SOME CRITICAL POINTS OF THE GLASSMELTING PROCESS

PART II - BUBBLE REMOVING PHENOMENA

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Received 15. 5. 1995

Bubbles may be removed from a glassmelt by dissolution or by separation, however, the dissolution process may be completed only at higher pressures. The simple relations expressing the influence of temperature, pressure and glass composition on the bubble separation process have been presented to demonstrate their significance. These theoretical equations have been compared with available experimental data. The results have shown the primary importance of reduced pressure, temperature and optimum refining agent concentration. The critical points of refining process at proposed conditions are heterogenous bubble nucleation at reduced pressures, and composition changes by evaporation as well as corrosion of refractory materials at very high temperatures. The modelling of the refining process faces the theoretical problems with involvement chemical reactions of present gases and influence of precipitated layers on bubble boundaries into the model.

INTRODUCTION

In the first part of this work, the critical points of the dissolution process are examined using the simplified kinetic equations of sand dissolution in a glass melt [1]. The results have quantitatively shown the importance of temperature and especially glass stirring intensity on the rate of dissolution as well as arising problems with corrosion resistance of the refractory materials. with rapid heating of glass batch and with appropriate arrangement of glass currents in the glassmelting space. As both processes, dissolution and bubble removing, may control the entire glassmelting, the same examination procedure should be applied for the bubble removing, with the aim to find the contemporary critical points of the refining process.

Bubble removing phenomena

Bubbles can be separated from glass using their different density compared with glass and applying usually gravitational or centrifugal forces. In special cases, surface tension forces and ultrasound waves have been tested. Two fundamental processes are therefore at disposal for bubble removing:

a) bubble dissolution
b) bubble separation from glass

a) bubble dissolution

As is known, the remaining bubbles in a glass melt contain the mixture of gases being dissolved in a glassmelt and present in atmosphere. The condition of bubble dissolution is

$$\sum_{i=1}^{n} p_i > \sum_{i=1}^{n} p_{i\ \mathrm{melt}} \tag{1}$$

where p_i is the partial pressure at i-th gas inside of a bubble and $p_{i\ \mathrm{melt}}$ is its equilibrium partial pressure in the melt. Unfortunately, the multicomponent bubbles may reach equilibrium with the glassmelt under normal melting conditions. Especially when some non-diffusing gas is present, the sum of partial pressures of diffusing gases inside of a bubble decreases quickly to its equilibrium value and consequently the bubble dissolution stops. As growing temperature increases the sum $\sum_{i=1}^{n} p_{i\ \mathrm{melt}}$ and glass composition variations only slightly influence the solubility of physically dissolved gases, the only way to dissolve bubbles is application of relatively high pressures. In this case, especially the transport of slowly diffusing gases should be enhanced, however, the dissolution is slowed down by the increasing density of gas inside of a bubble at very high pressures. This is apparent from results of mathematical modelling of bubble dissolution in Figure 1. The industrial application

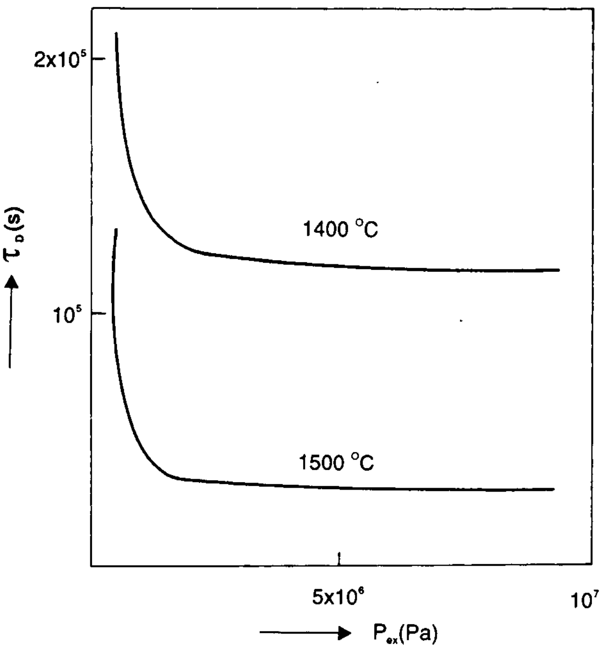

Figure 1. The dissolution time, τ_R, of $CO_2 + N_2$ bubbles in TV glass at elevated pressure (mathematical modelling) initial radius $a_0 = 5 \times 10^{-4}$ mm, $c_{CO2\,0} = 50$ %

of high pressures is nevertheless a technical problem as well as excluding the slowly diffusing gases (nitrogen) from the glassmelting process. As for high pressure attaining, the application of centrifugal refining seems to be also useful.

b) bubble removing by separation from glass

The rate of bubble separation from a glass melt is given by the bubble velocity relative to the glassmelt. This velocity is usually represented by the Stokes' formula if only gravitational forces control bubble separation and by the formula:

$$v_R = \frac{2\omega^2 R\rho a^2}{9\eta} \qquad (2)$$

if centrifugal forces are applied. Here ω is angular velocity, R is the radius of rotation, a is the bubble radius and ρ and η are density and viscosity of glassmelt, respectively.

