THE SEMIEMPIRICAL MODEL OF THE MULTICOMPONENT BUBBLE BEHAVIOUR IN GLASS MELTS

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A semi-empirical model of the bubble growth and dissolution in glasses with a fining agent has been derived. This model applies the experimental data from bubble observation at melting and fining temperatures. The experimental data needed for the model involved the temperature dependences of the average growth rate of the bubble radius and the average concentration of the fining gas in the bubbles. Both sets of values were measured in the laboratory in the glass of the float type and applied in the model. The measurements of the solubilities and diffusion coefficients of the gases present in the glass – needed for the analytical model of multicomponent bubbles – were thus avoided. The course of the partial bubble absorption with the temperature decreasing was simulated by means of two factors modifying the experimental values of the bubble growth rates at constant temperature. The temperature dependence of the resulting bubble growth rate qualitatively corresponded to the experimental observations in the soda-lime-silica glass, but a more detailed experimental and comparative study has yet to be performed. Such a study is being prepared.

INTRODUCTION

A reliable model of multicomponent bubble behaviour in glass melts, particularly during the glass melting process, is a crucial prerequisite for testing new fining procedures in industrial glass melting spaces, for the technological studies of glass fining and for the development of new glass melting and glass fining facilities. The need for the fining model arises especially in connection with the recent developments of special glasses characterised by high fining temperatures. Several physico-chemical models which describe the behaviour of multicomponent bubbles during glass melting are based on the fact that the fining process is controlled by mass transfer with the participation of several chemical reactions [1-8]. The differential equations expressing the diffusion of the individual gases present provide a picture of the bubble size, composition and position in the melt during the fining process. Whereas the equations describe the fining behaviour of individual bubbles with sufficient reliability despite some accepted simplifications, the data necessary for the models, including the properties of the relevant gases in the melt, are not available or they are measured with a limited accuracy. The low level of accuracy affects especially the measured solubilities and diffusion coefficients of hardly soluble gases (carbon dioxide, nitrogen, argon). The data of low quality may however substantially distort the bubble properties under the given conditions and the results of mathematical modelling may even qualitatively differ from the experimentally observed bubble behaviour under the given conditions. Therefore, especially the bubble characteristics at medium and low temperatures – important for the modelling of glass defects – are not sufficiently credible and prevent the identification and characterisation of the defect-bubble sources by the mathematical modelling.

Several data describing bubble behaviour may be obtained experimentally by bubble observation at different melting and fining temperatures and temperature regression [9-12]. It is nevertheless difficult to derive a more general model from these observations without considering the general features of the multicomponent bubble behaviour and without a targeted series of bubble observations. This study aims at deriving a semiempirical model describing the bubble size and approximate composition in the glass by using the relevant bubble observation data which were obtained in glasses containing a fining agent. The measurement of the necessary experimental data is also involved.

THEORETICAL

The bubble behaviour at constant and increasing temperatures

The sum of the internal partial pressures of present gases in molten industrial glasses almost always exceeds the total pressure inside the bubbles in the entire temperature interval of glass melting [13]:

$$\sum_{i=1}^{n} p_{imelt} > p_{tot} \tag{1}$$

where p_{imelt} (Pa) is the internal partial pressure of the i-th gas in the melt and p_{tot} (Pa) is the total pressure inside of the bubble.

Consequently, all the bubbles grow in the glass melt even at constant temperature and the value of the bubble growth rate increases with the temperature. The results of the mathematical modelling of bubble fining show that the character of the dependence between the bubble size and time is almost linear in the stationary state (as soon as the bubble attains the almost constant - stationary composition and the bubble growth rate depends only slightly on the bubble size). The fining behaviour of bubbles in the glass melt can thus be characterised by an average value of the bubble growth rate at the given temperature, $(\overline{da/d\tau})$, where a (m) is the bubble radius. The value of the bubble growth rate at the given temperature may be experimentally measured by the method of HTO (High-Temperature Observation) [9-10], and its value, $(da/d\tau)_{exp} = (\Delta a/\Delta\tau)_{exp}$, is received by observing the time history of a bubble in the melt.

