjected to an alkaline durability test by the following method. A glass sample was ground to 16–24 mesh (710–1000 μm) and 1.00 g granular pieces were placed in a platinum basket which were made of 50 mesh net; then they were rinsed with ethanol in order to remove the fine particles attached to them. The basket was immersed into 200 ml 2N NaOH aqueous solution which was kept at 82 ± 1 °C using an oil bath. The basket was taken out after certain intervals and weight loss was monitored throughout the durability test. Thus, the alkaline durability was evaluated by the weight loss during the test.

Some of the samples after durability tests were also characterized by scanning electron microscopy (SEM, Hitachi S-2500) and energy dispersive X-ray analysis (EDX, Kevex Delta Z-8000).

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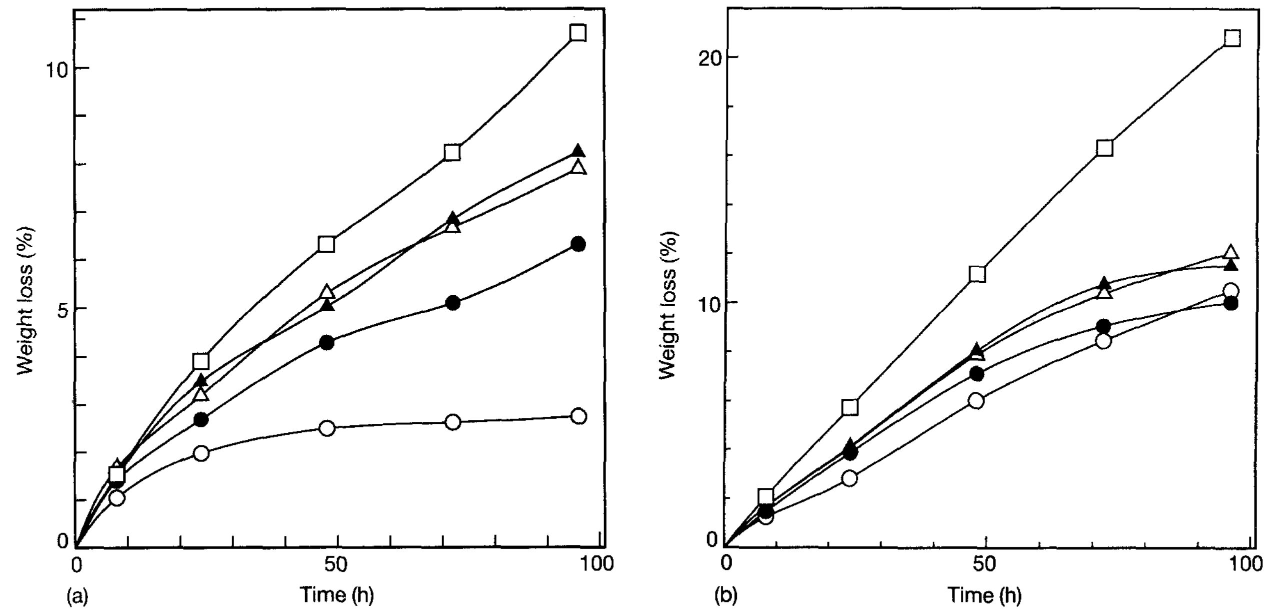

Figure 1 Alkaline durabilities of the glasses in 2N NaOH solution at 82 °C. (a) $5Na_2O \cdot (25 - x)CaO \cdot xMnO \cdot 70SiO_2$, (b) $10Na_2O \cdot (20\text{-}x)CaO \cdot xMnO \cdot 70SiO_2$, where x = (○) 0, (●) 5, (△) 10, (▲) 15 and (□) 20.

TABLE I Chemical composition of the samples

Sample	Composition (mol %)				
	Na_2O	CaO	MnO_2	SiO_2	$SiN_{4/3}$
A-1	5	25	0	70	0
A-2	5	20	5	70	0
A-3	5	15	10	70	0
A-4	5	10	15	70	0
A-5	5	5	20	70	0
B-1	10	20	0	70	0
B-2	10	15	5	70	0
B-3	10	10	10	70	0
B-4	10	5	15	70	0
B-5	10	0	20	70	0
C-1	10	20	0	65	5
C-2	10	20	0	60	10
C-3	10	20	0	55	15
C-4	10	20	0	50	20
C-5	10	20	0	45	25
D-1	10	10	10	65	5
D-2	10	10	10	60	10
D-3	10	10	10	55	15
D-4	10	10	10	50	20
D-5	10	10	10	45	25

