MODELLING OF GLASS REFINING KINETICS
PART 1. SINGLE BUBBLES

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Submitted April 16, 2003; accepted August 28, 2003

Keywords: Glass melt, Refining, Single bubble, Model

The modelling of glass refining kinetics plays the most important role for the industrial melting efficiency and glass quality control. Among different mathematical models of the process, the simplified descriptions of bubble behaviour, based on experimental measurements, may be most acceptable for mentioned applications. This work presents two models of single bubbles in glass melts: the steady state complete model and the simplified model utilizing the experimental data as are bubble growth rates and bubble stationary compositions. The verification of the simplified model is mentioned. The results of chemical and combined refining are presented, based on experimental data for the simplified model.

INTRODUCTION

The process of removing bubbles coming from different sources in a glass-melting furnace is traditionally called refining. The primary refining involves removing bubbles from gases inside of the glass batch, mainly gases coming from decomposition and chemical reactions of batch raw materials during batch melting. The primary bubbles are polydisperse, the most frequent size being several tenths of millimetres, the entering glass melt usually contains 10^8 - 10^9 bubbles per cubic meter of melt. The secondary bubbles come from further bubble sources, which can be classified according to mechanism of bubble arising:

- nucleation of bubbles in melt due to gas super saturation
- bubble arising due to chemical reaction of impurities
- bubble arising due to electrochemical reactions
- producing mechanical bubbles (bubbles from mechanical manipulation with glass, bubbles from pores of refractory materials).

Among defined bubble sources, the primary source (batch decomposition) and bubble evolution from refractory materials are massive sources. When examining the refining process, the size distribution of bubbles from massive bubble sources must be taken into account, as well as the impact of bubble multitude on melt flow and melt properties. Consequently, the advanced refining model should incorporate the bubble intensity and other properties of bubble sources, single bubble kinetics, bubble distributions in the melting space and bubble impact on glass flow and other glass properties. In any case, the kinetics of single bubble behaviour is fundamental for description of the entire refining process. Not only complete models considering separately mass transfer of single gases between a bubble and melt but also simplified description, utilizing in particular laboratory kinetic data, are formulated and applied. In following paragraphs, two models of single bubble behaviour (according to needed experimental data) and two distribution bubble models will be presented, developed in the Laboratory of Inorganic Materials and Glass Service.

THEORETICAL

Fundamental equations governing the behaviour of a single bubble

Bubble is a small spherical gas object in a liquid. Bubble rises to the liquid level owing to buoyancy force and may react with the liquid both physically and chemically. The behavior of very small bubbles is also influenced by surface tension; the decrease in hydrostatic pressure, as well as temperature increase, cause growth of the bubble volume.

Bubbles in glass are gas objects at very high temperature, consequently ideal behaviour of gases may be accepted and universal gas equation is valid. Bubbles in glasses are almost always multi component as some gases come from the batch, namely CO_2, H_2O, N_2, O_2, NO_x, SO_2, from impurities as CO_2, CO, H_2, H_2S, COS, or from atmosphere. Usually five or six gases are considered as most common according to refining agent applied: CO_2, N_2, Ar, H_2O, O_2, (SO_2). The refining gas, currently O_2 or the mixture O_2 and SO_2 are most active as for their interchange between bubbles and melt, therefore these gases particularly influence the bubble kinetics.

When deriving equations governing the bubble behaviour in the melt, the Gay Lussac's equation creates the base for derivation. Thus, its form for the entire bubble is following:

$$p_t 4/3\pi a^3 = \sum_{i=1}^{n} \frac{m_i}{M_i} RT \tag{1}$$

And for one gas only:

$$p_i 4/3\pi a^3 = \frac{m_i}{M_i} RT \tag{2}$$

The total pressure, p_t, is given by:

$$p_t = p_{ex} + \rho g Z + \frac{2\delta}{a} = \sum_{i=1}^{n} p_i \tag{3}$$

Where a is the bubble radius, m_i is the mass of the *i-th* gas inside the bubble and M_i is its molecular mass, R is the universal gas constant, T is absolute temperature, p_i is the partial pressure of the *i-th* gas in the bubble, p_{ex} is external pressure, Z is the depth of the bubble under melt level and δ is surface tension of the melt. After derivation of equations (1) and (2) and the appropriate arrangement, the equations describing the bubble growth or dissolution, as well as its composition changes, have the form:

