

Interaction between oxygen activity of Fe₂O₃ doped soda–lime–silica glass melts and physically dissolved oxygen

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The oxidation state of molten soda–lime–silica glass was studied by an electrochemical oxygen-sensor, based on an yttria-stabilized zirconia solid electrolyte. It is shown that the iron concentration of the glass melt influences the extent of oxygen activity variation during cooling. If the iron concentration is 0.2 mol% Fe₂O₃ or less, the redox ratio [Fe³⁺]/[Fe²⁺] cannot be assumed to be independent of temperature because the redox equilibrium is shifted by the reactivity of physically dissolved oxygen.

Sauerstoffaktivität von Fe₂O₃-dotierten Kalk-Natronsilicatglasschmelzen

Der Oxidationszustand von Kalk-Natronsilicatglasschmelzen wurde mit Hilfe eines elektrochemischen Sauerstoffsensors auf der Basis eines yttriumoxidstabilisierten Zirkondioxid-Festelektrolyten untersucht. Es konnte gezeigt werden, daß die Eisenkonzentration der Glasschmelze das Ausmaß der Sauerstoffaktivitätsänderung beim Abkühlen beeinflusst. Beträgt der Stoffmengenanteil $\leq 0,2$ % Fe₂O₃, so kann nicht vorausgesetzt werden, daß das [Fe³⁺]/[Fe²⁺]-Redoxverhältnis unabhängig von der Temperatur ist, da das Redoxgleichgewicht auf Grund der Reaktivität des physikalisch gelösten Sauerstoffs verschoben wird.

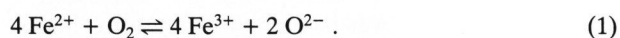
1. Introduction

The oxidation state of molten glass is important for the glass melting behavior, the glass forming process and many properties of the final glass product, especially the color. Industrially melted glasses are never in equilibrium with the furnace atmosphere and therefore, the oxidation state has to be adjusted via the oxidizing and reducing additions of the glass batch. Additionally the oxidation state is affected by the interaction of the glass melt with the furnace atmosphere and the bubbling gases, by the convection in the glass tank and by the temperature history [1 and 2]. Therefore, it is important to provide an in-situ technique in order to determine the oxygen activity in the molten glass. Since some years [1 to 5], it has been possible to measure the oxygen activity by means of sensors, based on oxygen ion-conducting solid electrolytes. Especially the refining process and in more general terms the “dynamic behavior” under temperature changes were investigated [6 and 7]. Laboratory experiments with industrially melted glasses showed that the oxygen activity can be correlated with the batch composition [1 to 8]. The effect of different multivalent ions on the oxygen activity during temperature changes was described, too [9]. However, there are still some questions, especially when more than one multivalent ion is present and when the concentration of the multivalent ion is small.

In this work, it will be shown that the iron concentration has a great impact on the “dynamic behavior” of the oxygen activity.

2. Theory

Oxygen is dissolved physically in the molten glass and is in equilibrium with the multivalent cations, for example with Fe²⁺ and Fe³⁺:



The free oxygen ions O²⁻ are in equilibrium with single-bonded O⁻ and double-bonded O⁰ oxygen:



Therefore, in glasses which contain considerable amount of alkali oxides, it can be assumed that the oxygen activity remains constant when the equilibrium, according to equation (1) is shifted. An equilibrium constant K can be defined:

$$a_{\text{O}_2} = K ([\text{Fe}^{3+}] / [\text{Fe}^{2+}])^4, \quad (3)$$

[Fe²⁺] and [Fe³⁺]: activities of Fe²⁺ and Fe³⁺, respectively. The equilibrium constant K depends on the composition of the glass melt [9] and on temperature [10 to 12]:

$$K = A e^{B/T}, \quad (4)$$

where A and B are constants.