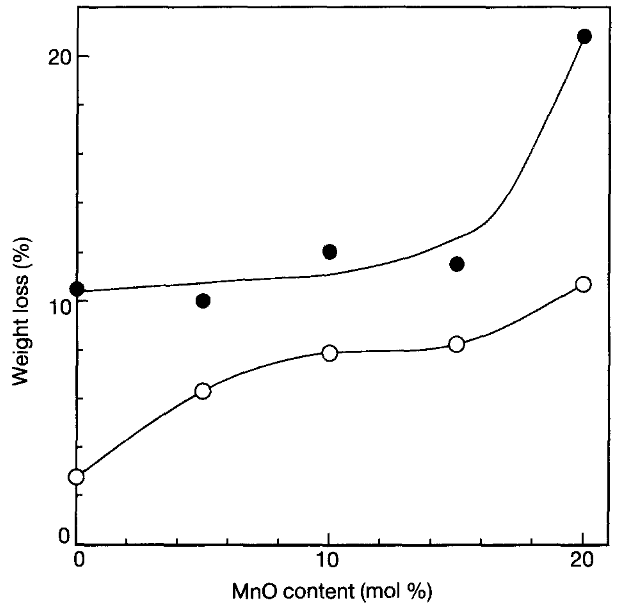

Figure 2 Effect of MnO content on the alkaline durability: 2N $NaOH_{aq}$, 82 °C; (○) $5Na_2O \cdot (25 - x)CaO \cdot xMnO \cdot 70SiO_2$, (●) $10Na_2O \cdot (20 - x)CaO \cdot x\,MnO \cdot 70SiO_2$.

3. Results

3.1. Effect of MnO contents on the alkaline durability

Fig. 1a and b show the weight change of the samples with time during the alkaline durability tests for series A and B, respectively. Fig. 2 shows the weight loss of each sample after 96 h testing. For series A, weight loss increases with increasing amount of MnO. For series B, little change was observed, so long as CaO existed. However, when all CaO was substituted by MnO, the weight loss became twice as much as that when CaO exists. These results are not consistent with those of Paul and Youssefi where MnO substitution for CaO in the Na_2O–CaO–SiO_2 system improved the alkaline durability with the solution of pH 10–12 [12].

Change in the surface composition of the samples was studied by EDX characterization after the test. Representative results for series A and B are shown in Fig. 3a and b, respectively. SiO_2 was selectively dissolved in the alkaline solution and MnO seemed to form the most stable hydroxide. This formation can be deduced by the comparison of scanning electron micrographs (Fig. 4a and b). Only when MnO was contained in the glasses, was a needle-like deposition observed.

3.2. Addition of nitrogen

For series C and D, 5–25 mol % SiO_2 was substituted by $SiN_{4/3}$ in order to introduce nitrogen into the

