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Prediction of Phase Separation in Multi-component Silicate Glass for Creating Porous Glass Materials from Waste Slag

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Keywords: slag; phase diagram; physical chemistry.

1. Introduction

Phase separation in glass represents a phenomenon in which a single glass phase separates into two or more glass phases with different compositions at a given temperature. To fabricate functional glass materials using waste slag discharged from metallurgical processes or waste melting processes, the authors have investigated the phase separation in multi-component oxide glass containing fundamental components in waste slag^{1,2}. Figure 1 shows schematic diagram for the process to create porous glass using phase separation in glass obtained from waste slag. For instance, spinodal decomposition forms three-dimensionally interconnected microstructure consisting of two different glass phases, and the porous glass can be obtained by leaching one of those phases with acid solution. Since its pore size can be easily controlled at a nano-scale level, the porous glass can be expected for widespread applications such as a filter to remove impurities from polluted water or air. Thus, slag can be transformed into value-added functional glass materials using phase separation in oxide glass.

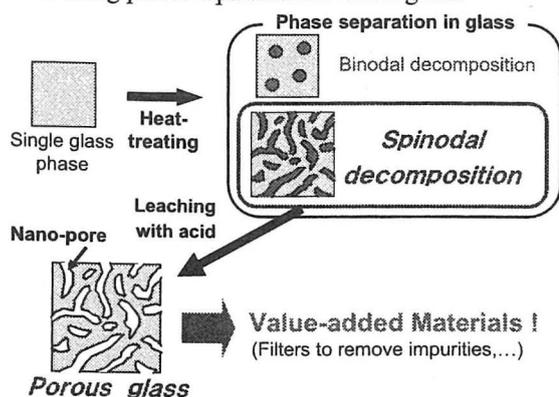


Figure 1 Schematic diagram of creating porous glass material using phase separation in glass.

To generate phase separation in glass obtained from waste slag, the composition ranges for metastable immiscibility and spinodal decomposition must be evaluated for multi-component slag systems. However, it is difficult to predict immiscibility boundaries empirically for multi-component oxide systems such as waste slag. Therefore, a thermodynamic evaluation must be performed for the prediction of phase separation in multi-component oxide systems.

In this study, the composition ranges have been predicted for phase separation and spinodal decomposition in multi-component silicate glasses by calculating the composition dependence of the Gibbs energy in the super-cooled liquid phase. The occurrence of spinodal decomposition was observed in heat-treated glasses at given compositions in the predicted immiscibility regions. Then, for creating porous glass material, a glass composition in multi-component borosilicate system was designed by substituting partial concentration of SiO_2 by B_2O_3 in the silicate glass composition included in the spinodal region. Since one of decomposed phases by spinodal decomposition in the borosilicate glass was leached out with acid solution, porous glass was obtained from the multi-component borosilicate glass.

2. Estimation of the Composition Ranges for Phase Separation and Spinodal Decomposition¹⁾

In the present study, the possibility of phase separation including spinodal decomposition was evaluated by calculating Gibbs energies and activities of SiO_2 in the metastable liquid phase, where glass in silicate systems is regarded as super-cooled liquid phase. The Gibbs energies and activities of SiO_2 were calculated with the FactSage thermodynamic computing program with the F*A*C*T oxide databases for molten oxide systems³⁾.

Liquid-liquid phase separation can be generally estimated from the Gibbs energy curve of the liquid phase. For instance, the miscibility gap in a binary system is determined from two points of contact on the Gibbs energy curve with a common tangent. The composition range for spinodal decomposition, referred to as the "spinodal region" in the present study, is obtained from two inflexion points in the Gibbs energy curve.

It has been found that many binary silicate systems have metastable miscibility gaps at high concentrations of SiO_2 ⁴⁾. In our previous study¹⁾, the Gibbs energy curves of the liquid phases were calculated for several binary silicate systems. The calculated results showed that the Gibbs energies change almost linearly in the high concentration range of SiO_2 with the composition. Therefore, it may be difficult to definitively determine the spinodal region from the inflexion points in the Gibbs energy curve for silicate systems.

