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Dissolution of bubbles in glassmelts with equilibrium redox reactions: approximations for a moving bubble boundary

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The solutions of the diffusion equations with a moving boundary for bubble dissolution (or growth) accompanied by a chemical reaction, were examined. From the viewpoint of the interaction between the convective transport and the chemical reactions, some approximations introduced to solve numerically the equations governing the bubble dissolution (or growth) were studied. For bubble dissolution in glassmelts with equilibrium redox reactions due to refining agents, the applicability of the convection transport approximations employed in the literature was discussed. It was found that our previously proposed model, in which the convective transport is neglected, agrees well with the rigorous finite-difference solution and is more reasonable compared with the approximate models proposed in the literature. Comparisons between our approximate model and the rigorous numerical solution indicate better agreement for dissolution of a bubble by simultaneous mass transfer and chemical reaction, compared with that by only mass transfer. © *1998 Chapman & Hall*

1. Introduction

Dissolution or growth of bubbles is important in many chemical and physical processes. Mathematically, this problem is diffusion with a spherical moving boundary. A bubble dissolves or grows by diffusion. The resulting motion of the bubble boundary introduces a convective transport in the diffusion equation which makes it very difficult to solve the problem. This moving boundary value problem is non-linear. Accurate solutions are obtained by using finite-difference techniques. For instance, Readey and Cooper [1], Cable and Evans [2], Duda and Vrentas [3] and Cable and Frade [4] have solved the differential equations numerically. The convection transport resulting from the bubble surface movement and which makes it very difficult to obtain a solution, has often been subjected to modification. In many industrial processes, dissolution or growth of bubbles is accompanied by chemical reactions. They increase the difficulty of solving problems, and numerical solutions of the differential equations are unavoidable. Because there is much to be gained by approximations, several investigators have used approximate solutions. The approximations require much less computational labour than the rigorous finite-difference solution. Furthermore, approximate solutions often provide insight into the structure of the dissolution or growth of a bubble. For instance, Epstein and Plesset [5] presented a quasi-stationary model in which moving boundary effects are ignored. 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 liquid. 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 has been known that the quasi-stationary model provides relatively reasonable approximations. Tao [6, 7] obtained the solutions in which the convective transport in the diffusion equation is ignored but it is retained in the mass balance at the bubble surface leading to an expression for the rate of change in bubble radius. Subramanian and Weinberg [8] discussed the modifications for the convective transport in the literature and stated that the approximation carried out by Tao [6, 7] is inconsistent. However, they studied only the system without chemical reactions.

Subramanian and Chi [9] discussed the effect of chemical reaction on bubble dissolution and compared the finite difference results with a perturbation expansion, a quasi-stationary approximation and a quasi-steady approximation. However, the reaction examined in their work is only a first-order irreversible chemical reaction.

One practical example of the moving boundary value problem is a removal of bubbles from glassmelts, or refining [2–4, 9]. Bubbles must be removed

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from the molten glass before cooling to produce high-quality glasses. Therefore, the dissolution or growth of stationary bubbles in an infinite glassmelt has been extensively studied. Refining agents, such as arsenic and antimony oxides, are often added to glass batch to enhance the removal of bubbles. The refining agents react with oxygen physically dissolved in the glassmelt, reduce its concentration and hence increase the rate of oxygen diffusion into the glassmelt. However, in most of the previous studies, the effects of the equilibrium redox reactions due to the refining agents on bubble dissolution or growth have not been considered quantitatively. Recently, Yoshikawa and Kawase [10] proposed a model for dissolution or growth of bubbles in glassmelts with equilibrium redox reactions of refining agents. Their model can be recognized to be a modification of the quasi-stationary model. It takes into account the change in bubble radius with time in the calculation of the concentration profiles, unlike the quasi-stationary analysis. Therefore, their model can provide more rational predictions as compared with the quasi-stationary model [10].

The objective of this work was to examine the effect of convective transport on the solution of the diffusion equation for bubble dissolution in the glassmelt with equilibrium redox reactions of refining agents. The predicted dissolution rates of a stationary bubble by our previously proposed approximate model [10] are compared with the results obtained from the finite-difference solution of the complete diffusion equation. The latter serves as the principal basis for assessing the general applicability and accuracy of our previously proposed approximation. The influence of the equilibrium redox reactions on the applicability of the approximations introduced for the convective trasnsport is examined.