Among influencing factors, especially the dependence of the relative bubble velocity on the square of its radius is important. However, as the application of centrifugal force enhances bubble dissolution, i.e. the diminishing bubble radius with time, the centrifugal refining is usually not advantageous for the separation process. The most applicable and reliable refining mecha-

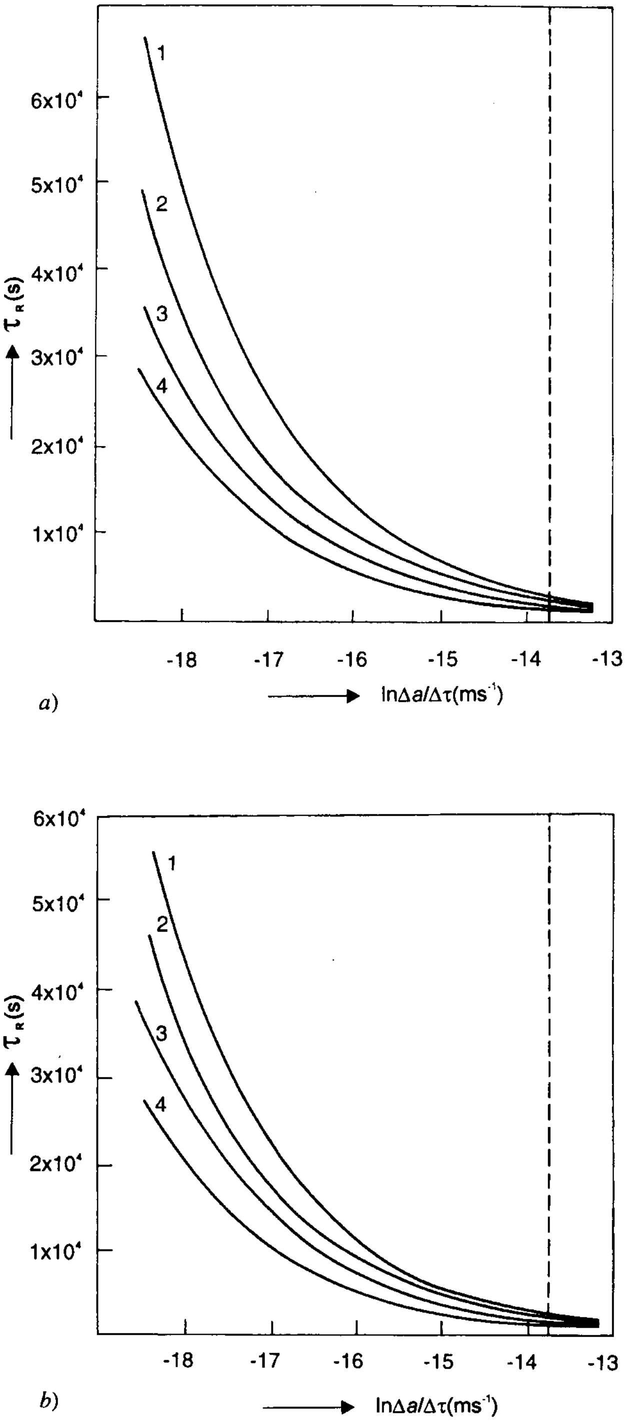

Figure 2. The dependence between the bubble refining time, τ_R, and bubble growth rate $\Delta a/\Delta\tau$

Float glass, $a_0 \leq 1 \times 10^{-4}$ m; The dotted line designates the limit of efficient refining ($\Delta a/\Delta\tau = 1 \times 10^{-6}$ m s^{-1})

a) At different values of glass viscosity, initial thickness of refined layer $h_0 = 0.25$ m

1 - 184 Pas (1200 °C), 2 - 65 Pas (1300 °C), 3 - 28 Pas (1400 °C), 4 - 13.5 Pas (1500 °C)

b) At different values of thickness of refined layer, $t = 1400$ °C

1 - 1 m, 2 - 0.5 m, 3 - 0.25 m, 4 - 0.1 m

nism applied up to this time is therefore accomplishing the bubble separation process by gravitational forces. Taking into account the Stokes' formula and geometrical conditions, the thickness of glass layer, glass viscosity, and the instantaneous bubble radius are three main factors determining the bubble separation process. The old experience with chemical refining and mathematical modelling of the refining process have however shown that only the bubble growth rate influences substantially the rate of effective refining. In Figures 2 and 3, respectively, there are dependencies between bubble refining times and mentioned factors - glass viscosity and thickness of glass layer - demonstrating the crucial significance of the bubble growth rate for the whole refining process.

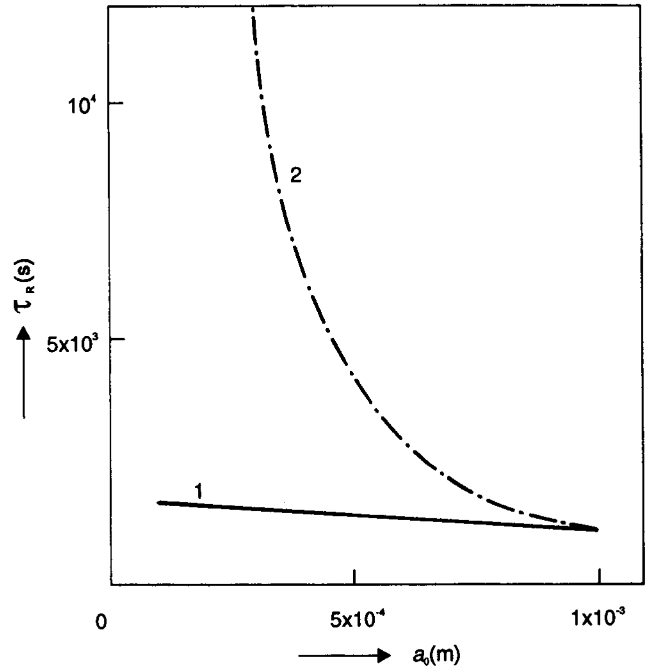

Figure 3. The dependence of the bubble refining time, τ_R, on the initial bubble radius, a_0. Float glass, t = 1400 °C, h_0 = 0.5 m
1 - $\Delta a/\Delta\tau = 1.2 \times 10^{-6}$ m s^{-1}, 2 - $\Delta a/\Delta\tau = 0$

As the bubble separation process under influence of gravitational forces and bubble growth is the most important variant of the refining process, the knowledge of influence of single parameters on this process is therefore important using simplified equations and experimental data.