$$\frac{da}{d\tau} = \frac{2g^2\rho^2 a^3}{27\eta\,(p_{ex} + \rho g Z + 4\delta/3a)} + \frac{a\,(p_{ex} + \rho g Z + 2\delta/a)}{3T\,(p_{ex} + \rho g Z + 4\delta/3a)} \frac{dT}{d\tau} + \\ + \frac{RT}{(p_{ex} + \rho g Z + 4\delta/3a)} \sum_{i=1}^{n} \frac{1}{M_i} \frac{dm_i}{d\tau} \tag{4}$$

And:

$$\frac{dp_i}{d\tau} = \frac{3RT}{M_i a} \frac{dm_i}{d\tau} - \frac{3p_i}{a} \frac{da}{d\tau} + \frac{p_i}{T} \frac{dT}{d\tau} \tag{5}$$

Where m_i is the mass of the *i-th* gas transferred between melt and the bubble.

In equation (4), the Stokes′ relation for the bubble rising velocity was applied, here having the negative value with respect to the orientation of Z-axis:

$$\frac{dZ}{d\tau} = -\frac{2g\rho a^2}{9\eta} \tag{6}$$

where η is melt viscosity.

To derive the value of $dm_i/d\tau$, the Levich's derivation was applied, relating to the mass transfer of gas between liquid and bubble of pure gas rising to the level [1], i.e. the steady state solution of the diffusive-convective equation of gas transfer between rising bubble and melt with constant gas concentration was applied among different approaches to the problem [2]. The steady state solution assumes the instant development of gas concentration gradient around a bubble and its further independence on time.

The value of $dm_i/d\tau$ is then given by:

$$\frac{dm_i}{d\tau} = \frac{D_i}{2a} + \frac{0.382 D_i^{2/3} \rho^{1/3} g^{1/3}}{\eta^{1/3}} (m_{ib} - m_{ia}) \tag{7}$$

The term $D_i/2a$ may be neglected for bubbles greater than about 0.1 mm. Consequently, the set of equations describing behaviour of bigger bubbles (which is normally used) after substituting equation (7) into (4-5) and rearrangement has the form [2]:

$$\frac{da}{d\tau} = \frac{2g^2\rho^2 a^3}{27\eta\,(p_{ex} + \rho g Z + 4\delta/3a)} + \frac{a}{3T} \frac{p_{ex} + \rho g Z + 2\delta/a}{(p_{ex} + \rho g Z + 4\delta/3a)} \frac{dT}{d\tau} + \\ + \frac{0.382 g^{1/3} \rho^{1/3} RT}{\eta^{1/3}\,(p_{ex} + \rho g Z + 4\delta/3a)} \sum_{i=1}^{n} \frac{D_i^{2/3}}{M_i} (m_{ib} - m_{ia}) \tag{8}$$

$$\frac{dp_i}{d\tau} = \frac{1.145\, RT\, D_i^{2/3} g^{1/3} \rho^{1/3}}{M_i \eta^{1/3} a} (m_{ib} - m_{ia}) - \frac{3p_i}{a} \frac{da}{d\tau} + \frac{p_i}{T} \frac{dT}{d\tau} \tag{9}$$

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

Equations (3), (6) and (8-9) are numerically solved to get unknown time development of a, p_i and Z. If the sodium sulphate is used as refining agent, the sulphate layer on the bubble surface may precipitate and influence mass transfer [3,4].

The application of the bubble model needs proper values of particularly quantities characterizing gases, namely their diffusion coefficients, solubilities and bulk concentrations (taking into account also chemical solubility of some gases). The values are acquired by laboratory measurements using different laboratory methods, as is high temperature extraction of gases from the melt and their subsequent analysis by gas chromatography, different methods of gas diffusivity determination and the measurement of equilibrium constants of chemically dissolved gases in the melt [5].

The simpler method of bubble modelling offers for bubbles reaching the almost constant composition. Any multi component bubble in a liquid reaches the composition after a sufficiently long time, which is independent from the bubble initial composition and under given conditions depends only on concentrations of gases dissolved in the melt. Thus, if the gas distribution in the melt is uniform, all bubbles reach the same composition, almost independent from time. In industrial glass melts, the amount of gases dissolved in the melt is sufficiently high, so the following inequality is fulfilled over the melting temperature interval [6]:

$$\sum_{i=1}^{n} p_{i\,melt} \succ p_t \tag{10}$$

Where $p_{i\,\mathrm{melt}}$ is the equilibrium partial pressure of the *i-th* gas in the melt.