When the temperature grows, the gas diffusion rate in the melt grows as well owing to the increasing values of diffusion coefficients and the decreasing, both physical and chemical, solubilities of the gases present in the melt. In addition, the concentration of the fining gas in the bubble increases, because the intensity of the fining agent decomposition grows steeply with the temperature. This leads to further bubble growth. Both the mathematical and semiempirical (experimental) models take the two processes into account as simultaneous. The main contributions to the total bubble growth rate are thus the bubble growth rate at a constant temperature and the bubble growth rate owing to the increase of the fining gas concentration in the bubble. The total growth rate of the bubble radius can be derived from the Gay-Lussac equation valid for a bubble, when ideal behaviour of gases is assumed:

$$\frac{4\pi a^3}{3} p_{tot} = nRT \tag{2}$$

where T (K) is the temperature, R (J/(K·mol)) is the universal gas constant, and n (mol) is the total amount of all gases present in the bubble which is a function of both time and temperature (temperature regime):

$$n = n[\tau, T(\tau)] \tag{3}$$

After a substitution and derivative of equations (2-3) at a varying bubble volume and temperature:

$$p_{tot} 4\pi a^2 \frac{da}{d\tau} = RT \frac{\partial n}{\partial \tau} + RT \frac{\partial n}{\partial T} \frac{dT}{d\tau} + nR \frac{dT}{d\tau} \tag{4}$$

where the first term on the right side represents the diffusion of all the gases at constant temperature, the second term is the contribution to the bubble growth owing to the increasing temperature and the third term expresses the contribution to the bubble growth owing to the thermal expansion of the gases. The value of n is given by the sum of moles of the fining gas n_F and other gases n_O present in the bubble:

$$n = n_F + n_O = \frac{4/3 \ \pi a^3}{2.24\times10^{-2} \ (T/273)} \tag{5}$$

The total amount of all gases present in the bubble can also be expressed by the ratio of the total volume of the bubble and the molar volume of the ideal gas, which is linearly temperature dependent (see the right side of the equation (5)).

In fact, the temperature dependence of the diffusion of the fining gas is much more significant than the temperature dependence valid for the other gases (owing to the steep temperature dependence of the solubility of the fining gas in the melt). Consequently, the transport of the gases at varying temperature – as expressed by the second term on the right side of equation (4) – can be represented only by the fining gas:

$$\frac{\partial n}{\partial T} = \frac{\partial n_F}{\partial T} \tag{6}$$

So, the expression $\partial n/\partial T$ in the second term on the right side in equation (4) is replaced by $\partial n_F/\partial T$ from equation (6).

The concentration of the fining gas in the volume percentage is expressed by:

$$c_F = \frac{100 n_F}{n} \rightarrow n_F = \frac{c_F}{100} n \tag{7}$$

By a derivation of equation (7) and by taking into account equation (6):

$$\frac{\partial n_F}{\partial T} = \frac{dc_F}{dT} \frac{n}{100} + \frac{\partial n_F}{\partial T} \frac{c_F}{100} \tag{8}$$

By applying equation (5) for n, the equation (8) then acquires the form:

$$\frac{\partial n_F}{\partial T} = \frac{dc_F}{dT} \frac{4/3 \ \pi a^3}{2.24\times10^{-2} \ (T/273)} \frac{1}{100 - c_F} \tag{9}$$

After an insertion of equation (9) into (4) and a rearrangement, we obtain the relation describing the time development of the bubble radius:

$$\frac{da}{d\tau} = \frac{\partial n}{\partial \tau} \frac{RT}{4\pi a^2 p_{tot}} + \frac{a}{3(100 - c_F)} \frac{dc_F}{dT} \frac{dT}{d\tau} +$$
$$+ \frac{aR}{6.72\times10^{-2} \ (T/273) p_{tot}} \frac{dT}{d\tau} \tag{10}$$

The first term on the right side of equation (10) represents the experimentally measurable diffusion

of all the gases at constant temperature, $(da/d\tau)_{exp}$, and equation (11) then acquires the final form:

$$\frac{da}{d\tau} = \left(\frac{da}{d\tau}\right)_{exp} + \frac{a}{3(100 - c_F)} \frac{dc_F}{dT} \frac{dT}{d\tau} + \frac{aR}{6.72 \times 10^{-2} (T/273) p_{tot}} \frac{dT}{d\tau}$$

$$(11)$$

The second term on the right side expresses the diffusion of the fining gas into the bubble to attain the stationary bubble composition, and the third one the thermal expansion of the present gases.

In order to obtain the temperature dependence of the fining gas concentration, dc_F/dT, bubble absorption is measured by the HTO method under temperature drop from the fining temperatures to temperatures characterised by an almost zero concentration of the fining gas in the bubble. The concentration of the fining gas in the bubble c_F at the given temperature is determined from the difference in bubble volumes. The diffusion of other gases is neglected.