Temperature influence

The simple equation of bubble growth at the presence of a refining agent and when taking into account the temperature dependencies of most important qualities, may be written as:

$$\frac{da}{dt} = K_R^T T \exp\left(-\frac{2a'}{3\beta T} - \frac{b'}{3\beta T} - \frac{c'}{\beta T}\right) \qquad (3)$$

Where a' and b' relate to the appropriate activation energies of the refining gas diffusion and viscosity, respectively, and c' to the enthalpy of reaction between refining gas and glass melt, β and K_R^T are constants. The subscripts in the constant K designate the controlling process (D - dissolution, R - refining), the superscripts the influencing factor (T - temperature, P - pressure, MaC - major components, MiC - minor components . . .). The appropriate equation for the refining time may be then written as:

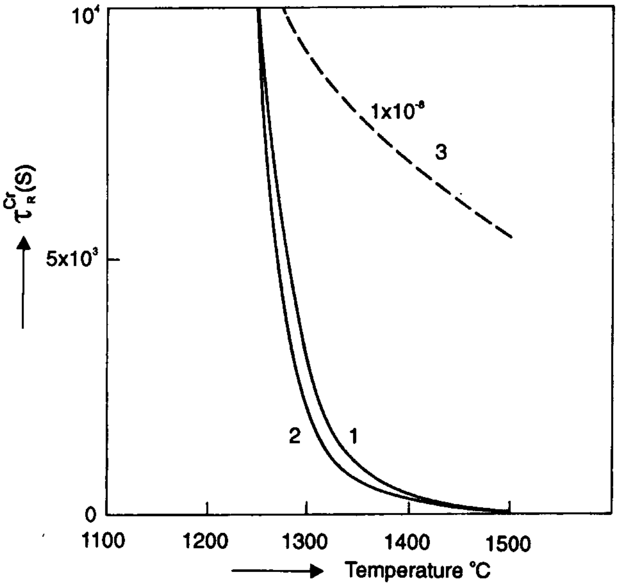

Figure 4. Temperature influence
The dependence of the refining time, τ_R, on temperature for the float glass refined by Na_2SO_4, h_0 = 1m, $a_0 = 5 \times 10^{-4}$ m
1 - the proposed Equation (4), 2 - the simplified equation using experimental data [8], 3 - $\Delta a/\Delta\tau = 1 \times 10^{-8}$ m s^{-1}

$$\tau_R = \frac{K_{R2}^T}{(\beta T)^{2/3}} \exp \frac{4a' + 5b' + 6c'}{9\beta T} \qquad (4)$$

where K_{R2}^T is independent from temperature. As the temperature dependence of the term with $T^{2/3}$ is not strong in the temperature interval of refining, the behaviour very similar to the sand dissolution may be expected. In Figure 4, the comparison of Equation (4) and refining times calculated using the experimental values of bubble growth rates show a good validity of the mentioned equation. At extremely high temperatures, the volatile components of glass may evaporate and diffuse into bubbles enhancing thus considerably the refining process (increasing the value of c'). At low temperatures or in the absence of refining agent, only viscosity represented by the constant b' in Equations (3, 4) is important, see curve 3 in Figure 4. In this case, the simple equation for the refining time may be accepted:

$$\tau_R = K_{R1}^T \exp\left(\frac{b'}{\beta T}\right) \tag{5}$$

K_{R1}^T is temperature independent constant.

Pressure influence

The presented discussion will be restricted to the effect of reduced pressure on gas diffusion leading to the accelerated bubble separation from a glassmelt. The instantaneous effect of the reduced pressure on the bubble growth being proportional to $p_{cx}^{-1/3}$ has not been taken into account. The main effect is characterized by a steady bubble growth due to the increased concentration gradient on bubble boundary and growing volume of the diffusing gas. If only refining gas is considered, the refining time can be expressed as:

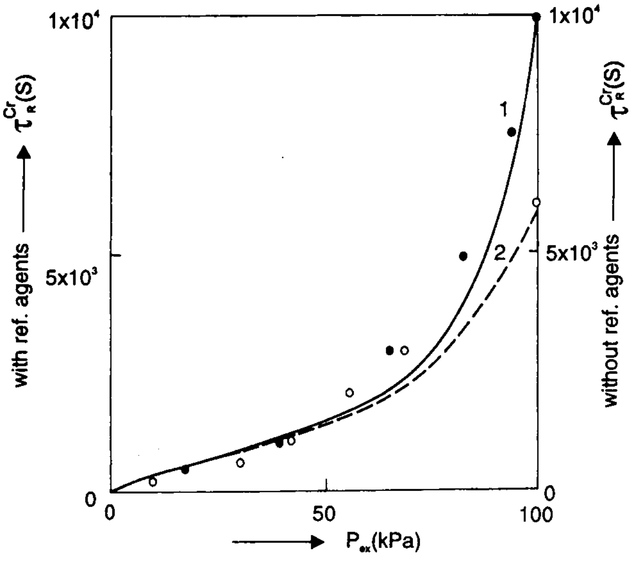

Figure 5. Pressure influence
The dependence of refining time, τ_R, on pressure for TV glass at 1400 °C, h_0 = 0.25 m, $a_0 = 1 \times 10^{-4}$ m
1 - with refining agent ——— Equation (6), • - calculated from exp. values; 2 - without refining agents – – – – theor. eq. in [1], ○ - calculated from exp. values

$$\tau_R = \frac{1}{(K_{R1}^P / p_{cx} - K_{R2}^P)^{2/3}} \tag{6}$$

Where p_{cx} is external pressure and both constants, K_{R1}^P and K_{R2}^P, are independent from pressure. The comparison of theoretical course of Equation (6) and refining times calculated using experimental values of bubble growth rate in TV glass shows an satisfactory agreement as may be seen from Figure 5. This effect is especially significant at slightly reduced pressures.

