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Prediction of phase separation in multi-component oxide glass for the fabrication of porous glass materials from waste slag

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Abstract. Thermodynamic analyses were performed to evaluate the composition ranges for metastable immiscibility including spinodal decomposition in multi-component silicate systems, where glass was regarded as a super-cooled liquid phase. Experimental studies on two-phase separation in glass were carried out, and the phase separation was observed in those silicate glasses corresponding to calculated metastable miscibility gaps.

The authors also attempted the fabrication of porous glass using phase separation in oxide glasses containing B_2O_3. A multi-component borosilicate glass composition was prepared based on the silicate glass composition where spinodal decomposition had been confirmed. One of the glass phases formed by the spinodal decomposition in the boro-silicate glass was selectively removed by acid leaching and porous glass was successfully obtained.

1. Introduction

Phase separation in glass represents a phenomenon in which a single glass phase separates into two glass phases with different compositions during the heat-treatment of the glass at a given temperature.

To create functional glass materials using waste glass and slag from metallurgical processes or waste melting processes, the authors have investigated phase separation in multi-component oxide glass. For instance, spinodal decomposition as one of phenomena of the phase separation forms three-dimensionally interconnected microstructure, and porous glass is obtained by leaching one of those phases with acid solution. This porous glass can be expected in many 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.

To obtain phase separation in glass from slag, the composition ranges for metastable immiscibility for multi-component oxide systems should be evaluated. In this study, the metastable immiscibility regions including spinodal decomposition were evaluated in several multi-component silicate systems by thermodynamic analyses, where glass was regarded as super-cooled liquid phase. Experimental studies were performed to confirm the phase separation in heat-treated glasses in the predicted miscibility gap. The fabrication of porous glass has been attempted using the phase separation in a multi-component oxide glass containing B_2O_3.

2. Estimation of the Composition Ranges for Phase Separation and Spinodal Decomposition [1,2]

Liquid-liquid phase separation can be generally predicted from the Gibbs energy curve of the liquid phase. For instance, the miscibility gap in a binary system is obtained 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," is determined from two inflexion points in the Gibbs energy curve.

In our study, the composition ranges for phase separation and spinodal decomposition were estimated by calculating Gibbs energies in the metastable liquid phase, where glass in silicate systems

was regarded as a super-cooled liquid phase. The Gibbs energies were calculated with the FactSage thermodynamic computing program and the F*A*C*T oxide databases for molten oxide systems [3].

To definitively determine the spinodal region, the activity of SiO_2 was calculated from the Gibbs energy in the super-cooled liquid phase. In an A-B binary system, the spinodal region is evaluated with the derivative of the activity with respect to composition derived 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} denotes the Gibbs energy for mixing in the liquid phase. μ_B and a_B are the chemical potential and activity of component B and described by Eq. (2) under 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 spinodal region is determined from the extremum points in the activity curve, because the second derivative of the Gibbs energy should be zero at its inflexion points.

The above estimation procedure for the spinodal region can be extended to ternary and multi-component systems as follows: 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 and C that correspond to tie-lines of the miscibility gap. The spinodal region in a quaternary system is derived, similarly, by calculating activities of A in A-$B_{1-x}C_x$-D quasi-ternary systems (here x varies from 0 to 1).

3. Experimental Procedure

3.1 Preparation of Two-phase Glass Materials

Phase separation in glass was investigated experimentally to verify the calculated results of the metastable miscibility gaps. SiO_2-CaO-MgO-Na_2O and SiO_2-CaO-Al_2O_3-Na_2O glasses were prepared from silica, magnesia, alumina, sodium carbonate and calcium carbonate. These raw materials were melted in air for 5 h at 1873 K, and glass samples were obtained by quenching the melts in water. The glasses were then heat-treated at 948 K or 993 K. X-ray diffraction analysis was conducted on annealed glasses to confirm that they were glassy. Microstructures in these glasses were observed by a transmission electron microscopy.

3.2 Fabrication of Porous Glass Materials using Phase Separation in Glass

Porous glass was fabricated using two-phase glasses obtained from spinodal decomposition by leaching one of decomposed phases with acid solution. In the leaching process, glass sample was immersed in a HCl solution for 14 h, where bulk size of the sample was less than 2 mm in diameter. Microstructure on the surface of the porous glass was observed by field emission scanning electron microscopy. Composition of the glass dissolved in acid was examined with ICP emission spectrometry.

