Numerical Modeling of Nucleation and Growth of Inclusions in Molten Steel Based on Mean Processing Parameters

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As an important aspect of inclusion engineering, numerical prediction of inclusion behavior in molten steel has attracted much attention in order to control inclusions in steel. Although considerable efforts have been made in the modeling of inclusion growth, it is still necessary to employ an initial particle size distribution (PSD) gained from experiments or assumptions as an input for numerical models. The present work focuses on the construction of a general nucleation-growth model, which combines thermodynamics, classical homogeneous nucleation theories and dynamics of particle collision and coagulation on the basis of mean processing parameters. This can be employed, without any initial PSD of inclusions in advance, to describe the time evolution of PSD in molten steel during inclusion nucleation, Ostwald ripening, and collision growth processes. With regard to collision-coagulation growth mechanisms of inclusions, four approaches, namely Brownian collision, turbulent collision, Stokes collision and gradient collision in laminar shear layers, have been investigated to estimate their role in the evolution of PSD during steel melt deoxidation process. In addition, an approximate numerical technique, termed the ‘DS method’, has been developed as a modification of the so-called (1) discrete-sectional representation and (2) Particle-Size-Grouping method in order for an efficient solution for population balance equations (PBE) at lower cost in CPU time. Finally, as an application of this general model, the evolution of nucleation and growth of alumina inclusions is demonstrated in the Fe–Al–O melt system. The predicted molten steel total oxygen and particle size distribution of alumina inclusions are compared with the experiment data cited from references.

KEY WORDS: modeling; nucleation; growth; alumina inclusion; Ostwald ripening; Brownian collision; turbulent collision; Stokes collision; gradient collision; particle size distribution (PSD); discrete-sectional representation; DS method.

1. Introduction

The description and control of morphology, size and distribution of inclusions in steel is an important aspect in inclusion engineering, which launches the necessity of combining thermodynamics, kinetics and even hydrodynamics for the numerical prediction of nucleation and growth of inclusions in molten steel. Based on classical nucleation theories, Turpin and Elliot,\(^1\) Turkdogan,\(^2,3\) and Mukai et al.\(^4\) analyzed deoxidation of molten steel and predicted homogeneous nucleation of inclusions. Those classical nucleation theories have been reviewed and summarized in depth by Christian in his monograph.\(^5\) Meanwhile, considerable attention has been paid to the prediction of inclusion growth and transport behaviors in molten steel in various metallurgical containers over the past several decades.\(^6-12\) The limitation of all these previous attempts for inclusion growth prediction is that one needs to employ an initial size distribution of inclusions, which comes from either experimental measurements or assumptions, as a starting point for numerical calculations. Therefore, the predicted results depend somewhat on the validity of the initial particle size distribution (PSD) selected.

An aim of metallurgy and material scientists is to predict inclusion behavior over the entire process range from nucleation to growth by a general model, which reflects the essential relationship between nucleation and growth, and covers substances from the molecular scale (several angstroms) to microscopic scale (several tens of micrometers), and has no necessity to introduce any initial PSD. Such a model is termed a ‘general nucleation-growth model’ here by the present authors.

A few researchers have tried to develop general nucleation-growth models in order for deoxidation prediction. Doo et al.\(^13\) gave a numerical analysis of alumina inclusion behavior in refining periods by considering a model that covered both nucleation and growth of inclusions. However, they treated the deoxidation process as several totally separate stages: particle nucleation, Ostwald ripening and the growth of inclusions due to various mechanisms, although the three stages mentioned above should occur simultaneously during the corresponding transition periods in a real case. They also reported that the outcome after Ostwald ripening was an even size distribution of inclusions of about 1.35 μm in diameter. Apparently, this kind of model should only be referred to as a growth model rather than a
real nucleation-growth model. Based on the work of Kampmann and Kahlweit,\textsuperscript{14} Zhang \textit{et al.}\textsuperscript{15} put forward a numerical model to predict the time evolution of particle nucleation, Ostwald ripening, and growth processes dominated by Brownian collisions and turbulent collisions. To abate the calculation load in the solution of population balance equations (PBE), they employed an approximate numerical approach, which is similar to the so-called Particle-Size-Grouping (PSG) Method termed by Nakaoka \textit{et al.}\textsuperscript{16} However, the problem of how to efficiently solve the PBE including Ostwald ripening over the entire nucleation-growth model was not shown in their paper, and moreover, their model neither evaluated the effect of Stokes collision and gradient collision nor predicted the acting time domains for different growth mechanisms.

