THE SIGNIFICANCE OF THE REDOX STATE OF GLASS ON THE BUBBLE BEHAVIOUR IN THE ISOTHERMAL GLASS MELTS

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The mathematical model for the calculation of the oxidation-reduction species distribution in a flowing glass melt under non-isothermal conditions was formulated. The results of calculations show that the initial oxidation-reduction state of a glass melt influences both the rate of bubble removing from the melt and the bubble composition development. The very high or very low values of the redox state accelerate the bubble removing process in glasses refined by sulphates while only high redox values are favourable in glasses refined by oxides. The concentration ratios CO_2/N_2 as well as N_2/Ar in analysed bubbles, used for the identification of bubble sources in a glass melting space, generally grow when the bubble removing process is accelerated.

INTRODUCTION

Bubbles in glass are a natural consequence of the melting process and the most frequent defects in glass products. The description of their behaviour faces the theoretical problems of multicomponent diffusion and simultaneous redox equilibria in a glassmelt as well as difficulties with measurement of necessary glass properties and parameters (gas diffusivities, solubilities and concentrations in glass, equilibrium constants of oxidation-reduction reactions, g.e.). The significance of the local equilibria of refining gases in glass melts was treated by several authors [1,2] and applied to bubble behaviour [3, 4]. This paper brings the construction of the model involving mass transport of CO_2, N_2, Ar, O_2, SO_2 and H_2O between bubbles and glass melt and taking into account the oxidation-reduction reactions of refining oxides or sulphates. Two important industrial glasses - glass for TV panels and float glass have been elected for presentation. The results showing the influence of the initial oxygen concentration on the bubble behaviour in the glass melt (redox state of glass) are aimed at the rate of the refining process and identification of some important bubble sources using bubble analyses.

THEORETICAL PART

The first aim of this work was to formulate the simple model of separation of single ascending bubbles in the static glass melt under isothermal conditions, involving the influence of oxidation - reduction reactions. The behaviour of multicomponent bubble may be described by a set of ordinary differential equations describing the size, partial pressure and vertical coordinate changes of the bubble [5]. The schematic set of equations for n present gases has the following form:

$$\frac{\mathrm{d}a}{\mathrm{d}\tau} = K_\mathrm{H} + K_\mathrm{D} \sum_{i=1}^{n} D_\mathrm{i}^\mathrm{m} (c_\mathrm{bi} - c_\mathrm{ii}),\ m=\text{konst.},\ i=1, 2, \dots, n \qquad (1)$$

$$\frac{\mathrm{d}p_\mathrm{i}}{\mathrm{d}\tau} = K_\mathrm{Pi} D_\mathrm{i}^\mathrm{m} (c_\mathrm{bi} - c_\mathrm{ii}) - \frac{3p_\mathrm{i}}{a}\frac{\mathrm{d}a}{\mathrm{d}\tau},\ i=1, 2, \dots, n-1 \qquad (2)$$

$$p_\mathrm{t} = p_\mathrm{a} + h\rho g + \frac{2\sigma}{a}, \qquad (3)$$

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = -\frac{2g\rho a^2}{9\eta}, \qquad (4)$$

where a is bubble radius, K_H is term including influence of the total pressure change in the bubble, K_D and K_pi include viscosity, temperature, total pressure of gases inside of bubble and molecular weight, D_i is diffusion coefficient of the i-th gas, c_bi is its bulk concentration in glass melt, c_ii is its surface concentration on the bubble boundary, p_i is partial pressure of the i-th gas inside of bubble, z is vertical coordinate of the bubble, ρ and η are glass density and viscosity, respectively.

The need of some material properties and constants follows from these equations, namely diffusion coefficients of gases in glass melt, their bulk concentrations in glass melt and concentrations on the bubble boundary.

For the physically soluble gases, the values of bulk concentrations, c_{bi}, in the melt should be measured by the gas chromatography analysis and surface concentrations on the bubble boundary, c_{ii}, should be obtained from Henry's Law:

$$p_i = H_i c_{ii} \;, \tag{5}$$

where H_i is the Henry's constant expressing gas solubility. The Henry's constant of a gas should be measured by equilibrating the appropriate gas and glass melt.