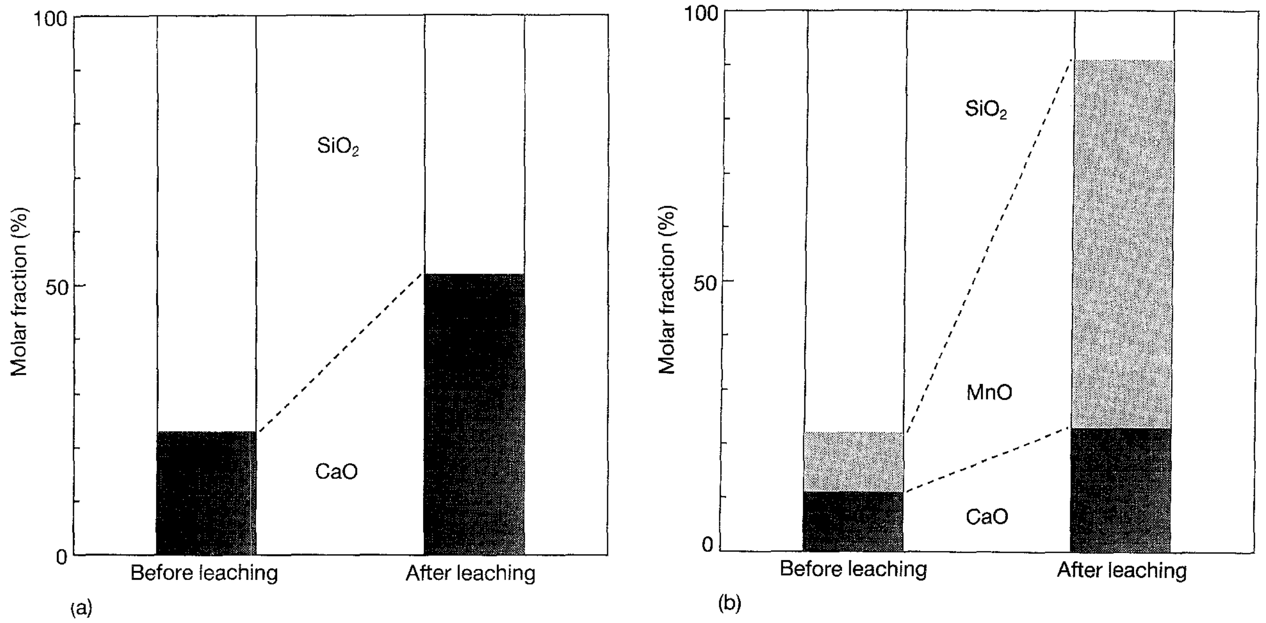

Figure 3 Change in surface composition of the glasses during a 96 h alkaline durability test. (a) $10Na_2O{\cdot}20CaO{\cdot}70SiO_2$, (b) $10Na_2O{\cdot}10CaO{\cdot}10MnO{\cdot}70SiO_2$.

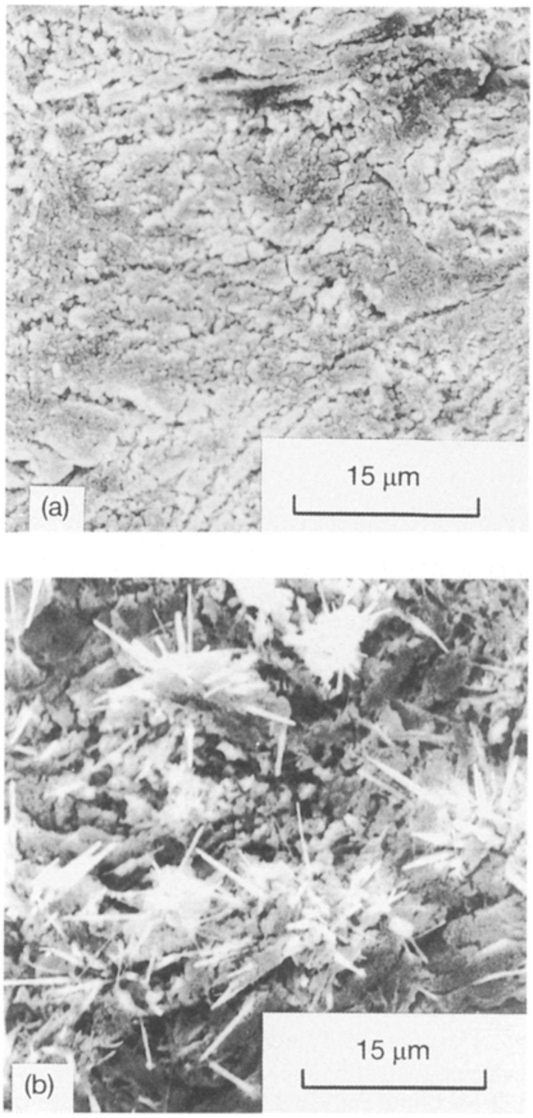

Figure 4 SEM image of the glasses after 96 h alkaline durability test. (a) $10Na_2O{\cdot}20CaO{\cdot}70SiO_2$, (b) $10Na_2O{\cdot}10CaO{\cdot}10MnO{\cdot}70SiO_2$.

