Phase field simulation study of the dissolution behavior of Al$_2$O$_3$ into CaO-Al$_2$O$_3$-SiO$_2$ slags

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Abstract

A quantitative phase-field model has been implemented to study the dissolution behavior of alumina (Al$_2$O$_3$) into CaO-Al$_2$O$_3$-SiO$_2$ slags. The simulations allowed evaluating the influence of temperature and composition on the diffusion paths and dissolution rates of Al$_2$O$_3$ into CaO-Al$_2$O$_3$-SiO$_2$ slags. The results obtained in the simulations are consistent with experimental observations and the predictions from an analytical dissolution model. The phase field simulations show that the dissolution rate of Al$_2$O$_3$ increases with temperature. Increasing CaO at a fixed Al$_2$O$_3$ content or decreasing Al$_2$O$_3$ content at a fixed CaO/SiO$_2$ ratio also results in a higher dissolution rate of Al$_2$O$_3$. The results are further interpreted based on thermodynamic and kinetic considerations.

Keywords: Phase-field model; Diffusion path; Dissolution rate; Alumina; CaO-Al$_2$O$_3$-SiO$_2$ slag
1. Introduction

A multitude of research efforts have been made to understand the behavior of oxide dissolution in metallurgical slags. Its significance is at least related with three applications, i.e. metal cleanliness, refractory degradation and slag formation in metallurgical processes. Different dissolution behaviors are desired for these applications. For example, in the case of refractory materials, one may target slow, indirect dissolution in order to enhance the service life-time of the refractory lining. In the other two cases, fast dissolution is required. As regards to the oxide inclusions during a typical clean steel production, inclusions need to dissolve promptly into the slag phase. If the kinetics of dissolution is not sufficiently fast, non-dissolved inclusions will rest near the slag/steel interface and thereby increase the risk of entrapment by the liquid steel [1].

A lot of experimental work has focused on the dissolution behavior of alumina in molten slags since Al$_2$O$_3$ is widely used as the key component in the refractory material as well as in the slag. Among molten slags, CaO-Al$_2$O$_3$-SiO$_2$ attracts continuous interest from both academic and industrial value due to its importance in ladle metallurgy for inclusion removal [2]. Therefore, obtaining a better understanding of its dissolution behavior will be helpful to improve both the refractory life-time and steel cleanliness [2-12]. For instance, the dissolution kinetics have been measured using a dip technique [3], whereby an Al$_2$O$_3$ cylinder is immersed into liquid slag. The dissolution mechanism and influence of the related experimental parameters can be understood by characterization of the sample after the test. However, this post mortem
determination of dissolution mechanisms and kinetics is an elaborate and intrinsically indirect procedure. Recently, the high temperature laser scanning confocal microscope (CSLM) [2,4-8] has become available, which allows an in-situ observation of Al₂O₃ dissolution in slags. Most macro dissolution studies have shown that alumina dissolution in liquid slags is a mass transfer controlled process [9-15]. Nevertheless, the limitations of the current experimental approaches are also apparent, e.g. the condition of a post-mortem observation is different from the real circumstances at higher temperature. Frequently, the obtainable results are averaged quantities from a few experiments, which might not reflect the underlying physicochemical mechanisms of the process entirely. In addition, full understanding of all the factors affecting the dissolution behavior of alumina, such as temperature, diffusivity and composition, will be very expensive, time consuming and difficult. In such situations, mathematical modeling and numerical simulation offer complementary insights in the interpretation of the experimental results and contribute to the determination of the fundamental phenomena at the root of the observed behavior.

Dissolution phenomena have been modeled using a broad range of approaches, ranging from analytical models [16,17] to numerical simulations, both of which are at the macroscopic [18-20] / lattice scale [21,22]. For instance, J.-H. Kang et al. [19] studied carbide dissolution behavior in a variety of bearing steel. It is found that precipitate dissolution is faster for an increasing alloying content, a smaller precipitate size and a higher initial precipitate volume fraction. In this work, alumina dissolution in CaO-Al₂O₃-SiO₂ slag systems is investigated at the mesoscale using the phase field
method (PFM). PFM is an elegant and simple technique to simulate the evolution of the microstructure of a multi-component and multi-phase material [23]. In contrast to other existing macroscopic and lattice models, the dissolution kinetics, diffusion profiles and the morphology of the individual phases can be described simultaneously by PFM. A recently developed phase field model for oxide melts [24] was used to simulate the dissolution of $\text{Al}_2\text{O}_3$ in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slags. First, simulated diffusion paths and dissolution rates were compared with those obtained from an analytical model and available experimental data in literature, in order to consolidate the validation of the model. In addition, the effect of temperature and composition on the dissolution kinetics of $\text{Al}_2\text{O}_3$ into molten $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ was then investigated using this validated phase-field modeling approach. A summary of the phase field simulation technique is given in Section 2. The numerical setup of the simulations is explained in Section 3. The simulation results are presented and discussed in Section 4. Finally, the conclusions are formulated in Section 5.