In the period of almost constant composition and under constant temperature, s.c. stationary state, the bubbles grow almost linearly, provided inequality (10) holds. The slight non-linearity is caused by the change of hydrostatic pressure. The developments of bubble compositions to the stationary value (determined by temperature, pressure, gas concentrations and their solubilities in the melt), valid for different initial bubble compositions, presents figure 1. The time necessary for a bubble to attain the stationary compositions increases linearly with bubble radius, increases exponentially with sinking temperature and decreases as the initial bubble composition approaches the stationary one. The high initial concentration of almost non-diffusing gas (N_2, Ar, e.g.) prolongates mostly the time to reach the stationary state.

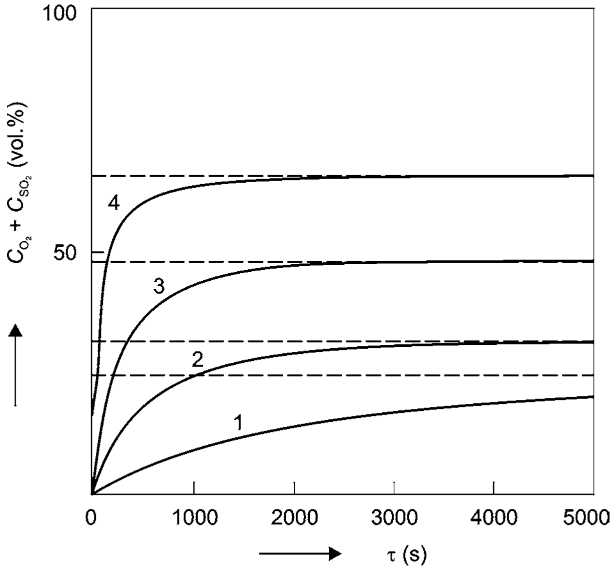

Figure 1. The time dependence of $SO_2 + O_2$ content in bubbles at constant temperature, obtained by mathematical modelling. Soda-lime-silica glass refined by 0.5 wt.% Na_2O as Na_2SO_4; $a_0 = 0.1$ mm, $Z_0 = 0.1$ m, $C_{0CO2} = 95$ vol.%, $C_{0N2} = 5$ vol.%, $c_{0O2} = 0.05$ mol m^{-3}; 1 - 1200°C, 2 - 1300°C, 3 - 1400°C, 4 - 1500°C.

As the behaviour of stationary bubbles is very simple (almost linear growth at constant temperature and pressure) and equivalent for all bubbles, the idea offers to replace the modelling of actual bubbles by stationary ones. The only necessary value, i.e. the bubble growth rate under stationary conditions, is measurable relatively easily by using the high temperature video recording of bubbles. At constant temperature and atmospheric pressure, equation (8) may be therefore replaced by:

$$\left(\frac{da}{d\tau}\right)_D = \Delta a/\Delta\tau \tag{11}$$

Where $(da/d\tau)_D$ is the bubble growth rate of stationary bubbles, measured in laboratory.

Equation (9) for partial pressures falls away, as all bubbles have the same stationary composition, constant with time.

Under non-isothermal conditions, however, the composition of bubbles changes, which fact brings about also changes of bubble sizes. Among present gases, especially chemically dissolved gases with their steep temperature dependence of solubility in the melt exhibit this effect. The refining gas fulfills the role of such gas in industrial glasses. In a simplified case, all present gases may be classified into two groups: refining gas, whose concentration substantially changes with temperature and other present gases, whose amount in bubbles is considered constant as temperature varies. Taking into account this assumption, the change of bubble size due to temperature variations (accompanied by the change of concentration of refining gas in the bubble) is given by [6]:

$$\left(\frac{da}{d\tau}\right)_T = \frac{a}{300-3C}\frac{dC}{d\tau} \tag{12}$$

Where C is the stationary concentration of the refining gas in the bubble in volume percents.