Influence of major components of glass

The glass basicity plays here an important role influencing the chemical equilibrium of refining agents in glass. In oxidized glasses, the decreasing basicity of glass causes an increase in efficiency of refining agents [3]. For the equilibrium of the sulphate ions in glass, e.q., is valid:

$$[SO_2][O_2]^{1/2} = \frac{K^{eq}\,[SO_4^{2-}]}{[O^{2-}]} \tag{7}$$

Here the quantities in brackets are activities, respectively concentrations of appropriate components in glassmelt and K^{eq} is equilibrium constant. As the refining efficiency grows with increasing concentrations of gases dissolved in the glassmelt, i.e. with $[SO_2]$ and $[O_2]$ values, the refining efficiency grows with decreasing basicity of glass expressed in Equation (7) as $[O^{2-}]$. Assuming proportionality between $[O^{2-}]$ and concentration of alkali oxides in glass, the diffusion of SO_3 instead of the mixture of SO_2 and O_2, the value of refining time is given by:

$$\tau_R = \frac{1}{\left(\frac{K_{R1}^{MaC}}{w_{R_2O}} - K_{R2}^{MaC}\right)} \tag{8}$$

Where w_{R_2O} is mass fraction of alkali oxides in glass and K_{R1}^{MaC} and K_{R2}^{MaC} are constants independent from the glass composition in the given composition interval. If there are no refining agents in glass, the refining time is influenced mostly by glass viscosity, and:

$$\tau_R = K_{R1}^{MaC} w_i - K_{R2}^{MaC} \tag{9}$$

Where w_i is the component of glass, mostly influencing its viscosity. As is obvious from Figures 6*a,b*, there is a good coincidence between theoretical and experimental data in the case without refining agents, however, only partial agreement between literary experimental data [3] and Equation (8) for the case involving refining agents.

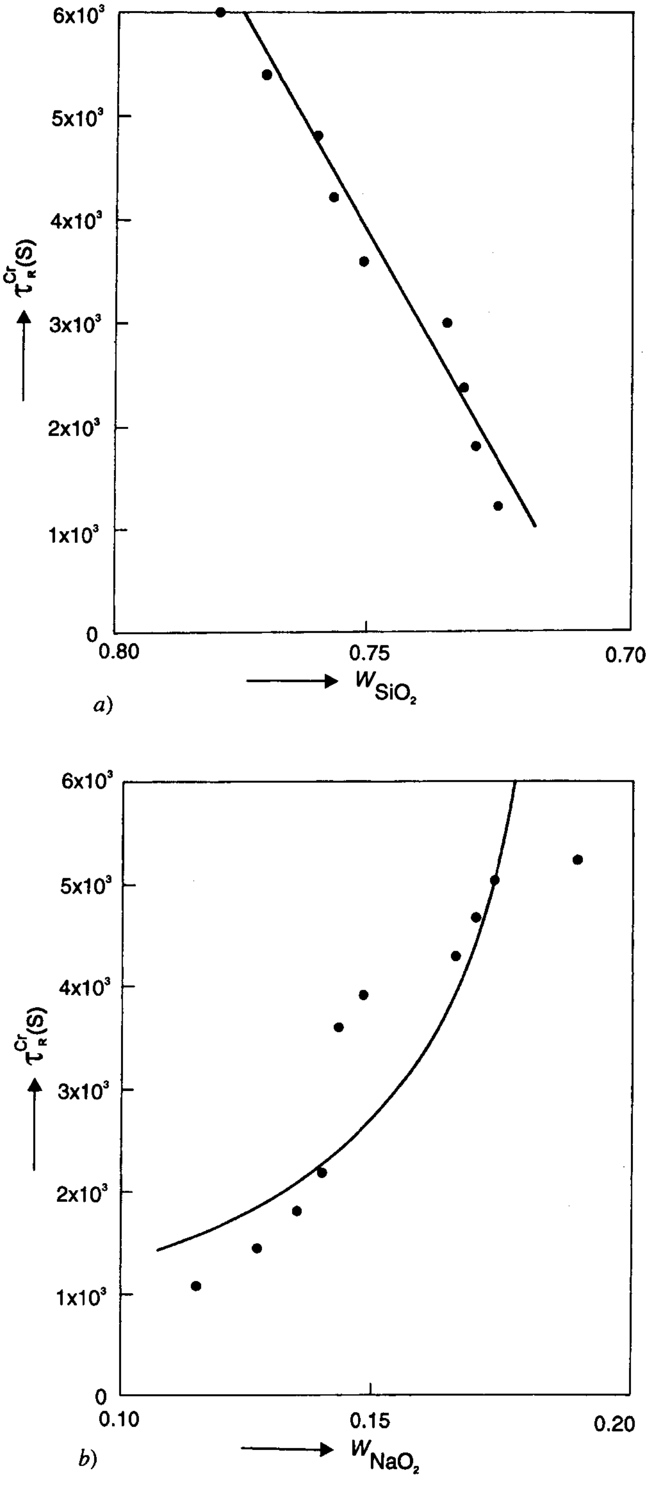

Figure 6. Influence of major components of glass
a) The dependence between the refining time,τ_R; and mass fraction of SiO_2, w_{SiO2}, in soda-lime glass (CaO = wt. 10 %), 1475 °C, without refining agents [3]; ——— Equation (9), • -exp. values
b) The dependence between the refining time, τ_R, and mass fracton of Na_2O,w_{SiO2}, in soda-lime glass (CaO = 10 wt. %), t = 1475 °C, 0.3 % SO_3 as refining agent [3]; ——— Equation (8), • - exp. values