Clearly, although much attention has been paid to the formation and growth of inclusions in molten steel by numerical ways, understanding of the nature of the process by which non-metallic inclusions nucleate and grow in steel deoxidation process, especially at the early stage, is still far from completion due to the complexity of high temperature chemical interactions in multi-component/multi phase systems.

Therefore, the present work has focused on the development of a general nucleation-growth model mentioned above, in which inclusions nucleate from homogeneous molten steel and grow due to the diffusion of oxygen and deoxidizer elements, Ostwald ripening and various collision-coagulation mechanisms, i.e., Brownian coagulation, turbulent coagulation, Stokes coagulation, and even gradient coagulation. A modified approach based on the discrete-sectional numerical technique and Particle-Size-Grouping method,\textsuperscript{16} the DS method in short, has been employed in order to solve population balance equations (PBE) in the general nucleation-growth model. Then, an attempt is given to evaluate the general model in a Fe–Al–O melt system. The effect of various approaches on inclusion growth after alumina nucleation and the acting time domains are investigated and discussed. The predicted total oxygen and PSD of alumina inclusions in molten steel at early stage are compared with the experimental data.

2. General Nucleation-growth Model

As Turkdogan\textsuperscript{3} described, deoxidation reactions in steel-making processes are usually considered to have three consecutive steps, \textit{i.e.}, nuclei formation with critical size in homogeneous mediums, growth of the reaction products due to different mechanisms, and the removal of inclusions from the melt. However, for the initial stage of steel deoxidation, during which inclusions nucleate and immediately grow, Turkdogan’s description needs to be detailed and modified. Following the ideas of Penrose\textsuperscript{17} on first-order phase transitions, the authors of the present work believe that the time evolution of deoxidation processes consists of several stages: 1) nucleation, during which nuclei of new phases, \textit{i.e.}, inclusions, are formed from the metastable parent phase; 2) rapid growth of nuclei formed by nucleation at the expense of the parent phase, during which the diffusion of oxygen or deoxidizer elements in melts is usually the controlling step; 3) Ostwald ripening or coarsening, when larger inclusions grow and become even larger at the expense of shrinkage or even vanishing of smaller particles so as to minimize the total surface energy between inclusions and the old phase; and then 4) collision and coagulation growth, when several collision mechanisms including Brownian collision, turbulent collision and Stokes collision may dominate. An important issue here is that the above steps may proceed simultaneously during certain transition periods rather than one by one separately.

In the following sections, a general nucleation-growth model is constructed with respect to reaction (1) in the Fe–M–O melt system.

\[ n[M]+m[O]=M_nO_m \]  \hspace{1cm} (1)

2.1. Modeling Assumptions

Following Turnbull and Fisher,\textsuperscript{18} Kampmann and Kahlweit,\textsuperscript{14} and Zhang and Pluschkell,\textsuperscript{15} some assumptions are made as follows:

(1) The products of reaction (1) in the system are pure $M_nO_m$ particles or drops;

(2) Before the formation of stable nuclei with oxide $M_nO_m$, there are plenty of single $M_iO_j$, ‘quasi molecules’, which are also termed monomers and designated as $[M_iO_j]$ in the present work. Quasi molecules are basic nucleus formation units and are unstable until assembled into groups large enough to attain critical size. Groups consisting of quasi molecules, \textit{i.e.}, embryos for inclusions are also unstable when they are smaller than the critical radius.

(3) The embryos or nuclei form and grow only by addition of monomers\textsuperscript{14,18};

(4) The rate-controlling step of nucleation is the diffusion of oxygen and deoxidizer elements to the surface of embryos or nuclei;

(5) Embryos, nuclei or inclusions during nucleation and later growth process are thought to be spherical;

(6) The Gibbs–Thomson equation\textsuperscript{19} holds for embryos or particles of all size classes\textsuperscript{14};

(7) The interfacial tension between particles and their parent phase is constant during nucleation and the growth process.

(8) Only those stable particles larger than critical size may collide with each other and form larger particles due to various collision-coagulation mechanisms.\textsuperscript{15}

2.2. Thermodynamics of Homogeneous Nucleation

Classical nucleation theory indicates that the change of volumetric free energy of a system, \textit{i.e.}, Fe–M–O here, should overcome the barrier due to interfacial energy between nuclei and its parent phase (molten steel) in order to precipitate oxide nuclei from the system Fe–M–O \textit{via} reaction (1).

