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The activity of sodium oxide in molten float glass by EMF measurements

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Abstract

The Na_2O activity in the molten float glass composed of 13.2 m/o Na_2O, 70.2 m/o SiO_2, 10.0 m/o CaO, 5.9 m/o MgO, etc. was determined in the temperature range from 1260 to 1380 K by means of galvanic cells using Na–β″-alumina as solid electrolyte. The Na_2O activity, a_{Na_2O}, accompanying the reaction Na_2O (dissolved in Na_2O–WO_3 melt) = Na_2O (dissolved in molten glass) was found to be given by $\log a_{Na_2O} = -5.88 - 6.32 \times 10^3\,T^{-1}$ as a function of temperature, and the relative partial molar enthalpy of Na_2O was calculated to be $\Delta\overline{H}_{Na_2O} = -121.0\,\mathrm{kJ/mol}$.

Keywords: Na_2O activity; Float glass; EMF measurements

1. Introduction

In the float glass process sodium is transferred, in various types of bond state, from the molten glass via the tin bath to the refractory lining of the bath casing, where it reacts with the refractory material. Due to the volume increase accompanying this reaction, the refractory lining is gradually destroyed [1,2]. The float glass melt is closely connected with sodium silicate melts, in which there are numerous literatures on the thermodynamic activity of Na_2O [3–14]. Kohsaka et al. [3] evaluated the partial molar Gibbs energy of Na_2O in the Na_2O–SiO_2 melts containing from 22.5 to 55 m/o Na_2O from electromotive force (EMF) measurements between 1390 and 1570 K, and Yamaguchi et al. [4] extended the range of the measurement to be $0.20 < \mathrm{m/o}\,Na_2O < 0.60$ and $1173\,\mathrm{K} < T < 1723\,\mathrm{K}$. Besides EMF measurements, Tsukihashi et al. [5] also investigated Na_2O activities in the melts containing more than 50 m/o Na_2O at 1373, 1473 and 1573 K employing a chemical equilibration technique, and Rego et al. [6] calculated them from the experimental data of the vapor pressure of Na for the composition range from 40 m/o Na_2O to silica saturation at 1573 and 1673 K. For ternary Na_2O–SiO_2–CaO melts, Neudorf and Elliott [7] reported Na_2O activities in the melts for the composition range of m/o Na_2O from 29.4 to 39.4 with up to 10 m/o CaO added between 1273 and 1373 K. Closely corresponding to float glass melts, Argent et al. [8] determined Na_2O ativities in soda–lime–silica melts between 1373 and 1673 K by the mass-spectrometric Knudsen method.

In order to investigate the “sodium problem” stated above, in this study, the Na_2O activity in the molten float glass has been determined between 1260 and 1380 K, i.e. temperatures of float bath, by EMF measurements. The measurement has been performed in galvanic cells using Na–β″-alumina as the electrolyte and Na_2O–WO_3 melt for the reference electrode. For trying the reliability performance of the cell, a sodium silicate melt having the same composition with that of Neudorf and Elliott’s work [7] has been chosen for the working melt. Finally, the Na_2O activity in the molten float glass measured by this work has been compared with that obtained from the mass-spectrometric Knudsen method by Argent et al. [8].

2. Experimental

The EMF cell employed in this work utilized a Na–β″-alumina electrolyte and the following galvanic cell