Influence of minor components of glass

As is apparent from Equation (7), the product $[SO_2][O_2]^{1/2}$ is proportional to the concentration of sulphate ions, $[SO_4^{2-}]$, in a glassmelt. Assuming proportionality between the portion of refining agent added, w_R, and its concentration in the glass melt, $[SO_4^{2-}]$, the value of τ_R can roughly be expressed as follows:

$$\tau_R = \frac{1}{(K_{R1}^{MiC} w_R^{n'} - K_{R2}^{MiC})^{2/3}} \qquad (10)$$

Where K_{R1}^{MiC} and K_{R2}^{MiC} are independent from the refining agent concentration in the glassmelt. For the very low and extremely high concentrations of refining agents, Equation (10) is not valid. The good agreement between the proposed Equation (10) and calculated refining times using the experimental values of bubble growth rates is obvious from Figure 7.

The redox state of glass melt, i. e. the concentration of dissolved oxygen in glass seems to influence refining

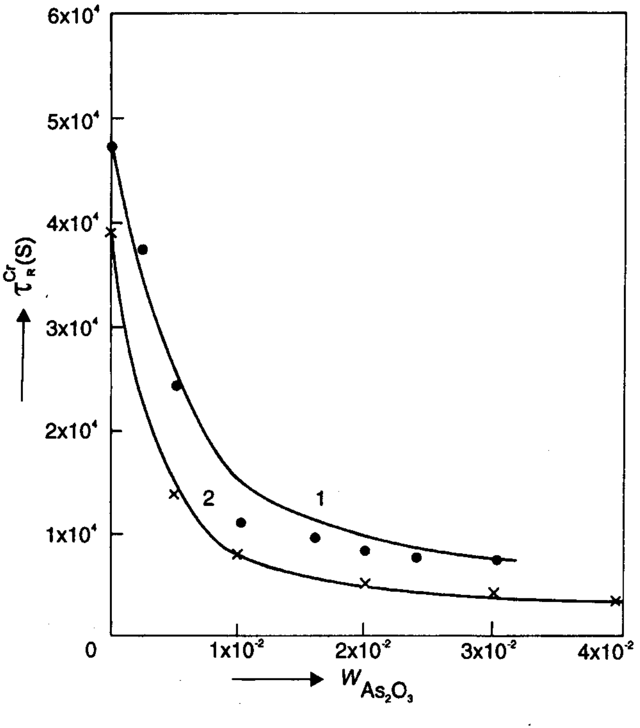

Figure 7. Influence of minor components of glass
The dependence between the refining time of the model glass (74 SiO_2, 16 Na_2O, 10 CaO, wt. %) and addition of As_2O_3 + $NaNO_3$
1 - 1400 °C, $a_0 = 5 \times 10^{-5}$ m, h_0 = 1 m; ——— Equation (10), • - from the exp. values
2 - 1450 °C, $a_0 = 5 \times 10^{-5}$ m, h_0 = 1 m; ——— Equation (10), × from the exp. values

ability in a similar way as the refining agent itself, i. e. Equation (10) may be proposed. The resulting concentration of oxygen in glass melt, however, is a complex function of initial melting conditions as well as presence of other oxidation - reduction pairs in the glassmelt. The predictions are therefore very approximate.

Influence of glass stirring

As bubbles are already moving in a glassmelt owing to gravitational, centrifugal or surface forces, the significance of glass convection for gas diffusion into bubbles seems to be restricted. The natural bubble movement in the gravitational or centrifugal field may be restrained by an intensive glass stirring. If the turbulent glass stirring is characterized by the average velocity value in vertical direction (gravitational field), $\pm\bar{v}_z$, and by the average time of force action in this direction, $\bar{\tau}_z$, then the most disadvantageous type of glass stirring is characterized by high values of $\bar{v}_z\bar{\tau}_z$ with relatively low values of $\bar{\tau}_z$. In this case, bubbles will be finally concentrated in the glass layer having thickness approximately $\bar{v}_z\bar{\tau}_z$ and being just under glass level. Only a small amount of these bubbles can be removed by bursting, owing to their low residence times on the glass level. Thus, the intensive glass stirring does not generally support refining and additional refining must be considered. When the less vigorous stirring is applied as is rotation with axis parallel to the throughput flow, e.g., the refining time seems to be only slightly influenced.

Summarization of bubble removing

As for the bubble dissolution process, the bubbles at normal melting conditions may reach equilibrium with glass; the high pressure seems to be therefore the best way to enhance the dissolution of gases slowly diffusing from bubbles. The technical problems with the instalment high external pressures or centrifugal forces in the industrial scale are the critical points of this process.