The total Gibbs energy change for the formation of nuclei is formulated as

\[ \Delta G = \frac{4\pi r^3}{3} \frac{\Delta G_m}{V_m} + 4\pi r^2 \sigma \]  \hspace{1cm} (2)

where $r$ is the radius of a nucleus corresponding to assumption (5), $\frac{4\pi}{3}r^3$ the volume of the nucleus, $4\pi r^2$ the surface area of the nucleus, $\Delta G_m$ bulk Gibbs energy change per mol, $V_m$ the molar volume of nucleus $M_nO_m$, and $\sigma$ the interfacial tension between nuclei and parent phase. Molar
Gibbs energy change \( \Delta G_m \) is given by
\[
\Delta G_m = -RT \ln S \quad \text{..............................................(3)}
\]
where \( S \) is the supersaturation degree defined as Eq.(4), \( ^{14,15} \)
\[
S = \frac{C_{\text{MO}}}{C_{\text{MO}}^*} = n_1 \quad \text{..............................................(4)}
\]

In Eq. (4), \( C_{\text{MO}} \) and \( C_{\text{MO}}^* \) represent the concentration of quasi molecules or monomers \([M_\text{O}n]\) in a supersaturated state and equilibrium state respectively. And \( n_1 \) and \( n_{1e} \) are the number density of free \([M_\text{O}n]\) monomers at moment \( t \) and in equilibrium respectively.

Nuclei of inclusions begin to form when \( \partial G/\partial t = 0 \), which corresponds to a critical radius \( r_c \) and critical free energy change \( \Delta G_c \).
\[
\Delta G_c = \frac{16\pi}{3} \frac{\sigma V_m^2}{(RT \ln S)^2} \quad \text{..............................................(6)}
\]

Accordingly, the critical number \( i_c \) of monomers forming an \( r_c \) nucleus is calculated by
\[
i_c = \left( \frac{2\sigma V_m}{RT \ln S} \right)^3 r_c^-3 \quad \text{..............................................(7)}
\]
in terms of monomer radius \( r_c \) and Avogadro’s number \( N_A \).
\[
n_1 = \frac{3V_m}{4\pi N_A^{1/3}} \quad \text{..............................................(8)}
\]

2.3. Dynamics of Particle Size Distribution: From Nucleation to Ostwald Ripening

In the initial stage of the deoxidation process under a homogeneous system, a nucleation process is followed by diffusion growth and coarsening (Ostwald ripening) of inclusions. Based on Smoluchowski’s formulation\(^{20}\) and considering the effect of the reversed dissociation of reaction products, the above process is mathematically described as a population balance equation (PBE), which is shown in Eqs. (9) and (10) as follows,
\[
n_k = n_k - \sum_{k=2}^{k-1} n_k \cdot k - \sum_{k=2}^{k-1} n_k \cdot k + \sum_{k=2}^{k-1} n_k \cdot k \quad \text{..............................................(9)}
\]
\[
\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1,j=k}^{k-1} \beta_{ij} n_i n_j - \sum_{i=1}^{k-1} \beta_{i} n_i n_k + \alpha_{k+1} A_k n_{k+1} + \alpha_k A_{k-1} n_{k-1} - \alpha_k A_k n_k \quad \text{for } k = 2, 3, \cdots \quad \text{..............................................(10)}
\]

where \( n_k \) (m\(^{-3}\)) is the number density of \( k \)-size particles or embryos \((k\)-mers\), \( n_j \) (m\(^{-3}\)) the number density of monomers produced by reaction (1), \( \beta_{ij} \) (m\(^{-3}\) s\(^{-1}\)) the rate constant of the reaction \((i) + (j) \rightarrow (i+j)\), \( \alpha_k \) (m\(^{-2}\) s\(^{-1}\)) the number of monomers dissociating from the unit surface area of a \( k \)-size particle in unit time, and \( A_k \) (m\(^2\)) the surface area of a \( k \)-size particle. The subscripts \( i, j \) and \( k \) represent embryos or inclusions assembled by \( i, j \) and \( k \) monomers \((i\)-mer, \( j\)-mer, and \( k\)-mer) respectively. The first term on the right-hand side of Eq. (10) represents the generation rate of \( k \)-mers by combining a smaller \( i \)-mer and a smaller \( j \)-mer subject to volume conservation, \( i.e., k = i+j \), the second term the depletion rate of \( k \)-mers due to the formation of larger assemblies by associating a \( k \)-mer with another, the third the formation of \( k \)-mers when a \((k+1)\)-mer loses a monomer by dissociation, and the last term the dissipation of \( k \)-mers caused from losing a monomer from a \( k \)-mer.

