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Title	Phase Separation of Halogen-Containing Sodium Borosilicate Glasses
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Citation	Journal of Ceramic Society of Japan, 100, 17-21
Issue Date	1992-01
Doc URL	https://hdl.handle.net/2115/17006
Type	journal article
File Information	JCSJ100-17.pdf



Phase Separation of Halogen-Containing Sodium Borosilicate Glasses

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[Received July 12, 1991; Accepted September 19, 1991]

Porous glasses were prepared by phase separation and leaching of NaF, NaCl and NaBr containing sodium borosilicate glasses with low silica content. Each sodium halide was added to $10\text{Na}_2\text{O} \cdot 50\text{B}_2\text{O}_3 \cdot 40\text{SiO}_2$ (wt%) glass and the effects of the additive on phase separation and leaching were investigated. The mean pore diameter, specific surface area and porosity were 300–2500 Å, 20–60 m²/g and 55–56%, respectively. The pore diameter increased and the specific surface area decreased with increasing temperature, time of heat treatment and halogen content. It was found that the halogen containing specimens were leached out in shorter soaking time than the halogen free specimen and that chlorine addition was most effective. The change in the leaching rate is probably caused by the dissolution of halogen containing sodium borate phase into hot water. For chlorine containing sample, leaching finished in a half time that of the halogen free sample.

Key-words: Phase separation, Porous glass, Sodium borosilicate glass, Spinodal decomposition, Halogen content, Leaching, Pore diameter, Surface area

1. Introduction

Porous silica glass has been studied for useful application for filters, desalination membrane and catalyst or enzyme carrier because of its micro-structure, chemical and thermal durability. Porous silica glass is usually prepared from sodium borosilicate glass with high silica content (ca. 60 wt%) by heat treatment for phase-separation and leaching sodium borate phase with acid solution. Hammel et al.¹⁾ have reported the preparation of porous glass which is made of relatively low silica content (about 40 wt% SiO₂) sodium borosilicate glass. This porous silica glass has many advantages as follows:

- (1) Low melting temperature (about 1200–1300°C).
- (2) Pore volume ranges up to 0.6 cm³/g, while porous glass prepared from high silica content was up to 0.3 cm³/g.
- (3) High silica content (about 99%) for porous glass.
- (4) Leaching treatment is carried out in hot

water.

As carrier of catalyst and enzyme, high pore volume is desired, thus the porous glass from sodium borosilicate glass with low silica content is favorable for this application.

Effect of fluorine addition on phase separation and leaching were reported by Takusagawa et al.²⁾ They reported the effect of fluorine addition for sodium borosilicate glasses with high silica content, and found that the fluorine promoted phase separation. However, effect of fluorine addition for low silica composition has not been reported.

In this study, the effect of halogen addition on phase separation and leaching was investigated for sodium borosilicate glasses with low silica content.

2. Experimental procedure

The composition of original glasses was 40 wt% of SiO₂ and molar ratio of Na/B was equal to 0.22. Without sodium halide, the glass composition was $10\text{Na}_2\text{O} \cdot 50\text{B}_2\text{O}_3 \cdot 40\text{SiO}_2$ (wt%). Halogen was added to be 1 or 2 wt% by using sodium halides (NaF, NaCl and NaBr) as starting chemicals.

The reagent grade chemicals of Na₂B₄O₇, B₂O₃, SiO₂ were mixed and in case of halogen addition, sodium halide was added, and the mixture was melted at 1400°C for 1 h in a platinum crucible under argon flow and melt was poured in a graphite crucible (23 mm o.d., 20 mm i.d. and 50 mm in height). These mother glasses are heated at various temperatures ranging from 500° to 600°C for 24 to 240 h to promote the phase-separation in glass samples.

The phase-separated samples were cut into disk form (20 mm in diameter and 2 mm in thickness) and leached in hot water at 95°C for 24 h. After leaching, porous glasses were dried at 140°C for 2 h in the air.

For the phase-separated and porous glasses, halogen content was determined with a halogen sensitive electrode. For the porous glasses, measurements of specific surface area, pore size distribution and electron microscopic observation were carried out by mercury porosimetry, gas adsorption and scanning electron microscopy.

3. Results

3.1 Halogen content of mother glasses

Compositions of prepared glasses are shown in Table 1. The halogen content of mother glasses and porous glasses were determined with a halogen sensitive electrode. The halogen contents of mother glasses are shown in Table 2 and some evaporation of halogens were observed. In the porous glasses, residual halogen contents were lower than 0.1 wt%. Thus most part of added halogen was included in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ phase and it was removed in leaching process.