In the present study, the activity of SiO₂ in the super-cooled liquid phase is calculated with concentration of SiO₂ to definitively determine the spinodal region. In an A-B binary system, the spinodal region is determined by calculating differentiation of the activity with respect to composition calculated by the following Equation (1):

$$\frac{\partial a_B}{\partial X_B} = \frac{\exp(\mu_B/RT)}{RT} \cdot \frac{\partial \mu_B}{\partial X_B} = (1 - X_B) \frac{a_B}{RT} \cdot \frac{\partial^2 G^{Mix}}{\partial X_B^2} \quad (1)$$

where G^{Mix} represents the Gibbs energy for mixing in the liquid phase. μ_B and a_B denote the chemical potential and activity of component B, and are expressed by Eq.(2) with respect to the pure liquid standard state:

$$\mu_B = RT \ln a_B = G^{Mix} + (1 - X_B) \frac{\partial G^{Mix}}{\partial X_B} \quad (2)$$

Equation (1) indicates that the first differential of the activity with respect to the concentration of B is directly proportional to the second differential of the Gibbs energy with respect to composition. Since the second composition derivative of the Gibbs energy becomes zero at its inflexion points, the spinodal region is determined from the extremum points on the activity curve.

The above estimation procedure for the spinodal region can easily be extended to ternary and multi-component systems on the condition that one of the separated phases consists of a pure component. If pure component A constitutes one of the separated phases, the spinodal region in an A-B-C ternary system is determined by calculating activity of component A across straight lines with constant composition ratios of components B to C that correspond to tie-lines of the miscibility gap. For quaternary or multi-component systems, the spinodal region is evaluated similarly by calculating the activities of A in A-B_{1-x}C_x-D quasi-ternary systems (here x is 0 to 1).

3. Experimental Procedure

3.1 Preparation of Two-phase Glass Materials

The occurrence of phase separation in glass was investigated experimentally to verify the calculated results of the metastable miscibility gaps. SiO₂-CaO-MgO-Na₂O and SiO₂-CaO-Al₂O₃-Na₂O glasses were prepared using silicon dioxide, magnesium oxide, aluminum oxide, sodium carbonate and calcium carbonate. These materials were melted in air for 5 h at 1873 K. Glass samples were obtained by quenching the melts in water and examined by X-ray diffraction analysis to confirm that they were glassy. The glasses were then heat-treated in air at 948 K or 993 K, and then cooled to room temperature. X-ray diffraction analysis was again carried out in the heat-treated glasses to confirm that they retained their glass state. Microstructures in these glasses were observed by a transmission electron microscope using an excitation voltage of 200 kV.

3.2 Fabrication of Porous Glass Materials using Phase Separation in Glass

Porous glass was produced for the two-phase glasses obtained from spinodal decomposition, by leaching one of decomposed phases with acid solution. The leaching process was performed by immersing the glass samples, whose bulk size were adjusted less than 2 mm in diameter, in HCl solution for 14 h. Microstructures on the surface of the porous glasses were observed by a field emission scanning electron microscopy using an excitation voltage of 15 kV. Glass compositions dissolved in the acid solution were analyzed using ICP emission spectrometry.

4. Results and Discussion

4.1 Prediction of Phase Separation in the Glass SiO₂-CaO-MgO-Na₂O^{1,2)}

The calculated results of the metastable miscibility gap and the spinodal region of the SiO₂-CaO-MgO-5mol%Na₂O system are shown in **Figure 2**, where the sum of the molar concentrations of all components except Na₂O is converted to unity. The spinodal region in the system was obtained by calculating the activities of SiO₂ in SiO₂-(CaO)_{1-x}(MgO)_x-Na₂O (here x is 0 to 1) quasi-ternary systems, because the calculated results of activities of SiO₂ in the super-cooled liquid phase indicated that one of the separated phases in the metastable immiscibility is regarded as pure SiO₂ metastable liquid phase¹⁾.

The occurrence of phase separation was investigated for the glasses A-D, having compositions indicated by square marks in **Fig. 2**. The selected chemical compositions of the glasses are shown in **Table 1**.

Figure 3 shows the electron micrographs in glasses A-D heat-treated for 192 h at 948 K, and they indicate the occurrence of phase separation. In glass A, an interconnected microstructure corresponding to spinodal decomposition was observed. The cross-section of the interconnected structure is estimated to be 80 to 100 nm in diameter. In glasses B and C, particle structures formed by binodal decomposition were observed. As the composition of glass D was outside the miscibility gap, no specific microstructure was observed after heat-treatment for 192 h. Since the electron diffraction patterns for each specimen in **Fig. 3** showed no evidence for the presence of crystalline phases, it was suggested that the annealed specimens were glassy in microscopic observation area.

