Original Paper

Oxygen activity change in soda–lime–silica glass melts with or without refining agent

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The effect of refining agents in soda–lime–silica melts was examined by measuring the oxygen activity with the method of electromotive force. When the melt contained antimony, the activity changed with temperature and the variation in activity increased as the antimony content increased. When the oxygen content in the atmosphere changed, the oxygen activity in the melt changed gradually by diffusion. The variation in oxygen activity with atmosphere decreased with increasing antimony content and almost disappeared when the Sb_2O_3 content was 1 mol%. In the case of sulfate addition, the activity value became unstable when the temperature was raised, which might be caused by bubble formation accompanied by the decomposition of sulfate.

Änderung der Sauerstoffaktivität in Kalk-Natronsilicatglasschmelzen mit oder ohne Läutermittel

Der Einfluß von Läutermitteln in Kalk-Natronsilicatschmelzen wurde durch Messung der Sauerstoffaktivität mit Hilfe der elektromotorischen Kraft-Methode untersucht. Enthielt die Schmelze Antimon, so änderte sich die Aktivität mit der Temperatur, und die Änderung nahm mit steigendem Antimongehalt zu. Bei einem Wechsel des Sauerstoffgehaltes in der Atmosphäre veränderte sich die Sauerstoffaktivität in der Schmelze allmählich infolge von Diffusion. Die Änderung der Sauerstoffaktivität mit der Atmosphäre verringerte sich mit steigender Antimonkonzentration und verschwand fast völlig, wenn der Sb_2O_3-Gehalt 1 Mol-% betrug. Im Falle einer Sulfatzugabe wurde der Aktivitätswert bei Temperaturerhöhung instabil, was durch Blasenbildung in Verbindung mit Sulfatzersetzung hervorgerufen sein könnte.

1. Introduction

The activity of oxygen in the glass melt can be measured by the EMF (electromotive force) method [1 to 4]. The study of the oxygen activity change is important since it relates to the formation or the disappearance of bubbles and to color change in glass. The dependence of the activity change on temperature differs from one additive in the glass melt to another. In a glass containing a redox element such as Fe^{2+}/Fe^{3+}, the oxygen activity changes with temperature change [3]. In this case, the equilibrium, Red + $n/4O_2 \rightleftarrows$ Ox + $n/2O^{2-}$, shifts with temperature. When the temperature is raised, the equilibrium moves to the left hand since ΔG of this reaction becomes high with temperature [5]. When arsenic or antimony is used as a redox element, the reaction occurs effectively since ΔG of this reaction crosses zero in the working temperature range [6]. In this case, released oxygen at a hot spot of a furnace expands bubbles in the melt and eases their escape from the surface. In a refining process where the temperature drops, the reverse reaction occurs and residual bubbles are absorbed in the melt. This is the refining mechanism in the glass melt containing arsenic or antimony [2 and 7]. The use of these elements, however, becomes difficult because of their toxicity in the environment [8].

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Instead of the redox elements, sulfate is also used as a refining agent in manufacturing window glass. In this case, though oxygen and sulfur dioxide gas are generated at high temperature by decomposition, the reverse reaction is said not to occur. Hence, oxygen activity does not become low with temperature drop [2].

In the glassmaking process, the oxygen concentration in the atmosphere may change at each melting step. Oxygen activity changes with atmosphere change were measured in some studies [2 and 3], sometimes for diffusion measurement [4 and 9]. However, the effect of refining agents on the activity in different atmospheres was not examined systematically.

In this study, oxygen activity changes with temperature change and with oxygen content change in the atmosphere were investigated. In order to prevent a local cell reaction between the electrode at melt/atmosphere interface and that in the bulk, which causes an undesirable oxygen activity change, the platinum lead of the electrode should be covered with an insulator, so that there is no contact between lead and interface [10]. Using melts with and without refining agents, the authors intended to clarify the behavior of the agents.