The bubble behaviour at decreasing temperature

When temperature decreases, the counter-diffusion of gases between the bubble and melt and the dramatic changes of the bubble composition occur in the interval of medium temperatures. The fining gas starts to diffuse outside from the bubble, so it does not longer take part in the bubble growth with the exception of the very low rates of temperature decrease. The important value is the temperature T_S (saturation temperature of the fining gas) at which the internal partial pressure of the fining gas in the melt reaches the value of the total pressure in the melt:

$$p_{Fmelt} = p_{tot} \qquad (12)$$

Now, if $T > T_S$, the bubble rises in the glass melt supersaturated by the fining gas and mostly steadily grows even at decreasing temperature. Equation (11) is then valid, but the terms $\frac{a}{3(100 - c_F)} \frac{dc_F}{dT} \frac{dT}{d\tau}$ and $\frac{aR}{6.72 \times 10^{-2} \frac{T}{273} p_{tot}} \frac{dT}{d\tau}$ are negative at $dT/d\tau < 0$.
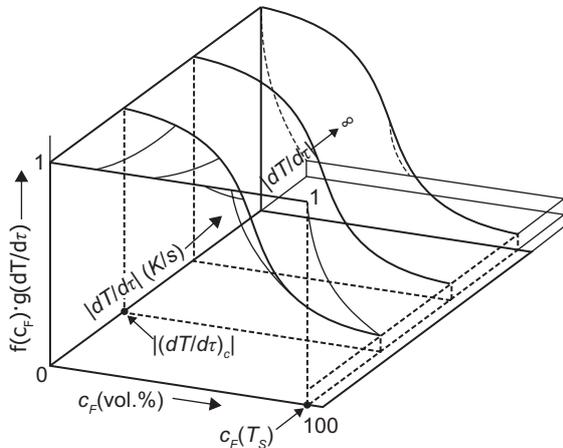

Figure 1. The schematic picture of the values of the product of $f(c_F) \cdot g(dT/d\tau)$ as a function of $c_F(T)$ and $|dT/d\tau|$ under a temperature decrease from T_S, $T < T_S$.

If $T < T_S$, the counter-diffusion of gases between the bubble and melt takes place, because the other gases diffuse permanently into the bubble; nevertheless, the fining gas is absorbed from the bubble into the melt. The fining gas is a rapidly diffusing gas with a steep temperature dependence of its chemical solubility in the melt. Consequently, its concentration in the bubble at the given temperature always approaches the equilibrium one and the other gases should diffuse into the bubble owing to their relatively high concentrations in the melt. Under these conditions, the composition of gases in the bubble at the given temperature remains almost constant (the stationary composition) even when the bubble grows or dissolves. If temperature decreases over the given temperature region, the concentration of the fining gas in the bubble rapidly decreases to its equilibrium value and the fraction of the other gases in the bubble should always correspond to the stationary composition of the bubble at the given temperature. The diffusion of the other gases into the bubble is then described by the factor:

$$f(c_F) = \frac{100 - c_F}{100} \qquad (13)$$

which multiplies the experimental value of the bubble growth rate at constant temperature, $(da/d\tau)_{exp}$, in the equation (11).

The complete equation for the bubble radius development in time valid in the interval $T < T_S$ is then:

$$\frac{da}{d\tau} = \left(\frac{da}{d\tau}\right)_{exp} \frac{100 - c_F}{100} + \frac{a}{3(100 - c_F)} \frac{dc_F}{dT} \frac{dT}{d\tau} +$$

$$+ \frac{aR}{6.72 \times 10^{-2} (T/273) p_{tot}} \frac{dT}{d\tau} \qquad (14a)$$

The validity of equation (14a) is based on the assumption that the fining gas is characterised by a rapid diffusion; consequently, its concentration in the bubble at any time-temperature regime has to be equivalent to the stationary concentration c_F. The validity of the assumption is fulfilled if the degree of bubble-volume absorption during glass cooling over the defined temperature interval is independent of the time-temperature regime, $dT/d\tau$. However, at very high values of the temperature decrease, $|dT/d\tau|$, the concentration of the fining gas in the bubble will be higher than the stationary one c_F.

If the temperature decrease is very slow, a part of the fining gas will diffuse into the bubbles even during the temperature decrease from T_S, because the necessary decrease of the concentration of the fining gas in the bubble is compensated by the dilution effect of the other gases diffusing into the bubble. The second multiplying factor of the value of the experimental bubble growth rate $(da/d\tau)_{exp}$ is therefore introduced into equation (14a) at the very low values of the temperature decrease. In the very narrow interval of the rates of the temperature decrease, close to 0, the fraction of the applicable value of