The above experimental results indicate that phase separation including spinodal decomposition occurs in the SiO₂-CaO-MgO-Na₂O glasses corresponding to the predicted metastable miscibility gap shown in **Fig. 2**.

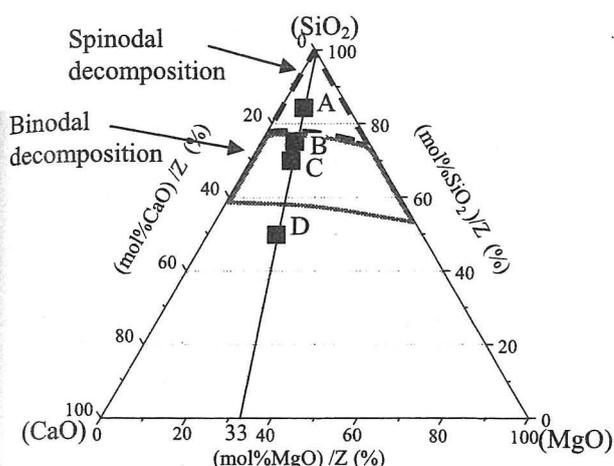


Table 1 Compositions of SiO₂-CaO-MgO-Na₂O glass samples used in the experiment

	Compositions [mol%]			
	SiO ₂	CaO	MgO	Na ₂ O
A	80.8	9.5	4.7	5.0
B	71.3	15.8	7.9	5.0
C	66.5	19.0	9.5	5.0
D	47.5	31.7	15.8	5.0

Figure 2 Calculated composition ranges for spinodal decomposition and bimodal decomposition at 948 K for the SiO₂-CaO-MgO-5mol%Na₂O system.

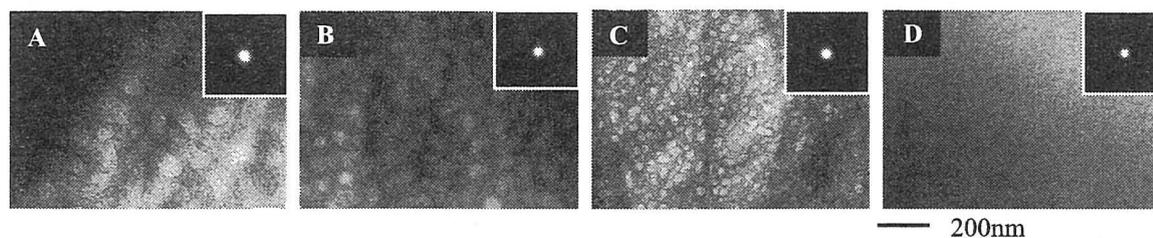


Figure 3 Electron micrographs of SiO₂-CaO-MgO-Na₂O glass specimens heated for 192 h at 948 K.

4.2 Prediction of Phase Separation in the Glass SiO₂-CaO-Al₂O₃-Na₂O

Figure 4 represents the calculated metastable immiscibility boundary and the spinodal region in the SiO₂-CaO-Al₂O₃-5mol%Na₂O system, where the sum of the molar concentrations of all components except Na₂O is converted to unity. The spinodal region in the quaternary system was determined by calculating the activities of SiO₂ in SiO₂-(CaO)_{1-x}(Al₂O₃)_x-Na₂O (here x is 0 to 0.5) quasi-ternary systems, because on the condition that molar ratios of CaO to Al₂O₃ were kept larger than unity, the calculated activities of SiO₂ indicated the phase separation where one of the decomposed phases is regarded as pure SiO₂ metastable liquid phase.

The occurrence of phase separation by spinodal decomposition in the SiO₂-CaO-Al₂O₃-Na₂O system was investigated for glass E, having composition indicated by filled circle mark in Fig. 4. Figure 5 represents the electron micrographs of annealed glass E. An interconnected microstructure was observed, and it indicates the occurrence of the spinodal decomposition in the glass. Since no evidence for the presence of crystalline phases was detected in the electron diffraction pattern for specimen shown in Fig. 5, it was revealed that the annealed specimens were glassy in microscopic observation area. Thus, the experimental result indicates that the spinodal decomposition occurs in the SiO₂-CaO-Al₂O₃-Na₂O glass in accordance with the thermodynamic prediction of the miscibility gap shown in Fig. 3.