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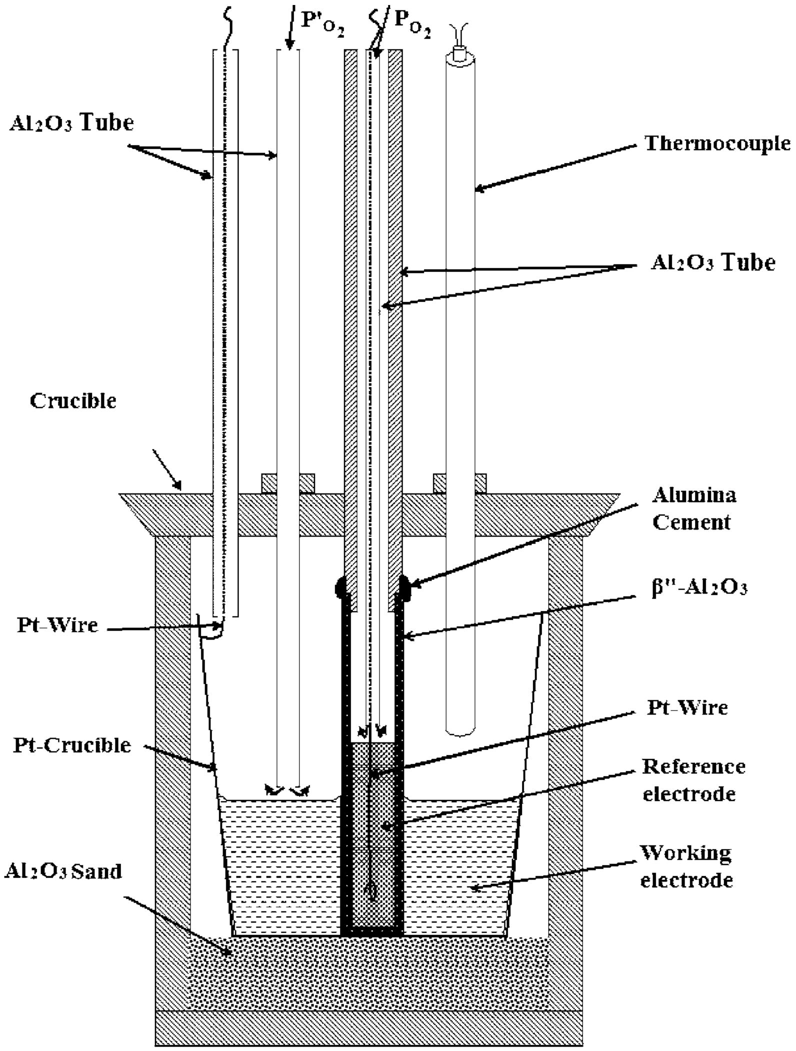

Fig. 1. Schematic of electrochemical cell.

was used for the temperatures from 1260 to 1380 K

$$\text{Pt, } O_2(1\,\text{atm})|(Na_2O)_R|Na^+\text{–}\beta''\text{-alumina}$$
$$|(Na_2O)_T|O_2(1\,\text{atm}),\ \text{Pt}$$

where $(Na_2O)_R$ designates sodium oxide in the Na_2O–WO_3 reference melt, and $(Na_2O)_T$ designates sodium oxide in the working melt, which was either the sodium silicate melt or the float glass melt. The general arrangement of the cell is shown in Fig. 1. The cell design is similar to that of Lin and Elliott [15]. The composition of the reference melt was 45.6 m/o Na_2O–54.4 m/o WO_3 [15], and an atmosphere of pure oxygen at 1 atm was maintained over both electrodes. The composition of the sodium silicate melt which was chosen to test the cell reliability was 65.7 m/o SiO_2–34.3 m/o Na_2O [7]. The composition of the float glass melt is listed in Table 1. The oxygen was dried before being passed into the cell.

For the cell of this study, the anodic reaction is

$$(Na_2O)_R = 2Na^+ + \tfrac{1}{2}O_{2(I)} + 2e^-$$

and the cathodic reaction is

$$2Na^+ + \tfrac{1}{2}O_{2(II)} + 2e^- = (Na_2O)_T$$

where $O_{2(I)}$ is the oxygen pressure at the anode, and $O_{2(II)}$ is the oxygen pressure at the cathode. Therefore, the overall reaction can be written as

$$(Na_2O)_R + \tfrac{1}{2}O_{2(II)} = (Na_2O)_T + \tfrac{1}{2}O_{2(I)}$$

Table 1
The composition of the molten float glass

Component	Content (m/o)
SiO_2	70.175
Na_2O	13.190
CaO	10.046
MgO	5.852
Al_2O_3	0.319
SO_2	0.242
Fe_2O_3	0.035
Cl	0.106
TiO_2	0.035

Table 2
Activities of Na_2O in sodium silicate melt

Temperature (K)	Measurement 1		Measurement 2	
	EMF (mV)	a_{Na_2O}	EMF (mV)	a_{Na_2O}
1268	−344.5	6.745×10^{-10}		
1272			−356.1	8.762×10^{-10}
1300			−346.4	1.028×10^{-9}
1307	−339.5	9.898×10^{-10}		
1325			−342.7	1.286×10^{-9}
1341	−336.5	1.385×10^{-9}		
1348			−338.5	1.548×10^{-9}
1373			−335.5	1.931×10^{-9}
1375	−331.2	1.834×10^{-9}		