4. Results and Discussion

4.1 Prediction of Phase Separation in Multi-component Silicate Glasses [1,2]

Figure 1 shows the calculated metastable miscibility gap and the spinodal region of SiO_2-CaO-MgO-5 mol% Na_2O system, where molar fractions of each component are divided by the sum of the molar concentrations of all components except Na_2O.

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

Electron micrographs of the heat-treated glasses A-C are shown in **Figure 2**, and they depict the occurrence of a phase separation. An interconnected microstructure is observed in glass A, and it corresponds to the spinodal decomposition. In glass B, a particle structure indicating the binodal decomposition was observed. As the composition of glass C is outside the miscibility gap, no specific microstructure was observed after annealing for 192 h. Since electron diffraction patterns for each specimen showed no evidence for the presence of crystalline phases, the heat-treated specimens were

glassy in microscopic observation area. The above experimental results indicated that the phase separation occurs in SiO_2-CaO-MgO-Na_2O glasses according to the predicted miscibility gap.

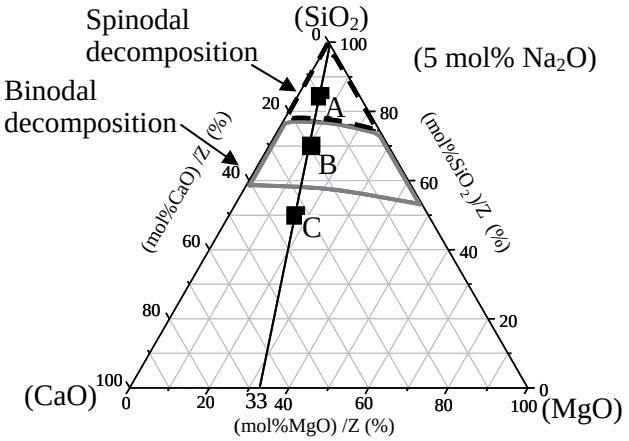

Figure 1. Calculated composition ranges for spinodal decomposition and binodal decom-position for the SiO_2-CaO-MgO-5 mol% Na_2O system at 948 K. (Z= mol% (SiO_2+CaO+MgO))

Table 1. Compositions of SiO_2-CaO-MgO-Na_2O glass samples used in the experiment.

	Composition [mol%]			
	SiO_2	CaO	MgO	Na_2O
A	80.8	9.5	4.7	5.0
B	66.5	19.0	9.5	5.0
C	47.5	31.7	15.8	5.0

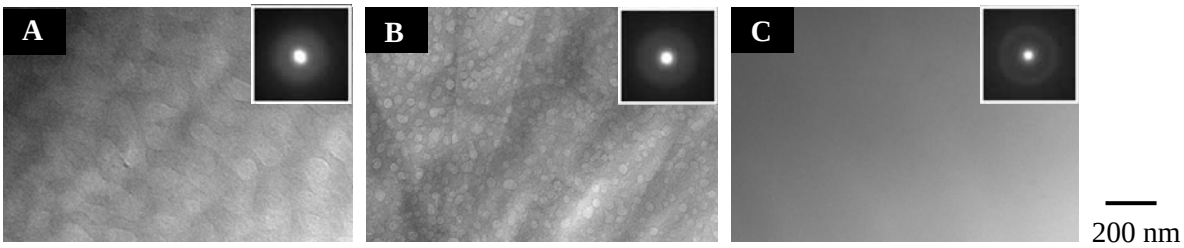

Figure 2. Electron micrographs of SiO_2-CaO-MgO-Na_2O glasses after annealing for 192 h at 948 K.

The metastable miscibility gap and the spinodal region in the SiO_2-CaO-Al_2O_3-5 mol% Na_2O system was calculated and is shown in **Figure 3**. Molar fractions of each component are divided by the sum of the molar concentrations of all components except Na_2O. The occurrence of spinodal de-composition in this system was investigated for glass D, whose composition is described by a square mark in **Fig. 3**. An interconnected microstructure indicating the spinodal decomposition was observed in the annealed glass D, as shown in **Figure 4**. This experimental result corresponds to the calculated miscibility gap as shown in **Fig. 3**.