2. The diffusion equation

An isolated spherical oxygen bubble, stationary in an infinite isothermal glassmelt, is considered as a numerical example of moving bubble boundary problems (Fig. 1).

The following assumptions are made for simplification [10].

1. The kinetics of equilibration at the bubble surface are rapid so that the rate-controlling process is diffusion in the glassmelt.
2. The physical properties, including diffusion coefficient and Henry's law constant of oxygen gas, are constant with concentration and time.
3. Oxygen gas is ideal.
4. The surface tension and viscosity effects are negligible.
5. The concentration of dissolved oxygen gas does not depend on the angular coordinates but only on the distance from the centre of the bubble.
6. The saturation concentration for oxygen at the surface of the bubble is independent of time.
7. The evaporation of refining agents is negligible.

A material balance for oxygen in the melt is given as [4, 10]

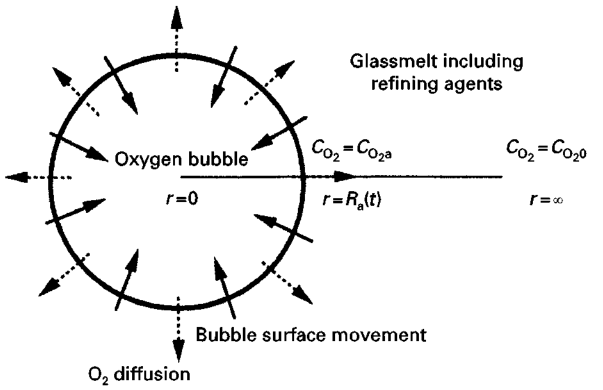

Figure 1 Dissolution of a stationary oxygen bubble in a glassmelt.

$$\frac{\partial C_{O_2}}{\partial t}+v(t,r)\frac{\partial C_{O_2}}{\partial r} = D_{O_2}\left(\frac{\partial^2 C_{O_2}}{\partial r^2}+\frac{2}{r}\frac{\partial C_{O_2}}{\partial r}\right)+R_{AO_2} \tag{1}$$

where C_{O_2} is the molar concentration of oxygen, $v(t, r)$ is the radial velocity of the solution, D_{O_2} is the diffusivity of oxygen in the melt, R_{AO_2} is the reaction term and r is the distance measured from the centre of the bubble.

Equation 1 is to be solved subject to the following initial and boundary conditions

$$C_{O_2}(r,0) = C_{O_20} \qquad r > R_a \tag{2a}$$

$$C_{O_2}(R_a,t) = C_{O_2a} = L_{O_2}P_{aO_2} \qquad t > 0 \tag{2b}$$

$$C_{O_2}(\infty,t) = C_{O_20} \qquad t \geqslant 0 \tag{2c}$$

where R_A is bubble radius, P_{aO_2} is oxygen partial pressure within the bubble and L_{O_2} is Henry's law constant. Because the equilibrium conditions are assumed at the interface, the interfacial oxygen gas concentration is related to the partial pressures of oxygen by Henry's law, Equation 2b. It is assumed that the volume of liquid is large compared with the diffusion distances from the bubble, Equation 2c.

The redox equilibrium reaction of refining agents, or variable-valence metal oxides, is described in generalized form as [11]

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

where $M^{(x'+n')+}$ is the oxidized species of variable-valence ion M and $M^{x'+}$ is the reduced species of 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+}. The above 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

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

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 glassmelts, the equilibrium constant for Equation 3, K_C, is defined as [11]

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

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

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

From Equations 6, 7 and 8, we have

$$\frac{\partial C_{O_2}}{\partial t} + v(t,r)\frac{\partial C_{O_2}}{\partial r} = D_{O_2}\left(\frac{\partial^2 C_{O_2}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{O_2}}{\partial r}\right) - \left(\frac{n'}{4}\right)^2 \frac{K_C m C_{O_2}^{n'/4-1}}{(K_C + C_{O_2}^{n'/4})^2}\frac{\partial C_{O_2}}{\partial t} \tag{9}$$