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When the glass melt is cooled from temperature T_1 to T_2 , the equilibrium according to equation (1) is shifted to the right side and the oxygen activity decreases. If the molten glass is cooled quickly, only the physically dissolved oxygen can react with Fe^{2+} ions. The oxygen of the furnace atmosphere cannot participate because the diffusion coefficients are too low. If besides oxygen only one type of polyvalent ion is present, equation (5) can be derived from equations (3 and 4) (index 1 for temperature T_1 and index 2 for T_2):

$$\ln \left(\frac{a_{\text{O}_2}^{(1)}}{a_{\text{O}_2}^{(2)}} \right) = B \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + 4 \ln \left(1 - \frac{4 \Delta \text{O}_2}{[\text{Fe}^{2+}]_1} \right) - 4 \ln \left(1 + \frac{4 \Delta \text{O}_2}{[\text{Fe}^{3+}]_1} \right), \quad (7)$$

when $\Delta \text{O}_2 < 0.1$ ($[\text{Fe}^{2+}]_1, [\text{Fe}^{3+}]_1$), equation (8) is a good approximation for equation (7):

$$\ln \left(\frac{a_{\text{O}_2}^{(1)}}{a_{\text{O}_2}^{(2)}} \right) = B \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - 16 \Delta \text{O}_2 \left(\frac{1}{[\text{Fe}^{2+}]_1} + \frac{1}{[\text{Fe}^{3+}]_1} \right), \quad (8)$$

$$c_{\text{O}_2}^{(1)} = \left[B \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - \ln \left(a_{\text{O}_2}^{(1)} / a_{\text{O}_2}^{(2)} \right) \right] \cdot \left[16 \left(1 - a_{\text{O}_2}^{(2)} / a_{\text{O}_2}^{(1)} \right) \left(\frac{1}{[\text{Fe}^{2+}]_1} + \frac{1}{[\text{Fe}^{3+}]_1} \right) \right]^{-1}. \quad (10)$$

If the amount of physically dissolved oxygen is small, then term (2) in equation (8) is zero and $\ln(a_{\text{O}_2}^{(1)} / a_{\text{O}_2}^{(2)})$ only depends on the temperature and the thermodynamic data ($B = \Delta H / R$) of the redox equilibrium, according to equation (1):

$$\ln \left(a_{\text{O}_2}^{(1)} / a_{\text{O}_2}^{(2)} \right) = B (1/T_1 - 1/T_2). \quad (11)$$

3. Experimental

The oxygen activity was measured by a sensor, based on an yttria-stabilized zirconia solid electrolyte. The sensor is described in detail in [7 and 13]. Figure 1 shows a schematic drawing of the electrochemical cell. The molten glass is inside a platinum-rhodium crucible, the ZrO_2 reference electrode and the platinum test electrode are immersed into the glass melt. The crucible was mounted inside a vertical alumina muffle tube with water-cooled flanges at the top and at the bottom. The alumina tube itself was gas tight and could be filled with various gases.

The quantity measured by the oxygen sensor is the electromotive force E of the electrochemical cell:

$$a_{\text{O}_2}(\text{glass melt}), \text{Pt} \parallel \text{ZrO}_2 (\text{Y}_2\text{O}_3 \text{ doped}) \parallel \text{Pt}, p_{\text{O}_2}(\text{air}).$$

The solid electrolyte possesses only ionic conductivity (transport number $t_{\text{O}^{2-}} = 1$) and therefore, the oxygen activity of the glass melt a_{O_2} can be calculated from the electromotive force by equation (12) [2]:

$$\ln a_{\text{O}_2} = \ln p_{\text{O}_2}(\text{air}) + 4 F E / R T. \quad (12)$$

$$\ln \left(a_{\text{O}_2}^{(1)} / a_{\text{O}_2}^{(2)} \right) = B \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + 4 \ln \left(\frac{[\text{Fe}^{3+}]_1 [\text{Fe}^{2+}]_2}{[\text{Fe}^{2+}]_1 [\text{Fe}^{3+}]_2} \right). \quad (5)$$