2. Model description

In this section, the phase field model used in the present work is briefly described. The details of the model and the implementation are given in Ref [24]. In the considered phase field model, the different phases $\rho$ are identified through independent non-conserved phase-field variables, $\eta_\rho$, with $\eta_\rho = 1$ representing the phase $\rho$ is present and $\eta_\rho = 0$ representing phase $\rho$ is absent at a certain point in the system. At the interface between two phases, the phase-field variables representing the adjacent phases vary smoothly and monotonously from 0 to 1 and vice versa. Conserved field variable $x_k$,
representing the local molar fraction of C-1 independent components \( k \), are used to describe the spatial variations in composition. In the present study, ternary systems are considered and therefore two conserved fields \( x_k \) are used, namely \( x_{\text{Al}_2\text{O}_3} \) and \( x_{\text{CaO}} \), and \( \text{SiO}_2 \) is taken as the dependent component. Two phases exist in this system, namely solid \( \text{Al}_2\text{O}_3 \) and molten liquid slag. Two phase-fields \( \eta \) are used to represent the two phases.

According to the principles of non-equilibrium thermodynamics, microstructure evolution in an isothermal system at constant pressure is driven by the minimization of the total Gibbs energy of the system. The total Gibbs energy \( F \) in the applied phase-field model is defined as

\[
F = \int \left[ m f_0(\eta_i) + \frac{k}{2} \sum_{i=1}^{2} \left( \nabla \eta_i \right)^2 + \sum_{i=1}^{2} \phi_i f'(x_i) \right] dV
\]

(1)

The first two terms in the integrand are responsible for the interface energy. The parameters \( m \) and \( \kappa \) are uniquely related to the interfacial energy \( (\sigma) \) and interface thickness \( (l) \) as \( \sigma = \sqrt{2km/3} \) and \( l = \sqrt{8\kappa km} \). \( f_0 \) is a fourth-order Landau polynomial of the phase-field variables. The third term in Eq. (1) is the contribution of the Gibbs energy densities of the phases as a function of composition and at a given temperature, \( f'(J/m^3) \) defined the ratios between the molar Gibbs energy and molar volume, to the total system energy, where \( \phi_i = \eta_i^2 / \sum_{j=1}^{2} \eta_j^2 \) is the phase fraction. Since in the considered model, the evolution of two phase-field variables is independent and their sum can be different from 1, a phase fraction \( \phi_i \) was defined based on the phase-field variables [24]. In conclusion, Eq. (1) expresses the total energy of the system, including both the interfacial and bulk energies.
The composition field of the independent components \(x_k\) is governed by the following mass balance equation

\[
\frac{\partial x_k}{\partial t} = \nabla \cdot \left( \sum_{i=1}^{2} \sum_{l=1}^{2} \phi_i (\sum_{j=1}^{2} M_{ij} \nabla \mu_j) \right)
\]  

(2)

Where \(\mu_i\) is the diffusion potential which is defined as the first derivatives of the Gibbs energy density functions of phase \(i\) with respect to the composition of \(l\). The elements \(M_{ik}\) form a mobility matrix \(M^i\) for phase \(i\), which relates to the interdiffusion matrix \(D^i\) through the thermodynamic factors matrix \(G^i\), i.e. a matrix containing the second derivatives of the Gibbs energy density functions with respect to the composition of CaO and Al\(_2\)O\(_3\), according to \(D^i = M^i G^i\) \[25,26\].

The evolution equation of each phase-field variable, \(\eta_\rho\), follows a time-dependent Ginzburg-Landau equation for non-conserved variables.

\[
\frac{\partial \eta_\rho}{\partial t} = -L \frac{\delta F}{\delta \eta_\rho}
\]

(3)

where the kinetic coefficient \(L\) is related to the interface mobility. For a typical diffusion-controlled growth \[27\], the \(L\) should be taken equal to

\[
L = \frac{4m}{3\kappa \zeta}
\]

(4)

with

\[
\zeta = \sum_{k=1}^{2} (x_{\eta,\rho,k} - x_{\eta,eq,k}) \sum_{m=1}^{2} m_{km} (x_{\eta,eq,m} - x_{\eta,eq,m})
\]

(5)

\(m_{km}\) are the elements of the inverse of the diffusion mobility matrix \((M^i)^{-1}\), \(x_{\eta,eq,k}\) is the equilibrium concentrations of component \(k\) in \(\alpha\) phase \[27\].

In the presented model, we assume that the dissolving particle can be considered to be settled in a distant and quiet part of the slag phase, and that therefore, any effect on
the dissolution process from convection is limited. To verify the validity of this assumption for the considered systems, the Rayleigh number (Ra), which describes the tendency for mass transport by thermal convection, must be calculated based on Eqs. (6) and (7), giving at 1550°C, for a typical slag composition considered in this study (namely slag A, as given in table 1):

$$Ra = \frac{g \Delta \rho L^3}{\nu \alpha} = \frac{9.8 \times 30 \times 0.125 \times 10^{-6}}{1.7}$$

(6)

where $g = 9.8 \text{[m.s}^{-2}\text{]}$, is the gravity acceleration, $\Delta \rho \text{[kg.m}^{-3}\text{]}$, the difference in density between the hotter and colder melt in the crucible, $L \text{[m]}$, a characteristic length of the crucible, $\nu \text{[Pa.s]}$, the viscosity of the melt and $\alpha \text{[m}^2\text{s}^{-1}\text{]}$, the thermal diffusivity. To calculate the upper bound of Ra, we assumed a characteristic length of 5mm (this is, for example, the crucible diameter during the CSLM experiments of [28], with which our simulation results are compared in section 4.1.2), and a maximum temperature difference over the sample was taken as 50°C, according to the calibration measurements [28]. Furthermore, $\Delta \rho = 30 \text{kg.m}^{-3}$ was taken from Ref. [29] and $\nu = 1.7 \text{Pa.s}$ was calculated at 1550°C. The thermal diffusivity was calculated from Eq.(7):

$$\alpha = \frac{\lambda}{\rho C_p} = \frac{0.3}{2650 \times 1252} = 9 \times 10^{-4} \text{m}^2\text{s}^{-1}$$