Substituting an explicit relation for the radial velocity of the liquid yields [4, 10]

$$\frac{\partial C_{O_2}}{\partial t} + \frac{R_a^2}{r^2}\frac{dR_a}{dt}\frac{\partial C_{O_2}}{\partial r} = D_{O_2}\left(\frac{\partial^2 C_{O_2}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{O_2}}{\partial r}\right) - \left(\frac{n'}{4}\right)^2 \frac{K_C m C_{O_2}^{n'/4-1}}{(K_C + C_{O_2}^{n'/4})^2}\frac{\partial C_{O_2}}{\partial t} \tag{10}$$

We assume that the ratio of the density of the bubble to the density of the outer liquid is small. This assumption has been introduced in many previous investigations because interest has been focused on the dissolution or growth of gas bubbles.

We introduce the following dimensionless variables [4]

$$\xi = \frac{r}{R_a(t)}, \tag{11a}$$

$$\zeta = \frac{R_a(t)}{R_{a0}}, \tag{11b}$$

$$\tau = \frac{D_{O_2} t}{R_{a0}^2}, \tag{11c}$$

$$\Phi = \frac{C_{O_2} - C_{O_2 0}}{C_{O_2 S}}, \tag{11d}$$

$$\Psi = \left(\frac{n'}{4}\right)^2 \frac{K_C m C_{O_2}^{n'/4-1}}{(K_C + C_{O_2}^{n'/4})^2} \tag{11e}$$

Where $C_{O_2 S}$ is the concentration of oxygen in the bubble.

Equation 10 may be rewritten as

$$(1+\Psi)\zeta^2\frac{\partial \Phi}{\partial \tau} + \zeta\{\xi^{-2} - (1+\Psi)\xi\}\frac{d\zeta}{d\tau}\frac{\partial \Phi}{\partial \xi} = \frac{\partial^2 \Phi}{\partial \xi^2} + 2\xi^{-1}\frac{\partial \Phi}{\partial \xi} \tag{12}$$

The transformation of the space variable into ξ implies the immobilization of the bubble surface [4]. When there is no equilibrium redox reaction in the melt ($\Psi = 0$), the above equation reduces to the equation derived by Cable and Frade [4]. Subramanian and Weinberg [8] discussed the role of convection transport in the dissolution or growth of a bubble and showed that the model proposed by Tao [6, 7] largely underestimates the dissolution rate. In Tao's model, the convective transport in the diffusion equation is neglected and the bubble surface movement in the mass balance at the bubble surface is retained. Tao's model extended to include the reaction term may be written as

$$(1+\Psi)\zeta^2\frac{\partial \Phi}{\partial \tau} - \zeta(1+\Psi)\xi\frac{d\zeta}{d\tau}\frac{\partial \Phi}{\partial \xi} = \frac{\partial^2 \Phi}{\partial \xi^2} + 2\xi^{-1}\frac{\partial \Phi}{\partial \xi} \tag{13}$$

This equation is obtained by omitting the first term in the brace in Equation 12. In other words, Equation 13 corresponds to $\zeta\xi^{-2} = 0$ in Equation 12. The term arising by the time derivative term and appearing by introduction of ξ remains. Because Tao [6, 7] did not clearly describe the pertinent diffusion equation [12], we obtained the above equation using the computational result given in Fig. 1 of Subramanian and Weinberg's paper [8]. The computational results of Equation 13 for $\Psi = 0$ completely coincide with the results presented by Subramanian and Weinberg [8]. This model is denoted by the NC model. As mentioned by Subramanian and Weinberg [8], the approximations are halfway. Although the convective transport in the diffusion equation seems to be neglected, as seen in Equation 13, a part of the second term in the left-hand side which appears due to the introduction of the dimensionless variables defined by Equation 11, remains. This problem will be discussed later.