For chemically dissolved gases, the local equilibria between their physically dissolved form and the appropriate complex ions chemically bound in glass should be considered. For an individual multivalent element, Me, in a glass melt, the general redox equilibrium reaction can be written as:

$$\frac{4}{b}\ \mathrm{Me}^{(a+b)+}(l) + 2\mathrm{O}^{2-}(l) \rightleftharpoons \frac{4}{b}\ \mathrm{Me}^{a+}(l) + \mathrm{O}_2\,(l, g)\;, \tag{6}$$

where b is the number of electrons transferred in the redox reaction. When several oxidation-reduction reactions take place, oxygen is shared by all of them.

If the concentrations of gases and appropriate complex ions in glass melt are assumed very low, the activities in the expression for the equilibrium constant may be replaced by concentrations and the equilibrium constant of reaction (6) has the following form:

$$K_{\mathrm{Me,\,eq}} = \frac{c_{\mathrm{Me}^{a+}}^{4/b}\, c_{\mathrm{O}_2}}{c_{\mathrm{Me}^{(a+b)+}}^{4/b}}\;. \tag{7}$$

Therefore, the equilibrium constants of the appropriate chemical reactions have to be known for the calculation of local concentrations of gases chemically dissolved in glass. The knowledge of equilibrium constants (their temperature dependences) is sufficient to calculate the simultaneous chemical equilibria in glass melt at isothermal conditions, however, under real non-isothermal conditions, the distribution of oxidation-reduction species in flowing glass melt must be calculated.

The determination of concentrations of dissolved oxygen, eventually sulphur dioxide, in the melt is the first step of the isothermal calculation. Temperature T = 1473 K was elected as the standard value. For the initial values of the redox state of glass, ranging from 1.56 mol O_2 m^{-3} glass (saturation concentration) to 10^{-3} mol O_2 m^{-3} glass, the appropriate concentrations of remaining oxidation - reduction species were calculated using equation (7). The same procedure was applied to calculate the oxidation - reduction state at different temperatures. In the case of simultaneous sulphate and iron equilibrium, the equation (7) has the form:

$$K_{\mathrm{SO}_4^{2-}}(T) = \frac{(c_{o\mathrm{SO}_2} + 2x)\,(c_{o\mathrm{O}_2} + x + y)^{1/2}}{(c_{o\mathrm{SO}_4^{2-}} - 2x)} \tag{8}$$

$$K_{\mathrm{Fe}}(T) = \frac{(c_{o\mathrm{Fe}^{2+}} + 4y)^4\,(c_{o\mathrm{O}_2} + x + y)}{(c_{o\mathrm{Fe}^{3+}} - 4y)^4}\;, \tag{9}$$

where the concentrations at standard temperature are designated by the index *o*. The new equilibrium concentrations at temperature T are:

$$c_{\mathrm{SO}_2}(T) = c_{o\mathrm{SO}_2} + 2x;\; c_{\mathrm{O}_2}(T) = c_{o\mathrm{O}_2} + x + y;\; c_{\mathrm{SO}_4^{2-}}(T) = c_{o\mathrm{SO}_4^{2-}} - 2x;$$

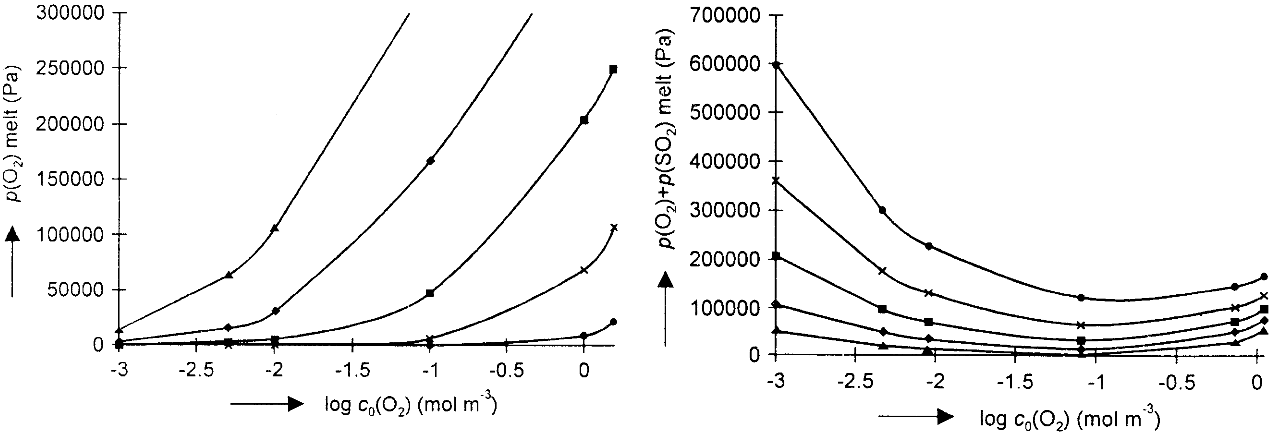
$$c_{\mathrm{Fe}^{2+}}(T) = c_{o\mathrm{Fe}^{2+}} + 4y;\; c_{\mathrm{Fe}^{3+}}(T) = c_{o\mathrm{Fe}^{3+}} - 4y\;.$$