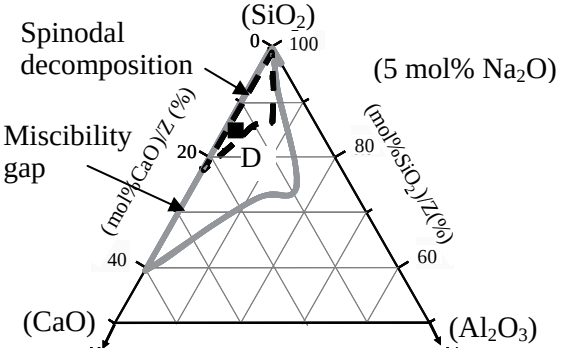

Figure 3. Calculated metastable immiscibility regions including spinodal decomposition in the SiO_2-CaO-Al_2O_3-5 mol% Na_2O system at 973 K. (Z= mol% (SiO_2+CaO+Al_2O_3))

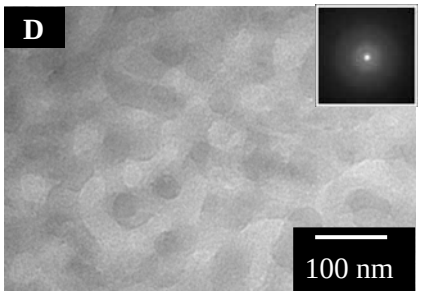

Figure 4. Electron micrograph of glass D (80.8SiO_2-11.7CaO-2.5Al_2O_3-5.0 mol% Na_2O) annealed for 96 h at 993 K.

4.2 Fabricating Porous Glass using Spinodal Decomposition in Multi-component Borosilicate Glass
The fabrication of porous glass was attempted using two-phase glasses with spinodal decomposition by leaching one of the decomposed glass phases with an acid solution.

It should be noted that in the spinodal decomposition in glasses containing B_2O_3, one of separated phases contains plenty of B_2O_3 and can be leached out with acid solutions [4,5]. In this study, a multi-component borosilicate glass composition D-2 was designed by partially substituting SiO_2 with B_2O_3 in the SiO_2-CaO-Al_2O_3-Na_2O glass D. Its composition is included in the spinodal region of the silicate system, and it was used to remove one of the separated phases in the leaching process.

Figure 5 shows microstructures of the borosilicate glass D-2 after heat-treatment and acid leaching. Morphology with interconnectivity was observed in the heat-treated glass, and an inter-connected porous structure was obtained after leaching. These microstructures indicate that one of the glass phases formed by spinodal decomposition was removed selectively with acid leaching. The chemical composition analysis for the glass phase dissolved into the acid solution revealed that a high proportion of B_2O_3 was dissolved in acid, and the porous glass contains a high concentration of SiO_2.

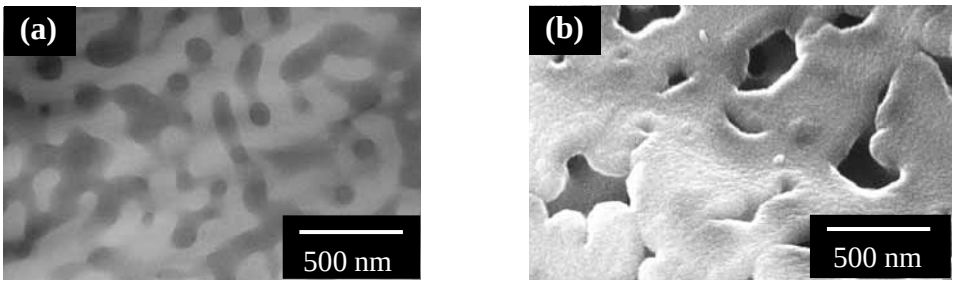

Figure 5. Microstructures in glass D-2 (59.7SiO_2-13.8CaO-2.9Al_2O_3-5.9Na_2O-17.7 mol% B_2O_3), (a) after annealing for 96 h at 993 K; (b) after leaching one of separated phases with acid solution.

5. Conclusions

Immiscibility regions in multi-component silicate glasses were determined by calculating Gibbs energies in the metastable liquid phase, where glass was regarded as a super-cooled liquid phase. The occurrence of phase separation in those silicate glasses was verified by observing microstructures in heat-treated glasses, and these experimental results corresponded to the predicted miscibility gaps.

For the fabrication of porous glass, a multi-component borosilicate glass was prepared by partially replacing SiO_2 with B_2O_3 in the silicate glass composition where spinodal decomposition had been confirmed. One of the glass phases formed by the spinodal decomposition in the borosilicate glass was leached out with an acid solution, and porous glass with a three-dimensional interconnected structure was obtained.

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