The model proposed recently by Yoshikawa and Kawase [10] may be written as

$$(1+\Psi)\zeta^2\frac{\partial \Phi}{\partial \tau} = \frac{\partial^2 \Phi}{\partial \xi^2} + 2\xi^{-1}\frac{\partial \Phi}{\partial \xi} \tag{14}$$

It is clear from a comparison between Equations 13 and 14 that the convection transport is completely neglected. Because, in other words, the second term in the left-hand side of Equation 10 is completely omitted, the convection term does not appear in Equation 14. When $\Psi = 0$, this form is the same as the quasi-stationary (QS) model. Therefore, the model previously proposed by us [10] can be recognized as a modification of the QS model and then is denoted as the MQS model. It should be emphasized, however, that there is a difference between them. While the QS analysis ignores convection transport in the mass transport equation and the boundary movement in the equation for the flux. The MQS model, in which the convection transport is neglected in the diffusion equation as well as the QS 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.

In the QS model, the mass flux at $t = t_1$ (arbitrary) is calculated by assuming that during $t = 0 \sim t_1$ the bubble boundary remains constant for R_a at $t = t_1$. Therefore the QS model overestimates the oxygen flux at the bubble surface and as a result the bubble dissolution rate. In the MQS model, on the other hand, the change of the bubble radius is considered at every increment of t in the numerical calculation [10].

3. Solution procedure

The dissolution of the bubble was calculated by the following procedure.

1. The concentration distributions of oxygen in the glassmelt at τ are calculated from Equations 12, 13 or 14.

2. The mass flux at the bubble surface is calculated using the numerical result for the concentration distribution obtained by the above calculation step. The oxygen molar flow from the bubble per unit time can be calculated from the following equation

$$\frac{\mathrm{d}n_{\mathrm{O}_2}}{\mathrm{d}t} = -4\pi R_{\mathrm{a}}^2 D_{\mathrm{O}_2}\left(\frac{\partial C_{\mathrm{O}_2}}{\partial r}\right)_{R_{\mathrm{a}}} \tag{15a}$$

$$\frac{\mathrm{d}n_{\mathrm{O}_2}}{\mathrm{d}\tau} = -4\pi R_{\mathrm{a}} R_{\mathrm{a}0}^2 C_{\mathrm{O}_2\mathrm{s}}\left(\frac{\partial \Phi}{\partial \xi}\right)_{\zeta} \tag{15b}$$

The mass flux or the concentration gradient at the bubble surface $(\partial\Phi/\partial\xi)_{\zeta}$ is evaluated by means of a three-point finite-difference approximation as well as the works of Cable and Evans [2] and Ramos [13]. The mesh sizes selected in this work are small enough to estimate the concentration gradient at the surface precisely. This will be discussed below.

3. The change in bubble radius is calculated by the following mass balance equation at the interface

$$\frac{\mathrm{d}R_{\mathrm{a}}}{\mathrm{d}t}\left(=\frac{D_{\mathrm{O}_2}}{R_{\mathrm{a}0}}\frac{\mathrm{d}\zeta}{\mathrm{d}\tau}\right) = \frac{R_{\mathrm{g}}T}{4\pi R_{\mathrm{a}}^2 P_{\mathrm{aO}_2}}\frac{D_{\mathrm{O}_2}}{R_{\mathrm{a}0}^2}\frac{\mathrm{d}n_{\mathrm{O}_2}}{\mathrm{d}\tau} \tag{16}$$

where T is temperature and R_g is gas constant.

The calculation procedure described above is similar to the quasi-stationary analysis of Epstein and Plesset [5].

4. Results and discussion

We discussed the approximations for the moving bubble boundary using the finite-difference solutions of the exact diffusion equation, Equation 12 (the EX solution), the model of Yoshikawa and Kawase [10] (MQS model), the quasi-stationary model (QS model) and the model of Tao [6–8] (NC model). The EX solutions, which can be considered to be excellent approximation to the exact solutions, were obtained in order to provide a precise solution against which the various approximations could be tested.

As a numerical example, a stationary pure oxygen bubble (partial pressure = 101.325 kPa) in an infinite glassmelt containing arsenic oxides as refining agents at 1473.15 K was considered (Fig. 1). In this case, the bubble shrinks due to oxygen absorption. Oxygen is absorbed in the glassmelt containing arsenic, by reacting with the lower valence form of As_2O_3 as well as physical absorption. The values used for the computer simulation are given in Table I. They were determined on the basis of the data in the literature [11, 13].