The values of c_{SO_2} and c_{O_2} were used as the bulk concentrations c_{bi} in equations (1-2). For the calculations of internal partial pressures of refining gases in the glass melt, $p_{i\mathrm{melt}}$, equation (5) and results of solution of equations (8-9) were applied. The values of further necessary constants were taken from literature [6] or measured in the laboratory [7].

RESULTS OF CALCULATIONS

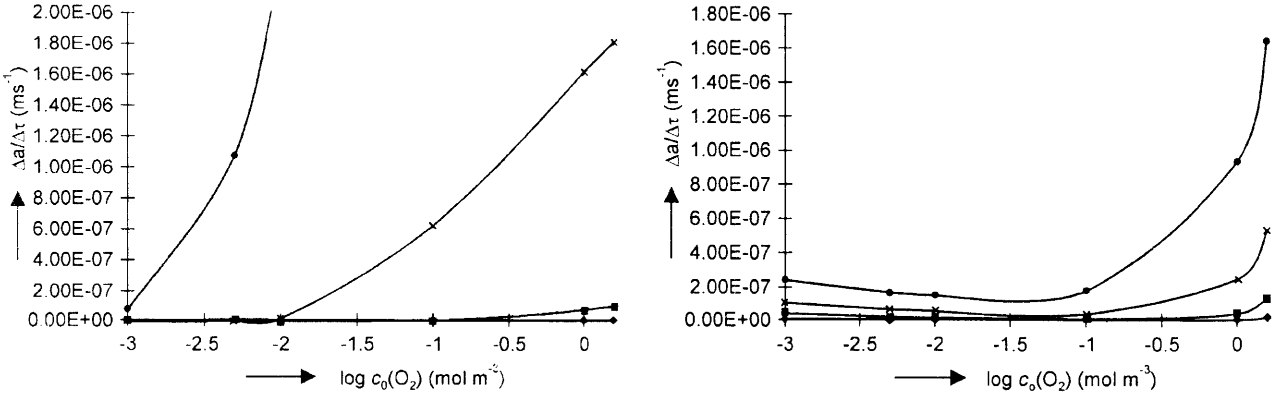
The calculations at isothermal conditions in the static glass melt were carried out. Initial bubble radius was 0.1 mm and bubble initial depth under glass level was always 0.1 m. The starting bubbles contained pure argon, CO_2 and air, respectively. The float glass and glass for TV panel production were used for calculations. The results of these calculations indicate the general behaviour of bubbles in glass melt at various initial concentrations of oxygen (initial redox state of glass).

The dependence of the internal partial pressures of refining gases on the initial redox state of glass is plotted in figures 1a, b. While the monotonous increase in $p_{\mathrm{O}_2\mathrm{melt}}$ with rising the initial redox characterizes the effect of the oxide refining agent (antimony oxides) in figure 1a, the corresponding dependences valid for the sulphate refining agent are more complicated. At higher values of the initial redox, the oxygen driving force is also dominating, however, the high internal partial pressures of SO_2 determine the mass transport into bubbles at very low values of the initial redox. This situation is reflected by the corresponding dependences of bubble growth rates and refining times on the initial redox state of glass. The rate of the refining process grows in the whole interval of increasing initial redox for the glass refined by antimony oxides, and exhibits extremes for the glass refined by sulphate (see figures 2 and 3).