Furthermore, taking notice of assumption (3), Eq. (10) is then simplified into
\[
\frac{dn_k}{dt} = \beta_{k-1} n_k (1+\delta(k=2)) - \beta_k n_k
+ \alpha_{k+1} A_k n_{k+1} - \alpha_k A_k n_k \quad \text{for } k = 2, 3, \cdots \quad \text{..............................................(11)}
\]

where the Dirac delta function \( \delta(k=2) \) has a value of 1 when \( k=2 \), otherwise it is equal to 0.

The value of \( \beta_{ik} \) and \( \alpha_k \) in Eq. (11) may be determined as follows\(^{14,21}\):
\[
\beta_{ik} = 4\pi \cdot D_1 \quad r_k \quad \text{..............................................(12)}
\]
\[
\alpha_k A_k = \beta_{ik} n_1 \quad \text{..............................................(13)}
\]

where \( r_k \) is the radius of a \( k \)-mer and \( D_1 \) stands for the diffusion coefficient of \([M_\text{O}n]\) monomers in melt. Considering that oxygen and deoxidizer elements diffuse in molten steel, one supposes that these diffusing oxygen and deoxidizer elements are assembled into monomers at the surfaces of embryos or inclusions, and then become a part of the embryos or inclusions. Hence, based on the fact that oxygen transfer in the melt controls molten steel deoxidation process\(^{12,23}\), \( D_1 \) in this model is assigned to take the value of the diffusion coefficient of oxygen in molten steel.

2.4. Contribution of Collision-coagulation Mechanisms to Particle Growth

Here, a general PBE\(^{20}\) as shown in Eq. (14) is employed to express the change rate of particle concentration due to collisions. Various collision-growth mechanisms including Brownian collision, turbulent collision, Stokes collision and gradient collision are investigated to evaluate their contribution to the change of particle size distribution.
\[
\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1,j=k}^{k-1} \beta_{ij} n_i n_j - \sum_{i=1}^{k-1} \beta_{i} n_i n_k \quad \text{for } k = 2i \quad \text{..............................................(14)}
\]

Here, total collision frequency function \( \beta_{ij} \) contains four terms, \( i.e., \beta_{ij}^B \) for Brownian collision, \( \beta_{ij}^T \) for turbulent collision, \( \beta_{ij}^S \) for Stokes collision and \( \beta_{ij}^G \) for gradient collision, being detailed by Eqs. (15a) through (15d)\(^{16,24,25}\).
\[
\beta_{ij}^B = \frac{2k_BT}{\mu_i} \left( \frac{r_i + r_j}{r_i + r_j} \right) \left( \frac{1}{r_i} + \frac{1}{r_j} \right) \quad \text{..............................................(15a)}
\]
\[
\beta_{ij}^T = 1.30 \pi^{1/2} \alpha (v/e)^{1/2} (r_i + r_j)^3 \quad \text{..............................................(15b)}
\]
\[
\beta_{ij}^S = \frac{2\pi (\rho_i - \rho_j)}{9\mu_i} |r_i - r_j| (r_i + r_j)^3 \quad \text{..............................................(15c)}
\]
\[ \frac{d}{dy} \beta_q^G = \left( \frac{4}{3} \right) (r_q + r_q) \times \text{with reference to Boltzmann's constant} \]

A combination of Eqs. (9), (11), (14) and (15) deduces

\[ \frac{d n_i}{d t} = \beta_{k,i-1} n_{k-1,i} / (1 + \delta(k=2)) - \beta_{k,i} n_{k,i} + \frac{\alpha_{k+1} n_{k+1,i}}{2} \]

where \( \delta(k=2l_q) \) equals 1 when the condition of \( k \geq 2l_q \) is true, otherwise 0.

Equations (9), and Eqs. (15) through (17) constitute the general dynamic equations in the general nucleation-growth model for molten steel coagulation.

3. Numerical Method

From a theoretical point of view, the general nucleation-growth model based on the population balance equation is sound and the basic ideas for integration of the set of differential equations are not complicated. However, there are still difficulties to obtain a numerical solution for the equations because the breadth of particle size distribution (PSD) may extend very rapidly due to Ostwald ripening and particle collisions. And the relevant calculation load is then too enormous to initiate a practical prediction. For instance, to estimate a PSD with 10^4-mers as the largest particles, corresponding to 0.01 mm diameter particles in the case of alumina inclusions, for a real time of 10^4 seconds, one has to solve a set of 10^4-dimension differential equations, which requires more than 40 h by using the Fourth-Order Runge-Kutta method with a time interval of 5 × 10^-4 s on a 1.4 GHz personal computer. However, in order to evaluate a particle size spectrum with the largest inclinations being 50 mm in diameter, roughly equivalent to 10^5-mers and which frequently appear in steelmaking processes, it is necessary to integrate a set of 10^15-dimension differential equations, which is computationally unworkable at present.