A Crank–Nicolson technique was employed to solve diffusion equations. The incremented variables were $\zeta$and τ. 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 computational results for the refining time required for the bubble to dissolve completely were independent of mesh sizes within 0.2%. In this work, the bubble refining time was defined as the time required for the bubble radius to become one-hundredth of the initial bubble radius. Unlike the works of Duda and Vrentas [3], Subramanian and Chi [9] and Ramos [13], a mapping was not used in this work. As well as the works of Readey and Cooper [1] and Cable and Evans [2], we set up a finite-difference mesh for a semi-infinite region. Although Duda and Vrentas [3] pointed out that Cable and Evans [2] underestimated the concentration gradients at the bubble surface in calculating the flux across the bubble surface and suggested the importance of the introduction of a mapping in a numerical solution, in this work no particular difficulty in convergence of the finite-difference solutions was experienced even at the higher dissolution rates, and therefore the mapping was not necessary to solve the governing equations for bubble dissolution. It should be mentioned that we had employed at least two-hundredths and five-thousandths of time and space mesh sizes used by Cable and Evans [2], respectively. Furthermore, the accuracy of the computational scheme without mapping in this work was confirmed by obtaining excellent agreement between the present numerical solutions of Equation 12 with the numerical results in the literature [3, 9]. 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 [9]. It varies for various values of the reaction rate and the driving force. The increment sizes selected to calculate

TABLE I Values used in the computational results

Equilibrium redox reaction
$n' = 2$ $\quad K_c = 0.1\ ((\mathrm{mol\,m^{-3}})^{-1/2})$ $\quad m = 100\ (\mathrm{mol\,m^{-3}})$

Mass transfer
$C_{\mathrm{O}_2 0} = 0\ (\mathrm{mol\,m^{-3}})$ $\quad D_{\mathrm{O}_2} = 1\times10^{-9} (\mathrm{m^2\,s^{-1}})$
$N_a = 0.01\text{–}1.0$ $\quad p_a = 101.325\,(\mathrm{kPa})$ $\quad T = 1473.15\ (\mathrm{K})$
$R_{a0} = 1\times10^{-4}\ (\mathrm{m})$

the concentration distributions of oxygen in the case with chemical reaction in the melt were smaller than those in the case of no chemical reaction. The calculations for the case of no reaction converged more readily compared with those for the presence of reaction. As mentioned above, we had to make mesh sizes of τ and ζ small to estimate numerically the concentration gradient at the bubble surface with accuracy. The oxygen concentration gradient at the bubble surface was estimated to evaluate the oxygen flux using a three-point finite-difference approximation (Equation 15) [3, 13]. 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. Because the oxygen concentration in the presence of the redox reaction was steeper than that in the absence of the reaction, the smaller mesh sizes for ζ and τ were required for the conversion of the calculations for the dissolution of a bubble in the presence of a redox reaction. We applied one-twentieth and one-tenth of space and time mesh sizes for the case of the absence of a reaction.

In Fig. 2, the dimensionless bubble radius, ζ, is plotted as a function of dimensionless time, τ, at small driving forces ($N_{\mathrm{a}} = (C_{\mathrm{O_2a}} - C_{\mathrm{O_20}})/C_{\mathrm{O_2S}} = 0.05$) when the glassmelt includes no refining agent. The MQS and QS models predict somewhat faster dissolution rates than the EX solutions as well as the results of Weinberg *et al.* [14]. This may be due to the neglect of the convection transport in the diffusion equation. The MQS and QS models overestimate the concentration gradient at the bubble surface by neglecting convective transport. For bubble dissolution, the radial velocity at the bubble surface is negative and the surface moves inwards. On the other hand, the diffusion mass flux is outwards. Therefore, the effect of boundary movement weakens the concentration gradient at the bubble surface and as a result reduces the dissolution rate. These approximate models neglect the effect of boundary movement. In other words, they ignore the reduction of the concentration gradient due to the convective transport. Consequently, they overestimate the bubble dissolution rate. 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 MQS model, the change in bubble radius with time is taken into account in the calculation of the concentration profiles of gases in the glassmelt by solving Equation 13, unlike in the QS analysis. Although in the MQS model the term for radial convection is neglected in the conservation equation, the gas concentration profiles accounting for the interface movement with time due to dissolution or stripping are used to calculate the change in the bubble size. Therefore, the MQS model provides somewhat better predictions compared with the QS model. On the other hand, the NC model examined by Subramanian and Weinberg [8] underestimates the dissolution rate.

