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Short communication

MEASUREMENT OF OXYGEN POTENTIAL IN Na_2SO_4-CONTAINING Na_2O-B_2O_3-Al_2O_3 MELTS BY ZrO_2 SENSOR

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1 INTRODUCTION

In the glass production process, the refining process where bubbles in glass melts are removed is very important to produce high quality glasses. The refining process is considered to be controlled by the redox reaction of a refining agent. Sodium sulfate is commonly used as a refining agent. The oxygen potential in glass melts is important in the analysis of the reaction of Na_2SO_4. Recently, it became possible to measure oxygen potential in glass melts directly by using ZrO_2 sensor. Schaeffer et al used ZrO_2 sensor to measure the variation of oxygen potential with time during refining process of silicate glass melts.[1] In this paper, the possibility to use ZrO_2 sensor in the measurement of oxygen potential in Na_2SO_4-containing Na_2O–B_2O_3–Al_2O_3 melts were investigated in order to clarify the thermodynamic behavior of sulfur.

2 EXPERIMENTAL

The reaction of sulfur in glass melts is expressed by Eq.(1). It is required to measure oxygen and sulfur potentials in order to investigate thermodynamic behavior of sulfur in glass melts. In this study, oxygen potential was measured by the oxygen sensor and sulfur potential was calculated from the sulfur content in silver which coexisted with glass melts. The thermodynamic data of sulfur in silver is given by Eq.(3)[2].

$$1/2S_2 + O^{2-} + 3/2O_2 = SO_4^{2-} \qquad (1)$$

$$1/2S_2(g) = S_{\text{in Ag}}(1\text{wt\%}) \qquad (2)$$

$$\Delta G_2^\circ = 54{,}800 + 4.26T \quad (\text{J/mol}) \qquad (3)$$

The constitution of the oxygen sensor is expressed as follows,

$$P_{O_2}(\text{ref.})|\text{Mo}|\text{Mo} + \text{MoO}_2||(\text{MgO})\text{ZrO}_2|| \text{melt} + \text{Ag–S}|\text{Pt}|P_{O_2}(\text{melt})$$

where P_{O_2}(ref.) is the oxygen potential at the reference electrode and is determined by the reaction of Eq.(4). The oxygen potential in the melt, P_{O_2}(melt), is determined by Eq.(6).

$$MoO_2(s) = Mo(s) + O_2(g) \qquad (4)$$

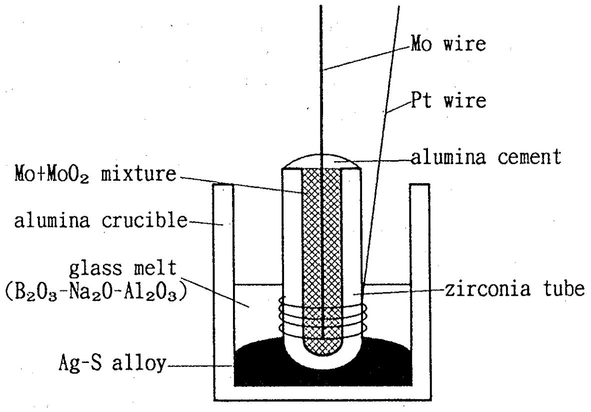

Fig.1. Structure of ZrO_2 sensor.

$$\Delta G_4^\circ = 578{,}000 - 167T \quad (\text{J/mol}) \ [3] \qquad (5)$$

$$S_{\text{in Ag}} + O^{2-} + 3/2O_2 = SO_4^{2-} \qquad (6)$$

The structure of ZrO_2 sensor is shown in Fig.1. In an MgO stabilized ZrO_2 tube, the mixture of Mo and MoO_2 powder (1:1 in molar ratio) was tightly stuffed and the upper side was sealed by alumina cement. Molybdenum and platinum wires were used as electrodes. In order to ensure the electrical contact between Pt wire and ZrO_2, the ZrO_2 tube was coated with Pt paste. The thermalelectromotive force between Pt and Mo was measured before experiments and experimental values of ZrO_2 sensor were corrected. The corrected electromotive force (E_{emf}) is expressed by Eq.(7), where R is gas constant, T absolute temperature, t_{ion} transport number of O^{2-} ion, and F Faraday constant. The transport number of O^{2-} ion in the MgO stabilized ZrO_2 is known to be unity.

$$E_{\text{emf}} = \frac{RTt_{\text{ion}}}{4F} \ln \frac{P_{O_2}(\text{ref.})}{P_{O_2}(\text{melt})} \qquad (7)$$

Glasses in the Na_2O–B_2O_3–Al_2O_3 system which contain about 1mol% Na_2SO_4 and Ag–S alloy (1wt%S) were equilibrated in Al_2O_3 crucibles at 1442K under Ar atmosphere. The ZrO_2 sensor was immersed in the crucible in order to contact with Ag.

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The electromotive force of the sensor was measured with a digital multimeter (YOKOKAWA 7561) and recorded by a personal computer. In the measurement of the solubility of Na_2SO_4, Na_2O–B_2O_3–Al_2O_3 glass and Na_2SO_4 were equilibrated at 1373K in Al_2O_3 crucible for 5hr. The sulfur in glasses and Ag after the experiments were analyzed by LECO.

