Original Paper

Significance of redox reactions in glass refining processes

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The role of the redox reactions due to refining agents in the glass refining processes was examined. A new approximate model for shrinkage (or growth) of gas bubbles in glassmelts in which redox reactions caused by refining agents were taken into account was developed. The proposed model is a modification of the quasi-stationary model by which the redox reactions due to refining agents can not be considered. It was found that the shrinkage (or growth) of gas bubbles in melts with refining agents is quite faster than that in those without refining agents. Numerical results for single-component and multicomponent gas bubbles indicate that the mechanism of the bubble shrinkage (or growth) in the refining process is significantly controlled by the oxidation of refining agents, which decreases (or increases) the oxygen concentration in the glassmelt and as a result causes the rapid oxygen transfer across the bubble/glassmelt interface and hence the fast shrinkage (or growth) of the gas bubble. The applicability of the proposed model was examined using the computational results and experimental measurements in the literature. It was also found that the proposed model provides better predictions compared with the quasi-stationary model.

Bedeutung von Redoxreaktionen bei Glasläuterungsvorgängen

Die Rolle, die von Läutermitteln ausgelöste Redoxreaktionen bei Glasläuterungsvorgängen spielen, wurde untersucht. Es wurde ein neues Näherungsmodell für das Schrumpfen (oder das Wachstum) von Gasblasen in Glasschmelzen entwickelt, wobei durch Läutermittel verursachte Redoxreaktionen berücksichtigt wurden. Das vorgeschlagene Modell ist eine Modifikation des quasistationären Modells, das die durch Läutermittel hervorgerufenen Redoxreaktionen nicht berücksichtigen kann. Man stellte fest, daß die Schrumpfung (oder das Wachstum) von Gasblasen in Schmelzen mit Läutermitteln sehr viel schneller erfolgt als in solchen ohne Läutermittel. Numerische Ergebnisse für ein- und vielkomponentige Gasblasen zeigen an, daß der Schrumpfungs- (oder Wachstums-)mechanismus während des Läuterungsprozesses durch die Oxidation der Läutermittel gesteuert wird, was die Sauerstoffkonzentration in der Glasschmelze vermindert (oder erhöht). Ferner führt dies zu einem raschen Sauerstoffdurchtritt an der Grenzfläche zwischen Blase und Glasschmelze und damit zu schnellem Schrumpfen (oder Wachstum) der Gasblase. Die Anwendbarkeit des vorgeschlagenen Modells wurde unter Benutzung der Ergebnisse von Berechnungen und experimentellen Messungen aus der Literatur überprüft. Es wurde auch gefunden, daß das neue Modell bessere Vorhersagen zuläßt als die quasistationäre Näherung.

1. Introduction

Removal of gas bubbles from glassmelts, or refining, is of importance in the glass producing process [1]. Gas bubbles are generated by the following mechanisms: first, air is trapped within the batch; second, gases are evolved from complex reactions within the refractories, and third, gases are produced during the melting process. Gas bubbles mix and homogenize the glassmelt, but they must be removed from the molten glass before cooling.

It has been suggested that gas bubbles are removed from glassmelts by either of two processes, i.e. rise of bubbles to the surface of the glassmelt or dissolution of the gases in bubbles into the glassmelt. While relatively large gas bubbles can be removed by rise to the surface of the melt, smaller gas bubbles can primarily be removed from melts by dissolution of their gases into the glassmelt. In order to elucidate these processes, the shrinkage or growth of stationary gas bubbles in an infinite glassmelt has been studied extensively [1].

Refining agents such as arsenic and antimony oxides are often added to glass batch to speed up the removal of gas bubbles. Greene et al. [2 to 4] found an enhancement of dissolution of oxygen bubbles in glassmelts due to refining agents. Doremus [5] discussed shrinkage of an oxygen bubble in a molten glass. It was suggested that the trivalent arsenic, which is a considerable portion of arsenic ions in glassmelts, reacts with oxygen physically dissolved in the melt, reduces its concentration and hence increases the rate of oxygen diffusion into the melt. However, the exact and quantitative role of refining agents in removing gas bubbles from glassmelts is still controversial. Therefore, the analysis of the shrinkage or growth of a gas bubble in a glassmelt containing refining agents is a problem of practical importance.

The shrinkage or growth of gas bubbles in glassmelts has been modeled to simulate the change in bubble size with time and to estimate the diffusivity of gases. In order to analyze the behavior of a gas bubble, some approximate methods (quasi-stationary, quasi-steady, etc.) have been used. Several investigators including Greene and Gaffney [2], Doremus [5], Epstein and Plesset [6] and Weinberg et al. [7] have modified the stationary

Received December 20, 1995, revised mauscript March 25, 1996.

boundary solution to obtain approximate solutions for the dissolution of gas bubbles, which is actually the moving boundary problem. In the quasi-stationary approximation, the motion of the bubble boundary or surface is neglected in solving the diffusion equation for the gas concentration profiles in the melt. The resulting concentration profiles are used to calculate the mass flux at the fixed boundary and then to determine the boundary motion or the change in bubble size. It is known that the quasi-stationary model provides relatively reasonable approximations. It should be emphasized, however, that at present the influence of redox equilibrium reactions due to refining agents can not be considered using the quasi-stationary model. In the quasi-steady state approximation, a further simplification of the diffusion equation by neglecting the time derivative is introduced.

Readey and Cooper [8], Cable and Evans [9] and Duda and Vrentas [10] solved the diffusion equation in which the motion of the melt caused by bubble shrinkage or growth was taken into account. Although their solutions may be more rigorous as compared with the quasi-stationary and quasi-steady state approximations, the diffusion equations must be solved numerically.