The results for the dimensionless bubble radius for the case of no redox reaction and high driving force ($N_{\mathrm{a}} = 1$) are plotted against dimensionless time in Fig. 3. It is seen that the MQS and QS models overestimate the refining time. The discrepancy from the EX solutions increases with driving force. The results obtained by the MQS model lie between those of the QS model and the EX solutions for every N_{a}. This implies that the present model provides better results compared with the QS model. In other words, the approximations utilized in the MQS model are more realistic than those in the QS model. The NC model predicts rather slow dissolution rates compared with the EX solutions.

Fig. 4 shows the computed dimensionless radius as a function of dimensionless time for bubble dissolution in the glassmelt with the refining reaction at

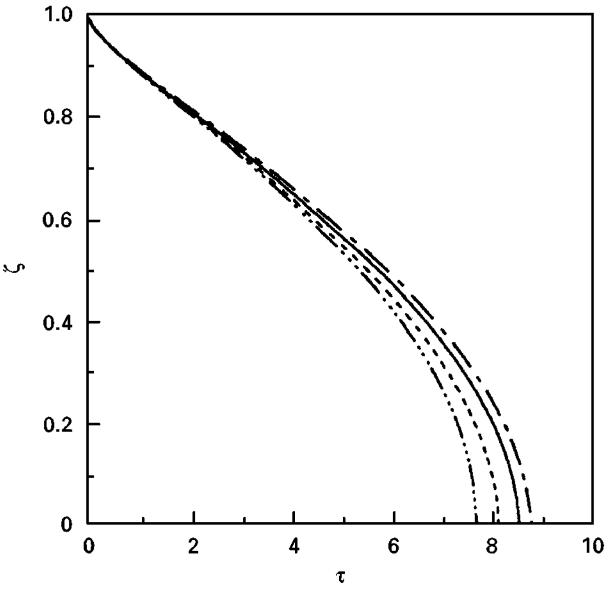

Figure 2 Dimensionless bubble radius versus dimensionless time for the absence of a redox reaction ($N_{\mathrm{a}} = 0.05$). (——) The EX solution (–––) MQS model, (----) QS model, (———) NC model.

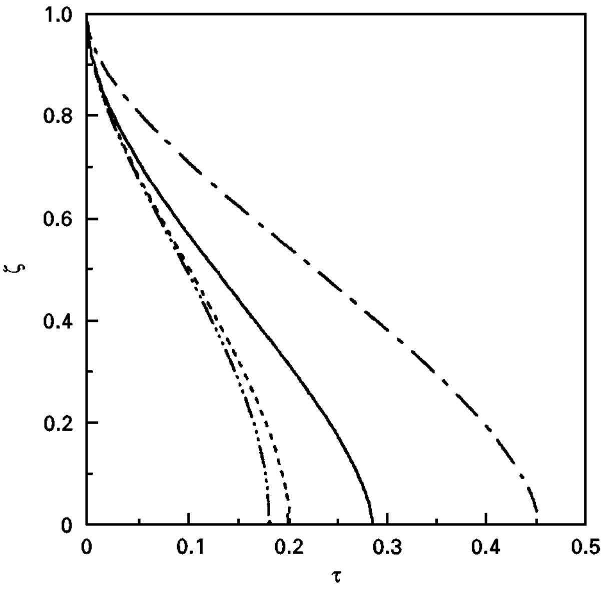

Figure 3 Dimensionless bubble radius versus dimensionless time for the absence of a redox reaction ($N_{\mathrm{a}} = 1.0$). (——) The EX solution, (–––) MQS model, (----) QS model, (———) NC model.

$N_a = 0.05$ which is the case when the driving force is small. It is found from Figs 2 and 4 that the refining time of the bubble with the refining reaction is shorter than without the reaction. It is clear that the dissolution of a stationary oxygen bubble is enhanced by the equilibrium redox reaction in the glassmelt. For the bubble dissolution, the equilibrium redox reaction of refining agents decreases the oxygen concentration in the glassmelts and as a result causes the rapid oxygen transfer from the bubble to the glassmelt and hence the fast dissolution of the bubble. The predictions of the MQS model are almost indistinguishable from the EX solutions. On the other hand, the NC model underpredicts the bubble dissolution rates and the discrepancy is somewhat larger compared with the results in the absence of an equilibrium redox reaction given in Fig. 2.