(7)

where $\lambda \text{[Wm}^{-1}\text{K}^{-1}\text{]}$ is the thermal conductivity of the melt which was taken from Ref.[30] and $C_p \text{[J kg}^{-1}\text{K}^{-1}\text{]}$ is the specific heat capacity of the slag melt. Ra=240 was found. Even for the upper bound, the value is still well below the critical values (650–1100) [28] above which convection may be expected. Therefore, it is reasonable to assume that convection is negligible in the current study. The dissolution is thus
dominated by diffusion, both in the experiments and the simulations, which was also suggested in Liang’s work [31].

3. Numerical implementation and simulation setup

3.1 Numerical implementation

The phase field and diffusion equations are discretized on a numerical grid using finite differences. The FORTRAN programming language is used. Neumann boundary condition is adopted.

3.2 Simulation setup

The presented model is employed for 1-D and 2-D simulations of the dissolution of a solid $\text{Al}_2\text{O}_3$ particle in $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ melts. In the simulations, a diffuse interface width of $l = 10^{-7}\text{m}$ is chosen. As shown before for this phase-field model [24], the choice of the diffuse interface width does not affect the simulation results noticeably, as long as it is chosen several times smaller than the grains (at least 5 times smaller) and sufficient grid points are present within the diffuse interface zone to resolve the smooth transition in phase-field values (at least 5 grid points over the interface zone). Choosing eight grid points in the diffuse interface yields a spatial discretization of $\Delta x = \Delta y = 0.125 \times 10^{-7}\text{m}$. The time step is restricted by the diffusion equations and is taken as $\Delta t = 1 \times 10^{-7}\text{s}$. Due to a lack of information on the temperature and composition dependence of the interfacial energy of $\text{Al}_2\text{O}_3$ in $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ melts, a value of $\sigma = 0.45\text{Jm}^{-2}$ is chosen for all simulations [32], which is implemented in the model using $\kappa = 0.3375 \times 10^{-7}\text{Jm}^{-3}$ and $m = 2.7 \times 10^7\text{Jm}^{-1}$. The molar volume of all components in all phases is taken to be constant, using the molar volume $V_m = 23.6 \times 10^6\text{m}^3\text{mol}^{-1}$ [24].
The interdiffusion matrix as a function of temperature is taken from Ref [33]. The composition dependence of the diffusion mobility was introduced through a composition dependent $G^i$ matrix by $D^i = M^i G^i$. The simulations were performed using 1000×2 and 160×160 domains for 1D and 2D, respectively. The initial particle size is taken $16\Delta x\times16\Delta y$ in 2D. This corresponds to a volume fraction of 0.008 in 2D. In experiment of Ref.[2](with which we will compare the 2D simulation results in section 4.1.2), volume fraction is 0.01.

The Gibbs energies of the different phases in Eq. (1), the diffusion potentials in Eq. (2) and thermodynamic factor as a function of composition and temperature were retrieved from the FACTSage Toxide database through ChemApp [34].

3.3 Variable parameters in this study

The effects of temperature and composition on the diffusion paths and dissolution rates of alumina were investigated in the present study, since we expected that both factors would strongly affect the dissolution behavior through their effects on the thermodynamic and kinetic properties of the phases.

3.3.1. Effect of initial composition

The dissolution behavior of $\text{Al}_2\text{O}_3$ was studied for the five distinct initial slag compositions as shown in Table 1 at a fixed temperature of 1550 °C. In the first three simulations, the CaO to SiO$_2$ ratio was kept constant with a ratio of 0.65, while the content of Al$_2$O$_3$ was gradually increased. For samples D and E, the same level of Al$_2$O$_3$ was taken as for sample A, however, the CaO to SiO$_2$ ratio varied. These compositions were chosen to investigate the effects of, respectively, basicity (the ratio between the...
amount of CaO and SiO\textsubscript{2} expressed in weight percent) and Al\textsubscript{2}O\textsubscript{3} content on the diffusion and dissolution behavior of Al\textsubscript{2}O\textsubscript{3}. Figure 1 shows the isothermal section of the CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system at 1550°C. The area OMS marked in Figure 1 is the liquid-alumina pseudo binary-phase region. The triangular zones marked as OSP and OMQ represent the liquid-alumina-mullite and liquid-alumina-CaAl\textsubscript{12}O\textsubscript{19} pseudo ternary phase region, respectively. In order to avoid the formation of any new phase at the interface, such as mullite and CaAl\textsubscript{12}O\textsubscript{19}, the initial compositions were intentionally chosen in the area lined by OM and OS.