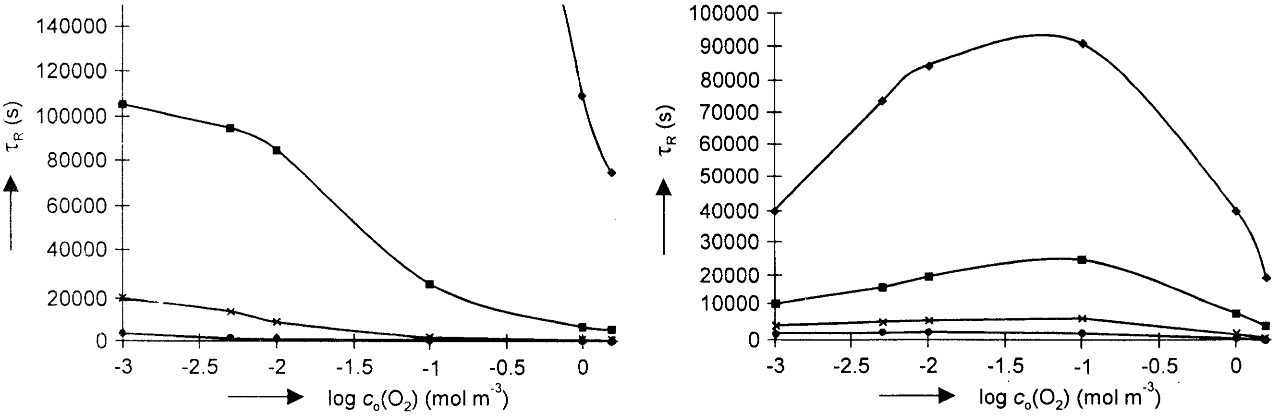
a) *b)*

Figure 1. The dependence of the internal partial pressures of refining gases, $p_{i\,melt}$, on the initial redox state of glass. Calculated from equations (5), (8) and (9).
a) $p_{O_2 melt}$, glass for TV panels; *b)* $p_{O_2 melt} + p_{SO_2 melt}$, float glass
▲ - 1100 °C, ♦ - 1200 °C, ■ - 1300 °C, X - 1400 °C, ● - 1500 °C



a) *b)*

Figure 2. The dependence of the bubble growth rate, $\Delta a/\Delta\tau$, on the initial redox state of glass. Calculated from equations (1-4).
a) glass for TV panels; *b)* float glass
▲ - 1100 °C, ♦ - 1200 °C, ■ - 1300 °C, X - 1400 °C, ● - 1500 °C



a) *b)*

Figure 3. The dependence between the time necessary the bubble of initial radius a_0 = 0.1 mm rised through the glass layer 0.1 m thick , τ_R, and the initial value of redox state of glass. Calculated from equations (1-4).
a) glass for TV panels; *b)* float glass
♦ - 1200 °C, ■ - 1300 °C, X - 1400 °C, ● - 1500 °C

DISCUSSION OF RESULTS

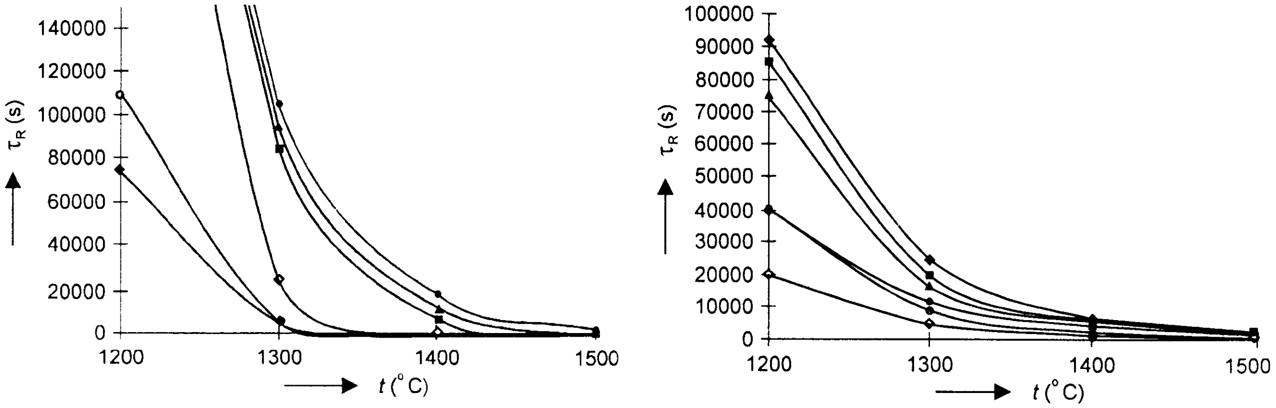
Two significant applications can be derived from the description of bubble behaviour at various levels of the redox state of glass: optimization of the refining process, and identification of bubble defect sources in glass melting furnaces, based on the bubble analysis in glass products. The relative impact of temperature on the rate of refining decreases with increasing value of the initial redox state of glass for both refining agents, so that the glass may be refined at lower temperature if the glass is saturated by the physically dissolved oxygen. The practical realization of this favourable state is however difficult. In glasses containing sulphates, the high concentration gradient exists for SO_2 diffusion into bubbles at very low values of the redox state of glass (high value of $p_{SO_2,melt}$). The similar acceleration of the refining process at relatively low temperatures can be therefore expected. However, the low values of diffusion coefficients of SO_2 at low temperatures prevent this acceleration. Temperature remains therefore the main factor of the refining process as is obvious from figures 4a, b.