$(da/d\tau)_{exp}$ should then grow from $(da/d\tau)_{exp} (100 - c_F)/100$ to $(da/d\tau)_{exp}$. An empirical factor $g(dT/d\tau)$ is proposed, multiplying the term with $(da/d\tau)_{exp}$ in equation (14a) along with $f(c_F)$ to describe the narrow range of the rates of the temperature decrease when the bubble behaviour changes from the dissolution to the growth:

$$g\left(\frac{dT}{d\tau}\right) = \frac{100}{100 - c_F}\left[1 - \frac{c_F}{100}\frac{|dT/d\tau|^{\frac{1}{2}}}{|(dT/d\tau)_C|^{\frac{1}{2}}}\right] \quad (15)$$

where $|(dT/d\tau)_C|$ is a critical rate of the temperature decrease. The factor $g(dT/d\tau)$ is applicable in the interval $\langle 0; |(dT/d\tau)_C|\rangle$ of the temperature decrease, and provides $g(dT/d\tau) = 1$ if $|dT/d\tau| = |(dT/d\tau)_C|$ and $g(dT/d\tau) = 100/(100 - c_F)$ if $|dT/d\tau| = 0$. If $|dT/d\tau| > |(dT/d\tau)_C|$, equation (14a) is valid without considering $g(dT/d\tau)$, see Figure 1. After a substitution of equation (15) into (14a) and a rearrangement, the equation for the bubble radius development in time in the interval $|dT/d\tau| \epsilon \langle 0; |(dT/d\tau)_C|\rangle$ has the form:

$$\frac{da}{d\tau} = \left(\frac{da}{d\tau}\right)_{exp}\left[1 - \frac{c_F}{100}\frac{|dT/d\tau|^{\frac{1}{2}}}{|(dT/d\tau)_C|^{\frac{1}{2}}}\right] +$$

$$+ \frac{a}{3(100 - c_F)}\frac{dc_F}{dT}\frac{dT}{d\tau} + \frac{aR}{6.72\times10^{-2}\,(T/273)\,p_{tot}}\frac{dT}{d\tau} \quad (14b)$$

The value of $|(dT/d\tau)_C|$ can be obtained at the temperature T_S from the equilibrium between the rate of diffusion of the other gases into the bubble and the rate of diffusion of the fining gas out of the bubble. In order to calculate $|(dT/d\tau)_C|$, equation (14b) should be used at $da/d\tau = 0$ and the last term on the right side of equation (14b) is neglected. After a rearrangement, we have:

$$\left|\left(\frac{dT}{d\tau}\right)_C\right| = \left(\frac{da}{d\tau}\right)_{expS}\frac{3(100 - c_{FS})^2}{100a_S\,(dc_{FS}/dT)} \quad (16)$$

where $(da/d\tau)_{expS}$, a_S and c_{FS} are the experimental bubble growth rate, the bubble radius and the volume concentration of the fining gas in the bubble at T_S. Equation (16) is applicable only when the temperature decrease starts at temperatures $T \geq T_S$. If the temperature decrease starts at a lower temperature than T_S, the value of $|(dT/d\tau)_C|$ cannot be obtained, because the value of a_S is not known (the relevant bubble history from T_S has not occurred). That is why the experimental estimation of the critical rate of the temperature decrease, $|(dT/d\tau)_C|$, should be applied, which is valid for most frequent bubble sizes at low values of $|(dT/d\tau)|$ (it should be obtained experimentally). For $|dT/d\tau| < |(dT/d\tau)_C|$, the equality is then simply put as $g(dT/d\tau) = 100/(100 - c_F)$, i.e. the equation (11) is valid.

The value of $|(dT/d\tau)_C|$ is experimentally estimated from the observation of bubble behaviour at very slow temperature decreases. The value of $|(dT/d\tau)_C|$ is approximately characterised by the rate of temperature decrease, at which the majority of the observed bubbles do not shrink more, i.e. the bubble size remains constant. The experiments with sodium sulphate as a fining agent

have indicated that the value of $|(dT/d\tau)_C|$ should be lower than 1 K/min. Consequently, the approximation of the function $g(dT/d\tau)$ by its marginal value valid for $dT/d\tau = 0$ will not substantially influence the entire picture of bubble behaviour.

The applicable part of the experimental term $(da/d\tau)_{exp}$ in the temperature interval $T < T_S$ is thus dependent on the multiplication factor $f(c_F)\cdot g(dT/d\tau)$. For $dT/d\tau \to 0$, the product rapidly approaches 1 and the entire value of $(da/d\tau)_{exp}$ is applicable. When $dT/d\tau \to \infty$, the fining gas remains in the bubble and the product retains its initial value (e.g. at T_S, the value of the product is $(100-c_{FS})/100$). In the wide range of the currently occurring values of $dT/d\tau$ – where the concentration of the fining gas in the bubble is almost in equilibrium with the melt – the product has the value of $(100 - c_F)/100$. The schematic dependence of the multiplication factor $f(c_F)\cdot g(dT/d\tau)$ on c_F and $dT/d\tau$ is presented in Figure 1.