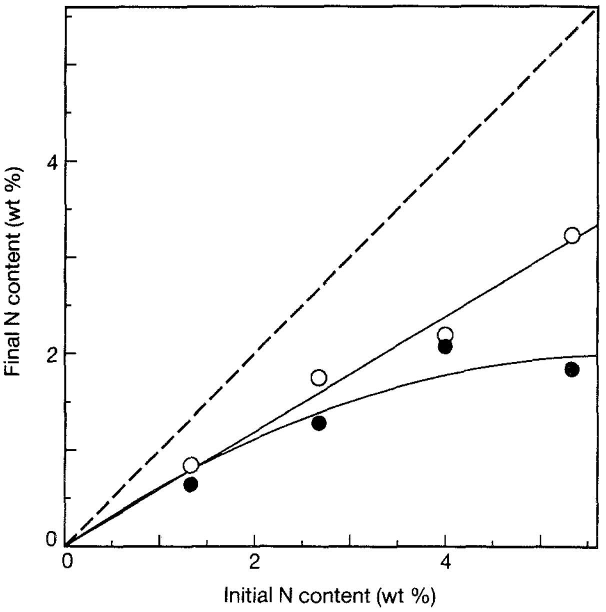

Figure 5 Nitrogen content in the glasses. (○) $10Na_2O{\cdot}20CaO{\cdot}70(SiO_2, SiN_{4/3})$, (●) $10Na_2O{\cdot}10CaO{\cdot}10MnO{\cdot}70(SiO_2, SiN_{4/3})$. (– – –) Without nitrogen loss.

glasses. With the higher amount of $SiN_{4/3}$ substitution, the yield of nitrogen introduction became less (Fig. 5). Nitrogen loss is possibly due to the oxidation during melting and/or quenching. For series C, 3.22 wt % N containing glass was obtained, while 2.07 wt % N was the largest value for series B. The introduction of nitrogen produced the density increase shown in Fig. 6. For series B, density increased by 4% with the addition of nitrogen. The introduction of nitrogen was also confirmed by the IR absorption spectra which are depicted in Fig. 7. The peak at about 970 cm^{-1}, which is considered to be due to the Si–N bond, has grown with increasing amount of nitrogen content. This suggests that nitrogen was substituted for oxygen to form networks in the glass.

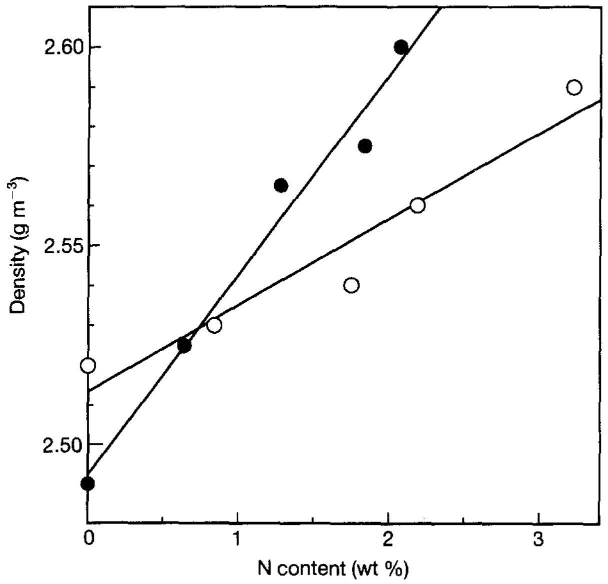

Figure 6 Density of glasses as a function of nitrogen content. (○) $10Na_2O \cdot 20CaO \cdot 70(SiO_2, SiN_{4/3})$, (●) $10Na_2O, 10CaO \cdot 10MnO \cdot 70(SiO_2, SiN_{4/3})$.

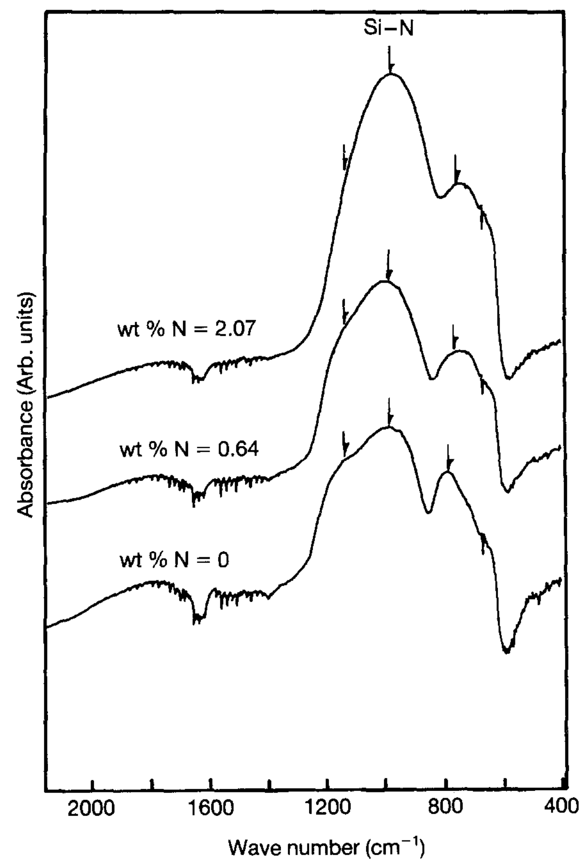

Figure 7 Infrared spectra of $10Na_2O \cdot 10CaO \cdot 10MnO \cdot 70SiO_2$–N glasses.