The regions of glass supersaturation by refining gases can be found when calculating the internal partial pressures of refining gases in the appropriate glass melts. Thus, the potential for oxygen bubble nucleation can be expected in the glass refined by antimony oxides at the initial redox 1×10^{-2} mol O_2 m^{-3} and more at 1500 °C, and at the redox value 3.24×10^{-2} mol O_2 m^{-3} ($\log c_{O_2} = -1.49$) and more at 1400 °C (see figure 5a). When the glass is refined by sulphate, the SO_2 bubbles can be nucleated at very low values of the redox state of glass and O_2 bubbles at the very high ones, when p_{imelt} exceeds 100 kPa (see Fig. 5b). The SO_3 (SO_2+O_2) bubbles can be expected when $p_{O_2,melt} \rangle 33.3$ kPa and simultaneously, $p_{SO_2,melt} \rangle 66.6$ kPa. This mentioned case is also obvious from figure 5b. The SO_2 + O_2 bubbles, can be nucleated in the region of the initial redox between 0.17 and 0.66 mol O_2 m^{-3}.

The expensive analysis of bubble defects in glass products and their rather uniform results pose the question about the actual usability of bubble analysis when revealing the source of defect bubbles. The mathematical modelling of bubbles can contribute to this problem by some general qualitative conclusions. The most frequent gases found by bubble analysis, are CO_2, N_2, refining gas and Ar. The concentration ratios of CO_2/N_2 and N_2/Ar, as well as resulting bubble pressure, are often used for characterization of the most important groups of bubble sources, however, no general tendency could be unfortunately derived from the laboratory experiments. The CO_2/N_2 ratio has the initial zero value for bubbles coming from air sources, and shows its very high values for bubbles coming from glass batch or from other sources with initial high content of CO_2 (reduction). After elapsing sufficiently long time, the composition of all those mentioned bubbles reaches the stationary value being independent from the initial state, i.e. from the nature of bubble source. It is very interesting to know how this stationary value depends on the process parameters. Figures 6a, b present the calculated stationary values of the CO_2/N_2 concentration ratios in bubbles as a function of temperature and initial value of the redox state of glass. CO_2 generally diffuses with higher rate between bubbles and glass melt when compared with N_2 diffusion and consequently, the CO_2/N_2 stationary concentration ratio increases both with temperature and driving force of diffusion of refining gases into bubbles. As was already mentioned this driving force is dependent from the initial redox state of glass. To distinguish the bubble sources according to the actual CO_2/N_2 concentration ratio, the redox state of glass should be therefore taken into account. The development of the actual CO_2/N_2 ratios with time for both kinds of glasses and temperatures 1100 as well as 1300 °C, are obvious from figures 7a, b. Their identification ability (i.e. their different values) for both sources at 1100 °C is seen up to 20000 s and 30000 s, respectively. The N_2/Ar concentration ratio can serve as an auxiliary criterion to estimate the age of bubbles originally containing air. As Ar can be considered the non-diffusing gas, the value of N_2/Ar ratio, starting from about 87 (air), steadily grows with time in bubbles in glass melts. As in the previous case, the N_2/Ar ratio steeply grows with temperature; this fact is obvious from figure 8. The problem of N_2/Ar ratio application lies in the needed high accuracy of Ar analysis in bubbles. Using the CO_2/N_2 and N_2/Ar criterion, the sources of air bubbles in the glass melting space can be characterized as follows:

- air bubbles from high temperature regions: relatively high or almost stationary value (see figure 6a,b) of the CO_2/N_2 ratio, high value of N_2/Ar ratio (thousands)
- old air bubbles from the low temperature regions: the value of CO_2/N_2 close to the stationary value, low value of N_2/Ar ratio (100 - 200).
- relatively fresh air bubbles: low value of CO_2/N_2 ratio ($CN << CN_{stat}$), low value of N_2/Ar ratio ($NA \approx 80 - 100$).