2. Experimental

The base glass composition (in mol%) was chosen as 70 SiO_2, 20 Na_2O, 10 CaO. The raw materials were reagent grade SiO_2, Na_2CO_3 and $CaCO_3$. For the glass

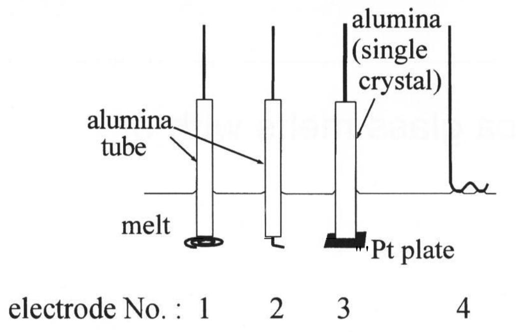

Figure 1. Shapes of platinum electrodes. Type 1: platinum wire of 1 mm in diameter; the part contacting the melt surface was covered with an alumina tube. Type 2: the electrode with smaller surface area. Type 3: Pt-13 % Rh plate; the lead was covered with an alumina single crystal. Type 4: the electrode of this type was used for surface activity measurements, which was used for all measurements except those for figure 4.

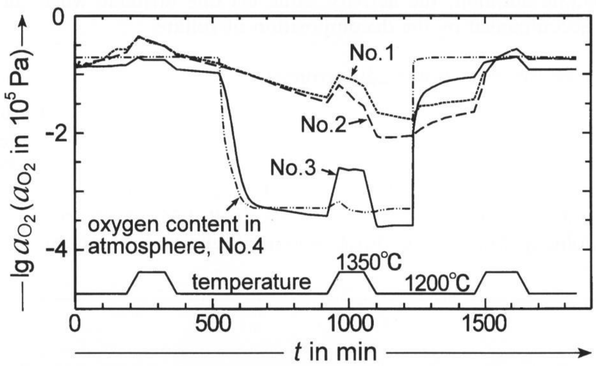

Figure 2. Oxygen activity change in the melt without additives. Two electrodes of type 1 (see figure 1) were used for the measurements given by curves no. 1 and 2. The curve no. 3 follows the value at the surface of the melt measured with the electrode type 4 (see figure 1). Atmosphere was changed from air $\rightarrow N_2 \rightarrow$ air. The oxygen content in the atmosphere, shown in curve no. 4, was measured with a handmade zirconia sensor. Temperature change is shown at the bottom of this figure.

containing a redox element as a refining agent, Sb_2O_3 was added to the base glass composition. For the glass containing sulfate, 5 % of total Na_2CO_3 was replaced by Na_2SO_4. A mixture of these materials was melted in a platinum crucible at 1400 °C in an electric furnace. The melt was cast onto a graphite plate. About 150 g of the blocks were remelted in an Al_2O_3 crucible (pure special alumina with an Al_2O_3 content > 99.95 %) set in the center of an Al_2O_3 tube in an atmosphere-controlled furnace.

For oxygen activity measurement by the EMF method, zirconia and platinum electrodes were used. An yttria-stabilized zirconia rod attached in an alumina tube was used as a zirconia reference electrode. The preparation method of the electrode was described elsewhere [11]. Four types of platinum electrodes (no. 1 to 4) were used as shown in figure 1. The oxygen activity in the bulk glass was measured with the electrode no. 1, 2 or 3, in which a part of the lead including the liquid/atmosphere interface was covered with alumina as an insulator [10]. In the case of electrode no. 3, an alumina single crystal was used for the insulator since the solidity of alumina influenced the corrosion rate in the glass melt. The activity at the melt surface was measured with the electrode no. 4. A combination of these electrodes was immersed simultaneously in the melt after the temperature was raised.

The oxygen activity, a_{O_2}, in the melt was calculated from the EMF (ΔE) value between platinum and zirconia electrodes with the Nernst equation

$$\Delta E = (RT/4F)\ln(a_{O_2}/p_{O_2}) \,, \tag{1}$$

where R is the gas constant, T the temperature, F the Faraday constant and $p_{O_2} = 0.20$ for the oxygen partial pressure of reference air (80 % N_2 and 20 % O_2) introduced in the zirconia electrode.

During the experiment, 200 to about 500 cm^3/min of dried air (80 % N_2 and 20 % O_2) or N_2 were introduced as an atmospheric gas. An oxygen concentration in atmosphere in the tube was measured with a zirconia sensor, which has another platinum electrode and the same type of zirconia electrode used for reference in the melt. The atmosphere was changed from air to N_2 and to air again. In each atmospheric condition, the temperature was raised and dropped. The concentration of oxygen in the N_2 atmosphere was adjusted to a constant value by adding a slight amount of oxygen through a microvalve.