The addition of a fining agent releasing a gas chemically insoluble in the glass melt or a gas with its chemical solubility being almost temperature independent requires the application of equation (11) at increasing temperature and the application of equation expressing only the thermal contraction of the gases in the bubble during the glass cooling:

$$\frac{da}{d\tau} = \frac{aR}{6.72\times10^{-2}\,(T/273)\,p_{tot}}\frac{dT}{d\tau} \quad (11b)$$

The fining by the chemically insoluble gas occurs in the case of the sulphate reduction fining. The physically soluble sulphur dioxide is released by the direct reduction of the sulphate during the earlier melting stages and by the reaction of the remaining sulphate and produced sulphide during the later fining period [11-12]. The fining only by a physically soluble gas or by a gas showing the chemical solubility almost independent of temperature is advantageous at the regimes of fluctuating temperature. No chemical absorption of the bubble and, consequently, no fining retardation occurs then at the regimes of decreasing temperature.

EXPERIMENTAL

The application of the model for the float glass fined by the sodium sulphate

The float glass was applied with 0.62 wt. % of SO_3 in the glass, added to the glass batch. The values of the growth rate of the bubble diameter were measured between 1123-1500°C using the high temperature observation method [10, 12]. The values of the growth rates of bubble diameters obtained by the observation of the individual bubbles, their average values and the standard deviation of measurements are shown in Table 1. On average, 10 bubbles were followed at each temperature. The scattering of the results at lower temperatures is caused by the glass inhomogeneity. The experimental

dependence between $(\overline{dd}/d\tau)_{exp}$ has been expressed by the exponential relation:

$$\left(\frac{\overline{dd}}{d\tau}\right)_{exp} = \exp\left(120.343 - 3.804\times10^5/T + 2.608\times10^8/T^2\right) \text{ (m/s)} \tag{17}$$

where T is the temperature in K; the equation (17) with the experimental points are presented in Figure 2.

Table 1. The values of the experimentally measured growth rates of bubble diameter as a function of the temperature.

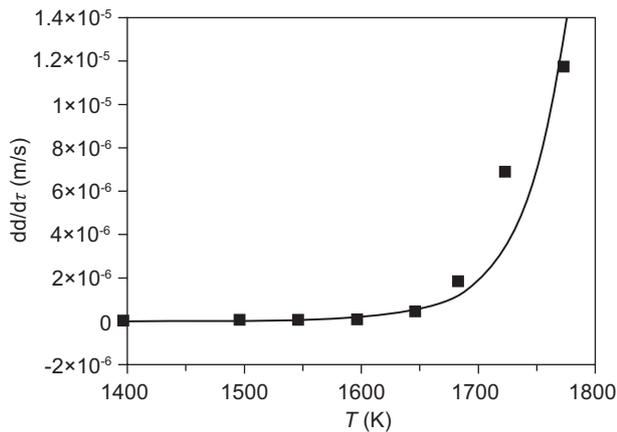| t (°C)	T (K)	$dd/d\tau$ (m/s)	standard deviation (m/s)
1123	1396	9.42×10^{-9}	3.58×10^{-9}
1223	1496	5.70×10^{-8}	2.97×10^{-8}
1273	1546	5.31×10^{-8}	4.09×10^{-8}
1323	1596	5.82×10^{-8}	1.65×10^{-8}
1373	1646	4.44×10^{-7}	1.72×10^{-7}
1410	1683	1.84×10^{-6}	4.94×10^{-7}
1450	1723	6.90×10^{-6}	8.08×10^{-7}
1500	1773	1.17×10^{-5}	1.69×10^{-6}

Figure 2. The values of the experimentally measured average rates of the growth of bubble diameter as a function of the temperature (square points) and the fitted empirical function.

The concentrations of the fining gas in the bubbles were measured at temperatures of 1380, 1400, 1420, 1450, 1480, 1500 and 1520°C from the observed bubble contraction after a temperature drop to 1280°C [12]. On average, 5 bubbles were observed at each temperature. The values of the concentrations of the fining gas in the individual bubbles observed, the average concentrations and the standard deviation of the measurements are presented in Table 2 and plotted in Figure 3.

The value of the saturation temperature t_S read from Figure 3 was 1450°C (T_S = 1723 K). The amounts of both the fining and the other gases in the bubble grow approximately exponentially. Since the relation $c_F = 100n_F/(n_F+n_O)$ expresses the percentage concentra-

tion of the fining gas in the bubble, the values of both n_F and n_O should not express the actual number of moles of both gases in the bubble. Two significant points along the experimental dependence $c_F(t)$ were elected for fitting the dependence to the experimental data: c_F = 27.6 vol. % of the fining gas at 1400°C and c_F = 97.1 vol. % of the fining gas at 1450°C. The values of n_F and n_O are then:

$$n_F = 3.52\times10^{-7}\exp[8.36\times10^{-2}(t-1200)] \tag{18a}$$

$$n_O = \exp[0.01(t-1200)]+10 \tag{18b}$$

and the $c_F(t)$ dependence has the form:

$$c_F(t) = \frac{100\,n_F}{n_F+n_O} = \tag{19}$$

$$= 100\frac{3.52\times10^{-7}\exp[8.36\times10^{-2}(t-1200)]}{3.52\times10^{-7}\exp[8.36\times10^{-2}(t-1200)] + \exp[0.01(t-1200)]+10} \text{ (vol.\%)}$$