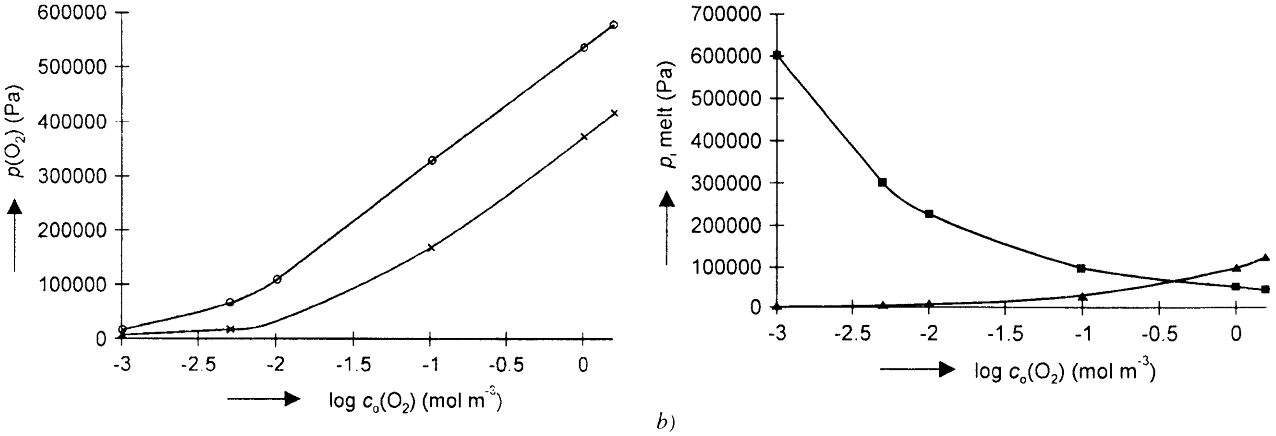
As is already obvious, the identification of a bubble source is feasible only when the actual CO_2/N_2 concentration ratio in analyzed bubbles differs from CN_{stat}. Figure 7 shows that the identification can be successful at low temperatures, however, the indication value of CN criterion fails for bubbles coming from high temperature regions (see 1300 °C in figure 7a, b). The resulting pressure in analysed bubbles can be expected between 25 - 30 kPa as a consequence of gas content contraction in bubbles „frozen“ in the solid cooled glass.



a)

b)

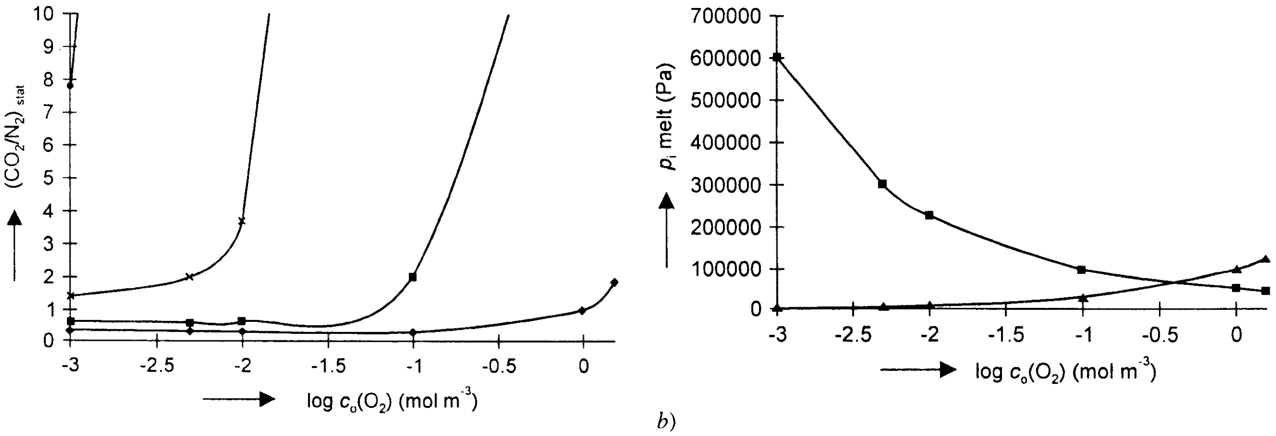
Figure 4. The temperature dependence of the time τ_R for different initial values of redox state of glass. Calculated from equations (1-4).
a) glass for TV panels; *b*) float glass
■ - 1.56 mol O_2 m^{-3}, ▲ - 1 mol O_2 m^{-3}, ● - 0.1 mol O_2 m^{-3}, * - 0.01 mol O_2 m^{-3}, ♦ - 0.005 mol O_2 m^{-3}, × - 0.001 mol O_2 m^{-3}



b)

a)