3. Results and discussion

3.1 Oxygen activity change in the melt without refining agent

Figure 2 shows an oxygen activity change in the melt without additives. The value at the melt surface (curve no. 3) quickly responded to the change in the atmosphere. Curves no. 1 and 2 slightly differed in the activity value, which might be caused by the nonuniformity of the melt. When the temperature was changed, the oxygen activity also changed a little. Theoretically, the activity would not change with temperature in the melt without additives. Actually, the oxygen activity change with temperature change was not clear in a previous experiment as shown in figure 3 [11]. Hence, the change might have occurred by some redox ions in the melt as contamination. When the oxygen content in the atmosphere was lowered, the oxygen activity slowly dropped as shown in figure 2. This was caused by an oxygen diffusion from the bulk to the surface of the melt. With the EMF method, however, the diffusion of only molecular or atomic oxygen dissolved in the melt can be detected. This means that the diffusion of total oxygen including oxide ion (O^{2-}) remains unknown.

3.2 Oxygen activity change in the melt with antimony

Figure 4 shows an oxygen activity change in the soda–lime–silica melt with 1 mol% Sb_2O_3 [10]. When

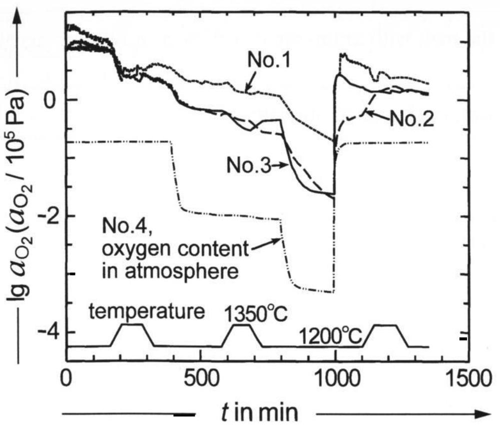

Figure 3. Oxygen activity change in the melt without additives [11]. For the measurement of curves no. 1 to 3, electrodes of type 2 (figure 1) were used simultaneously. Oxygen content in atmosphere, shown in curve no. 4, was adjusted by mixing air and N_2. Other conditions were similar to the measurement given in figure 2. The activity values were unstable at the beginning of the measurements.

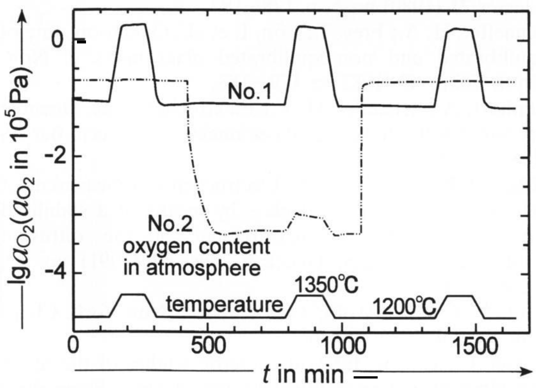

Figure 4. Oxygen activity change in the melt with 1 mol% Sb_2O_3 [10]. The electrode type 1 (figure 1) was used for curve no. 1. Oxygen content in the atmosphere was shown in curve no. 2. Other conditions were similar to the measurement given in figure 2.

the temperature was raised or lowered, the oxygen activity went up or down. This was caused by the shift of the equilibrium

$$Sb^{5+} + O^{2-} \rightleftharpoons Sb^{3+} + 1/2O_2 \, , \tag{2}$$

which moves to the right hand side with increasing temperature. This behavior is fundamental to the refining process of redox elements such as antimony [2 and 7]. Figures 5 and 6 show the results in the melt with 0.3 and 0.1 mol% Sb_2O_3, respectively. The initial activity values were different in these figures. This might be caused by a difference in the conditions in batch melting or by carbon contamination in the casting process. The behavior of the oxygen activity shown in figures 5 and 6 was slightly different from that in figure 4. The variation of activity during the temperature change became larger as the antimony content became higher. This behavior was similar to the case of an iron-containing glass melt [12].

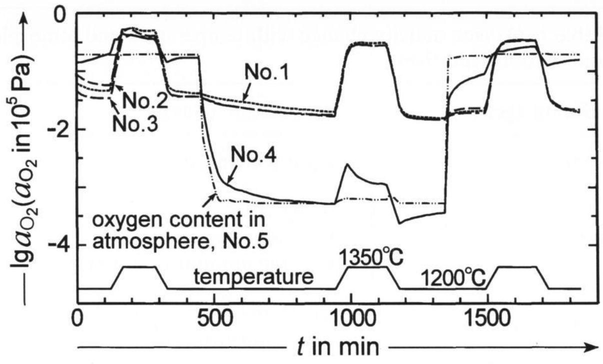

Figure 5. Oxygen activity change in the melt with 0.3 mol% Sb_2O_3. Three electrodes of type 3 (figure 1) were used for curves no. 1 to 3. The curve no. 4 follows a value at the surface of the melt. Other conditions were similar to the measurement represented in figure 2.