The Particle-Size-Grouping (PSG) method has proved its effectiveness in the calculation of PSD with respect to collision-coagulation growth problems. The main idea in this technique is to divide the entire PSD range into several particle size groups subject to the relation of \( v_q = R_q v_{q-1} \), where \( v_q \) is the volume of particles in section \( q \), and \( v_{q-1} \) the volume of particles in section \( q-1 \), and \( R_q \) the volume ratio. However, when the method is employed to solve a PSD problem resulting from nucleation and Ostwald ripening in the initial stage of coagulation, mathematically described by Eq. (11), it is found that the PSD may not actually be extended by addition of monomers in the size group manner because addition of a monomer to a particle in a particular group can never support enough particle growth in order for it to be listed in the neighboring larger size group. Apparently, the phenomena are inconsistent with real PSD dynamics.

In order to account for the above problem, an approximate numerical method has been developed in the present work on the basis of the so-called discrete-sectional technique developed by Gelbard and Seinfeld, and Wu and Flagan, and the Particle-Size-Grouping (PSG) method. In the following text, this numerical method is abbreviated as the DS method, which is described in brief as follows:

1. The entire particle size spectrum is divided into two parts. The first part is termed discrete regime, which begins from monomer followed by dimer, trimer, ..., \( k \)-mer, ..., and \( M \)-mer. \( M \)-mer is the largest particle in this part.

2. The second part immediately follows \( M \)-mer and is termed sectional regime. All the particles in the sectional part are assembled into sections (or groups), in which there is a unique equivalent size for each section, i.e., particle volume \( v_q \) (or particle radius \( r_q \) for section \( q \).

3. Equivalent particle sizes in the sectional manner are determined subject to the condition of \( v_q = R_q v_{q-1} \), where \( v_q \) is formulated by \( R_q^{v_q} R_{q-1}^{v_{q-1}} \), in terms of integers \( q_0 \) and \( q \), monomer volume \( v_1 \) and the equivalent particle volume \( R_q^{v_q} R_{q-1}^{v_{q-1}} v_{q-1} \) of the first section \( q=1 \) in the sectional part. The threshold of section \( q \), the size division point between section \( q-1 \) and section \( q \), is set to be the middle point between section \( q-1 \) and section \( q \) in terms of the equivalent particle radius \( r_{q-1} \) and \( r_q \) which yields \( r_{q-1} = (1/2) (r_{q-1}^{-1} + r_q) \) and \( r_q = (1/2) (1 + r_{q-1}^{1/3}) r_{q-1} \). Accordingly, the threshold of section \( q \) in terms of particle volume is \( V_q = \frac{1}{8} (1 + R_{q-1}^{1/3}) R_{q-1} \), where the volumetric sizes \( V_q \) of particles in section \( q \) match the condition of \( V_q < V_{q-1} \leq V_{q+1} \), i.e., \( (1/8) (1 + R_{q-1}^{1/3}) \leq V_{q-1} \leq V_q \leq (1/8) (1 + R_{q+1}^{1/3}) R_{q+1} \).

4. The first section in the sectional regime immediately follows the \( M \)-mer in the discrete regime. The two parts of particle size space are connected by \( M = Int(V_q/v_1) = Int((1/8) (1 + R_{q-1}^{1/3}) R_{q-1}^{v_q}) = Int(C_q R_q^{v_q}) = h_1 \), where \( Int \) is a mathematical operator extracting the integer part of a real number, and \( C_q \) a coefficient equal to \( (1/8) (1 + R_{q-1}^{1/3}) \). In the case of \( R_q = 2 \), for instance, the first particle in the first section is \( (h_1 + 1) \)-mer subject to the relation of \( h_1 = Int(C_q R_q^{v_q}) = M \).

5. The mass density of particles of different sizes in an identical section in the sectional part is assumed to be constant.