Tao [11] obtained approximate solutions in which the motion of the melt is ignored, but that of the bubble surface is considered.

In most of the previous studies such as the literature mentioned above, the effects of the redox reactions on bubble shrinkage or growth have not been considered quantitatively. Subramanian and Chi [12] discussed the effect of chemical reaction on bubble dissolution. They compared the finite difference results with a perturbation expansion, a quasi-stationary approximation and a quasi-steady approximation. It was found that in spite of its simplicity the quasi-stationary approximation is an excellent one in the presence of a fast chemical reaction. However, the reaction examined in their work is only a first-order irreversible chemical reaction.

Němec [13] examined the chemical reaction of the gas on the bubble surface. The chemical reaction due to the refining agents was considered in describing the equilibrium concentration of the gas at the surface of rising bubbles. Hübenthal and Frischat [14] and Krämer [15] also examined the growth of gas bubbles in the glassmelts with chemical reaction.

Papanikolau and Wachters [16] formulated the diffusion- and viscosity-controlled growth of a stationary gas bubble with chemical reaction and solved the numerical example of hydrogen reboil in fused silica. In their analysis, the chemical reaction rate was fast, so that the reaction was assumed to be in equilibrium.

Recently, Beerkens and de Waal [17] applied Papanikolau and Wachters' analysis [16] to obtain the concentration profile of gas in glassmelts which contain a refining agent. The redox reactions of refining agents were represented in a more generalized form [18]. Their computational results indicate that the concentration profiles for diffusing oxygen in glassmelts with refining agents are steeper than those without refining agents. However, their discussion was limited to only one-dimensional diffusion in rectangular coordinates.

Beerkens [19] examined the release of gases from rising bubbles due to redox reactions in glassmelts. Unfortunately, the calculation procedure for bubble growth or shrinkage is indistinct. In addition, the estimations of mass transfer coefficient and driving force considering the effects of redox reactions are not described clearly.

As described above, the detailed mechanisms of the agents in the refining processes are not yet clear. In the present work, therefore, the diffusion equation including the effect of redox equilibrium reactions of refining agents for diffusion-controlled shrinkage or growth of a gas bubble is solved using the method of finite differences. Since the reaction term is included in the diffusion equation, analytical solutions are impossible in contrast with the quasi-stationary model. The mass flux at the bubble surface is used to calculate the shrinkage or growth of a gas bubble in glassmelts which contain a refining agent. Unlike the quasi-stationary analysis, the change in bubble radius with time is taken into account in the calculation of the concentration profiles. For the shrinkage or growth of a gas bubble in melts without refining agents, therefore, the present model can provide more rational predictions as compared with the quasi-stationary model. The present model can be recognized as an improvement of the quasi-stationary analysis. The effects of refining agents on bubble shrinkage or growth in glassmelts are examined, and the significance of redox reactions of refining agents in bubble behavior is illustrated. Since gas bubbles in glassmelts often contain several gases [20], besides a single-component gas bubble a multicomponent one was also discussed. The proposed approximate model provides some mechanistic insights into the refining process. The computational results are compared with the approximate solutions and the measurement on shrinking oxygen bubbles in the literature.

2. Theoretical

An isolated spherical bubble being stationary in an infinite isothermal glassmelt is considered (figure 1).

The following assumptions are made for simplification:

a) The kinetics of equilibration at the bubble surface is rapid, so that the rate-limiting process is diffusion in the melt.

b) The physical properties including the diffusion coefficient and the Henry's law constant of gases are constant with concentration and time.

c) The gases are ideal.

d) The surface tension and viscosity effects are negligible.

e) The concentrations of dissolved gases do not depend on the angular coordinates but only on the distance from the center of the gas bubble.

f) The saturation concentrations for gases at the surface of the gas bubble are independent of time.

g) The convective transport in the melt is negligible.

h) The evaporation of refining agents is negligible.

Even with the utilization of these simplifying assumptions, the problem remains quite complicated.

A material balance for the i-th gas component in the melt is given as:

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) + R_{A_i} , \tag{1}$$

This equation is to be solved subject to the following initial and boundary conditions:

$$C_i(r, 0) = C_{i0} \quad \text{for } r > R_a , \tag{2a}$$

$$C_i(R_a, t) = L_i \, P_{ai} \text{ for } t > 0 , \tag{2b}$$

$$C_i(\infty, t) = C_{i0} \quad \text{for } t \geq 0 . \tag{2c}$$

Since the equilibrium conditions are assumed at the interface, the interfacial gas concentrations are related to the partial pressures of gases by Henry's law (equation (2 b)). It is assumed that the volume of the melt is large compared with the diffusion distances from the gas bubble (equation (2c)).

The redox equilibrium reaction of refining agents, or variable-valence metal oxides, is described in a generalized form as [18]:

$$M^{(x'+n')+} + \frac{n'}{2} O^{2-} \rightleftarrows M^{x'+} + \frac{n'}{4} O_2 \tag{3}$$

where $M^{(x'+n')+}$ stands for the oxidized species of the variable-valence ion M, and $M^{x'+}$ stands for the reduced species of the variable-valence ion M. For example, the redox couple $M^{x'+}/M^{(x'+n')+}$ could be As^{3+}/As^{5+} and Sb^{3+}/Sb^{5+}. This redox reaction due to the refining agents may be a main chemical reaction in the refining process.