Under non-isothermal conditions of bubble moving through the melting space, we have for $dC/d\tau$:

$$\frac{dC}{d\tau} = \frac{dC}{dT}\left[\frac{\partial T}{\partial x}v_x + \frac{\partial T}{\partial y}v_y + \frac{\partial T}{\partial z}\left(v_z - \frac{2g\rho a^2}{9\eta}\right)\right] \tag{13}$$

Where v_x, v_y, v_z are the velocity components of melt flowing.

The value of dC/dT may be obtained from the experimentally measured dependence $C = C(T)$. The high temperature video-recording of shrinking bubbles under conditions of dropping temperature is used to get $C = C(T)$. Notice that $(da/d\tau)_T$ is negative when decreasing temperature.

For the behaviour of stationary bubbles at constant glass composition and pressure, the additives of both contributions to the change of bubble size is assumed, therefore:

$$\frac{da}{d\tau} = \left(\frac{da}{d\tau}\right)_D + \frac{a}{300-3C}\frac{dC}{d\tau} \tag{14}$$

The application of equation (14) in the real melting space needs corrections of the bubble volume when going from experimental conditions of $da/d\tau$ and $C = C(T)$ measurements to real conditions in the melting space. If the experimental values were measured at external pressure p'_{ex}, the average depth of the bubble under glass level $\bar{Z}$ and average bubble radius during measurement was $\bar{a}$, these conditions and values should be considered in appropriate equations.

The appropriate equation for $da/d\tau$ has then the form:

$$\frac{da}{d\tau}=\frac{2g^2\rho^2a^3}{27\eta(p_{ex}+\rho gZ+4\delta/3a)}+\frac{a\ p_{ex}+\rho g\overline{Z}+2\delta/\overline{a}}{3T(p_{ex}+\rho gZ+4\delta/3a)}\frac{dT}{d\tau}+ \\ +\frac{(p_{ex}+\rho g\overline{Z}+2\delta/\overline{a})}{(p_{ex}+\rho gZ+4\delta/3a)}\left[\left(\frac{da}{d\tau}\right)_D+\frac{a}{300-3C}\frac{dC}{d\tau}\right] \tag{15}$$

It is recommendable to measure the values of $(da/d\tau)_D$ and $C = C(T)$ in laboratory under the same external pressure as is characteristic for the model, i.e. $p'_{ex} = p_{ex}$, as external pressure influences also the diffusion transport between bubble and melt. The values of members $\rho g\overline{Z}$ and $2\delta/\overline{a}$ are negligible compared to p_{ex}, especially when $p_{ex} = p_a$. Equation (15) has then the form usable for modelling melting spaces working under atmospheric pressure:

$$\frac{da}{d\tau}=\frac{2g^2\rho^2a^3}{27\eta(p_a+\rho gZ+4\delta/3a)}+\frac{ap_a}{3T(p_a+\rho gZ+4\delta/3a)}\frac{dT}{d\tau}+ \\ +\frac{p_a}{p_a+\rho gZ+4\delta/3a}\left[\left(\frac{da}{d\tau}\right)_D+\frac{a}{300-3C}\frac{dC}{d\tau}\right] \tag{16}$$

To get the bubble radius development and its rising in the melting space, equations (6), (13) and (16) are numerically solved.

The application of simplified equations (14) and (16) introduces inaccuracy into bubble modelling. The simplified model neglects the initial non stationary period of bubble behaviour, thus a bubble having initially low concentration of the preferentially transferred gas grows faster than the simplified model indicates while bubbles with high concentration of this gas initially dissolves and subsequently grows. At varying temperature, the real bubble exhibits greater inertia in growing or dissolution due to bubble composition changes compared to bubble behaviour according to simplified model. The verification of the simplified model is therefore always necessary. The results of recent verification have shown [7] that the impact of varying temperature during the melting process may be neglected but problems may arise when neglecting the initial non stationary period. The less accurate results are obtained for bubbles having initial composition distinctly different from the stationary one and simulated at lower temperatures. The mentioned case, however, is not frequent in technological practice. A typical example of bubble simulation according to both bubble models is plotted in figure 2.