According to equation (1), $[\text{Fe}^{2+}]_2$ and $[\text{Fe}^{3+}]_2$ can be related to $[\text{Fe}^{2+}]_1$ and the concentration of physically dissolved oxygen ΔO_2 , which actually reacts with Fe^{2+} ions, when the glass is cooled from T_1 to T_2 :

$$\begin{aligned} [\text{Fe}^{2+}]_2 &= [\text{Fe}^{2+}]_1 - 4 \Delta \text{O}_2, \\ [\text{Fe}^{3+}]_2 &= [\text{Fe}^{3+}]_1 + 4 \Delta \text{O}_2. \end{aligned} \quad (6)$$

Inserting equation (6) into equation (5) results in:

ΔO_2 can be related to the real concentration of physically dissolved oxygen $c_{\text{O}_2}^{(1)}$:

$$a_{\text{O}_2}^{(1)} / a_{\text{O}_2}^{(2)} = c_{\text{O}_2}^{(1)} / (c_{\text{O}_2}^{(1)} - \Delta \text{O}_2). \quad (9)$$

From equation (8) and (9) $c_{\text{O}_2}^{(1)}$ can be calculated:

All experiments were carried out in a glass melt with the basic composition of 74 % SiO_2 , 16 % Na_2O , 10 % CaO (in mol%), which was modified by adding Fe_2O_3 . The glasses were heated to 1250 °C with a rate of 600 K/h, then the electrodes were immersed in the glass melt. The oxygen activity was measured continuously by a high Ohmic ($R > 10^{11} \Omega$) digital voltmeter. The temperature was cycled between 1250 and 1400 °C (30 min heating time, 30 min holding time and 30 min cooling time).

4. Results and discussion

Figure 2a shows the oxygen activity of a glass melt with an iron concentration of 0.35 mol% as a function of time when the temperature is varied. The oxygen activity decreases with decreasing temperature over one and a half decade. Figure 2b shows the same type of measurement of a glass melt with an iron concentration of 0.1 mol%. Here, the oxygen activity

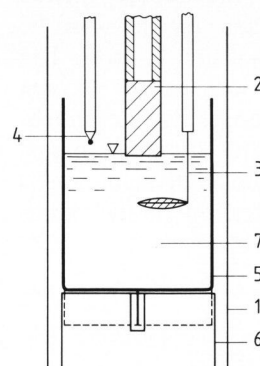
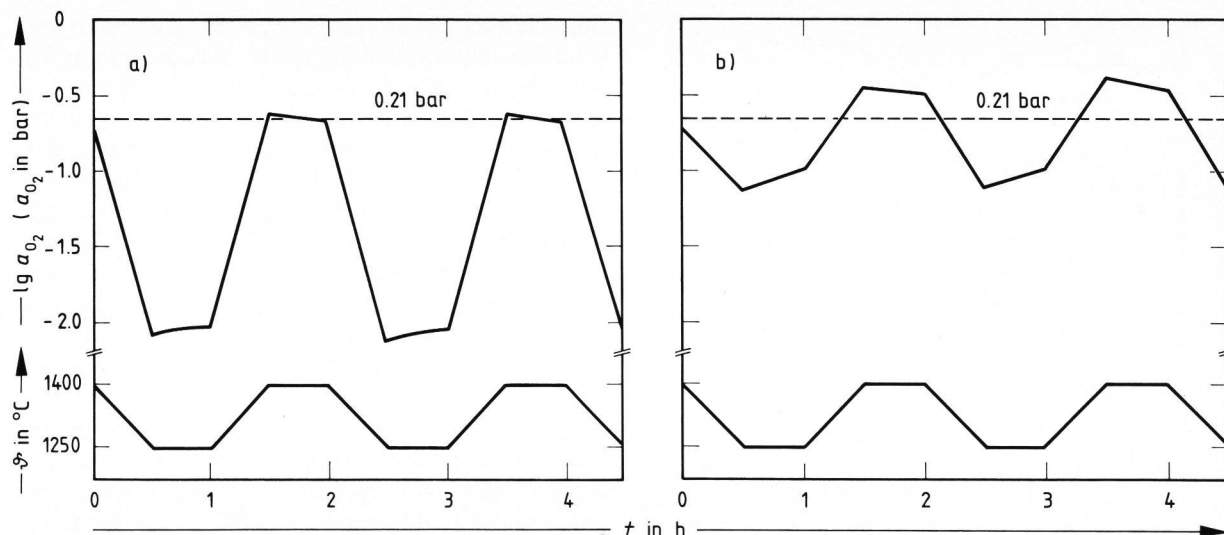