The concentration changes in O_2, $M^{x'+}$ and $M^{(x'+n')+}$ are related to each other as

$$\Delta[O_2] = \frac{n'}{4} \Delta[M^{x'+}] = -\frac{n'}{4} \Delta[M^{(x'+n')+}] . \tag{4}$$

Therefore, the molar rate of production of oxygen per unit volume R_{AO_2} is written as:

$$R_{AO_2} = -\frac{n'}{4} \frac{\partial [M^{(x'+n')+}]}{\partial t} . \tag{5}$$

The diffusion equation for oxygen including chemical reaction is given by:

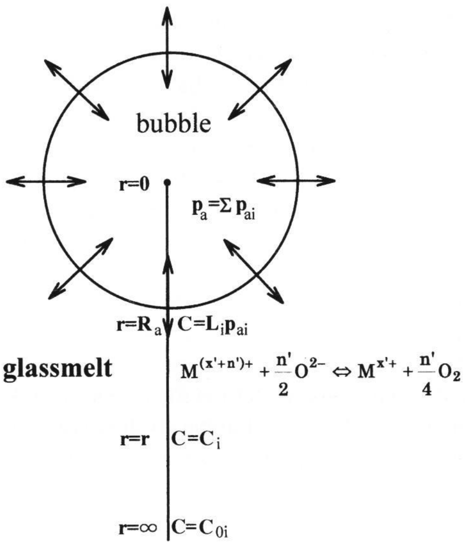

Figure 1. Shrinkage or growth of a stationary bubble in an infinite glassmelt.

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2} \left(\frac{\partial^2 C_{O_2}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{O_2}}{\partial r} \right) - \frac{n'}{4} \frac{\partial [M^{(x'+n')+}]}{\partial t} . \tag{6}$$

It should be noted that the diffusion of the variable-valence ions in the glassmelt is neglected in equation (6).

For the constant activity of oxygen ions in the glassmelt, the equilibrium constant for equation (3), K_c, is defined as

$$K_c = \frac{[M^{x'+}][O_2]^{n'/4}}{[M^{(x'+n')+}]} . \tag{7}$$

The summation of the concentrations of the oxidized and reduced ions is constant and equals to the concentration of refining agents m.

$$m = [M^{x'+}] + [M^{(x'+n')+}] . \tag{8}$$

Introducing the variable $u_i = r \, C_i$ and substituting equations (7 and 8) into equation (6) give the following differential equation having the same form as the equations for other gases

$$\frac{\partial u_i}{\partial t} = D_i \frac{\partial^2 u_i}{\partial r^2} . \tag{9}$$

For oxygen reacting with refining agents, the diffusion coefficient, D_i, is replaced by the modified diffusion coefficient for oxygen, D_{cO_2}, given as

$$D_{cO_2} = D_{O_2} \, 1 + m \, (n'/4)^2 \left(\frac{K_c \, C_{O_2}^{(n'/4)-1}}{(K_c + C_{O_2}^{n'/4})^2} \right) .$$

Since D_{cO_2} is a function of dissolved oxygen concentration, it depends on time and distance. It should be noted that for other gases the reactions of which are not considered in this work $D_{ci} = D_i$ in equation (9).

A Crank-Nicolson technique was used to solve equation (9). The incremented variables were r and t. The increment size was varied to ensure that the results were independent of increment sizes. In other words, convergence of the finite-difference solutions was established by varying the mesh sizes for the radial and time variables. The increments of r and t to calculate the concentration distributions of gases in the glassmelt for the case without chemical reaction in the melt were taken to be $5 \cdot 10^{-7}$ m and $2 \cdot 10^{-4}$ s, respectively. The computational results for the refining time (the bubble lifetime in the case of bubble shrinkage) were independent of mesh sizes within 0.2%. The bubble lifetime for bubble shrinkage is the time required for the bubble to dissolve completely. In this work, the bubble lifetime is defined as the time required for the bubble radius to become a hundredth of the initial bubble radius. Since the concentration distributions of gases were considered only in the melt and the concentration distributions of gases in the gas bubble were assumed to be uniform, the bubble surface was always a starting point of the mesh. At every time interval, new mesh points starting from the bubble surface were introduced. Unlike the works of Duda and Vrentas [10], Subramanian and Chi [12] and Ramos [20], a mapping was not used in this work. As well as in the examinations of Readey and Cooper [8] and Cable and Evans [9], a finite-difference mesh for a semi-infinite region was set up. Duda and Vrentas [10] pointed out that Cable and Evans [9] underestimated the concentration gradients at the bubble surface in calculating the flux across the bubble surface and suggested the importance of immobilization of the bubble surface in a numerical solution by introducing a mapping. In this work, however, because no difficulty in convergence of the finite-difference solutions was experienced even at the higher dissolution or growth rates, the mapping was not necessary. It should be mentioned that at least two hundredths and five thousandths of time and space mesh sizes used by Cable and Evans [9], respectively, have been employed. Furthermore, the accuracy of the computational scheme without mapping in this work was confirmed by obtaining good agreement with the numerical results including the cases for higher dissolution rates in the literature [10 and 12] (Yoshikawa and Kawase [21]). The present model contains no significant errors due to finite-difference approximations for the concentration gradients at the bubble surface [21]. It should be emphasized that even though the exponential transformation is applied, the parameter included in the transformation must be selected in the usual manner by varying the mesh sizes for the radial and time variables (Subramanian and Chi [12]). It varies for various values of the reaction rate and the driving force.