RESULTS AND DISCUSSION

Chemical refining

Chemical refining applies minor chemical components increasing the melt saturation by gases under proper conditions. Among potential refining agents, additions of sulphates, sulphates with reducing agent, antimony and arsenic oxides with oxidants and chlorides are most frequent. Besides chemical influence of refining agents, the initial oxidation - reduction state of the batch material, as well as the contents of major batch components (determining the basicity of glass) play role in the refining process.

The chemical effect of refining agents is reflected by the high value of m_{ib} (in equation (8) bulk concentration of the refining gas in the melt), increasing substantially at high refining temperatures. The refining effi-

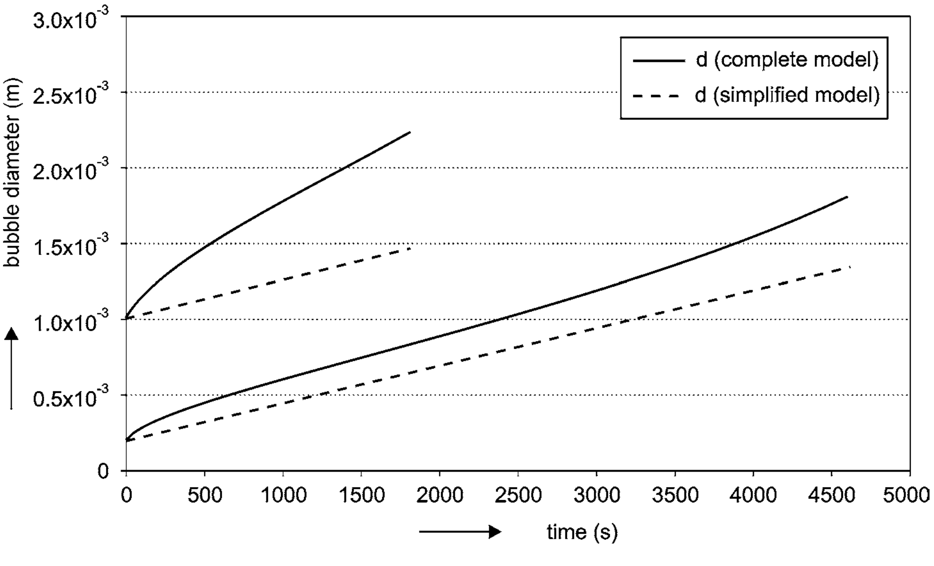

Figure 2. The behaviour of s.c. melting bubbles containing initially 95 vol.% CO_2 and 5 vol.% N_2 in TV glass melt at 1400°C. Initial bubble diameters 2×10^{-4} m and 1×10^{-3} m.

ciency of the melt substantially improves with increasing concentration of the refining agent, this dependence having approximately hyperbolical shape as is obvious from figure 3. The refining effect of mentioned agents is approximately exponentially dependent from temperature. This fact results especially from the exponential dependence of the diffusion coefficient of the refining gas, refining ion stability and glass viscosity on temperature. Figure 4 presents the almost linear dependence between natural logarithm of refining times of a quiescent glass layer and reciprocal value of temperature.

The impact of initial redox is significant especially for glasses refined by the combination of sulphate and reducing agent (mostly carbon). The proper carbon additions support the melt convection during batch reactions and set up the low redox value of glass, beneficial for rapid refining.

Figure 5 shows that the potential equilibrium concentration in the melt steeply grows with initial additions of carbon. The glass super saturation by sulphur dioxide increases the glass refining ability, as the internal partial pressure of SO_2 in the melt is proportional to

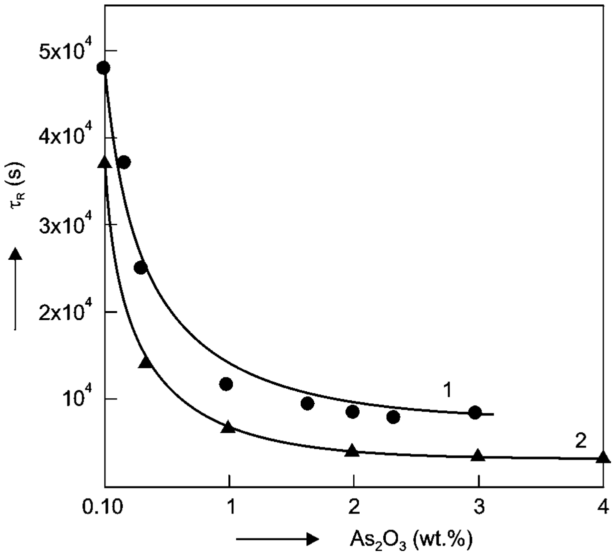

Figure 3. The dependence between refining time of a quiescent glass layer (τ_R) and concentration of the refining agent in the soda-lime-silica glass, refined by As_2O_3 + $NaNO_3$. The values of τ_R were obtained from bubble growth rates, measured experimentally; $a_0 = 5 \times 10^{-5}$ m; $Z_0 = 1$ m. 1 - 1400°C, 2 - 1450°C, — theoretical equation.