The bubble separation process is enhanced by the bubble growth. The gravitational forces are mostly applied as easily applicable when comparing with centrifugal ones. In addition, the centrifugal forces increase pressure in a glass melt and inhibit therefore the bubble growth. As is obvious from the previous text, the bubble growth is mostly supported by high temperatures, low pressures and by the presence of component having the high value of internal pressure of gas, $p_{\mathrm{i\,melt}}$, (refining agents, volatile components). The application of extreme temperatures causes the volatile components being currently present in glass (alkali oxides, B_2O_3) accelerate the bubble growth, however, the local composition changes of glass decreasing its homogeneity may be expected. When a low pressure is applicated, the refining process should be separated into a special refining space; bubble nucleation on the boundaries of such a space is the potential disadvantage of this refining procedure. The critical points of both mentioned possibilities are therefore technical problems with introducing low pressures into a separated space, the intensive bubble nucleation on boundaries or in glassmelt and potential deteriorating of glass quality by evaporation and corrosion.

According to the contemporary results and models, the classical refining process, applying current refining agents and temperatures, can be relatively fast when comparing with the dissolution of solid and liquid inhomogeneities. That is why the good knowledge and appropriate control of refining may be urgently needed. Especially important are the behaviour of secondary bubbles and the knowledge of conditions of their arising as well as other aspects of refining as is redox state of glass batch and glass melt and the presence of redox impurities. Thus, the complex knowledge of the refining process becomes the special critical point of the glassmelting process.

Redox state of glass

Oxygen plays an important role during the glassmelting process as its concentration and solubility in glass influences the bubble and foam behaviour as well as colour of glass. The present oxidation - reduction equilibria can be summarized in the following reactions:

$$SO_4^{2-}(l) \rightleftarrows SO_2(g,l) + 1/2O_2(g,l) + O^{2-} \tag{11}$$

$$C(s,l) + O_2(g,l) \rightarrow CO_2(g,l) \tag{12}$$

$$2S^{2-}(l) + 3O_2(g,l) \rightleftarrows 2SO_2(g,l) + 2O^{2-}(l) \tag{13}$$

$$4/b\ Me^{(a+b)+}(l) + 2O^{2-}(l) \rightleftarrows 4/b\ Me^{a+}(l) + O_2(g,l) \tag{14}$$

Reaction (12) is significant especially in the earlier stages of the glassmelting process enhancing the sulphate decomposition and thus influencing the glass convection, i.e. the dissolution process. The remaining carbon can influence the redox state of glassmelt during the later melting stages. If Me in reaction (14) is iron, the redox reactions (11), (13) and (14) determine the colour of glass as well as the refining process. The presence of oxide refining agents involves only reaction (14).

In a very simplified way, the dependence between the refining time and redox state of glass may be described by Equation (10) where the concentration of refining agent, w_R, is replaced by the concentration of dissolved oxygen, as already mentioned. Thus, the increasing oxygen concentration in glass enhances refining in the later stages of glassmelting process.

In the real glassmelting space, the resulting distribution of oxidation - reduction species is determined by their dynamical and chemical equilibria in any point of the glassmelting space, i.e.:

$$K_{SO_4^{2-}} = \frac{C_{SO_2} C_{O_2}^{1/2}}{C_{SO_4^{2-}}} \; ; \qquad K_C = \frac{C_{CO_2}}{C_C C_{O_2}} \qquad (15)$$

And:

$$D_i\left(\frac{\partial c_i^2}{\partial x^2} + \frac{\partial c_i^2}{\partial y^2} + \frac{\partial c_i^2}{\partial z^2}\right) + \frac{\partial}{\partial x}(v_x c_i) + \frac{\partial}{\partial y}(v_y c_i) + \frac{\partial}{\partial z}(v_z c_i) = 0 \qquad (16)$$

Where c_i is any component in Equations (11 - 14) and v_x, v_y and v_z are velocity components of the glassmelt. The obtained concentration fields of single oxidation - reduction components create the refining potential of the glassmelting space.

Reactions controlling bubble behaviour

As is already obvious from reactions (11 - 14), the mentioned oxidation - reduction equilibria influence considerably the behaviour of bubbles in glass melt. The concentration difference of diffusing components (O_2, SO_2, CO_2) in the bulk glass - being given by the resulting distribution of oxidation - reduction species in the glassmelting space - and on the bubble boundary is the driving force of bubble dissolution and namely bubble growth.

The complete description of bubble behaviour requires, however, the involvement of chemical reactions being consequence of interaction between glass melt and impurities. Among these reactions, especially these producing chemically reacting gases, as is CO and H_2, are important for the description of bubble behaviour. These secondary bubbles containing CO and H_2 undergo the changes evoked by the reactions of their gas content with the oxidation - reduction glass species present in glass. In the stage of CO and H_2 presence in bubbles, the following reactions can be expected:

$$2CO(g) + O_2(l) \rightarrow 2CO_2(g,l) \qquad (17)$$

$$2H_2(g) + O_2(l) \rightarrow 2H_2O(g,l) \qquad (18)$$

$$3CO(g) + SO_2(l) \rightarrow 2CO_2(g,l) + COS(g,l) \qquad (19)$$

$$3H_2(g) + SO_2(l) \rightarrow 2H_2O(g,l) + H_2S(g,l) \qquad (20)$$

$$4CO(g) + SO_4^{2-}(l) \rightarrow 3CO_2(g,l) + COS(g,l) + O^{2-}(l) \qquad (21)$$

$$4H_2(g) + SO_4^{2-}(l) \rightarrow 3H_2O(g,l) + H_2S(g,l) + O^{2-}(l) \qquad (22)$$

The significance of reactions should be proved experimentally, however, both COS and H_2S are currently found in bubbles by the mass spectrometry if components containing sulphur are present in glass. The subsequent reactions of COS and H_2S, respectively, must be taken into account:

$$2COS(g) + 3O_2(l) \rightarrow 2CO_2(g) + 2SO_2(g) \qquad (23)$$

$$2H_2S(g) + 3O_2(l) \rightarrow 2H_2O(g) + 2SO_2(g) \qquad (24)$$

$$COS(g) + 3SO_4^{2-}(l) \rightarrow CO_2(g) + 4SO_2(g) + 3O^{2-}(l) \qquad (25)$$

$$H_2S(g) + 3SO_4^{2-}(l) \rightarrow H_2O(g) + 4SO_2(g) + 3O^{2-}(l) \qquad (26)$$

The relatively complicated behaviour of bubbles containing reducing gases will be subjected to the experimental study.