The increment sizes selected to calculate the concentration distributions of gases in the case with chemical reaction in the melt were $2.5 \cdot 10^{-8}$ m and $2 \cdot 10^{-5}$ s, respectively. The result was independent of mesh size within a few percentages of the bubble lifetime for bubble shrinkage. The calculations for the case of no reaction converged more readily compared with those for the presence of reaction. This problem will be discussed later.

The shrinkage or growth of a gas bubble was calculated by the following procedure:

- The concentration distributions of gases in the glassmelt at t are calculated from equation (9).
- The mass flux at the bubble surface is calculated using the numerical result for the concentration distribution obtained by the above calculation step. The molar flow for the i-th component from the gas bubble per unit time can be calculated by the following equation:

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = -4\pi R_\mathrm{a}^2 D_i \left(\frac{\partial C_i}{\partial r}\right)_{R_\mathrm{a}} . \tag{10}$$

  The mass flux or the concentration gradient at the bubble surface $(\partial C_i / \partial t) R_\mathrm{a}$ is evaluated by means of a three-point finite-difference approximation as well as in the studies of Cable and Evans [9] and Ramos [20]. As described above, the mesh sizes selected in this work are small enough to estimate the concentration gradient at the surface precisely.
- The change in bubble radius is calculated by the following mass balance equation at the interface:

$$\frac{\mathrm{d}R_\mathrm{a}}{\mathrm{d}t} = \frac{R_\mathrm{g} T}{4\pi R_\mathrm{a}^2 P_{\mathrm{a}i}} \sum_i \frac{\mathrm{d}n_i}{\mathrm{d}t} . \tag{11}$$

The calculation procedure described above is similar to the quasi-stationary analysis of Epstein and Plesset [6]. In the quasi-stationary approximation, the motion of the bubble boundary is neglected and the mass flux at the boundary obtained by solving the simplified differential equation is used to determine the boundary motion. However, in the present model the change in bubble radius with time is taken into account in the calculation of the concentration profiles of gases in the melt by solving equation (9) unlike the quasi-stationary analysis. Although in the present model the term for radial convection is neglected in the conservation equation, the gas concentration profiles taking into account the interface movement with time due to dissolution or stripping is used to calculate the change in the bubble size. This difference between the proposed model and the quasi-stationary analysis is discussed below.

3. Results and discussion

3.1 Single-component bubble

A stationary pure oxygen bubble (partial pressure = = 101.325 kPa) in an infinite glassmelt containing arsenic oxides as refining agents at 1473.15 K is considered. In this case, the gas bubble shrinks due to oxygen absorption. The values used for the computer simulation are given in table 1. They were determined on the

Table 1. Values used in computational results for a single-component bubble (O_2) (figures 2 to 4)

$n' = 2$ for As^{3+}/As^{5+}
$K_c = 0.1\ (mol\ m^{-3})^{1/2}$
$m = 100\ mol\ m^{-3}$
$R_{a0} = 10^{-4}\ m$
$T = 1473.15\ K$
$P_a = 101325\ Pa$

$C_{0O_2} = 0.0\ mol\ m^{-3}$
$D_{O_2} = 10^{-9}\ m^2\ s^{-1}$
$L_{O_2} = 3 \cdot 10^{-6}\ mol\ m^{-3}\ Pa^{-1}$

basis of the data in the literature [17, 19 and 20]. It should be noted that the values of the solubility and diffusion coefficients of gases in glassmelts are not well known [20].

Figure 2 shows the concentration profiles of physically dissolved oxygen in glassmelts at $t = 2000$ s, which are numerical solutions of equation (9), The concentration profile for diffusing molecular oxygen into glassmelts with refining agents or variable-valence ions extends a relatively short distance from a bubble surface as compared with the profile in a melt without these ions. In other words, the concentration profile for the molecularly dissolved oxygen in the melts with variable-valence ions is steeper than that in the melts without these ions. Of course, the difference of the two curves is due to the redox reaction consuming physically dissolved oxygen during oxidation of the variable-valence ions in the glassmelts. Oxygen is absorbed in the glassmelt containing arsenic by reacting with the lower-valence form of As_2O_3 besides physical absorption. This coincides with the computational result for one-dimensional diffusion in rectangular coordinates [17].

The oxygen concentration gradient at the bubble surface is estimated in order to evaluate the oxygen flux using a three-point finite-difference approximation (equation (10)) [10 and 20]. As mentioned above, the mesh sizes of t and r had to be made small to estimate numerically the concentration gradient at the bubble surface with accuracy. In particular, the oxygen concentration gradient at the surface in the presence of a redox reaction could not be obtained readily. This difficulty increased with an increase in the steepness of the concentration gradients. Since the oxygen concentration in the presence of a redox reaction was steeper than that in the absence of the reaction (figure 2), the smaller mesh sizes for r and t were required for the conversion of the calculations for the dissolution of a gas bubble in the presence of a redox reaction. However, no particularly complicated difficulty was experienced in the accurate calculation of the concentration gradients even at the higher dissolution rates. As described previously, therefore, a mapping was not introduced to solve the governing equations for bubble dissolution.