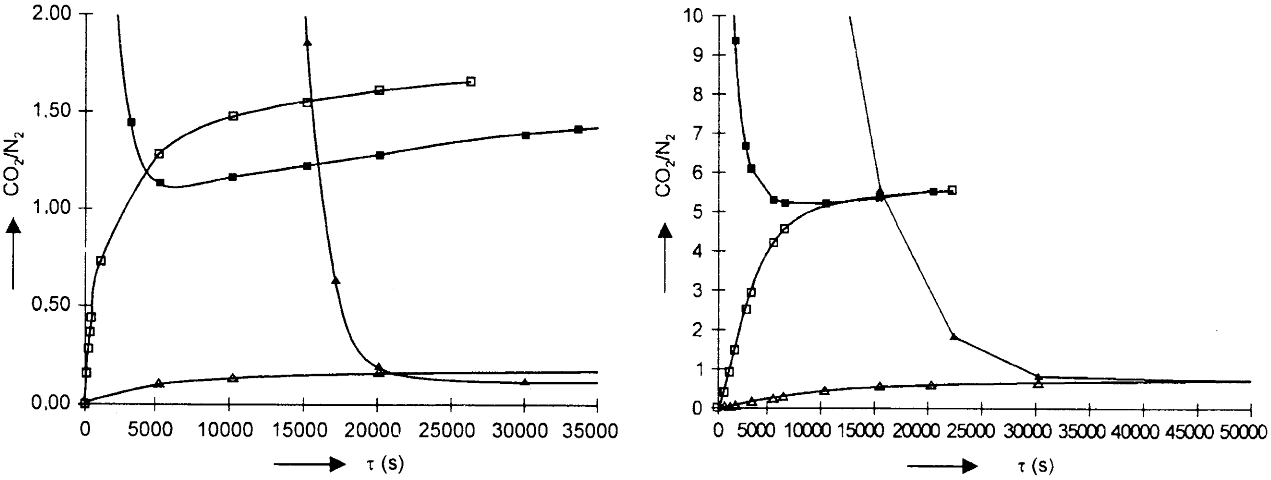
Figure 5. The dependence of $p_{O_2,melt}$ and $p_{SO_2,melt}$, respectively, on the initial value of redox state of glass. Calculated from equations (5), (8) and (9).
a) glass for TV panels, 1400 and 1500 °C; ○ - 1500 °C, × - 1400 °C
b) float glass, 1500 °C; ■ - p_{SO_2}, ▲ - p_{O_2}



b)

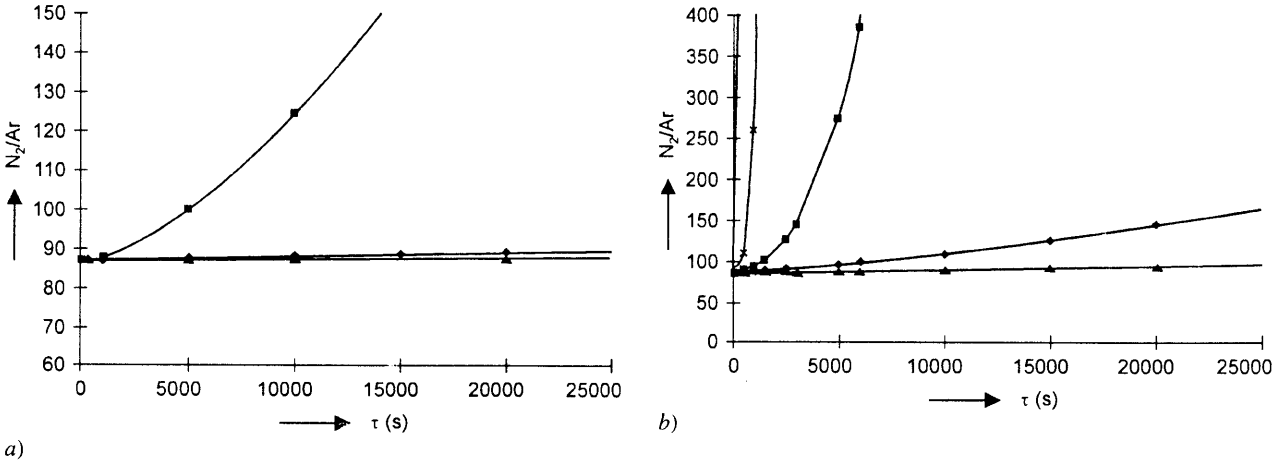
a)