Precipitation
of the sulphate layer
on the phase boundaries

This well known phenomenon determines the description of bubble behaviour in glasses containing sulphates at oxidation conditions. When the conditions inside of a bubble and in glass cause the product of partial pressures of SO_2 and $O_2^{1/2}$ in the bubble is greater than its saturation value, the sulphate layer is excluded on the bubble boundary.

The equilibrium constant of the sulphate layer may be written as:

$$K_{SO_4^{2-}} = [SO_2][O_2]^{1/2}[O^{2-}] \qquad (27)$$

where $[SO_2]$, $[O_2]$ and $[O^{2-}]$ are activities of appropriate components and $[SO_4^{2-}] = 1$;

The excluded sulphate layer may then be considered as the solution of SO_2, O_2 and Na_2O, respectively, in sulphate. The change of conditions leads to the diffusion of components through the layer and consequently, to the growth or dissolution of the bubble and layer. The very quick absorption of bubbles or gas volumes containing high partial pressures of SO_2 and O_2 may be therefore explained by the fast diffusion of Na_2O through the layer (see Figures 8a - b) [10]. The quantitative description of bubbles containing sulphate layer faces the problem of obtaining properties of the layer, especially diffusion coefficients and solubilities of penetrating components.

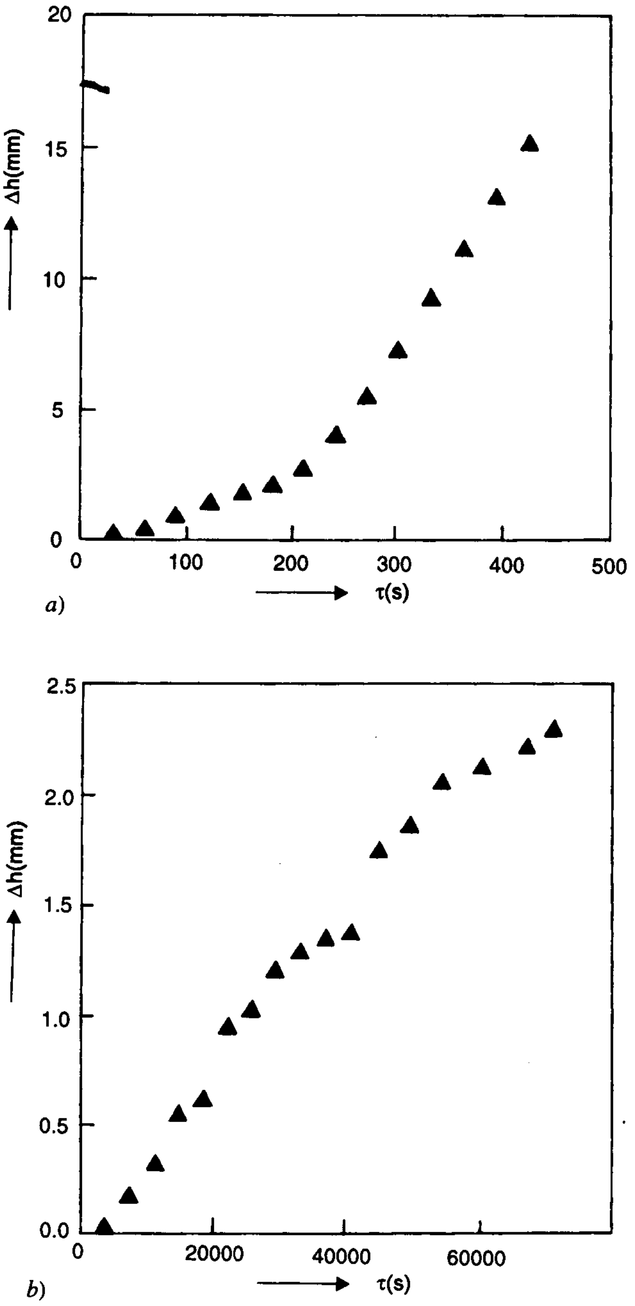

Figure 8. The shifting of the phase boundary gas - glass melt in the diffusion vessel as the consequence of gas absorption by the glassmelt Glass 74 SiO_2, 16 Na_2O, 10 CaO, wt. %, [10]
a) mixture of SO_2 (66.6 %) and O_2 (33.3 %), t = 1450 °C
b) SO_2, t = 1350 °C

Equations controlling bubble behaviour

The general equation describing mass transfer between single multicomponent bubble and glassmelt involves the bubble motion in the melt, the diffusion of single components between bubble and glass - being dependent on the actual bubble composition, gas concentrations and redox distribution - and the influence of appropriate chemical reactions. Thus, the general equation for the i-th diffusing component, c_i, may be given by:

$$\frac{\partial c_i}{\partial \tau} = D_i \Delta c_i + \mathrm{div}(v c_i) + P(\tau) \qquad (28)$$

where v is glass velocity and $P(\tau)$ expresses the source of i-th component by the chemical reaction.