Figure 1. Schematic drawing of the electrochemical cell. 1: alumina furnace tubing, 2: zirconia-based solid electrolyte (reference electrode), 3: platinum measuring electrode, 4: thermocouple, 5: Pt/Rh crucible, 6: rotary alumina support, 7: glass melt.



Figures 2a and b. Oxygen activity a_{O_2} of a glass melt as a function of time, with temperature variations between 1250 and 1400 °C; contains a) glass melt with 0.35 mol% Fe₂O₃, b) glass melt with 0.1 mol% Fe₂O₃.

decreases only by slightly more than half a decade. By comparing the figures 2a and b, it can be seen clearly that the effect of the temperature on the oxygen activity depends on the iron concentration. In order to point out this correlation the expression $\Delta \lg a_{O_2}$ is defined as the difference between the oxygen activities at 1250 and 1400 °C:

$$\Delta \lg a_{O_2} = \lg a_{O_2} (\vartheta = 1400 \text{ °C}) - \lg a_{O_2} (\vartheta = 1250 \text{ °C}). \quad (13)$$

$\Delta \lg a_{O_2}$ can be used as a measure of the temperature dependence on the oxygen activity. Figure 3 displays the dependence of $\Delta \lg a_{O_2}$ on the iron concentration. As already shown in [6 and 10] the oxygen activity is nearly independent of temperature, when no polyvalent ion is present in the glass melt. In this case $\Delta \lg a_{O_2}$ is zero. With increasing Fe₂O₃ concentration, $\Delta \lg a_{O_2}$ increases, too and a limiting value is nearly reached at 0.35 mol% Fe₂O₃.

If the real concentration of physically dissolved oxygen is too small to influence the redox ratio $[Fe^{2+}]/[Fe^{3+}]$, the curves in figures 2a and b should have the same shape and $\Delta \lg a_{O_2}$ will have a constant value for all iron concentrations. Since $\Delta \lg a_{O_2}$ is not independent of the iron concentration for $[Fe_2O_3] \leq 0.2 \text{ mol\%}$, the values of small iron concentrations in figure 3 must be described by equation (8) instead of equation (12). For $[Fe_2O_3] \geq 0.35 \text{ mol\%}$, a limiting value is nearly reached (see dotted line in figure 3) and $\Delta \lg a_{O_2}$ does not depend on the iron concentration. In this case, the second term in equation (8) is zero and $\Delta \lg a_{O_2}$ depends only on the thermodynamic data of equation (1). Therefore, from the limiting value ($\Delta \lg a_{O_2}^\infty = B(1/T_1 - 1/T_2) = 1.45$), the enthalpy of reaction (1) can be calculated ($\Delta H = RB = -472 \text{ kJ/mol}$). When the iron concentration is small, ($[Fe_2O_3] \leq 0.2 \text{ mol\%}$), the second term in equation (8) cannot be neglected and