In Fig. 5, the dimensionless bubble radii are plotted against the dimensionless time for $N_a = 1.00$ with refining reaction. While the MQS model agrees reasonably well with the EX solution even at large driving force, the NC model is in poor agreement with the EX solution. When the time is small, there is no significant difference in the curves between the MQS model and the EX solution. Because the change in the bubble size is small for small time, the neglect of bubble surface movement has only a slight effect on oxygen transfer.

Figs 6 and 7 indicate the relative errors based on the refining times, t_r, of the MQS and NC models without refining reaction and with refining reaction, respectively. The accuracy of the predictions of the approximate models is expressed in terms of the relative error in t_r defined as

$$\text{Relative error}(\%) = \frac{t_r(\text{approximate model}) - t_r(\text{the EX solution})}{t_r(\text{the EX solution})} \times 100 \tag{17}$$

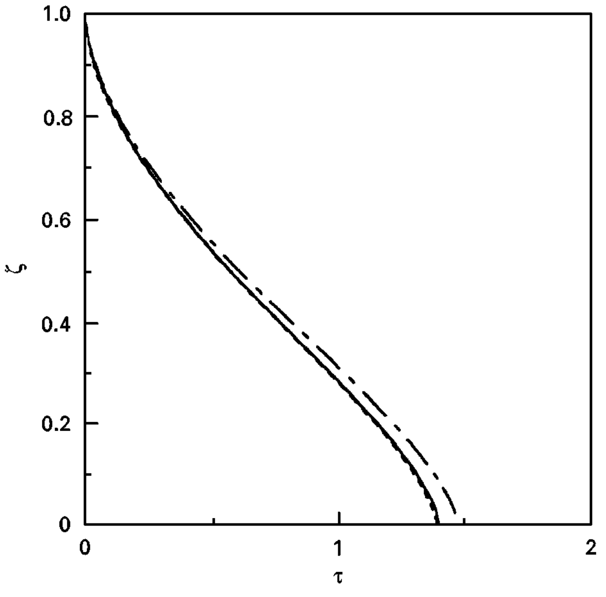

Figure 4 Dimensionless bubble radius versus dimensionless time for the presence of a redox reaction ($N_a = 0.05$). (——) The EX solution, (- - -) MQS model, (— — —) NC model.

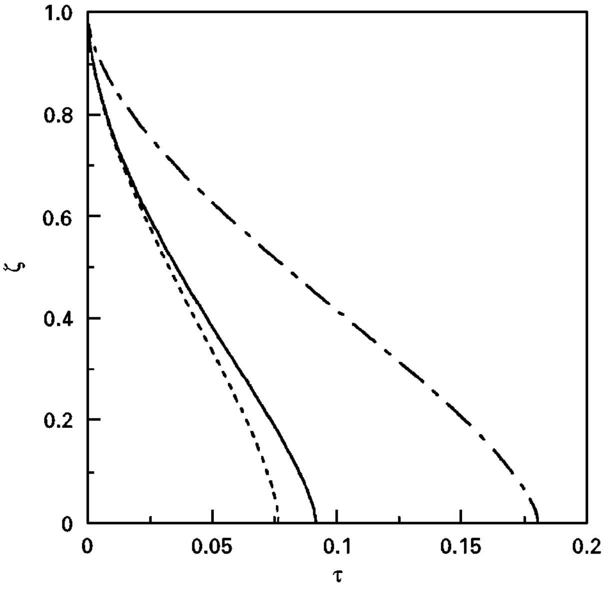

Figure 5 Dimensionless bubble radius versus dimensionless time for the presence of a redox reaction ($N_a = 1.0$). (——) The EX solution, (- - -) MQS model, (— — —) NC model.