Table 1 Slag compositions of the considered slag systems

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>C/S ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>wt%</td>
<td>mol%</td>
</tr>
<tr>
<td>A</td>
<td>30.0</td>
<td>34.8</td>
</tr>
<tr>
<td>B</td>
<td>27.6</td>
<td>33.0</td>
</tr>
<tr>
<td>C</td>
<td>25.5</td>
<td>31.3</td>
</tr>
<tr>
<td>D</td>
<td>27.0</td>
<td>31.4</td>
</tr>
<tr>
<td>E</td>
<td>32.1</td>
<td>37.2</td>
</tr>
</tbody>
</table>

Fig.1 Isothermal section of CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system at 1550°C, which was calculated
using Factsage Toxide.

3.3.2. Effect of temperature

The isothermal section of CaO-Al$_2$O$_3$-SiO$_2$ system at another two temperatures (1500°C and 1600°C) is shown in Figure 2, which clearly shows that the liquidus line SM changes with temperature. Therefore, in this work, a series of temperatures, namely 1500°C, 1550°C and 1600°C, were considered in the simulations to investigate the influence of temperature on the obtained diffusion path and dissolution behavior of Al$_2$O$_3$ in a slag with composition A (see Table 1).

![Isopleths](image.png)

Fig.2 Isothermal section of the CaO-Al$_2$O$_3$-SiO$_2$ system at (a)1500°C and (b)1600°C, which were calculated using Factsage Toxide.

4. Results and discussion

The phase field simulation results are presented and discussed in this part. The considered conditions for all the simulations are listed in Table 2. Firstly the proposed phase-field approach is validated against analytical theory and experimental data.
(section 4.1). Then, the effects of slag composition and temperature on the diffusion path for Al$_2$O$_3$ dissolution (section 4.2) and dissolution rate (section 4.3) are investigated based on a series of phase-field simulations for varying temperature and initial slag composition.

Table 2 Conditions for the simulations of Al$_2$O$_3$ dissolution performed in this work

<table>
<thead>
<tr>
<th>Case</th>
<th>Slag Composition ((x_{\text{CaO}},x_{\text{Al}_2\text{O}_3}))</th>
<th>Temperature (^{\circ}\text{C})</th>
<th>Initial Al$_2$O$_3$ size</th>
<th>Simulation time(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>A</td>
<td>1550</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.0025</td>
</tr>
<tr>
<td>#2</td>
<td>(0.453,0.124)</td>
<td>1500</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.005</td>
</tr>
<tr>
<td>#3</td>
<td>A</td>
<td>1500</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.005</td>
</tr>
<tr>
<td>#4</td>
<td>A</td>
<td>1600</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.0015</td>
</tr>
<tr>
<td>#5</td>
<td>(0.187,0.122)</td>
<td>1500</td>
<td>- (\times16\Delta x\times16\Delta y)</td>
<td>0.005</td>
</tr>
<tr>
<td>#6</td>
<td>(0.187,0.122)</td>
<td>1550</td>
<td>- (\times16\Delta x\times16\Delta y)</td>
<td>0.004</td>
</tr>
<tr>
<td>#7</td>
<td>B</td>
<td>1550</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.003</td>
</tr>
<tr>
<td>#8</td>
<td>C</td>
<td>1550</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.004</td>
</tr>
<tr>
<td>#9</td>
<td>D</td>
<td>1550</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.0035</td>
</tr>
<tr>
<td>#10</td>
<td>E</td>
<td>1550</td>
<td>20(\Delta x\times2\Delta y) (\times16\Delta x\times16\Delta y)</td>
<td>0.025</td>
</tr>
</tbody>
</table>

4.1 Validation of the phase-field model

4.1.1 Diffusion controlled Al$_2$O$_3$ dissolution (flat interface)

Validation of the phase-field model by comparison with an analytical model (simulation case #1 in Table 2)

The time dependence of the molar fraction fields \((\chi_{\text{CaO}} \text{ and } \chi_{\text{Al}_2\text{O}_3})\) were obtained from Eq. (2), and \(x_{\text{SiO}_2}\) can then be calculated as the molar fraction of the dependent component SiO$_2$. The diffusion path obtained in 1D phase-field simulations of the dissolution of Al$_2$O$_3$ at 1550°C is shown in Figure 3 (a). The movement of a flat interface due to a diffusion controlled transformation in a binary system is one of the
few moving boundary problems for which an analytical solution exists. With $X(t)$ the location of the interface at a given time $t$, the solution for $X$ is given by [35]

$$X_0 - X = K \sqrt{Dt}$$

(8)

with $X_0$ the initial position of the interface, $D$ the interdiffusion coefficient and $K$ a constant given by

$$\Delta = \frac{\sqrt{\pi}}{2} K \exp\left(\frac{K^2}{4}\right) \left[1 + \text{erf}\left(\frac{K}{2}\right)\right]$$

(9)

$$\Delta = \frac{x_{eq} - x_b}{x_e - x_b}$$

(10)

where $\Delta$ is a measure of the saturation. At the solid-liquid interface, $x_{eq}$ and $x_e$ indicate the equilibrium concentrations of the liquid and solid, respectively, $x_b$ is the initial concentration of the slag. Although Eq. (10) was derived for binary systems, it can be applied to the system considered here, because the saturation concentration of both independent components CaO and Al$_2$O$_3$ appeared to be almost equal for the considered composition. It is namely obtained in the simulated microstructures that $\Delta_{\text{CaO}}=0.195$ and $\Delta_{\text{Al}_2\text{O}_3}=0.190$. The change of interface position in the considered ternary system can then be calculated based on Eq. (8). Here, $D$ was taken as the diffusion coefficient of Al$_2$O$_3$ since the dissolution rate of Al$_2$O$_3$ is controlled by the diffusion of Al$_2$O$_3$ in the slag.