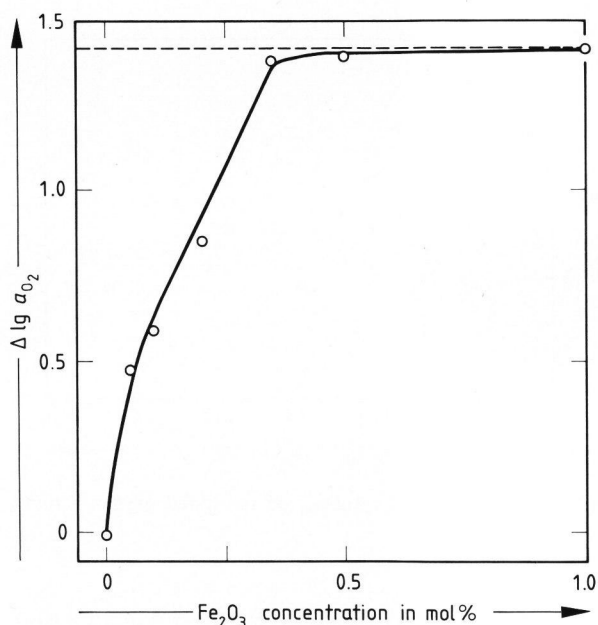


Figure 3. Dependence of $\Delta \lg a_{O_2}$ ($= \lg a_{O_2} (\vartheta = 1400 \text{ °C}) - \lg a_{O_2} (\vartheta = 1250 \text{ °C})$) on the Fe₂O₃ concentration.

the change of the oxygen activity with temperature is smaller. Then the concentration of physically dissolved oxygen influences the temperature dependence. When the iron concentration decreases further, the second term in equation (8) increases more and more and $\Delta \lg a_{O_2}$ approaches zero. The deviation of $\Delta \lg a_{O_2}$ from the limiting value $\Delta \lg a_{O_2}^\infty = 1.45$ (figure 3 (accords to $16 \Delta O_2(1/[Fe^{2+}] + 1/[Fe^{3+}])$) (equation (8)) and to the numerator of equation (10). From this deviation, the concentration of physically dissolved oxygen can be calculated by the aid of equation (10). From data in [1] the redox ratio $[Fe^{3+}]/[Fe^{2+}] = 9$ could be calculated for 1400 °C and an oxygen activity of 0.38 bar (figure 2b) for the glass

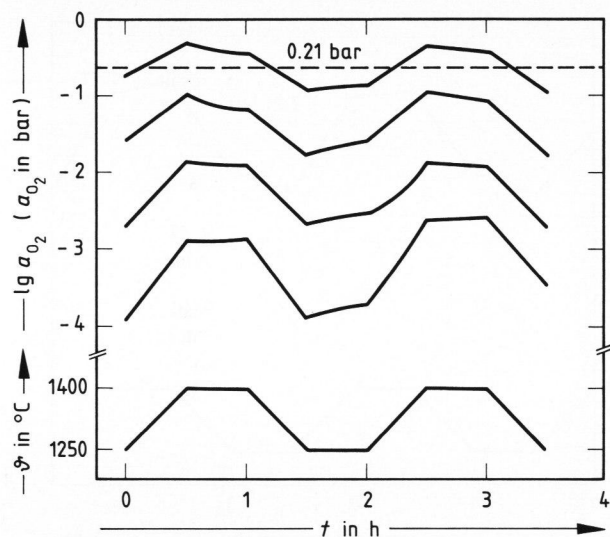


Figure 4. "Dynamic behavior" of the oxygen activity a_{O_2} of a soda-lime-silica glass melt with 0.05 mol% Fe_2O_3 for different initial oxygen activities.

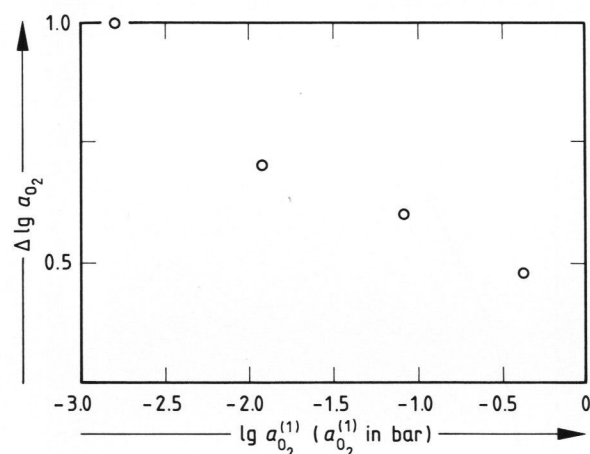


Figure 5. Dependence of $\Delta \lg a_{O_2}$ on the initial oxygen activity $\lg a_{O_2}^{(1)}$ at 1400 °C.