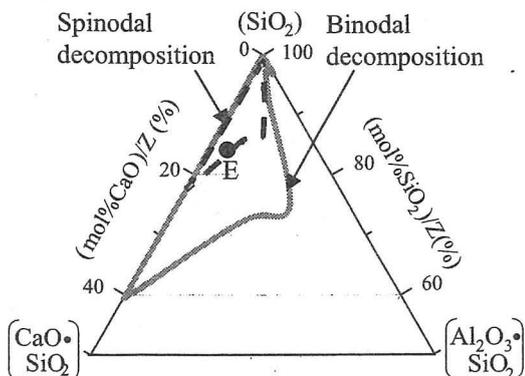


Figure 4 Calculated composition ranges for spinodal decomposition and bimodal decomposition at 973 K for the SiO₂-CaO-Al₂O₃-5mol%Na₂O system.

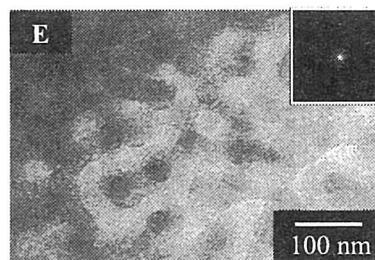


Figure 5 Electron micrographs of glass E (80.8SiO₂-11.7CaO-2.5Al₂O₃-5.0mol%Na₂O) heat-treated for 96 h at 993 K.

4.3 Fabrication of Porous Glass Materials using Spinodal Decomposition in Glass

In the present study, porous glass was fabricated using annealed glasses with spinodal decomposition, by leaching one of decomposed glass phase with acid solution. The leaching process was performed for the annealed SiO_2 -CaO-MgO- Na_2O glass A in which spinodal decomposition was observed, but it was found that the proportion of the glass sample dissolved into acid solution was quite low. Since the separated phases by spinodal decomposition in glass A contain high concentrations of SiO_2 , it may be difficult to leach one of the phases selectively with acid solution.

It should be noted that in the spinodal decomposition in glasses containing B_2O_3 , one of separated phases contains lots of B_2O_3 and can be leached out with acid solutions^{5,6}. In this study, to remove one of the decomposed phases, multi-component borosilicate glass compositions was designed by replacing part of molar concentration of SiO_2 by B_2O_3 in the silicate glasses included in the spinodal regions.

The microstructure on the surface of porous glass material obtained from SiO_2 -CaO- Al_2O_3 - Na_2O - B_2O_3 multi-component glass E-2, whose composition was designed from glass E, is shown in **Figure 6**. An interconnected porous structure was observed. This microstructure suggests that one of separated phases formed by spinodal decomposition in the borosilicate glass was removed selectively with acid leaching process. The chemical composition analysis for the glass dissolved into acid solution revealed that high proportion of B_2O_3 in glass E-2 was dissolved into acid and that the porous glass contains high concentration of SiO_2 .

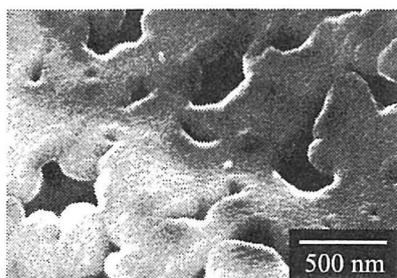


Figure 6 Microstructure on the surface of porous glass made from glass E-2 (59.7SiO_2 - 13.8CaO - $2.9\text{Al}_2\text{O}_3$ - $5.9\text{Na}_2\text{O}$ - $17.7\text{mol}\%\text{B}_2\text{O}_3$), annealed for 96 h at 993 K and leached one of decomposed phases with acid solution.

5. Conclusions

Thermodynamic analyses were performed to predict composition ranges for glass-glass immiscibility including spinodal decomposition in multi-component silicate glass, where glass was regarded as super-cooled liquid phase. The metastable miscibility gaps in SiO_2 -CaO-MgO- Na_2O and SiO_2 -CaO- Al_2O_3 - Na_2O systems were obtained by calculating Gibbs energies in the metastable liquid phase. The occurrence of spinodal decomposition in those glasses was confirmed by observing microstructures in heat-treated glasses, and these experimental results corresponded to the predicted miscibility gaps.

The leaching process was carried out for the two-phase glasses formed by spinodal decomposition to remove one of decomposed phases and to fabricate a porous glass. Multi-component borosilicate glass was prepared by replacing partial concentration of SiO_2 by B_2O_3 in the silicate glass compositions included in the predicted spinodal regions. One of separated phases by spinodal decomposition in the borosilicate glass can be leached out with acid solutions, and then porous glass having three-dimensional interconnected structure was obtained.

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