In Figure 3(b), the interface position as a function of time was obtained from the phase-field simulations and the relationship between $X_0 - X$ and $t$ was calculated from Eq. (8). The comparison of the two curves in Figure 3(b) indicates that the PFM results reproduce well the analytical solution.
Fig. 3 (a) Diffusion path obtained in a 1-D phase-field simulations for the dissolution of Al₂O₃ in slag composition A at 1550 °C (case#1) (b) Comparison of the interface position obtained by the phase-field simulations and the analytical solution for the movement of a flat interface due to diffusion controlled dissolution evaluated for slag composition A at 1550°C.

II Validation of the phase-field model by comparison with experiments (simulation case #2 in Table 2)

In order to further validate the phase-field model, we compare simulation results with available experimental data [36]. The interface between solid Al₂O₃ slab and molten liquid slag was assumed to be flat under the condition of dip technique [36,37]. The diffusion path and dissolution rate obtained in the phase-field simulations for case #2 are shown in Figure 4(a) and (b) respectively, together with the experimental data and results from an analytical model obtained [37] for similar conditions as in our simulation case #2. The diffusion path obtained for Al₂O₃ dissolution in a slag at the conditions specified for case #2 in the phase-field simulation is very similar to that
obtained in the previous calculations. For the dissolution rate, however, there is a remarkable difference between the PFM results and the previously calculated values, where the PFM results are much closer to the experimental data.

Fig.4 (a) Diffusion path obtained from a phase field simulation for the solution of a particle with a flat interface for case # 2 (open circle) compared with previously calculated data [37] (red line) (b) Comparison of interface position as obtained in the phase-field simulations with experimental [36] and previously calculated data [37]

4.1.2 Diffusion-controlled dissolution of circular $\text{Al}_2\text{O}_3$ (cases #1, 3-6, 2D)

A one-dimensional PFM problem represents a planar interface. A curved interface must be considered when the dissolution of a circular $\text{Al}_2\text{O}_3$ is considered in two dimensions. In the 2D simulations, a quarter of a circular $\text{Al}_2\text{O}_3$ particle with radius $16\Delta x$ is initially placed at the left bottom of the simulation cell ($160\Delta x \times 160\Delta x$). The initial particle size is chosen small enough to guarantee complete dissolution. The relationship between $R/R_0$ (with $R$ the alumina radius as a function of time and $R_0$ the initial alumina radius) and $t/t_0$ (with $t$ time and $t_0$ the total dissolution time) can be
obtained from the phase-field simulations and is plotted for different temperatures in Figure 5.

Fig. 5 Normalized particle radius as a function of normalized time for an initial composition of the liquid oxide of $x_{\text{CaO}} = 0.348$, $x_{\text{Al}_2\text{O}_3} = 0.153$ and at different temperatures: (a) 1500°C, (b) 1550°C and (c) 1600°C. A comparison of experimental data [2] with data obtained from phase-field simulations (the different symbols for data coming from Ref [2] indicate different samples).

Experimental data at different temperatures and for an Al$_2$O$_3$ particle in the initial composition of the liquid oxide $x_{\text{CaO}} = 0.348$, $x_{\text{Al}_2\text{O}_3} = 0.153$ [2] (i.e. the same conditions as assumed in the cases #1 and 3-4 simulations in this study) are plotted together with the phase field predictions. The results clearly show that there is excellent
agreement between the phase field simulations, assuming diffusion controlled
dissolution, and the experimental data.

In addition, two more simulation results (i.e. the same conditions as assumed in
the cases # 5-6 simulations in this study) were compared with experimental data from
another source [38], the initial composition of the liquid oxide was set as: $x_{CaO}^0 = 0.187,$
$x_{Al_2O_3}^0 = 0.122$ (Figure 6). Again, the present phase-field simulations agree well with
the experimental data [38].

![Fig.6 Normalized particle radius as a function of the normalized time for an initial
composition of the liquid oxide of $x_{CaO}^0 = 0.187,$ $x_{Al_2O_3}^0 = 0.122$ and temperature: (a)
1500°C and (b) 1550°C. A comparison of experimental data [38] with the data obtained
from phase field simulations.](image)

In principle, a phase field model can consider the effect of variations in interface
energy. However, no data are available on the interface energy as a function of
temperature and composition for the CAS system. Therefore, we took a fixed interface
energy for all the simulations. Still, a good agreement between simulation and
experiment was achieved. Therefore, we conclude that the role of interfacial energy is of minor importance in controlling the dissolution process. In addition, F. J. Vermolen [20] also pointed out that the effect of the interface energy on the dissolution of stoichiometric particles in a binary Fe-C alloy is relatively small.