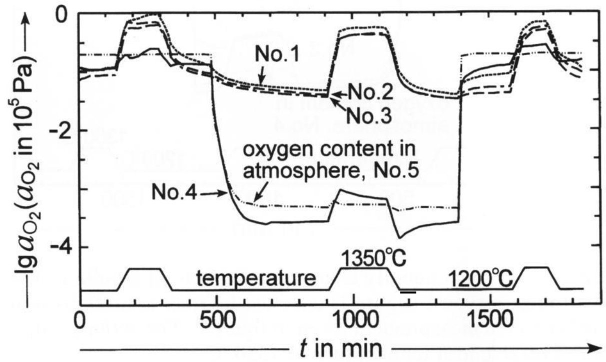

Figure 6. Oxygen activity change in the melt with 0.1 mol% Sb_2O_3. Electrode configuration and conditions were the same as in figure 5.

In contrast, the activity dependence on the oxygen content in the atmosphere decreased with increasing content of antimony. In the case of 1 mol% Sb_2O_3, even though the oxygen content in the atmosphere was changed from 20% to 400 ppm, an oxygen activity change was not apparent in the bulk. This means that the apparent diffusion was much slower than that in the melt without a redox element. This 'buffering' phenomenon must be caused by the reaction between oxygen and antimony as a redox element. When the oxygen activity dropped, the equilibrium equation (2) moved to the right and oxygen was produced. This caused the apparent slow diffusion.

3.3 Effect of sulfate

Figure 7 shows an oxygen activity change in a melt containing sulfate. When the temperature was raised, not only the activity went up, but the value became unstable. Since the instability was reproducible in the melt with sulfate [11] and was not seen in other melts, it is considered that the cause is bubble formation of sulfur dioxide gas on the electrodes produced by thermal decomposition of sulfate given by the following equation:

$$SO_4^{2-} \rightarrow SO_2 + 1/2O_2 + O^{2-} \, . \tag{3}$$

Table 1. Oxygen activity change with temperature and atmosphere changes in the melt with antimony or sulfate as a refining agent and without additives

refining agent	temperature change	oxygen content change in atmosphere
none	slightly changed	changed
antimony	changed The value was increased with the amount of antimony	The value decreased with antimony content and not observed in the melt with 1 mol% Sb_2O_3
sulfate (Na_2SO_4)	raised and became unstable with temperature	changed

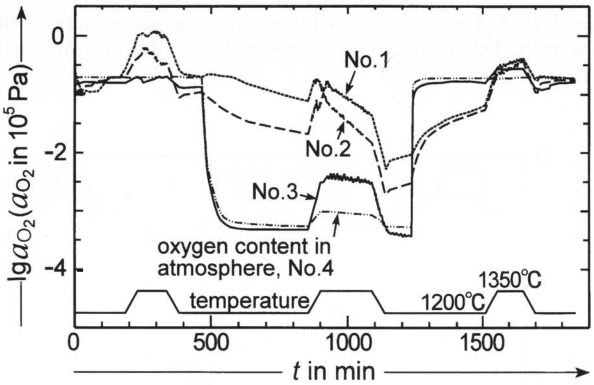

Figure 7. Oxygen activity change in the melt with sulfate. Two electrodes of type 1 (figure 1) were used. Other conditions were similar to the measurement given in figure 2. The activity values were unstable at a temperature of 1350 °C.

When the concentration of oxygen in the atmosphere was lowered, the activity of oxygen in the melt decreased like in the melt without additives. This means that sulfate had no buffer effect in contrast to the melt with a redox element. As shown in figure 7, the activity became low when the temperature was decreased. However, this kind of refining effect is not seen in the melt with sulfate in [2], and was not observed in the authors' previous experiment, either [11]. Since the phenomenon has no reproducibility, this might be caused by the similar reason as in the melt with no additives.

4. Summary

The oxygen activities were measured with the EMF method in melts with or without refining agents. By changing temperature and atmosphere, the behavior of refining agents was examined. The difference in behavior is summarized in table 1.

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