The activity of sodium oxide in the working melt, $a_{Na_2O(T)}$, can be evaluated from the Nernst equation as follows:

$$\log a_{Na_2O(T)} = \log a_{Na_2O(R)} + \frac{1}{2}\log\left(\frac{P_{O_2(II)}}{P_{O_2(II)}}\right) - \frac{2FE}{2.303RT}$$

where E is the EMF (V) of the cell, R is the universal gas constant, and F is the Faraday constant. The value of the standard potential, E^0, for the overall cell reaction is zero. The activity of sodium oxide in the Na_2O–WO_3 reference melt was obtained by the measurement of Lin and Elliott [15] who evaluated it to be $\log a_{Na_2O(R)} = -2.64 - 11.73 \times 10^3 T^{-1}$. At 1 atm of oxygen pressure over both electrodes, the above equation can be simplified as follows:

$$\log a_{Na_2O(T)} = \log a_{Na_2O(R)} - \frac{2FE}{2.303RT}$$

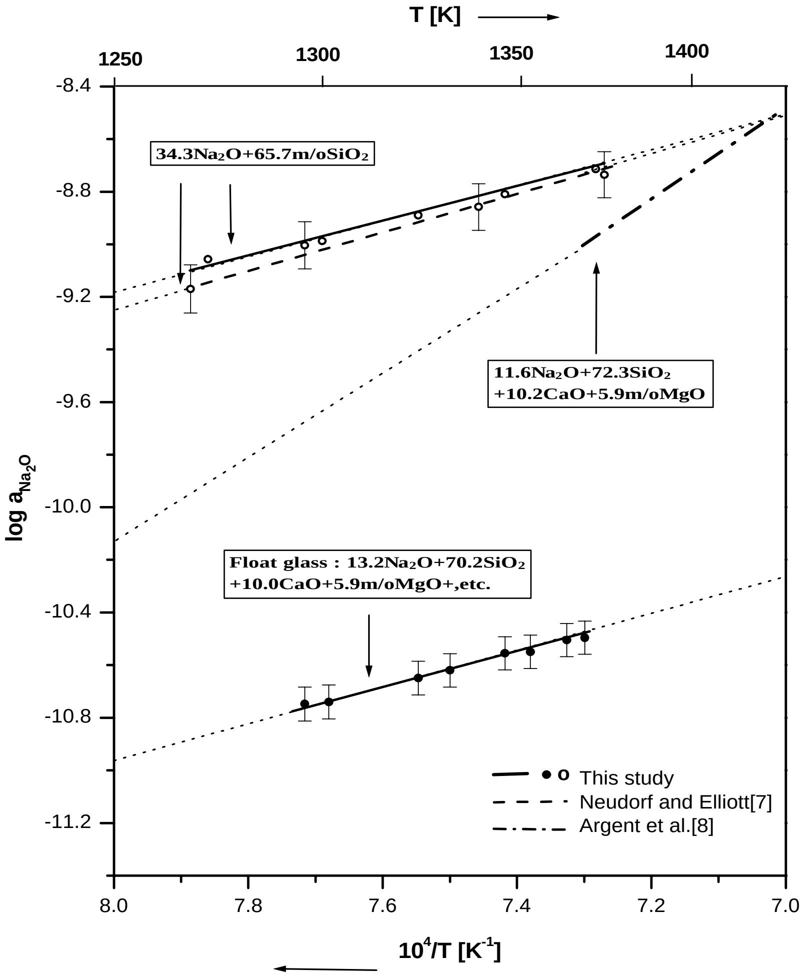

Fig. 2. Activities of Na_2O in various silicate melts as a function of temperature. Error bars correspond to an uncertainty of approximately ±10 mV in the potential of the cell.

Table 3
Activities of Na_2O in molten float glass

Temperature (K)	Measurement 1				Measurement 2	
	EMF (mV)	a_{Na_2O} (at elevating temperature)	EMF (mV)	a_{Na_2O} (at lowering temperature)	EMF (mV)	a_{Na_2O}
1296	−121.9	1.76×10^{-11}	−123.4	1.81×10^{-11}		
1302					−118.5	1.81×10^{-11}
1325	−110.8	2.21×10^{-11}	−112.3	2.27×10^{-11}		
1333					−108.4	2.38×10^{-11}
1348	−103.2	2.69×10^{-11}	−106.7	2.86×10^{-11}		
1354					−100.6	2.80×10^{-11}
1365	−97.4	3.10×10^{-11}	−98.4	3.14×10^{-11}		
1370					−95.2	3.19×10^{-11}

and thus represented as a function of temperature with the given reference data and the measured EMF values.