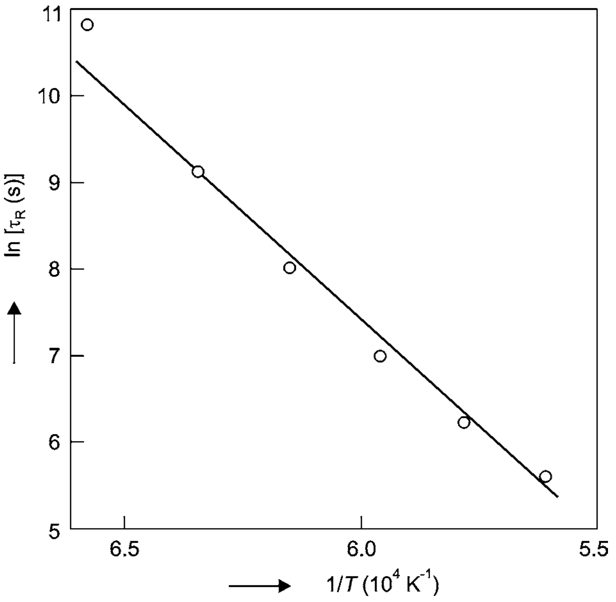

Figure 4. The experimentally obtained temperature dependence of refining times of a quiescent glass layer, float glass; $a_0 = 0.5$ mm, $Z_0 = 1$ m, $C_{0CO_2} = 83$ vol.%, $C_{0SO_3} = 17$ vol.%.

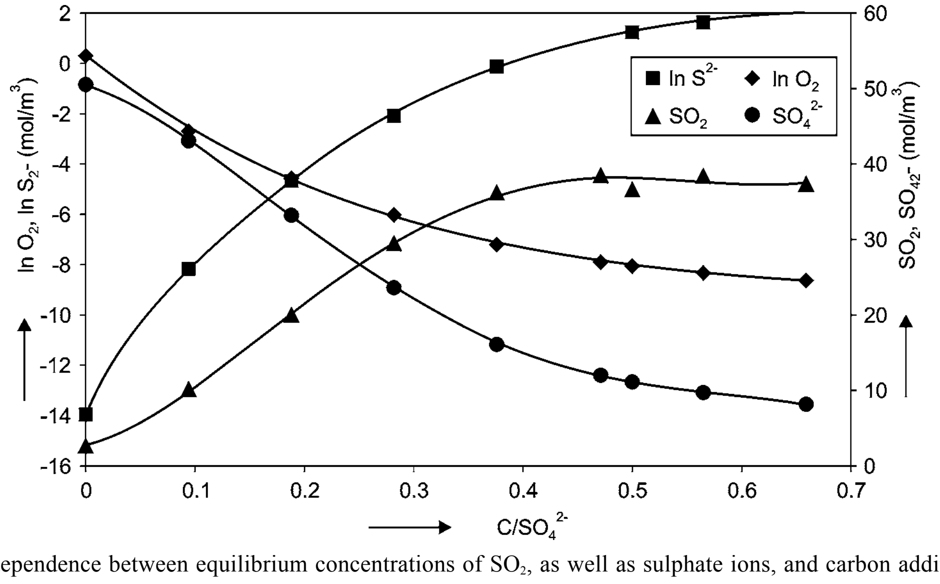

Figure 5. The dependence between equilibrium concentrations of SO_2, as well as sulphate ions, and carbon additions in the container glass.

the value m_{ib} in equation (9). In fact, however, most of SO_2 is removed from the melt by bubble nucleation, growth and rising, as well as by melt foaming during early stages of melting. The melt stirring by SO_2 and CO_2 accelerates particle dissolution and removes chemical inhomogeneities. At higher additions of carbon, the concentration of remaining sulphate may be too low to ensure efficient refining at subsequent higher temperatures.