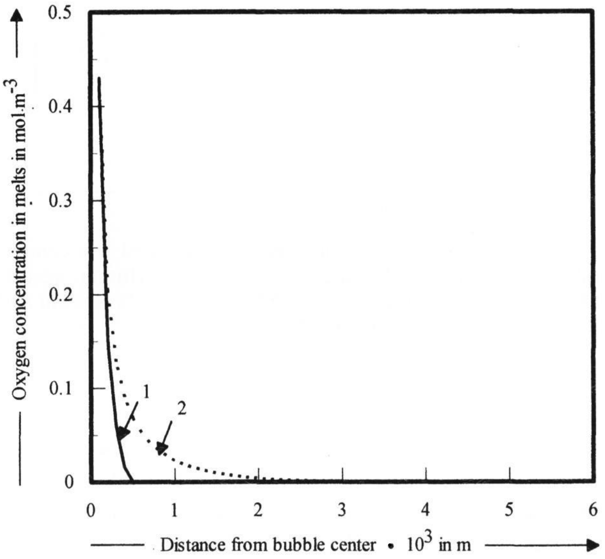

Figure 2. Oxygen concentration profiles in a melt around a bubble ($t = 1200$ s, $R_{a0} = 1 \cdot 10^{-4}$ m. Curve 1: with refining agents (As^{3+}/As^{5+}), curve 2: without refining agents.

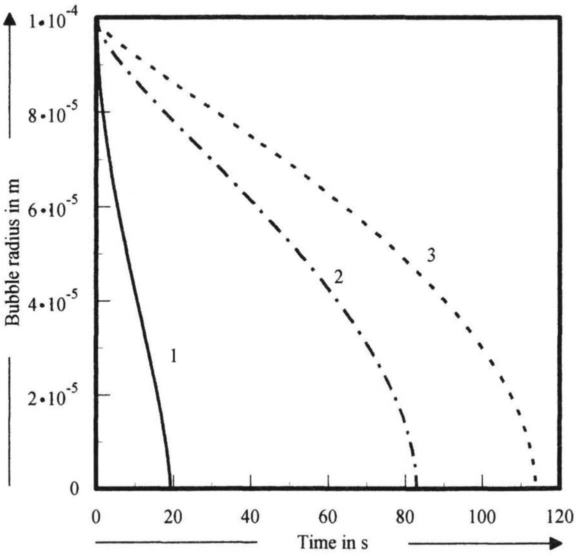

Figure 3. Shrinkage of an oxygen bubble in a melt ($R_{a0} = 1 \cdot 10^{-4}$ m). Curve 1: with refining agents (As^{3+}/As^{5+}), curve 2: with refining agents (Fe^{2+}/Fe^{3+}), curve 3: without refining agents.

Figure 3 shows the shrinkage of a bubble in melts with and without refining agents or variable-valence ions, As^{3+}/As^{5+}. The lifetime of a bubble in melts with variable-valence ions is shorter than that in those without these ions. The rate of transfer of oxygen through a

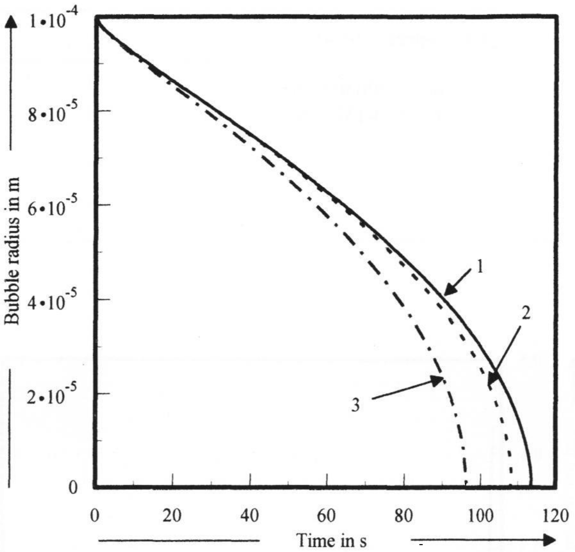

Figure 4. Comparison of the present result and the computational results in the literature (without refining agents) ($R_{a0} = 1 \cdot 10^{-4}$ m). Curve 1: present work, curve 2: Epstein and Plesset [6], curve 3: Doremus [5].

bubble surface is given by equation (10). The concentration gradient for the molecularly dissolved oxygen at the gas/liquid interface with variable-valence ions is steeper than without these ions. The absolute value of the rate of transfer is higher for melts including variable-valence ions than that in melts without these ions under the same conditions. Hence, the rates of shrinkage of a bubble are faster in the case of variable-valence ions added. The more the concentration of variable-valence ions increases, the faster is the rate of shrinkage of the gas bubble. The dissolution of a stationary gas bubble is enhanced by the redox reaction in the glassmelt. For further comparison, the rate of bubble shrinkage in melts with the refining agents or variable-valence ions, Fe^{2+}/Fe^{3+}, is also plotted in figure 3. The equilibrium constant for variable-valence ions Fe^{2+}/Fe^{3+} was estimated to be 18 $(\text{mol m}^{-3})^{1/4}$ from the data reported by Rüssel und Freude [22]. In the case of the variable-valence ions Fe^{2+}/Fe^{3+} the number of electrons transferred is unity and, as a result, the consumption of physically dissolved oxygen during oxidation of these ions in glassmelts is less than that in the case of the variable-valence ions As^{3+}/As^{5+}. As seen in figure 3, therefore, the effect of the former variable-valence ions on the rate of bubble shrinkage is rather smaller as compared with that of the latter.

In figure 4, the present results for the absence of a chemical reaction are compared with the approximate quasi-stationary solutions in the literature. In other words, the quasi-stationary analysis ignoring convection transport in the mass transport equation and the boundary movement in the equation for the flux is compared with the present model in which the convection transport is neglected in the diffusion equation as well as in the quasi-stationary model, but the change in bubble radius with time is taken into account in the calculation of the concentration profiles of oxygen in the melt.