3 RESULTS

The E_{emf} showed a stable value soon after the sensor was immersed into the melts. When the temperature was changed during the measurement, E_{emf} was stabilized within 1hr and the ZrO_2 sensor showed a good response to the change of oxygen potential.

The ZrO_2 sensor was attacked by glass melts, especially by melts rich in Na_2O. For example, ZrO_2 tube was completely melted in the $40Na_2O$–$60B_2O_3$ melt in 1hr. However, the damage was not serious for the melts in which B_2O_3 content was higher than 70mol%, or Al_2O_3 was almost saturated and it was shown that the ZrO_2 sensor can be used for such melts. Therefore, the melts for the measurement of oxygen potential were saturated with Al_2O_3(19∼34mol%).

The results of oxygen potential measurement are shown in Table 1. The sulfur content in glass melts are shown as SO_3 content in this table for the convenience of the following discussion. The sulfur potential was calculated from the sulfur content in Ag according to Eq.(3).

Table 1 Oxygen and sulfur potential in Na_2O–B_2O_3–Al_2O_3 melts containing sulfur measured at 1442K.

X_{Na_2O}	$X_{B_2O_3}$	$X_{Al_2O_3}$	X_{SO_3}	P_{O_2}	P_{S_2}
(molar fraction)				(atm)	(atm)
0.203	0.609	0.188	7.28×10^{-6}	3.78×10^{-7}	5.65×10^{-5}
0.228	0.545	0.227	2.28×10^{-5}	1.43×10^{-6}	2.50×10^{-5}
0.271	0.506	0.223	2.75×10^{-4}	4.65×10^{-6}	1.14×10^{-4}
0.321	0.452	0.224	2.01×10^{-3}	1.94×10^{-5}	2.58×10^{-9}
0.357	0.385	0.256	2.34×10^{-3}	4.25×10^{-5}	1.55×10^{-9}
0.361	0.303	0.335	4.24×10^{-5}	6.41×10^{-10}	2.73×10^{-5}

4 DISCUSSION

Though the real reaction of sulfur in glass melts is expressed by Eq.(6), it is difficult to analyze the behavior of sulfur numerically based on Eq.(6) because the pure ionic species, for example O^{2-} and SO_4^{2-}, are not available as a reference state. Therefore, the analysis in this study was based on Eq.(8) and the activity of SO_3 in melts was calculated.

$$1/2S_2 + 3/2O_2 = SO_3 \qquad (8)$$

$$\Delta G_8^\circ = -458,000 + 163T \quad (\mathrm{J/mol})\ [3] \qquad (9)$$

Activity coefficient is an important parameter to express the thermodynamic behaviors of a component in melts. The activity coefficient of SO_3, $\gamma_{SO_3} = P_{SO_3}/X_{SO_3}$, in melts was also shown in Fig.2, where reference state is SO_3 gas of 1atm.

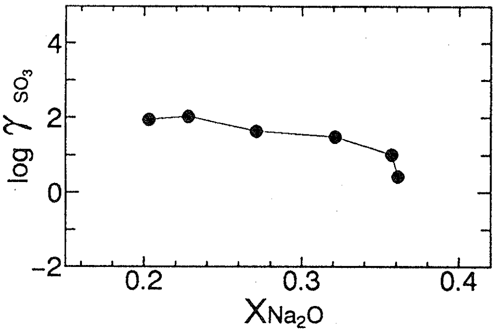

Fig.2. Activity coefficient of SO_3 in the Na_2O–B_2O_3–Al_2O_3–Na_2SO_4 system with saturated Al_2O_3 content at 1442K.

The B_2O_3–Na_2SO_4 system does not show any miscibility and addition of Na_2O to this system increases miscibility which drastically decreases the activity coefficient of SO_3[4]. However, such a drastic change is not shown in the Na_2O–B_2O_3–Al_2O_3 system. This difference would be attributed to Al_2O_3. The solubility of Na_2SO_4 in Na_2O–B_2O_3–Al_2O_3 and Na_2O–B_2O_3 melts at 1373K is shown in Fig.3. The solubility of Na_2SO_4 in Na_2O–B_2O_3–Al_2O_3 melts would not change much with temperature like that in Na_2O–B_2O_3 melts reported by Nezu[4]. It is found that the addition of Al_2O_3 increases the solubility of Na_2SO_4 when X_{Na_2O} is lower than 0.2, so that the change of activity coefficient of SO_3 is small compared with that in the Na_2O–B_2O_3 system. This supports the validity of the measurement of oxygen potential by ZrO_2 sensor.

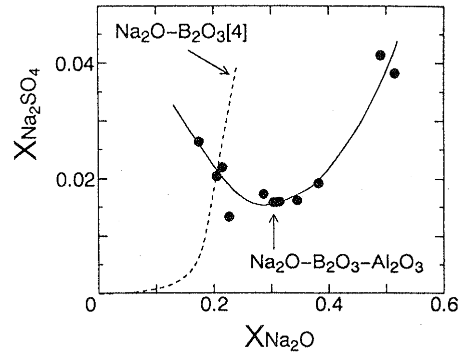

Fig.3. Solubility of Na_2SO_4 in the Na_2O–B_2O_3–Al_2O_3–Na_2SO_4 system with saturated Al_2O_3 content at 1373K.

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