The growing basicity of glass increases the refining ion stability in the melt. Thus, less refining gas is evolved under given conditions and refining is less intensive. The literary data of Lyle [8] demonstrate this fact in figure 6. In both mentioned cases, the value of m_{ib} of the refining gas in equation (8) is influenced.

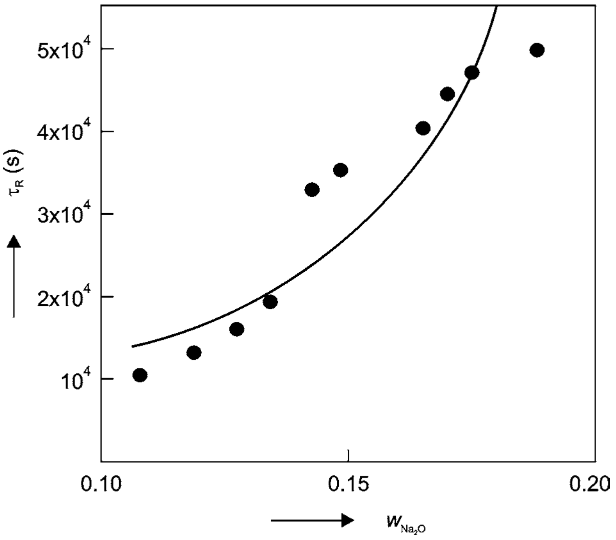

Figure 6. The experimentally obtained dependence between refining times of a quiescent glass layer and Na_2O content in the soda-lime-silica glass refined by sodium sulphate, temperature 1475°C. ● - experimental values [8], — simplified theoretical equation.

Physical and combined refining

Generally, the refining process by bubble separation from the melt (usually bubble rising) is controlled by temperature, pressure, melt composition and external force (bubble separation). The effect of glass composition was mentioned in previous paragraph; the temperature effect is bound above all with chemical refining and therefore was treated in that paragraph. The range of physical refining involves then the impact of pressure and other external force.

The centrifugal force may accelerate the bubble separation by their rapid wandering to the rotation axis of the melt volume. However, the effect of centrifugal force is followed by pressure increase in the melt and reduced by subsequent partial bubble contraction. In addition, the technical realization of continuous centrifugal refining is difficult and therefore not recommendable.

Pressure may support both bubble dissolving and growth according to conditions. Increasing pressure supports bubble dissolution by increasing the value of m_{ia} in equation (8). But the low mobility of some present gases (N_2, Ar) prevents the technological application owing to demanded high pressures and resulting long dissolution times of bubbles. Sinking pressure decreases the value of m_{ia} in equation (8) for all gases, thus enhancing the gas diffusion into bubbles. The volume of diffusing gases and consequently, the bubble volume, grows as p_{ex} in equation (8) decreases due to gas expansion. Figure 7 presents the approximately hyperbolical dependence between refining times of a layer of quiescent TV glass melt and external pressure showing that the pressure reduction is promising for efficient refining. The substantial refining acceleration by pressure reduction gives a chance to decrease the refining temperature, refining agent concentration in the batch or both. This may have a beneficial effect on energy consumption of refining or on process ecology (evaporation of ref. agents).

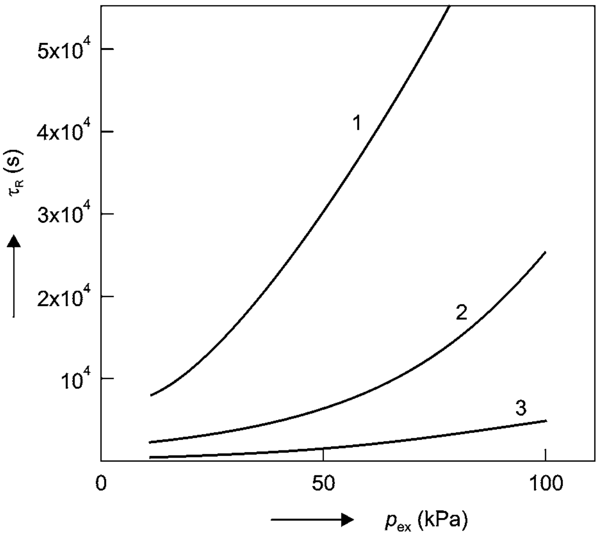

Figure 7. The dependence between refining time of a quiescent glass layer (τ_R) and pressure in the soda-lime-silica glass refined by sodium sulphate. The values of τ_R were calculated by using bubble growth rates measured experimentally; soda-lime-silica glass refined by sulphate, a_0 = 0.1 mm, Z_0 = 1 m. 1 - 1200°C, 2 - 1300 °C, 3 - 1400°C.