4.2 Effect of temperature and slag composition on the diffusion path obtained for Al₂O₃ dissolution in CaO-Al₂O₃-SiO₂ slags (simulation cases #1, 3-4, 7-10, 1D, see Table 2)

In this part, several one-dimensional simulations were performed to investigate the influence of temperature and liquid oxide composition on the diffusion path for the dissolution of Al₂O₃ in the slag. As the initial condition, a solid phase extending over 20 grid points is placed at the left side of the simulation domain. The initial liquid concentration is as listed in Table 1, while the solid (Al₂O₃) was initialized at its stoichiometric composition, i.e. \( x_{\text{Al}_2\text{O}_3} = 1 \). As a representative example, Figure 7 shows the resulting composition profiles obtained for the dissolution of a Al₂O₃ particle in a CaO-SiO₂-Al₂O₃ slag (case #7). Further away from the solid-liquid interface, the slag concentration does not noticeably change during the simulations, since the amount of Al₂O₃ in the simulations is chosen far below its solubility limit in CaO-SiO₂-Al₂O₃ slags.
Fig. 7 Concentration profiles of CaO and Al₂O₃ obtained as a function of time in a phase field simulation of dissolving Al₂O₃ in CaO-Al₂O₃-SiO₂ (case #7). The dashed line is the initial composition profile. The time between the plotted profiles is 5 ms and the total system length was 12.5 µm.

For three temperatures, the resulting diffusion paths of slag A are plotted on an isothermal section in Figure 8. It is found that, after a short initial transition time, the direction of the diffusion path becomes constant in time. The heavy solid line is the liquidus line. Point N represents the concentrations at the interface, as obtained in the phase-field simulations. Point W shows the initial slag composition. \( v₁ \) and \( v₂ \) present the directions of the major and minor eigenvector of the diffusion coefficient matrix \( D \), respectively, for which the values are given in Table 3. From figure 8, to fulfill the mass balance conditions at any given time \([39]\), the composition must lie within the
parallelogram formed by the two eigenvectors drawn at the starting compositions. The
diffusion paths for Al₂O₃ dissolution in CaO-Al₂O₃-SiO₂ melts are in the direction of
the fast eigenvector (v₁) in the neighborhood of the initial melt composition. In addition,
the diffusion path deviates more a straight line as the ratio of the eigenvalues of the
diffusion coefficient deviates more from unity (Figure 8(a)).

Fig. 8 Simulated diffusion path for the dissolution of Al₂O₃ into slag A in the isothermal
section at: (a) 1500°C, (b) 1550°C and (c) 1600°C. N represents the concentrations at
the interface, W is the initial slag composition. v₁ and v₂ present the directions of the
major and minor eigenvector of the diffusion coefficient matrix.
Table 3 Eigenvalues and eigenvectors of the diffusion coefficient matrices D assumed in the simulations

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Eigenvalues (cm²/s⁻¹)</th>
<th>Eigenvectors</th>
<th>Eigenvectors angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Major</td>
<td>Minor</td>
<td>Major</td>
</tr>
<tr>
<td>1500</td>
<td>1.328</td>
<td>0.538</td>
<td>(0.765, -0.644)</td>
</tr>
<tr>
<td>1550</td>
<td>2.118</td>
<td>1.035</td>
<td>(0.738, -0.675)</td>
</tr>
<tr>
<td>1600</td>
<td>3.330</td>
<td>1.870</td>
<td>(0.691, -0.722)</td>
</tr>
</tbody>
</table>

The resulting diffusion profiles for initial slag compositions B, C, D and E at 1550°C are plotted in Figure 9. These diffusion profiles (square dot) clearly show the influence of the slag composition on the local equilibrium or tie-line at the solid-liquid interface. The dashed line connects pure alumina with the slag composition at the interface. The alumina-liquid two phase area is surrounded by the vertices of O, M and S.

![Fig.9 Simulated diffusion paths for the dissolution of Al₂O₃ at 1550 °C in: (a) Slag B, (b) (c), (d)]
(b) Slag C, (c) Slag D and (d) Slag E. The alumina-liquid two-phase region is the area surrounded by the vertices OMS.

From the above, it is clear that in a ternary system the exact location of the slag melt composition at the solid-liquid interface depends on the diffusion mobility, the liquidus and the initial melt composition.

4.3 Dissolution rate of Al$_2$O$_3$ into CaO-Al$_2$O$_3$-SiO$_2$ Slags

The dissolution rate of Al$_2$O$_3$ into CaO-Al$_2$O$_3$-SiO$_2$ slags, $dR/dt$, is governed by Eq. (11) [40]:

$$\frac{dR}{dt} = -A k \left[ (x_{Al_2O_3})_{eq} - (x_{Al_2O_3})_b \right]$$  \hspace{1cm} (11)

Where $A$ is a constant, $k$ is the mass transfer coefficient and $(x_{Al_2O_3})_{eq}$ and $(x_{Al_2O_3})_b$ are the molar fraction of Al$_2$O$_3$ in the slag at the interface and in the bulk, respectively. Apparently, the driving force of Al$_2$O$_3$ dissolution is related to $[(x_{Al_2O_3})_{eq} - (x_{Al_2O_3})_b]$ and will thus be constant in time since the diffusion path is constant in time (see section 4.2).