Epstein and Plesset [6] derived the equation for the bubble radius using the quasi-stationary approximation:

$$\frac{\mathrm{d}R_a}{\mathrm{d}t} = \frac{D\,\Delta C}{R_a\,\varrho_g}\left\{1 + \frac{R_a}{(\pi\,D\,t)^{1/2}}\right\}. \tag{12}$$

When the time is short, there is no significant difference in the curves between the present and the quasi-stationary models (figure 4). Since the change in the bubble size is small for short time, the deviations might be almost indistinguishable. It is also seen from the figure that equation (12) predicts a slightly faster shrinkage of the bubble as compared with the present result for long time. It is assumed, in the quasi-stationary approximation, that a bubble boundary or surface does not change with time by dissolution. In other words, the mass flux at $t = t_1$ (arbitrary) is calculated by assuming that during $t = 0-t_1$ the bubble radius remains constant for R_a at $t = t_1$. Even though the bubble radius decreases from the initial bubble radius R_{a0} to R_a ($R_{a0} > R_a$ for bubble shrinkage) during $t = 0-t_1$, the bubble radius is assumed to be constant for R_a. It is seen from equation (12), therefore, that the quasi-stationary approximation overestimates the oxygen flux at the boundary and hence the bubble dissolution rate. Since, on the other hand, the change of the bubble radius with time in the calculation of the concentration distribution is considered in the present model, it predicts a slightly longer dissolution time as compared with that obtained by the quasi-stationary approximation. The results obtained by the present approximate model lie between those of the quasi-stationary model and the rigorous numerical solutions [21]. This implies that the present model provides better results compared with the quasi-stationary model. In other words, the approximations utilized in the present model are more realistic than those in the quasi-stationary model.

Weinberg et al. [7] and Subramanian and Weinberg [23] indicated that the inclusion of the bubble boundary motion and the associated fluid motion for a stationary gas bubble slows the bubble dissolution rate. On the other hand, Cable and Evans [9] found opposite results. According to Ramos [20], since both the diffusion flux and the melt for dissolution of a gas bubble move radially outward relative to the bubble surface, the concentration gradients and hence the rate of bubble dissolution will be smaller than those for a fixed boundary. Subramanian and Weinberg [22] discussed the significance of convective transport in bubble dissolution. As well as the present result in figure 4, their comparison indicates that the model ignoring only the motion of the melt underestimates the dissolution rate while the quasi-stationary approximation overestimates it. The negative radial velocity in the case of shrinkage tends to reduce oxygen transfer from the gas bubble to the melt, and as a result causes a decrease in the rate of bubble dissolution. Therefore, the solution in which the convective transport is considered may predict a longer bubble lifetime as compared with the present solution. It should be mentioned that the negative radial velocity due to the bubble shrinkage may also tend to make a concentration gradient at the bubble surface gentler, hence the rate of shrinkage lowers (Cable and Evans [9]). However, on the whole, the deviations between the radius–time curve obtained in the present work for oxygen bubble shrinkage and that calculated from the quasi-stationary model are rather small.

Subramanian and Weinberg [23] stated that the approximation which neglects the convection term in the mass transport equation but retains boundary movement with time in the equation for the flux (the NC approximation) deviates much more from the numerical solution than does the quasi-stationary approximation which ignores the convective transport in the mass transport equation and the boundary motion in the flux equation. It is to be noted that in their calculations based on the NC approximation the moving boundary was immobilized by the mapping in solving the mass transport equation even though the convective transport term was ignored. Their computational results, therefore, show rather large discrepancy between the rigorous numerical solution and the solution of the NC approximation. The NC approximation significantly underestimates the bubble shrinkage rates. On the other hand, the present model slightly overestimates the bubble shrinkage rates unlike the NC approximation. As mentioned previously, the predictions of the present approximate model lie between those of the quasi-stationary model and of the rigorous numerical solutions [21].

Assuming that R_a in parentheses in equation (12) is constant, integration gives (Doremus [5])

$$R_{a0}^2 - R_a^2 = 2\,D\,\Delta C\,t\left(1 + \frac{2\,R_{a0}}{\sqrt{\pi\,D\,t}}\right). \qquad (13)$$

It is clear from figure 4 that equation (13) rather underestimates the dissolution time for long time.

3.2 Multicomponent gas bubble

Since several gases are usually contained in glassmelts, the behavior of a gas bubble in a glassmelt containing several dissolved gases is also examined. As numerical examples, a gas bubble is considered which initially consists of nitrogen in a glassmelt containing oxygen, water, carbon dioxide, sulfur trioxide and nitrogen. Table 2 presents the values used for the computer simulation. They are based on the data in the work of Ramos [20 and 24]. In figure 5, the amounts of five substances in the gas bubble are plotted as a function of time. It should be noted that only the redox reaction of refining agents with oxygen is taken into account in the present simulation. The solid curves represent results where the redox reaction due to the refining agent (As^{3+}/As^{5+}) is taken into account, while the broken curves represent results without consideration of refining agents. Since the inital concentrations of O_2, CO_2, H_2O and SO_3 in the gas bubble are zero, they diffuse into the gas bubble. On the other hand, N_2 diffuses away from the gas bubble. It is seen from figure 5 that the O_2 diffusion in the melt containing the refining agent is somewhat faster than that without the refining agent since the redox reaction due to the refining agent increases the driving force or the concentration difference between the gas/liquid surface and the glassmelt bulk. The somewhat quick increases in CO_2 and H_2O concentrations with the refining agent are caused by the relative decrease in their concentrations at the gas/liquid interface due to rapid influx of O_2 into the gas bubble. The influence of the redox reaction on N_2 diffusion is quite small. The inflows of O_2, CO_2, H_2O and SO_3 dilute the N_2 concentration in the gas bubble and decrease the driving force for N_2 diffusion. Since, however, the diffusion coefficient of N_2 is small as compared with those of O_2, CO_2 and H_2O, the influence of the redox reaction on N_2 concentration in the gas bubble is quite small as well as that on SO_3 concentration.