Figure 6. The dependence of the stationary value of the CO_2/N_2 volume concentration ratio in bubbles, CN_{stat}, on the initial value of redox. Calculated from equations (1-4).
a) glass for TV panels; *b*) float glass
♦ - 1200 °C, ■ - 1300 °C, × - 1400 °C, ● - 1500 °C



a) *b)*

Figure 7. The time development of the actual value of CO_2/N_2 concentration ratio in bubbles initially containing air or CO_2, a_0 = 0.1 mm. Calculated from equations (1-4).
a) glass for TV panels, c_{0O_2} = 0.1 mol m^{-3}, 1100 and 1300 °C; *b)* float glass, c_{0O_2} = 0.01 mol m^{-3}, 1100 and 1300 °C
■ - 1300 °C (CO_2), □ - 1300 °C (air), ▲ - 1100 °C (CO_2), Δ - 1100 °C (air)



a) *b)*

Figure 8. The time development of the concentration ratio N_2/Ar in bubbles initially containing air, a_0= 0.1 mm. Calculated from equations (1-4).
a) glass for TV panels, c_{0O_2} = 0.1 mol m^{-3}; *b)* float glass, c_{0O_2} = 0.01 mol m^{-3}
▲ - 1100 °C, ♦ - 1200 °, ■ - 1300 °C, × - 1400 °C, ● - 1500 °C

The presence of SO_2 in outcoming bubbles, however, leads to its disproportionation in the transformation interval to the elementary sulphur and sulphate and therefore further pressure decrease in analysed bubbles can be expected [8]. As the amount of SO_2 in the bubble is proportional to the highest temperature the bubble passed, the bubble pressure is often used for the identification of source location in a glass melting space. Figure 9 presents the resulting pressures in bubbles calculated under the assumption that most of SO_2 and O_2 gas from the bubble had been absorbed by the glass melt to form sulphate, and the superfluous sulphur dioxide has succeedingly disproportionated. The mentioned expected temperature dependence of the resulting bubble pressure can be, however, found only at medium values of the redox state of glass.

CONCLUSION

Taking into account the redox state of glass melt shows to be significant for both glass refining and identification of bubble sources. As regards the significance of the redox state of glass for the refining process, its high value accelerates the glass refining, the driving force of oxygen diffusion into bubbles becoming high. The low redox values accelerate the SO_2 diffusion and therefore refining in glasses refined by sulphates. The favourable influence of both high and low redox values on gas transport is generally decreased by the low values of diffusion coefficients of refining gases at low temperatures. That is why the high temperature remains the dominant factor of refining.

Regarding the significance of the redox state of glass for the identification of bubble sources, it was found that the redox value considerably influences both the stationary concentrations of gases in bubbles and the resulting pressure inside of bubbles.

The present model still gives rather qualitative information, and its verification by laboratory experiments is intended in the near future. The extension of the model to the non-isothermal flowing glass will be presented in the next work.

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VÝZNAM OXIDAČNĚ-REDUKČNÍHO STAVU SKLOVINY PRO CHOVÁNÍ BUBLIN V IZOTERMNÍ SKLOVINĚ

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Účinek většiny čeřících přísad je založen na průběhu oxidačně - redukčních reakcí ve sklovinách. Počáteční oxidačně--redukční stav skloviny, jenž je možno charakterizovat koncentrací fyzikálně rozpuštěného kyslíku ve sklovině, proto podstatně ovlivňuje chování bublin. V této práci byl sledován vliv počátečního redox stavu skloviny na chování bublin v sodnovápenaté sklovině a ve sklovině pro výrobu televizních baněk. V prvním případě byl výsledný oxidačně - redukční stav dán simultánní rovnováhou $S^{6+} \rightleftarrows S^{4+}$ a $Fe^{3+} \rightleftarrows Fe^{2+}$, v druhém případě rovnováhou $Sb^{5+} \rightleftarrows Sb^{3+}$. Výsledky výpočtů chování bublin ukázaly, že vysoké hodnoty počáteční koncentrace kyslíku v obou sklovinách urychlují růst a odstraňování bublin, zatímco velmi nízké hodnoty urychlovaly proces u skloviny obsahující síranové ionty (růst koncentrace SO_2 ve sklovině). Konečné složení bublin, tj. zejména koncentrace CO_2, N_2, případně Ar jsou rovněž silně ovlivněny počátečním oxidačně - redukčním stavem skloviny. Tento fakt musí být brán v úvahu při identifikaci zdrojů bublin v tavicích prostorech na základě analýz bublin.