3.2 Electron microscopic images of sample glasses

Halogen free and F, Cl, Br added specimens (composition 1, 3, 5, 6) are treated at 580°C for 48 h and electron microscopic observations were carried out. As Figs. 1(b)–(d) show, porous glasses prepared

Table 1. Compositions of halogen containing sodium borosilicate glasses.

Composition	Na_2O	B_2O_3	SiO_2	NaX
1	10.0	50.0	40.0	---
2	8.6	49.7	39.8	1.9wt%NaF (2.9mol%)
3	7.8	49.6	39.7	2.9wt%NaF (4.3mol%)
4	9.5	49.8	39.8	0.9wt%NaCl (1.0mol%)
5	9.2	49.7	39.7	1.4wt%NaCl (1.6mol%)
6	9.4	49.4	39.5	1.7wt%NaBr (1.1mol%)

Table 2. Halogen content of glasses listed in Table 1.

Composition	halogen	before melting	after melting
1	---	---	---
2	F	1.0wt%	0.85wt%
3	F	2.0wt%	1.3 wt%
4	Cl	1.0wt%	0.54wt%
5	Cl	2.0wt%	0.88wt%
6	Br	2.0wt%	1.3 wt%

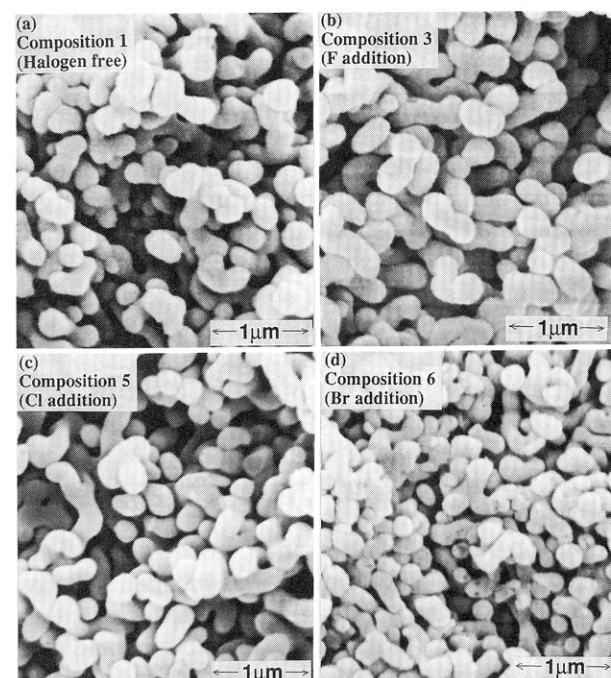


Fig. 1. SEM images of porous glasses prepared from halogen free and F, Cl and Br containing glasses.

from halogen containing glasses have the SiO_2 interconnecting structures which were probably resulting from spinodal decomposition. Their micro-structures were similar to the porous glass from halogen free glass shown in Fig. 1(a).

3.3 Effect of heat treatment conditions and halogen additions on phase separation

Pore size distributions are shown in Fig. 2 for compositions 3, 5 and 6. All specimens show sharp pore distribution curves and pore size increased with increasing heat treatment temperature. Mean pore diameter and specific surface area of samples treated at various temperatures for 48 h are shown in Table 3.

For the fluorine added specimens, the relationship between pore diameter and specific surface area and temperature of heat treatment is shown in Fig. 3. The heat treatment time is 48 h. The pore diameter increases from about 300Å to 2500Å and the specific surface area decreases from 60 m^2/g to 20 m^2/g with increasing the treatment temperature from 500° to 600°C. Thus the micro-structure of porous glass enlarged with increasing of treatment temperature.

The pore diameter slightly increased with increasing fluorine content. This may show the promotion of phase separation with fluorine addition. The promotion of phase separation by fluorine was reported by Takusagawa et al.²⁾ for $7\text{Na}_2\text{O}\cdot 23\text{B}_2\text{O}_3\cdot 70\text{SiO}_2$ (wt%) glass. Same effect was observed for this glass system. Same tendency was observed for chlorine containing samples as shown in Table 3, however the bromine addition was not so effective on pore diameter change.