The equation (19) fits well the experimental values of c_F at temperatures higher than 1400°C. The deviation from the experimental values is obvious at lower temperatures, where a further decrease of c_F with the temperature should be expected, but the measurement showed only a small decrease of the fining gas concentration. The problem most probably consists

Table 2. The concentrations of the fining gas in the bubbles as a function of the temperature.

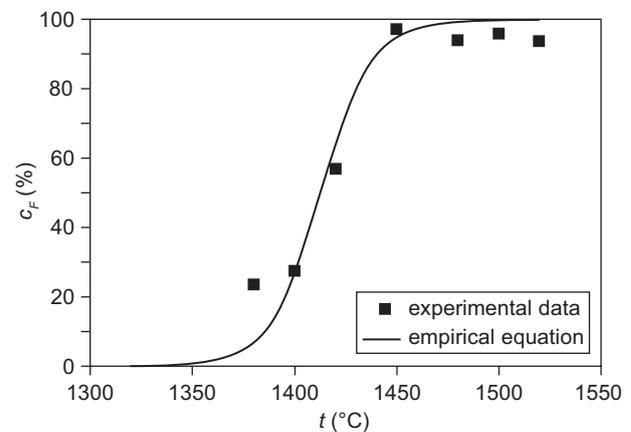| t (°C)	T (K)	c_{Favg} (vol.%)	standard deviation
1380	1653	23.67	3.14
1400	1673	27.64	3.68
1420	1693	56.83	5.50
1450	1723	97.07	0.43
1480	1753	93.98	1.48
1500	1773	95.95	0.92
1520	1793	93.68	2.51

Figure 3. The average concentrations of the fining gas in the bubbles as a function of the temperature (square points) and the fit of the experimental points to equation (19).

in the low accuracy of the experimental measurements below 1400°C. The value of dc_F/dt is then given by:

$$\frac{dc_F}{d\tau} = \frac{8.36n_F(n_F + n_o) - n_F[8.36\,n_F + (n_o - 10)]}{(n_F + n_o)^2} \quad \text{(vol.\%/°C)} \quad (20)$$

DISCUSSION

The presented model clearly works at growing temperature when the total bubble growth rate is composed of two increments: the bubble growth rate at constant temperature caused by the diffusion of all the gases present into the bubble, which is expressed by the value of the term $(da/d\tau)_{exp}$, and the bubble growth rate caused by the growth of the fining gas concentration in the bubble, expressed by equation (9). Figure 4 presents the bubble growth rates as a function of the temperature for different values of the product of $a \cdot dt/d\tau$. The bubble growth rates grow with both temperature and the product of $a \cdot dt/d\tau$. The values of the bubble radii a and the temperature increases $dt/d\tau$ used for the products are given in the Table 3. The equation confirms the experimentally observed rapid increase of the fining rate with the temperature. The expected progressive growth of bubble sizes at the regime of growing temperature will be presented in the next work.

Table 3. The values of the bubble radii a, the temperature increases $dt/d\tau$ and their products $a \cdot dt/d\tau$. At decreasing temperature the values of products will have the negative sign (in Figure 5)

No.	a (m)	$dt/d\tau$ (°C/min)	$dt/d\tau$ (°C/s)	$a \cdot dt/d\tau$ (m·°C/s)
1	1.25×10^{-4}	5	8.33×10^{-2}	1.04×10^{-5}
2	2.5×10^{-4}	5	8.33×10^{-2}	2.08×10^{-5}
3	2.5×10^{-4}	10	1.67×10^{-1}	4.17×10^{-5}
4	5.0×10^{-4}	10	1.67×10^{-1}	8.35×10^{-5}
5	5.0×10^{-4}	20	3.33×10^{-1}	1.67×10^{-4}
6	1.0×10^{-3}	20	3.33×10^{-1}	3.33×10^{-4}

The behaviour of the bubbles at decreasing temperature is a more complicated case, as the 'other' gases diffuse permanently into the bubbles while the fining gas is absorbed from the bubbles into the melt. The development of the total rate of the bubble radius change with the temperature shows then both the positive and negative trend with the minimum. Such a development for several values of the product of $a \cdot dt/d\tau$ is plotted in Figure 5.