When deriving the equations describing the bubble behaviour, the role of chemical reaction is usually neglected despite the fact that oxidation - reduction equilibria (Equations 11 - 14) and reactions of reducing gases (Equations 17 - 26) influence the mass transfer of the respective components. If no chemical reactions are assumed, the mass balance equation for the i-th diffusing component is given by:

$$\frac{d}{d\tau}(4/3\pi a^3 \rho_i') = 4\pi a^2 k_i (c_{ib} - c_{is}) \qquad (29)$$

where ρ_i' is partial density of i-th component in the bubble, c_{ib} and c_{is} are bulk and bubble surface concentrations of the i-th component in the glass, respectively, and k_i is its coefficient of mass transfer.

The value of coefficient of mass transfer, k_i, depend on whether or not the boundary motion is considered and on the value of Reynolds number. When the value of Re is low and the bubble behaves as a rigid sphere, the Stokes' law for bubble rising velocity is valid. The set of equations describing the bubble behaviour involves the equation for the change of bubble radius (involving the influence of hydrostatic pressure and surface tension) and equations for the changes of partial pressures of single gases inside of a bubble. In a simplified way, for n diffusing gases [4]:

$$\frac{da}{d\tau} = K_h + \frac{C}{p_t} \sum_{i=1}^{n} \frac{D_i^{2/3}}{M_i}(c_{ib} - c_{is}) \qquad (30)$$

$$\frac{dp_i}{d\tau} = \frac{3CD_i^{2/3}}{M_i a}(c_{ib} - c_{is}) - \frac{3p_i}{a}\frac{da}{d\tau} \qquad (31)$$

$i = 1, 2, \ldots, n - 1$

where K_h is the therm expressing the influence of hydrostatic pressure and surface tension, C is constant, M_i is molecular weight of the i-th component, p_t is total pressure and p_i is the partial pressure of i-th component inside of a bubble, respectively.

Considering the moving bubble surface, the Hadamard - Rybczynski law for bubble rising velocity is valid and its higher value results in larger mass transfer coefficients [5]. The experimental following bubble rising velocities and further studies have shown that both bubble rising laws can be valid [6, 7], and that Stokes' law is rather valid in longer refining times and for bigger bubbles. The comparisons between experimental observations of bubble growth and dissolution rates and theoretical equations also did not provide unambiguous results because of low accuracy of the diffusion coefficients and solubilities of gases applied in theoretical equations [8].

When a new phase is precipitated on the bubble surface (sulphate layer, g.e.) the additional equation describing the growth or dissolution of the layer must be taken into account as well as diffusion of gasses through it. An attempt to treat this problem theoretically has been presented in [9].

Summarizing the complex description of behaviour of multicomponent bubbles in glass melt, several critical points arise. From the theoretical point of view, the involvement of precipitated layer and especially considering the influence of chemical reactions on the mass transfer between bubble and glassmelt are needed. The last but not least critical points of this subjects are experimental methods for the verification of bubble behaviour (bubble size and composition development) and methods for the determination of concentrations and diffusion coefficients of gasses in glassmelts.

CONCLUSION

The considerable acceleration of the glassmelting process leads to the application of extreme conditions, especially extreme temperatures and intensive glass stirring. The application of extreme temperatures faces ecological problems with the glass component evaporation and troubles with the fast refractory corrosion. The expectable high pulls from these advanced furnaces demand introducing high amount of energy into the heated glass. The dispersion of the glass batch into the heating gas or in the glass phase accelerates considerably the heating, however, the economic and technical problems are always present. Thus, the application of extreme temperatures has the main critical points in the choice of the resistant refractory material and the rapid heating of the dispersed glass batch to the melting temperature.

The application of intensive glass stirring requires separation of the dissolution and refining process. The glass stirring arrangement in the glassmelting space may be set using results of the mathematical modelling of glass flow. The problems with rapid batch heating are here better soluble as the melting temperatures are not high. Nevertheless, the corrosion resistant refractory material and rapid heating of the glass batch remain the critical points of the dissolution process.

As for the refining process, the bubble separation using gravitational or centrifugal force is more hopeful in comparison with the bubble dissolution. The reduced pressure accelerates the bubble growth and therefore the refining process at lower temperatures and without current refining agents. The critical point of this refining arrangement is the bubble nucleation in the low pressure refining space. Applying proper conditions, the refining process may be also accelerated using classical refining agents, however, the perfect control of the refining process is necessary. The sufficiently true model of the refining process is the critical point of this approach. The most troublesome problems are joint with the involving influence of chemical reactions on the mass transfer between bubble and glass melt, and with obtaining sufficiently precise values of concentrations and diffusion coefficients of gases in glass.

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Submitted in English by the author

NĚKTERÉ KRITICKÉ STRÁNKY TAVICÍHO PROCESU SKEL

ČÁST II - PROCESY ODSTRAŇOVÁNÍ BUBLIN

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Bubliny lze ze skloviny odstranit rozpuštěním nebo separací účinkem vnějších sil. Proces rozpouštění je možno uskutečnit pouze za zvýšených tlaků, je však pomalý vzhledem k technologickým požadavkům. Vliv základních vnitřních faktorů jako je teplota, tlak a složení na separaci bublin účinkem gravitačních sil byl vyšetřen pomocí zjednodušených rovnic a jejich srovnáním s dostupnými experimentálními daty. Za nejdůležitější parametry lze považovat snížený tlak, teplotu a přítomnost optimálního množství čeřiv. Kritickými stránkami procesu je praktická aplikace sníženého tlaku v reálném tavicím prostoru, doprovázející nukleace bublin a snížení kvality skloviny odpařováním jakož i koroze rozhraní při aplikaci extrémních teplot. Efektivního odstranění bublin lze dosáhnout i za běžných podmínek aplikací přesných teoretických modelů. Kritickou stránkou aplikace modelů je jejich složitost a z ní vyplývající snížená věrnost.