melt composition investigated. By the aid of equation (10), $c_{O_2}^{(1)}$ was estimated: for $[Fe_2O_3] = 0.1$ mol% ($[Fe^{2+}] = 0.02$ mol% and $[Fe^{3+}] = 0.18$ mol%), $c_{O_2}^{(1)}$ amounts to $8 \cdot 10^{-4}$ wt% O_2 . A mean value, calculated from $[Fe_2O_3] = 0.05, 0.1, 0.2$ mol%, amounts to $(7.5 \pm 2.5) 10^{-4}$ wt% O_2 . $c_{O_2}^{(1)}$ is always much smaller than $[Fe^{2+}]$, $[Fe^{3+}]$ as required when equation (8) was derived.

Previously only very few investigations of the oxygen solubility in glass melts have been carried out [13 to 16]. In the literature most values are related to glass melts refined with arsenic and therefore besides the physically dissolved oxygen the chemically dissolved oxygen was recorded, too. Only Zluticky et al. [16] measured a soda-lime-silica glass melt without any refining agent employing a high temperature vacuum extraction method and found an oxygen concentration of $3 \cdot 10^{-5}$ wt%. However, the oxygen activity of this glass melt is unknown and therefore,

this value cannot be compared directly to the oxygen solubility measured in this study, because the amount of physically dissolved oxygen strongly depends on the oxygen activity of the glass melt. For investigating this effect in more detail, glass melts with an iron concentration of 0.05 mol% Fe_2O_3 were exposed to gas atmospheres with different oxygen partial pressures at 1500 °C. After some hours of stirring the glass melt was nearly in equilibrium with the gas atmosphere. Then the temperature was decreased to 1400 °C and the oxygen activity was measured while the temperature was cycled (figure 4). The initial values of the oxygen activity at 1400 °C varied over nearly three decades, according to the gas atmospheres in the furnace. At the upper curve, the oxygen activity does not change very much when the temperature is decreased to 1250 °C. At the lower curve, the variation of the oxygen partial pressure with temperature is much larger. For a better illustration, figure 5 shows the dependence of $\Delta \lg a_{O_2}$ on the initial values of the oxygen activity at 1400 °C. $\Delta \lg a_{O_2}$ increases from a value of 0.48 for a glass melt with high oxygen activity to a value of 1.0 for a glass melt with a low initial oxygen activity. This is in accordance with equation (8). When the initial oxygen activity a_{O_2} is small, the oxygen concentration ΔO_2 reacting with Fe^{2+} ions during cooling is small. Then term two in equation (8) is small, $\ln(a_{O_2}^{(1)}/a_{O_2}^{(2)})$ and therefore, $\Delta \lg a_{O_2}$ is large. When $a_{O_2}^{(1)}$ increases, term two in equation (8) increases, too and $\Delta \lg a_{O_2}$ is smaller. It should be remarked that even when the glass melt is equilibrated with air at 1400 °C, $c_{O_2}^{(1)}$ is always much smaller than $[Fe^{2+}]$ and $[Fe^{3+}]$ as required when equation (8) was derived.

5. Conclusions

In former investigations it was mostly assumed, that the concentration of physically dissolved oxygen compared to the concentration of multivalent ions is too small to influence their redox ratios during cooling. But from figures 3 and 5 it can be seen, that the concentration of the multivalent ion and the initial oxygen activity are important for the temperature dependence of the oxygen activity. If the iron concentration is low (≤ 0.2 mol% Fe_2O_3), it cannot be assumed that the redox ratio $[Fe^{2+}]/[Fe^{3+}]$ remains constant during cooling. Then the redox equilibrium according to equation (1) is remarkably shifted by the reaction of physically dissolved oxygen with Fe^{2+} ions.

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