Under the condition of a steady decrease of the temperature from the high fining temperatures, most bubbles steadily grow at temperatures $T > T_S$ but their growth rate decreases because of the growing negative

value of the second term on the right side of equation (11). The large bubbles at high values of $dT/d\tau$ dissolve already at $T > T_S$. As soon as the temperature attains a value of around the saturation temperature t_S (here 1450°C), the glass supersaturation by the fining gas vanishes and the concentration of the fining gas in the bubble, c_F, drops abruptly. This fact is demonstrated by the sudden shift of the total rate of the bubble radius change to the negative values – most bubbles will dissolve. Equation (14a) with the term $(100 - c_F)/100$ will be valid below T_S. A further temperature decrease below T_S leads to an increase of the fraction of the 'other' gases diffusing permanently into bubbles and subsequently to a decrease of the bubble dissolution rate. In the relatively broad temperature interval around 1400°C, the bubble begins to grow slowly again owing to the prevailing diffusion of the 'other' gases into the bubble. The specific course
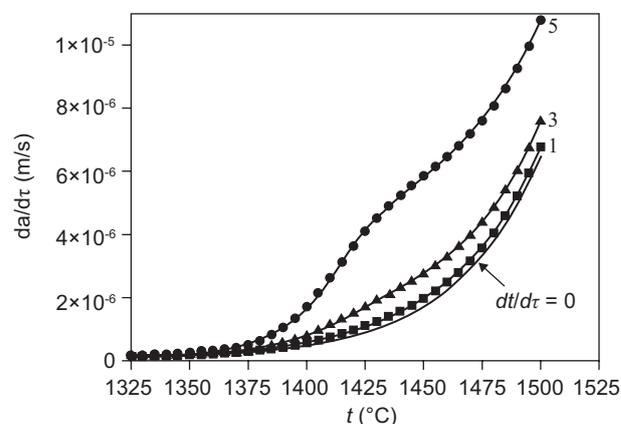
Figure 4. The dependence of the total growth rate of the bubble radius on the temperature at growing temperature and at different values of $a \cdot dt/d\tau$: ■1 - $a \cdot dt/d\tau = 1.04 \times 10^{-5}$, ▲3 - $a \cdot dt/d\tau = 4.17 \times 10^{-5}$, ●5 - $a \cdot dt/d\tau = 1.67 \times 10^{-4}$ (m·°C/s).
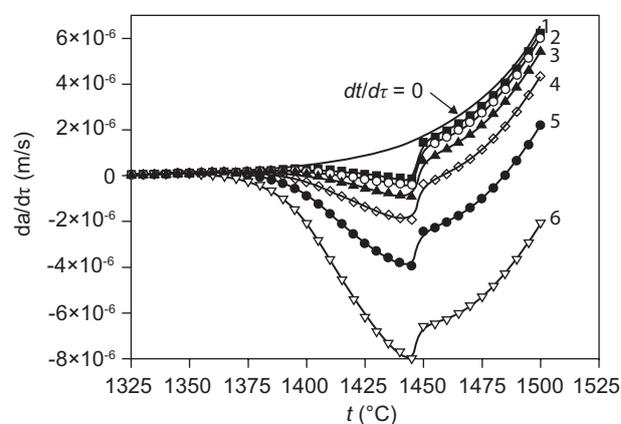
Figure 5. The dependence of the total rates of the bubble radius changes on the temperature at decreasing temperature and at different values of: ■1 - $a \cdot dt/d\tau = -1.04 \times 10^{-5}$, ○2 - $a \cdot dt/d\tau = -2.08 \times 10^{-5}$, ▲3 - $a \cdot dt/d\tau = -4.17 \times 10^{-5}$, ◊4 - $a \cdot dt/d\tau = -8.35 \times 10^{-5}$, ●5 - $a \cdot dt/d\tau = -1.67 \times 10^{-4}$, ∇6 - $a \cdot dt/d\tau = -3.33 \times 10^{-4}$ (m·°C/s).

of the described dependence is dependent on the bubble size and the rate of temperature decrease; the larger bubbles at a quickly decreasing temperature dissolve in a broader temperature interval and with a higher rate than the small ones. The high bubble dissolution rates around the temperature 1450°C correspond to the experimental observations and will be discussed in the following work. According to equation (14a), a bubble below T_S cannot be dissolved completely, because the term $(da/d\tau)_{exp}$ is permanently positive and the absolute value of the negative term rapidly decreases at lower temperatures. This fact is in agreement with the experimental observations, as well. The complex behaviour of bubbles at temperatures around and below T_S becomes evident during fining under industrial melting conditions characterised by an oscillating temperature along the bubble pathways.