3.3. Effect of nitrogen addition on the alkaline durability

Alkaline durability tests were performed for series C and D. Results are shown in Fig. 8a and b, and weight loss after 96 h is shown in Fig. 9 as a function of nitrogen content. For series C, a drastic improvement was seen on the addition of nitrogen, and the weight loss linearly decreased with nitrogen content. By introducing as much as 3.22 wt % nitrogen, the weight loss after 96 h testing decreased to one-third. For series D, although the effect was smaller, weight loss linearly decreased with increasing nitrogen content. This improvement in alkaline durability by nitrogen introduction is consistent with other studies on oxynitride glasses [14–19].

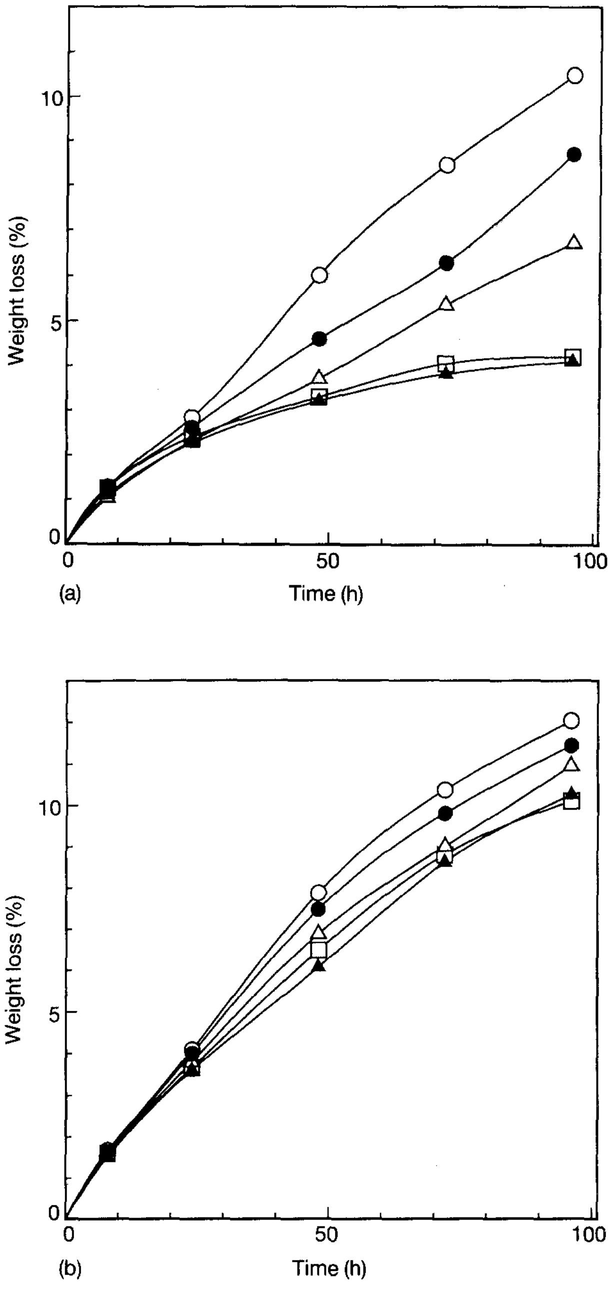

Figure 8 Alkaline durabilities of the glasses in 2N NaOH solution at 82 °C. (a) $10Na_2O \cdot 20CaO \cdot 70(SiO_2, SiN_{4/3})$; (○) base glass, (●) 0.84, (△) 1.75, (▲) 2.19 and (□) 3.22 wt % of N. (b) $10Na_2O \cdot 10CaO \cdot 10MnO \cdot 70(SiO_2, SiN_{4/3})$; (○) base glass, (●) 0.64, (△) 1.28, (▲) 1.84 and (□) 2.07 wt % N.