Figure 6 illustrates the change in bubble radius with time of an initially pure N_2 bubble. It is seen that a faster growth occurs due to the redox reaction of the refining agent.

3.3 Comparison with the experimental data

The calculation result is compared with the available experimental data [25] in figure 7. The glass used in the experiments is an alkali alumina silicate glass containing 51 mol m^{-3} Sb_2O_3 as a refining agent. The approximate composition (in wt%) is: $62SiO_2$, 19RO, $15R_2O$ and $2Al_2O_3$. An isolated bubble of $R_{a0} = 7.8 \cdot 10^{-4}$ m was formed by injecting the oxygen gas into the glassmelt in the cell at 1473.15 K and 101.325 kPa. Diameter measurements were carried out using a microscope. The values used for obtaining computational results are quoted in table 3. The value of K_c was obtained using the data of Rüssel and Freude [22]. It is seen from the figure that the computational results agree reasonably well with the experimental data. In the later stages of bubble shrinkage, the shrinking becomes slower. It may be caused by the decrease in the concentration gradient at the surface of the bubble. The diffusion of foreign gases into the bubble may be another explanation.

Generally speaking, difficulties preclude making precise comparisons between the present calculations and the experimental data in the literature [7 and 26]. Accurate gas diffusion coefficient and solubility coefficient data in the glassmelts are not available at present. Furthermore, the melt conditions including the initially dissolved oxygen concentration in the melt for the data in the literature are usually not well characterized.

Table 2. Values used in computational results for a multicomponent bubble (O_2, N_2, CO_2, H_2O and SO_3) (figures 5 to 6)

$n' = 2$ for As^{3+}/As^{5+}
$R_{a0} = 10^{-3}$ m
$K_c = 0.1\ (\mathrm{mol\ m^{-3}})^{1/2}$
$T = 1473.15$ K
$m = 100\ \mathrm{mol\ m^{-3}}$
$P_a = 101325$ Pa

	D_i in $m^2\,s^{-1}$	L_i in $mol\,m^{-3}\,Pa^{-1}$	C_{0i} in $mol\,m^{-3}$
O_2	$6.41 \cdot 10^{-11}$	$2.21 \cdot 10^{-4}$	7.813
N_2	$7.00 \cdot 10^{-12}$	$1.76 \cdot 10^{-7}$	0.016
CO_2	$5.00 \cdot 10^{-11}$	$5.16 \cdot 10^{-7}$	3.977
H_2O	$1.80 \cdot 10^{-10}$	$1.37 \cdot 10^{-3}$	23.611
SO_3	$1.30 \cdot 10^{-11}$	$5.53 \cdot 10^{-2}$	77.500

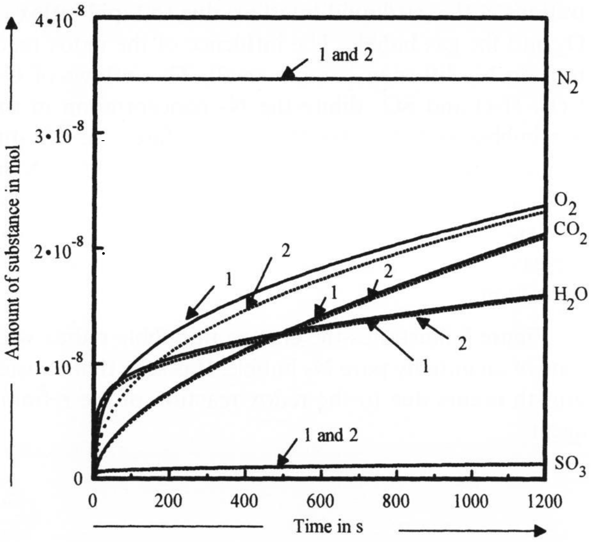

Figure 5. Amounts of substances in a multicomponent gas bubble as a function of time ($R_{a0} = 1 \cdot 10^{-3}$ m. Curve 1: with refining agents (As^{3+}/As^{5+}), curve 2: without refining agents.

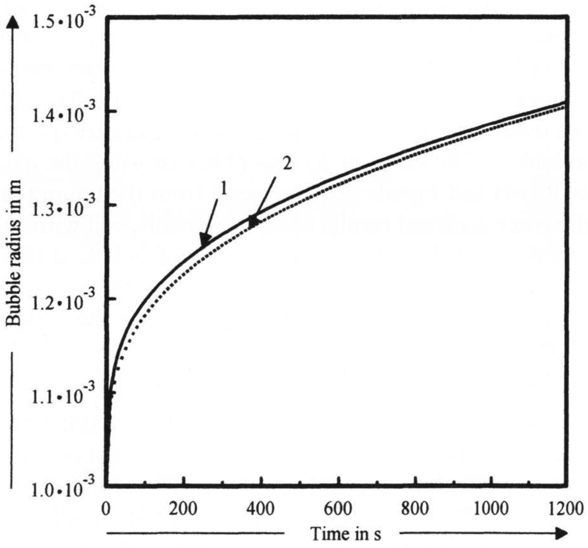

Figure 6. Growth of a multicomponent bubble ($R_{a0} = 1 \cdot 10^{-3}$ m). Curve 1: with refining agents (As^{3+}/As^{5+}), curve 2: without refining agents.