In Eq. (11), the mass transfer coefficient ($k$) is related to the viscosity of the slag ($v$) and the diffusivity of Al$_2$O$_3$ ($D$) through Eq. (12) [40].

$$k = C v^{-0.344} D^{0.644}$$  \hspace{1cm} (12)

where $C$ is a constant, $D$ is the diffusion coefficient of alumina. The effect of composition on the diffusion coefficient in Eq. (12) should be taken into account. As the diffusivity of Al$_2$O$_3$ particles is due to Brownian motion within the melt phase, the composition will influence the diffusion coefficient by changing the viscosity of the slag according to Einstein-Stokes equation [41]:

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\[ D = \frac{k_B T}{6\pi \eta r} \quad (13) \]

where \( k_B \) is the Boltzmann’s constant, \( T \) refers to the absolute temperature and \( r \) is the hydrodynamic radius of the diffusing species which we assume to be composition and temperature independent as a first approximation.

Introducing Eqs. (12) and (13) into Eq. (11), one obtains:

\[
\frac{dR}{dt} = -AC(k_B T)^{0.888}[(x_{Al2O3})_{eq} - (x_{Al2O3})_b]^{0.988} \quad (14)
\]

From Eq. (14), \( \frac{dR}{dt} \) is expected to be proportional to temperature (T), the driving force \([(x_{Al2O3})_{eq} - (x_{Al2O3})_b]\) and viscosity to a power -0.988.

4.3.1 The effect of temperature on dissolution rate (case #1, 3-4, 2D)

Figure 10(a) and Figure 11(a) show the effect of temperature on the dissolution rate of alumina into slag A, as obtained from phase-field simulations. Figure 11 shows that the dissolution rate is constant over a long time period, which can be interpreted from the constant diffusion path in time and Eq. (14). When the diffusion path is constant, the driving force \([(x_{Al2O3})_{eq} - (x_{Al2O3})_b]\) in Eq. (14) is also constant, resulting in a constant dissolution rate. At the beginning and end there are some transition effects, which are related to both realistic effects (e.g. evolution towards the steady-state concentration profile near the solid-liquid interface) and modeling effects (evolution towards a diffuse interface profile for the conserved and non-conserved phase-field variables at the start, an artificially increased dissolution rate when the particle size approaches the width of the diffuse transitions in the values of the phase-field variables at interfaces).
Moreover, it is seen that a higher dissolution rate of alumina is achieved at a higher temperature. This temperature effect is caused by both a thermodynamic and a kinetic effect. Thermodynamically, the driving force for Al₂O₃ dissolution, i.e. \( (x_{\text{Al}_2\text{O}_3})_{\text{eq}} - (x_{\text{Al}_2\text{O}_3})_b \), can be calculated from the interface compositions obtained in the phase-field simulations. Increasing the temperature from 1500°C to 1600°C augments the equilibrium concentration of Al₂O₃ in the slag at the particle/slag interface from 0.294 to 0.375. Thus, the concentration difference between the bulk and the interface is enlarged (from 0.141 to 0.222), and the driving force for Al₂O₃ dissolution is increased.

From a kinetic point of view, the mass transfer coefficient \( k \) increases with increasing temperature and decreasing viscosity (and viscosity decreases with temperature).

Fig.10 Normalized particle radius as a function of the absolute time as obtained from phase-field simulations of the dissolution of Al₂O₃ into slags, (a) at different temperatures and for slag A, (b) for different slag compositions at 1550°C
Fig. 11 Dissolution rate as a function of time obtained from phase-field simulations of the dissolution of Al$_2$O$_3$ particles in oxide liquids, (a) at different temperatures and for slag A, (b) for different slag compositions at 1550°C

4.3.2 The effect of slag composition on the dissolution rate (case #1, 7-10, 2D)

Figure 10(b) and Figure 11(b) shows the dissolution rate of Al$_2$O$_3$ for five different slag compositions at 1550°C obtained from phase-field simulations. The dissolution rate varies largely with slag composition. The highest dissolution rate occurs in Slag E with the highest C/S ratio and the lowest Al$_2$O$_3$ content. The lowest dissolution rate occurs in Slag C with the highest Al$_2$O$_3$ content. A general trend is that the dissolution rate increases with increasing C/S ratio for a fixed Al$_2$O$_3$ content and with decreasing Al$_2$O$_3$ content for a fixed C/S ratio (Figure 11(b)). The driving force, i.e., $[(\chi_{\text{Al}_2\text{O}_3})_{\text{eq}} - (\chi_{\text{Al}_2\text{O}_3})_{\text{b}}]$ is affected to a great extent by changes in the slag composition (See Figure 9). $[(\chi_{\text{Al}_2\text{O}_3})_{\text{eq}} - (\chi_{\text{Al}_2\text{O}_3})_{\text{b}}]$ for the five slag compositions A, B, C, D and E can be obtained from the phase field simulations and are listed in Table 4. It is descending in an order of slag E > slag A > slag D > slag B > slag C. In addition, the slag composition affects the mass transfer coefficient $k$ in Eq. (11) by its effect on the slag viscosity. Based on
calculations [42], it is found that the sequence of the slag viscosity for the different compositions is as follows, slag D > slag C > slag B > slag A > slag E. According to Eq. (14), the dissolution rate is determined by the thermodynamic driving force and mass transfer coefficient and can be calculated analytically, with the interface concentrations determined from the phase-field simulations. The details for the analytical calculation are listed in Table 4. Based on the calculation, a good agreement between PFM and the analytical model was obtained, i.e. the order of the dissolution rate was the same for both approaches (slag E > slag A > slag B > slag D > slag C) as shown in Table 4 and Figure 11(b).