If the rate of the temperature decrease is very low, the fining gas begins to diffuse into the bubbles despite the fact that the concentration of the fining gas in the bubble still decreases (the decrease is compensated by the dilution effect of the 'other' gases diffusing into the bubble). This behaviour is particularly apparent at high concentrations of the fining gas in the bubble, i.e. at temperatures slightly below T_S. The empirical factor $g(dT/d\tau)$ has therefore been proposed to bridge the value of the bubble growth rate from $(da/d\tau)_{exp}$ $(100 - c_F)/100$ to $(da/d\tau)_{exp}$ at low values of the temperature decrease $(dT/d\tau)$ (see eq. 15). In order to ascertain the significance of the factor $g(dT/d\tau)$, the values of the critical temperature decrease $|(dT/d\tau)_C|$ were calculated for the different initial bubble radii at $T_S = 1723$ K ($t_S = 1450$°C). The dependence between $|(dT/d\tau)_C|$ and a_S is plotted in Figure 6. The results show that the values of $|(dT/d\tau)_C|$ increase with the decreasing value of the bubble radius at T_S and are very low for bubbles of the current sizes around 1mm. The factor $g(dT/d\tau)$ will therefore be applied only to a minor extent.
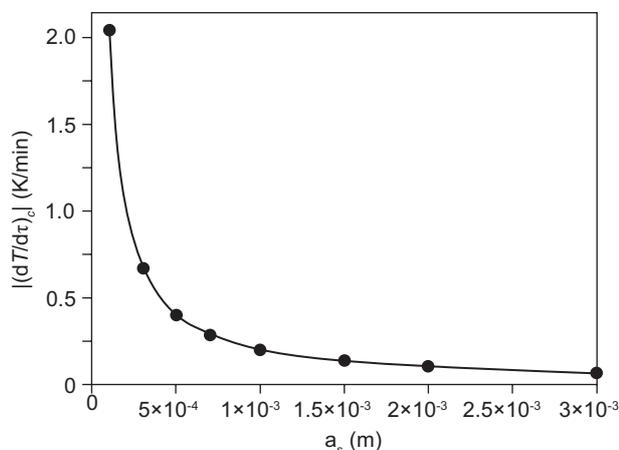

Figure 6. The values of the critical temperature decrease $|(dT/d\tau)_C|$ as a function of the bubble radius a_S at the saturation temperature T_S ($T_S = 1723$ K).

CONCLUSION

The study has proposed equations able to describe the bubble behaviour in glass melts under the conditions of time-temperature regimes. The derived equations result from the experimental examination of bubble growth at constant temperature and from the determination of the concentration of the fining gas in the bubbles as a function of the temperature. Thus, the long-term measurements of the data characterising the equilibrium and kinetics of the gases are avoided and the model of the bubbles in the relevant glass may be easily realised for application in industrial facilities. Two factors have been proposed to modify the experimental values of the bubble growth rates at decreasing temperature and to simulate the partial bubble dissolution in the melt. It seems, however, that only the first one, $f(c_F)$, taking into account the instant concentration of the 'other' gases in the bubble, will be relevant for the practical modelling applications. The up-to-date experimental results are in qualitative agreement with the experimental bubble observations. An experimental study of the bubble behaviour at different time-temperature regimes to verify the model in detail is in progress.

References

1. Němec L.: Glass Technol. *21*, 134 (1980).
2. Onorato P. I. K, Weinberg M.C.: J. Am. Ceram. Soc. *64*, 676 (1981).
3. Cable M., Frade J. R.: Glastechn. Ber. *60*, 355 (1987).
4. Ungan A.: Glastechn. Ber. *63K*, 19 (1990).
5. Beerkens R.: 7th Int. Conf. on Advances in Fusion and Processing of Glass III, Rochester, July 27-31, 2003.
6. Balkanli B., Ungan A.: Glass Technol. *37*, 101 (1996).
7. Matyáš J., Němec L.: Glass Sci. Technol. *76*, 71 (2003).
8. Oda K., Kaminoyama M.: J. Cer. Soc. Japan *117*, 736 (2009).
9. Jebavá M., Němec L., Kloužek J.: Ceramics − Silikáty *48*, 121 (2004).
10. Jebavá M.: Ph.D. Thesis, Institute of Chemical Technology Prague (2008).
11. Kloužek J., Arkosiová M., Němec L., Cincibusová P.: Glass Technol.: Eur. J. Glass Sci. Technol. A *48*, 176 (2007).
12. Vernerová M.: Ph.D. Thesis, Institute of Chemical Technology Prague (2011).
13. Němec L., Mühlbauer M.: Glastechn. Ber. *54*, 99 (1981).
14. Kloužek J., Arkosiová M., Němec L.: Ceramics − Silikáty *50*, 134 (2006).