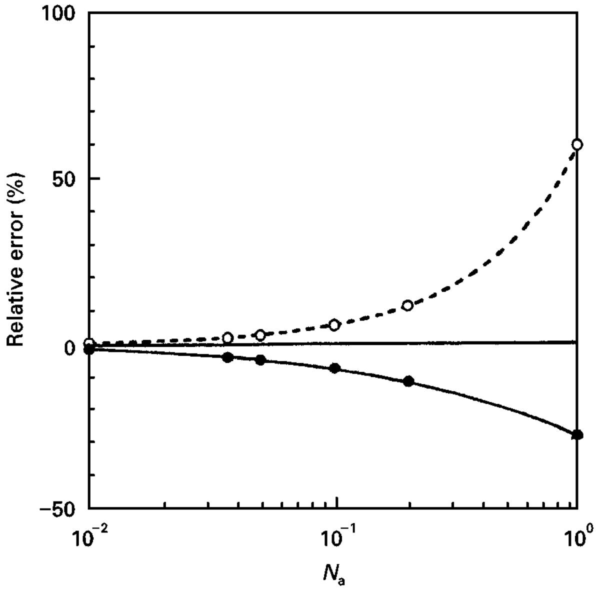

Figure 6 Relative errors of the MQS and NC models for the absence of a redox reaction. (—●—) MQS model, (- - -○- - -) NC model.

The results in Fig. 6 indicate that for small N_a the NC model predicts slightly more accurate refining times compared with the MQS model. For larger N_a, however, the accuracy of the NC model is rather poor. It is clear from Figs 6 and 7 that the effect of the convective transport on the bubble dissolution in the MQS model is reduced by the equilibrium redox reaction. In the NC model, on the other hand, the discrepancy from the EX solution is enlarged by the presence of an equilibrium redox reaction due to the refining agents. While the terms having a negative sign on the left-hand side of Equation 12 delay the dissolution rates, those having a positive sign hasten the dissolution rates. The terms relating to the equilibrium redox reactions appear on the left-hand side of Equation 12

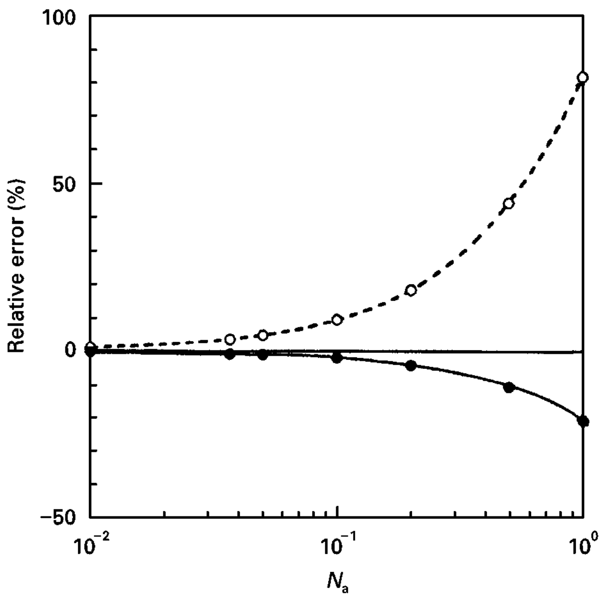

Figure 7 Relative errors of the MQS and NC models for the presence of a redox reaction (—●—) MQS model (---○---) NC model.

and have positive signs. Therefore, the redox reaction hastens the bubble dissolution rates. In the NC model, the term for convective transport remained on the left-hand side of Equation 12 and has a negative sign.

5. Conclusions

The approximate model previously proposed by the present authors [10] predicts slightly longer refining time compared with that obtained by the quasi-stationary approximation, and its predictions are somewhat shorter than the exact finite-difference solutions. The negative radial velocity due to the bubble dissolution may tend to produce a gentler concentration gradient at the bubble surface, and hence a lower dissolution rate. Therefore, the rigorous numerical solution in which the convective transport is considered may predict longer refining time compared with the our previously proposed model. However, on the whole, the deviations between the radius–time curve obtained from our previously proposed model for oxygen bubble dissolution and the finite-difference solution of the complete diffusion equation, are rather small.

It was found that the equilibrium redox reaction of the refining agents reduces inaccuracy caused by ignoring the convection transport in the diffusion equation. The redox reaction enhances the dissolution rate and as a result decreases the influence of the convection transport on the bubble dissolution.

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