4. Discussion

In this research, MnO addition did not provide any improvement in alkaline durability, as was also reported by Ohta and Suzuki [20]. This inconsistency with Paul and Youssefi's result could be mainly due to the difference in pH. Because the alkaline content in the solution was much higher in this experiment,

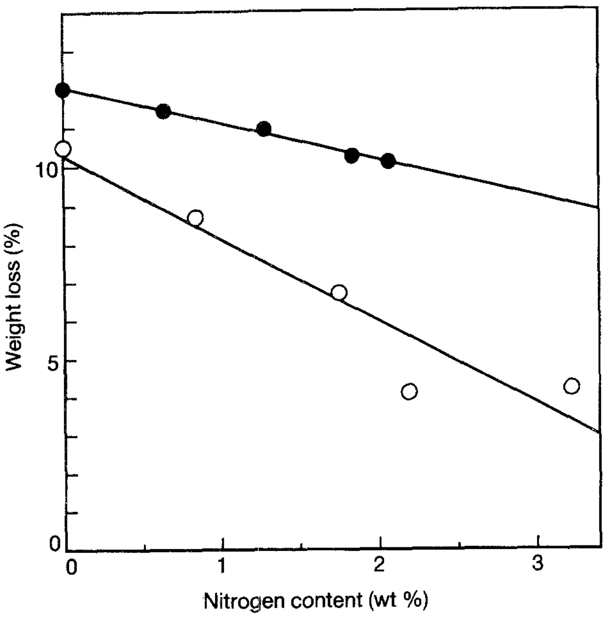

Figure 9 Effect of nitrogen content on the alkaline durabilities. 2N NaOH, 82 °C, 96 h. (○) $10Na_2O \cdot 20CaO \cdot 70(SiO_2, SiN_{4/3})$, (●) $10Na_2O \cdot 10CaO \cdot 10MnO \cdot 70(SiO_2, SiN_{4/3})$.

manganese hydroxide could be formed more easily according to the reaction

$$Mn^{2+} + 2OH^- = Mn(OH)_2 \qquad (1)$$

As a result, manganese could remain as a deposited hydroxide, and the activities of other components, such as Na_2O, CaO and SiO_2, was increased, and thus the dissolution of the glass was enhanced.

The reason for the greater loss of nitrogen with MnO is considered to be as follows. Manganese is known to exist mainly as Mn^{2+} in oxide melts at such a high temperature. However, when the oxygen partial pressure becomes lower, the vapour pressure of metallic manganese becomes higher. A larger amount of nitrogen in the glass under a certain nitrogen partial pressure causes a lower oxygen partial pressure. Therefore, the following reaction can be considered

$$2MnO + SiN_{4/3} = 2Mn + SiO_2 + 2/3N_2 \qquad (2)$$

$$K_2 = p_{Mn}^2 a_{SiO_2} p_{N_2}^{2/3} / (a_{MnO_2} a_{SiN_{4/3}}) \qquad (3)$$

where K_2 is the equilibrium constant for Equation 3, and p_x and a_y denote a partial pressure of x and an activity of y, respectively.

In this study, p_{N_2} is unity. Because nitrogen is known to have stronger bonding with silicon than with manganese, nitrogen is considered to exist preferably around the silicon. Thus, a_{MnO} is assumed to remain constant with variation of nitrogen content. Then the following relationship is obtained

$$p_{Mn} \simeq (a_{SiN_{4/3}} / a_{SiO_2})^{1/2} \qquad (4)$$

From this equation, it is predicted that a larger amount of nitrogen stimulates Reaction 2, thus a greater loss of nitrogen was observed with the existence of manganese. Recently, Wusirika [21] reported that the presence of nitrogen itself in the systems $CaO-SiO_2$, $CaO-BaO-SiO_2$ and $Y_2O_3-Al_2O_3-SiO_2$ did not improve the durability of glass fibres in 10% NaOH solution at 96 °C. The improvement in alkaline durability of the glass by nitrogen introduction is reasonable, and it is possibly due to, as has been explained, the higher packing density of the oxynitride glasses [14].

5. Conclusions

The effect of MnO, CaO and N on the alkaline durability of sodium silicate glasses was studied. Substitution of MnO for CaO did not provide any improvement in alkaline durability in 2N NaOH solution at 82 °C. Nitrogen was introduced into $Na_2O-CaO-SiO_2$ and $Na_2O-CaO-MnO-SiO_2$ glasses up to 3.22 and 2.07 wt %, respectively. Although the existence of MnO demonstrated poorer alkaline durability, nitrogen introduction improved it drastically. By introducing 3.22 wt % nitrogen, the weight loss of the glass was reduced to one-third for $10Na_2O \cdot 20CaO \cdot 70SiO_2$.

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