To confirm the reproducibility and reversibility for EMF, all the measurements have been repeated two times, and carried out at elevating temperatures and lowering temperatures, respectively.

3. Results

The results of the test measurement carried out with the sodium silicate melt (34.3 m/o Na_2O–65.7 m/o SiO_2) are shown in Table 2 and Fig. 2. For comparison, results obtained by Neudorf and Elliott [7] also are given in Fig. 2. Both experimental data show good correspondence with the activities of Na_2O. The results of measurements of Na_2O activity in molten float glass are shown in Table 3 and Fig. 2, where the line is the least squares line for all point; its equation is $\log a_{Na_2O} = -5.88 - 6.32 \times 10^3 T^{-1}$ with the 99% confidence limit, and the relative partial molar enthalpy was calculated using Gibbs–Helmholtz equation to be $\Delta\overline{H}_{Na_2O} = -121.0\,\mathrm{kJ/mol}$ with uncertainty of approximately ±1400 J/mol. These results are compared with those reported by Argent et al. [8] who measured the Na_2O activity in soda–lime–silica melts having the composition of 11.6 m/o Na_2O, 72.3 m/o SiO_2, 10.2 m/o CaO and 5.9 m/o MgO, closely corresponding to the float glass, in the temperature range from 1373 to 1673 K by the mass-spectrometric Knudsen method and found it to be $\log a_{Na_2O} = 2.57 - 15.81 \times 10^3 T^{-1}$. As can be seen in Fig. 2, the data of Argent et al. [8] is shown considerably higher than this work. In Fig. 3, the activities of sodium oxide ($\log a_{Na_2O}$) in various melts are represented in dependence of Na_2O content (m/o) at 1343 K. With the assumption that the effect of 5 m/o MgO on the Na_2O activity might not be so significant as that of CaO [16], the activity of sodium oxide from this work is placed right in close vicinity to the line extended by values from Neudorf and Elliott's work [7], whereas the value obtained by Argent et al. [8] deviates definitely from that estimated. It is considered that the mass-spectrometric Knudsen method could be accompanied with some errors in evaluating the measured values in the low-temperature range owing to several conversion factors.

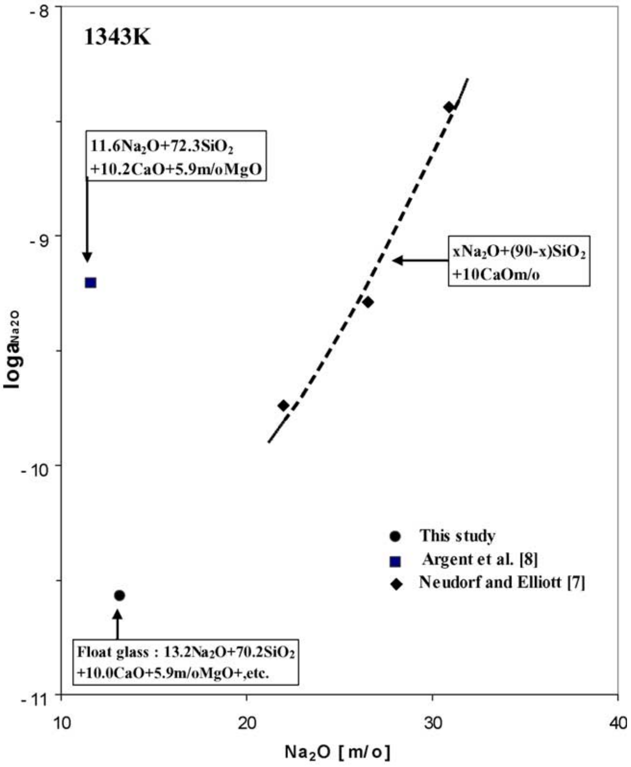

Fig. 3. Activities of Na_2O in various silicate melts as a function of Na_2O (m/o) content.

4. Conclusions

A galvanic cell employing Na–β″-alumina as a solid electrolyte has been used to measure the activity of Na_2O in the molten float glass as a function of temperature. The Na_2O activity has been represented by $\log a_{Na_2O} = -5.88 - 6.32 \times 10^3 T^{-1}$ between 1270 and 1370 K. These experimental data are expected to be useful applied to analysis of the "sodium problem" occurring in the float glass process.

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