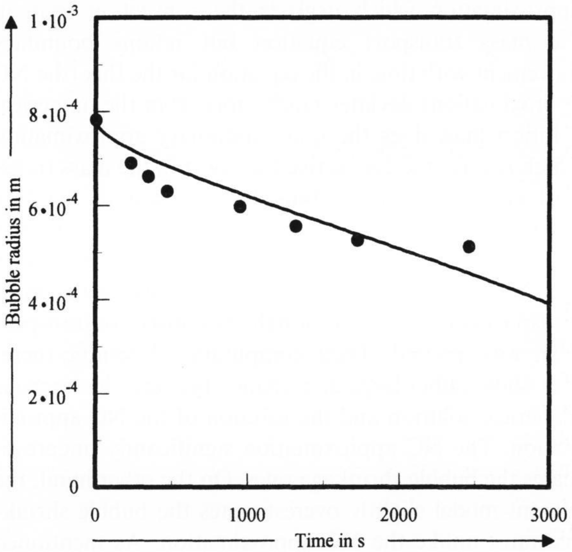

Figure 7. Shrinkage of an oxygen bubble at 1473.15 K with refining agents (Sb^{3+}/Sb^{5+}) ($R_{a0} = 7.8 \cdot 10^{-4}$ m). The curve is the result of this work, the points (●) are data from Kato [25].

4. Conclusions

A new approximate model of bubble dissolution or growth in glassmelts was formulated by taking account of the redox reactions due to refining agents. Using the method of finite differences, the resulting equations which can be recognized as a modification of the quasi-stationary approximation were solved. The significance of redox reactions due to refining agents in the refining process was examined. The applicability of the proposed approximate model was discussed using the computational results and experimental measurements in the literature.

The results of the numerical analysis indicate that the dissolution or growth of the stationary bubble is enhanced by the redox reaction due to refining agents. The mechanism of the bubble shrinkage or growth in the refining process is significantly controlled by the oxidation of the refining agents. For the bubble shrinkage, the redox reaction of the refining agents decreases the oxygen concentration in the glassmelt and as a result causes the rapid oxygen transfer from the bubble to the glassmelt and hence the fast shrinkage of the bubble. The present

Table 3. Values used for a comparison of the present model with experimental data [25] (figure 7)

$n' = 2$ for Sb^{3+}/Sb^{5+}
$R_{a0} = 7.8 \cdot 10^{-4}$ m
$K_c = 10\,(\mathrm{mol\,m^{-3}})^{1/2}$
$T = 1473.15$ K
$m = 51\,\mathrm{mol\,m^{-3}}$
$P_a = 101325$ Pa

$C_{0O_2} = 0.0\,\mathrm{mol\,m^{-3}}$
$L_{O_2} = 3 \cdot 10^{-6}\,\mathrm{mol\,m^{-3}\,Pa^{-1}}$
$D_{O_2} = 10^{-9}\,\mathrm{m^2\,s^{-1}}$

analysis was compared with the quasi-stationary model and the experimental data in the literature. Reasonable agreements were found. The present model predicts a slightly longer dissolution time as compared with that obtained by the quasi-stationary approximation. The growth of a multicomponent gas bubble was also examined. It was found that the bubble growth is enhanced by the redox equilibrium reaction of the refining agents as well as the bubble shrinkage.

In the literature, there have been several experimental results describing the behavior of a single gas bubble in a glassmelt. It must be recognized that there exist difficulties for a precise comparison between theoretical and experimental results [7 and 26]. In general, little precaution has been taken to ensure the experimental conditions. Furthermore, there is the recurrent problem of thermodynamic and transport data, i.e., the diffusivities and solubilities of oxygen have not been accurately determined [27]. For example, Doremus [5] and Terai and Oishi [28] reported $D_{O_2} = 6.4 \cdot 10^{-11}$ and $2.4 \cdot 10^{-12}\,\mathrm{m^2\,s^{-1}}$, respectively, at 1473.15 K. Most of their measurements include the influence of refining agents or chemical reaction and hence they are apparent values instead of real values.

The present work is a first step of attempts to gain insight into the bubble dissolution process in glass refining.

6. Nomenclature

C	concentration in the melt in $\mathrm{mol\,m^{-3}}$
C_0	initial concentration in the melt in $\mathrm{mol\,m^{-3}}$
D	diffusion coefficient of oxygen in the melt in $\mathrm{m^2\,s^{-1}}$
D_c	modified diffusion coefficient in $\mathrm{m^2\,s^{-1}}$
K_c	equilibrium constant for equation (1) in $(\mathrm{mol\,m^{-3}})^{n'/4}$
L	Henry's law solubility constant in $\mathrm{mol\,m^{-3}\,Pa^{-1}}$
m	concentration of refining agents in $\mathrm{mol\,m^{-3}}$
n	number of moles in mol
n'	number of electrons transferred
P_a	gas partial pressure within the bubble in Pa
R_A	molar rate of production per unit volume in $\mathrm{mol\,m^{-3}\,s^{-1}}$
R_a	bubble radius in m
R_g	gas constant in $\mathrm{J\,mol^{-1}\,K^{-1}}$
r	radial distance from the center of the stationary bubble in m
T	temperature in K
t	time in s
u	variable ($= r\,C$) in $\mathrm{mol\,m^{-2}}$
ϱ_g	density of gas in $\mathrm{kg\,m^{-3}}$

7. References

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