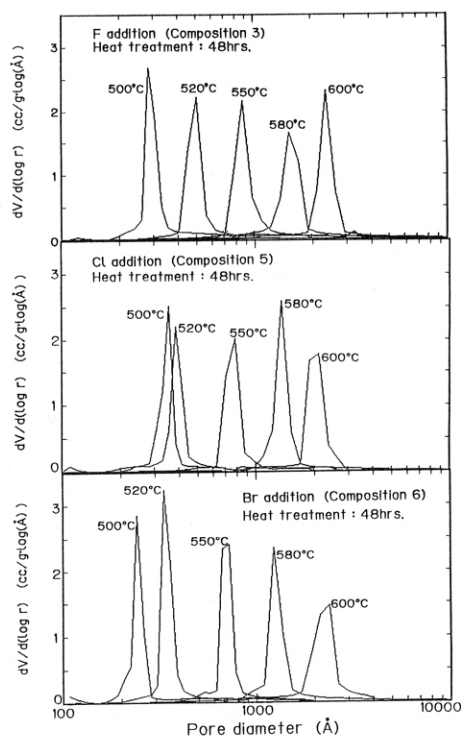


Fig. 2. Pore size distribution curves of porous glasses.

Table 3. Mean pore diameter and specific surface area of porous glasses treated at various temperatures.

Composition of mother glass	Condition of heat treatment	mean pore diameter (Å)	specific surface area (m ² /g)
1	500°C × 48hrs.	260	32.6
	520°C × 48hrs.	358	
	550°C × 48hrs.	800	
	580°C × 48hrs.	1320	
	600°C × 48hrs.	2634	
2	500°C × 48hrs.	294	70.4
	520°C × 48hrs.	462	
	550°C × 48hrs.	846	
	580°C × 48hrs.	1562	
	600°C × 48hrs.	2150	
3	500°C × 48hrs.	352	68.7
	520°C × 48hrs.	560	
	550°C × 48hrs.	988	
	580°C × 48hrs.	1574	
	600°C × 48hrs.	2388	
4	500°C × 48hrs.	246	70.4
	520°C × 48hrs.	420	
	550°C × 48hrs.	794	
	580°C × 48hrs.	1400	
	600°C × 48hrs.	2102	
5	500°C × 48hrs.	382	68.7
	520°C × 48hrs.	562	
	550°C × 48hrs.	800	
	580°C × 48hrs.	1464	
	600°C × 48hrs.	1994	
6	500°C × 48hrs.	292	70.4
	520°C × 48hrs.	366	
	550°C × 48hrs.	714	
	580°C × 48hrs.	1162	
	600°C × 48hrs.	2064	

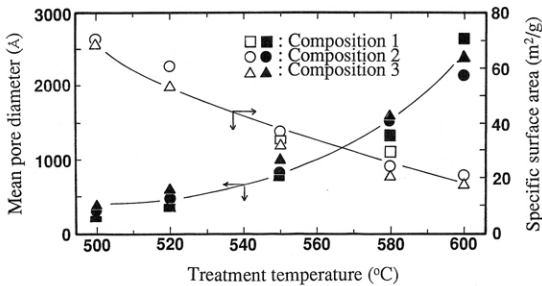


Fig. 3. Relationship between pore diameter, specific surface area and heat treatment temperature.

For the fluorine added specimens, the dependence of pore diameter and specific surface area on heat treatment time is shown in Fig. 4. The heat treatment temperature is 550°C. The pore diameter increases from about 600Å to 1200Å and the specific surface area decreases from 50 m²/g to 30 m²/g with increasing the treatment time from 24 h to 120 h. Thus the micro-structure of porous glass enlarged with increasing of treatment time.

3.4 Weight changes in hot water leaching

Behavior in leaching of phase separated glass was observed for same samples shown in Figs. 1(a)–(d). Weight changes in hot water leaching are shown in Fig. 5. Samples were treated at 580°C for 48 h and cut into disk form and leached in hot water (95°C)

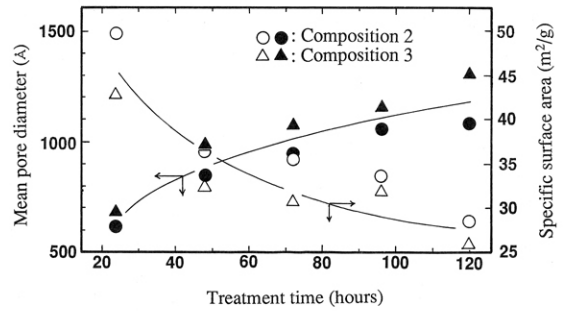


Fig. 4. Relationship between pore diameter, specific surface area and heat treatment time.