Table 4 The parameters used for evaluating the analytical relation (14).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Driving force ([x_{Al_2O_3}]<em>{eq} - [x</em>{Al_2O_3}]_b)</th>
<th>Viscosity (\nu) (Poise)</th>
<th>(\nu^{0.988} \times [x_{Al_2O_3}]<em>{eq} - [x</em>{Al_2O_3}]_b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.160</td>
<td>17.105</td>
<td>0.0097</td>
</tr>
<tr>
<td>B</td>
<td>0.126</td>
<td>18.585</td>
<td>0.0070</td>
</tr>
<tr>
<td>C</td>
<td>0.079</td>
<td>18.836</td>
<td>0.0043</td>
</tr>
<tr>
<td>D</td>
<td>0.153</td>
<td>30.739</td>
<td>0.0052</td>
</tr>
<tr>
<td>E</td>
<td>0.176</td>
<td>11.732</td>
<td>0.0155</td>
</tr>
</tbody>
</table>

5. Conclusion

This study investigates the influence of the initial composition of the liquid slag and its temperature on the diffusion path and dissolution rate for the dissolution of Al\(_2\)O\(_3\) into molten CaO-Al\(_2\)O\(_3\)-SiO\(_2\) slags by phase field simulations. A phase field model for a two-phase solid-liquid system with diffusion-controlled conditions at the solid-liquid interface was implemented. The simulation results fit well to the analytical solution for dissolution in a one dimensional system and the dissolution rate of a circular Al\(_2\)O\(_3\)
particle. The simulations also agree well with experimental data. Furthermore, the simulation results demonstrate that (1) the dissolution rate of $\text{Al}_2\text{O}_3$ increases with temperature, (2) the dissolution rate increases with increasing CaO content and with decreasing $\text{Al}_2\text{O}_3$ content for a fixed CaO/SiO$_2$ ratio.

**Acknowledgements**

The author, Jingjing Liu, thanks to the financial support from Chinese Scholarship Council (CSC).
Reference


Table and Figure captions:

Fig.1 Isothermal section of CaO-Al2O3-SiO2 system at 1550°C, which was calculated using Factsage Toxide.

Fig.2 Isothermal section of the CaO-Al2O3-SiO2 system at (a)1500°C and (b)1600°C, which were calculated using Factsage Toxide.

Fig.3 (a) Diffusion path obtained in a 1-D phase-field simulations for the dissolution of Al2O3 in slag composition A at 1550 °C (case#1) (b) Comparison of the interface position obtained by the phase-field simulations and the analytical solution for the movement of a flat interface due to diffusion controlled dissolution evaluated for slag composition A at 1550°C.

Fig.4 (a) Diffusion path obtained from a phase field simulation for the solution of a particle with a flat interface for case # 2 (open circle) compared with previously calculated data [37] (red line) (b) Comparison of interface position as obtained in the phase-field simulations with experimental[36] and previously calculated data [37].

Fig.5 Normalized particle radius as a function of normalized time for an initial composition of the liquid oxide of $x_{CaO} = 0.348$, $x_{Al2O3} = 0.153$ and at different temperatures: (a) 1500°C, (b) 1550°C and (c) 1600°C. A comparison of experimental data [2] with data obtained from phase-field simulations (the different symbols for data coming from Ref [2] indicate different samples).

Fig.6 Normalized particle radius as a function of the normalized time for an initial composition of the liquid oxide of $x_{CaO} = 0.187$, $x_{Al2O3} = 0.122$ and temperature: (a) 1500°C and (b) 1550°C. A comparison of experimental data [38] with the data obtained.
from phase field simulations.

Fig. 7 Concentration profiles of CaO and Al₂O₃ obtained as a function of time in a phase field simulation of dissolving Al₂O₃ in CaO-Al₂O₃-SiO₂ (case #7). The dashed line is the initial composition profile. The time between the plotted profiles is 5ms and the total system length was 12.5um.

Fig. 8 Simulated diffusion path for the dissolution of Al₂O₃ into slag A in the isothermal section at: (a) 1500°C, (b) 1550°C and (c) 1600°C. N represents the concentrations at the interface, W is the initial slag composition. v₁ and v₂ present the directions of the major and minor eigenvector of the diffusion coefficient matrix.

Fig. 9 Simulated diffusion paths for the dissolution of Al₂O₃ at 1550 °C in: (a) Slag B , (b) Slag C, (c) Slag D and (d) Slag E. The alumina-liquid two-phase region is the area surrounded by the vertices OMS.

Fig. 10 Normalized particle radius as a function of the absolute time as obtained from phase-field simulations of the dissolution of Al₂O₃ into slags, (a) at different temperatures and for slag A , (b) for different slag compositions at 1550°C.

Fig. 11 Dissolution rate as a function of time obtained from phase-field simulations of the dissolution of Al₂O₃ particles in oxide liquids, (a) at different temperatures and for slag A, (b) for different slag compositions at 1550°C.

Table 1 Slag compositions of the considered slag systems
Table 2 Conditions for the simulations of Al₂O₃ dissolution performed in this work
Table 3 Eigenvalues and eigenvectors of the diffusion coefficient matrices D assumed in the simulations
Table 4 The parameters used for evaluating the analytical relation (14)