The attained results offer an idea of combination of chemical and physical refining (temperature, pressure concentration of refining agent) to reach the optimum state for given glass and melting facility. Thus, the optimum state of the refining process would be characterized by mentioned three values: temperature, pressure and refining agent concentration. The criterion of good refining parameters involves not only rapid bubble removing but also disturbing processes as is foaming at lower temperatures and pressures, and bubble nucleation from a supersaturated melt. Figure 8 presents areas of proper temperatures and pressures to insure rapid refining and prevent stable foam or bubble nucleation in a glass with and without refining agent, obtained by laboratory experiments [6].

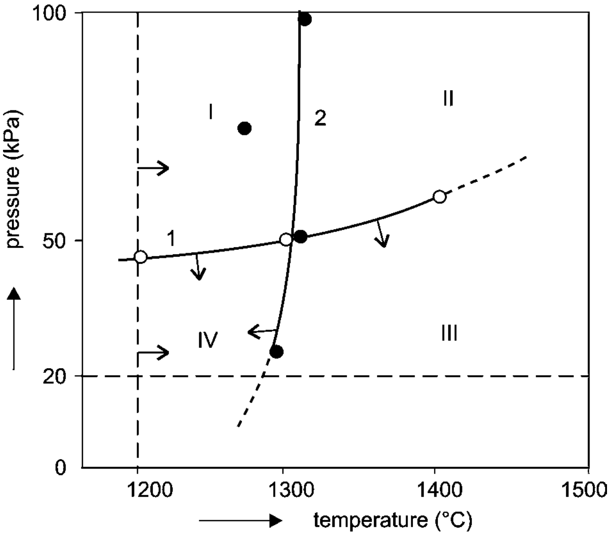

Figure 8. Definition of the temperature - pressure area, applicable to the refining of the lead silica glass melt containing refining agent; ---- - the temperature of the stable foam on the glass level, ○ - the curve defining the bubble growth rate $da/d\tau = 10^{-6}$ m/s, ● - the curve defining the bubble nucleation temperature, IV - the area of high refining rate without foam and bubble nucleation.

CONCLUSION

Models of single particles in glass melts form the base for the physico-chemical modelling of the glass melting process. The models of bubble behaviour are complex by their nature and difficult for adequate mathematical description. In addition, they need a lot of experimental data; particularly gas data in glass melts are hardly obtainable, the value acquired by different methods have limited accuracy. That is why simplified models coming from direct observations of bubble behaviour in melts are also applied. A verification process should nevertheless confirm their reliability. The application of simplified models plays its irreplaceable role when formulating the particle distribution models as will be presented in the following part of this work.

Acknowledgement

This work was supplied with the subvention by the Grant Agency of ASCR, Project No. S4032103 and by Schott Glass, Mainz, Germany.

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MODELOVÁNÍ KINETIKY BUBLIN V TAVICÍM PROCESU SKEL
ČÁST 1. JEDNOTLIVÉ BUBLINY

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Řízení kvality průmyslově vyráběných skel vyžaduje používání příslušných matematických modelů popisujících chování defektů v reálných podmínkách. Mezi různými matematickými modelu chování bublin se jako nejvhodnější pro tento účel hodí zjednodušený model založený na laboratorním sledování defektů typu bublin. Tato práce prezentuje podrobněji dva používané modely jednotlivých bublin: tzv. kompletní model popisující vývoj složení a rozměrů bublin s časem a zjednodušený model, popisující pouze vývoj rozměrů na základě experimentálních sledování rychlosti růstu bublin a vývoje jejich ustáleného složení. Jsou rovněž uvedeny výsledky verifikace zjednodušeného modelu a chemického i kombinovaného chemického a fyzikálního čeření vycházející z experimentálních dat.