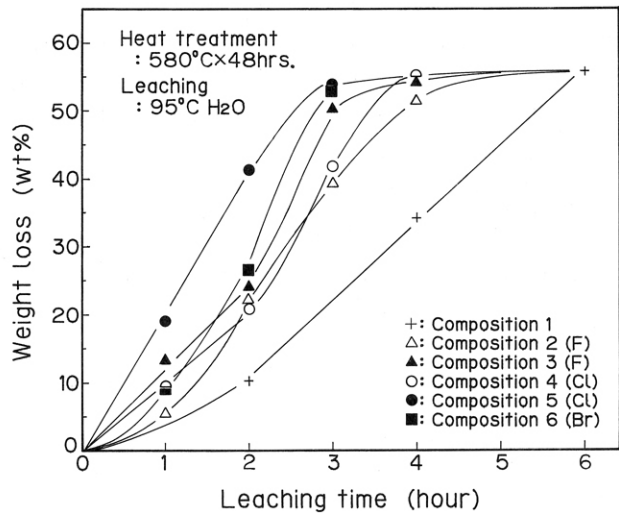


Fig. 5. Weight loss in leaching treatment.

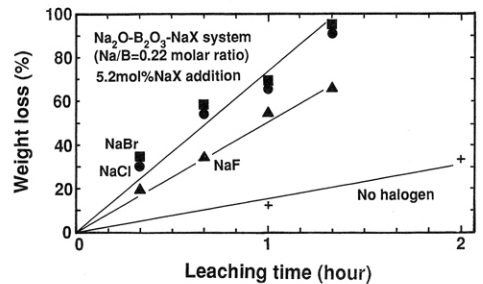


Fig. 6. Weight loss of Na₂O-B₂O₃-NaX (X: F, Cl, Br) in water at 95°C.

for 1 to 6 h. The halogen containing glass was leached out in shorter soaking time than halogen free glass and leaching rate was increased with increasing halogen content. For chlorine containing sample (Composition 5), the leaching finished in a half time of halogen free sample (Composition 1).

Change in dissolving rates in 17Na₂O·83B₂O₃ (wt%) glasses with halogen addition was observed as Fig. 6. This sodium borate glass composition is considered as the soluble phase of phase separated glass and 5.2 mol% of sodium halides were added. The dissolving rate of sodium borate glass increased

by the addition of halogen and the dissolving rate of chlorine and bromine containing samples were higher than fluorine containing sample.

4. Discussion

The relationship between the surface area and treatment time was studied by Haller³⁾ and different relations were presented for each transport mode in microphase rearrangement process of phase separated glasses as Table 4. For sodium borosilicate glass with 68 wt% of SiO₂ content, $t^{-1/2}$ proportionality was also reported by Haller³⁾ as Eq. (1).

$$A = K \cdot t^{-1/2} \quad (1)$$

where A : specific surface area, t : treatment time
 K : constant

The shape of micro pore is usually described by cylindrical model. In this case, the relationship between pore radius ' r ' and surface area ' A ' is described as Eq. (2).

$$A = 2 V/r \quad (2)$$

where V : pore volume

Thus, surface area would be in proportion to reciprocal of pore radius and Eq. (3) is derived from Eqs. (1) and (2).

$$r = 2 V \cdot t^{1/2}/K \quad (3)$$

Nakashima et al.⁴⁾ reported the $t^{1/2}$ proportionality of pore radius as Eq. (3) for Na₂O-B₂O₃-SiO₂-Al₂O₃-CaO glass with 63 wt% of SiO₂ content and this relation is agreed with that of Haller.³⁾ Morimoto⁵⁾ reported $t^{1/3}$ relation of pore diameter for SiO₂-B₂O₃-Al₂O₃-ZrO₂-RO-Na₂O glasses with 56-66 wt% of SiO₂ content. Morimoto concluded that phase separation of SiO₂-B₂O₃-Al₂O₃-ZrO₂-RO-Na₂O glass took place by the nucleation growth mechanism resulting in the different time dependence of pore diameter. For the present glass composition (low silica content), the dependence of pore radius and specific surface area on treatment time were plotted in Fig. 7 and it was shown that specific surface area is in proportion to $t^{-0.3}$ and pore radius is to $t^{0.4}$. The $t^{-0.3}$ dependence of surface area corresponds to the case 2 or case 3 in Table 4. Micro-structure of the present glass is larger than that of sodium borosilicate glass with high silica content as studied by Haller. Thus, the rearrangements of micro phase would proceed by the way of bulk diffusion for large distance. If cylindrical model of micro-pore is adequate for the present glass, decrease of surface area and increase of pore diameter should show same time dependence, however different dependency was observed as Fig. 7 for the present study. The reasons for this discrepancy is unknown at present but one of the reasons is that the cylindrical model would not be suitable to interpret the rearrangement of the spherical structure as observed in Figs. 1(a)-(d).

Pore diameters of halogen free and F, Cl, Br containing samples shown in Fig. 5 were 1320Å, 1562Å, 1400Å and 1162Å, respectively, and their differences are relatively small in comparison with the leaching rate. Change in dissolving rate of Na₂O-B₂O₃ glass with halogen addition in Fig. 6 shows the same tendency as leaching rate in Fig. 5. Thus, the shortening of the leaching time with halogen addition would be mainly ascribed to differences in dissolving rate of sodium borate phases. One of the authors⁶⁾ reported that the addition of P₂O₅, WO₃ and V₂O₅ to the present mother glass is effective to increase the leaching rate. Takusagawa et al.⁴⁾ reported the promotion of leaching rate by fluorine addition to sodium borosilicate glasses with high silica content. In the present study, the same effect was observed for other halogen containing glasses and for the mother glass of low silica content.

5. Conclusion

The porous glasses were prepared from halogen containing sodium borosilicate glass and sharp pore size distribution curves were observed for all samples. The pore diameter increased and the specific surface area decreased with increasing heat treatment temperature, heat treatment time and halogen content. The dependence of pore radius and specific surface area on treatment time were different from

Table 4. Time dependence of surface area for different theoretical growth models.

Transport mode	Decrease of surface area
Volume diffusion: (Case 1) Fast diffusion across small distances Process at interfaces is rate-controlling step	$A \propto t^{-1/2}$
(Case 2) Rapid mass transfer across interface Slow diffusion across large distances is rate-controlling step	$A \propto t^{-1/3}$
Surface diffusion: (Case 3) Fast diffusion across small distances Vacancy formation is controlling	$A \propto t^{-1/3}$
(Case 4) Rapid vacancy formation Slow diffusion across large distance is controlling	$A \propto t^{-1/4}$

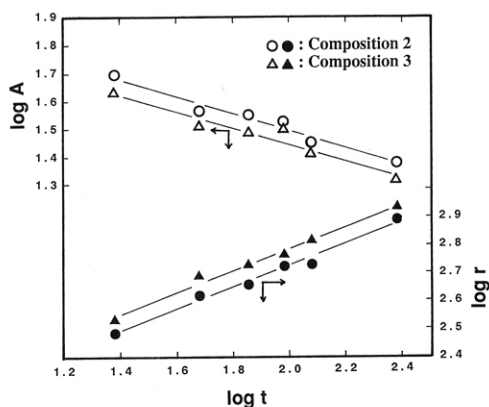


Fig. 7. Dependence of pore radius ' r ' and specific surface area ' A ' on treatment time ' t '.

that of sodium borosilicate glass with high silica content. For the present glass composition, specific surface area is in proportion to $t^{-0.3}$ and pore radius is to $t^{0.4}$. The halogen containing specimen was leached out in shorter soaking time than halogen free specimen and chlorine addition was most effective. The change of the leaching rate would be mainly ascribed to dissolving rate of halogen containing sodium borate phase into hot water.

Acknowledgements The authors would like to acknowledge Dr. H. Inoue of The University of Tokyo for much helpful advice

in the preparation on this manuscript. In addition the authors thank to Mr. K. Kotani of National Institute for Research in Inorganic Materials for pore size measurements.

References

- 1) J. J. Hammel and T. Allersma, US Pat., 3,843,341 (1974).
- 2) N. Takusagawa, K. Yamamoto and K. Kitajima, *J. Non-Cryst. Solids*, **95-96**, 1055-62 (1987).
- 3) W. Haller, *J. Chem. Phys.*, **42**, 686-93 (1965).
- 4) T. Nakashima and Y. Kuroki, *Nippon Kagaku Kaishi*, **8**, 1231-38 (1981).
- 5) S. Morimoto, *Seramikkusu Ronbunshi*, **98**, 1093-96 (1990).
- 6) A. Makishima and J. D. Mackenzie, *J. Non-Cryst. Solids*, **31**, 377-83 (1979).