Thus, in DS representation, Eq. (11) may be transferred into

\[ \frac{d n_q}{d t} = \beta_{k,i} n_{k,i} / (1 + \delta(k=2)) - \beta_{k,i} n_{k,i} + \frac{\alpha_{k+1} n_{k+1,i}}{2} \]
\[
\begin{align*}
\frac{dn_k}{dt} &= \beta_{h,k} n_k n_{k-1} + \alpha_{h,k+1} n_{k+1} n_{k-1} - 2 \alpha_{k-2} n_k n_{k-3} + \sum_{i=1}^{k-1} \beta_{i,k} n_i n_k - 1 \\
&+ \alpha_{k-1} A_{i,k} n_{i+1} n_i - \delta_{k} n_k
\end{align*}
\]

for particles in the sectional part of the particle size spectrum. In Eq. (18), \( k \) is the number of monomers assembling a \( k \)-mer, \( n_i \) the number density of \( k \)-mers, \( n_i \) the number density of monomers, and \( \delta (k=2) \) Dirac delta function. When \( k \) is equal to \( M \), the change rate of number density \( n_M \) of \( M \)-mer particles in the discrete regime is calculated. In Eq. (19), \( q \) represents the section number in the sectional part. Section \( q \) covers particles ranging from \( (h_q+1) \)-mer, the smallest particle, to \( (h_q+1) \)-mer, the largest particle, in this section sequentially in terms of \( h_q = \text{Int}(C R^{k-1}) \) and \( h_q+1 = \text{Int}(C R^{k+1}) \). \( n_q \) is the number density of \( (R_h^{k+1}) \)-mers, equivalent particles in section \( q \) according to mass conservation. Moreover, constants \( \xi_1, \xi_2, \xi_3, \), and \( \xi_4 \) in Eq. (19) are correction factors according to the law of mass conservation and are formulated as Eqs. (20) through (23).

\[
\begin{align*}
\xi_1 &= \frac{1 + h_q}{R_h \cdot h_q (h_q - h_q-1)} \\
\xi_2 &= \frac{1}{h_q+1 - h_q} \\
\xi_3 &= \frac{1}{i - (h_q+1 - h_q)} \\
\xi_4 &= \frac{R_h \cdot h_q+1}{(h_q+2 - h_q+1)(1 + h_q+1)} 
\end{align*}
\]

4. Predicted Results and Discussion

To test the above general model, a Fe–Al–O system prediction is illustrated in the following sections. In the case of molten steel deoxidation at 1600°C by addition of aluminum, alumina inclusions are expected to form in the steel melt. To model the nucleation and coarsening of Al2O3 particles in such a Fe–Al–O system, some important parameters are necessary and listed in Table 1. It is supposed that the initial total oxygen is about 300 ppm and that the free oxygen is roughly 3 ppm after the deoxidation process. Correspondingly, the equilibrium number density of [Al2O3] monomers \( n_{1e} \) and the total dimensionless number density \( N^* = (R_h \cdot h_q - h_q) \) of monomers produced by the reaction (1) are estimated to be 2.635 x 10^23 m^-3 and 100 respectively. Additionally, it is supposed that alumina inclusions larger than 50 \( \mu m \) in diameter are immediately removed from molten steel.

4.1. DS Numerical Method Accuracy Estimation

In order to evaluate the accuracy of the DS method, a numerical solution to the dynamic balance equations of the accurate discrete representation, formulated as Eq. (11) and which covers nucleation and Ostwald ripening (termed model NO), is computed by means of the Fourth-Order Runge–Kutta method. The time step size in the numerical calculation is set to be 5.0 x 10^-10 s. The largest inclusion in the particle spectrum is assembled with 2^{14} (=16 384) Al2O3 monomers in the comparison calculation. The computed results are mapped in Figs. 1 and 2. Figure 1, in which the left y-axis represents the dimensionless number density \( N_t \) of total particles normalized by monomer number density \( n_{1e} \) in equilibrium state, and the right y-axis the number density \( n_t \) of total particles with a unit of n·m^-3, illustrates the variation of total particle concentration over

Table 1. Simulation parameters.

| Parameters       | Unit   | Value  |
|------------------|--------|--------|
| Molten steel density \( \rho_i \) | Kg·m^-3 | 7000   |
| Inclusion density \( \rho_i \) | Kg·m^-3 | 3010.31 |
| Dynamic viscosity of melt \( \mu_i \) | Kg·m^-1·s^-1 | 0.0062 (32) |
| Molar volume of alumina \( V_n \) | m^3·mol^-1 | 34.33 x 10^-6 |
| Diffusion coefficient of oxygen in molten steel \( D_{ij} \) | m^2·s^-1 | 2.7 x 10^-9 |
| Interfacial tension \( \sigma \) between \( \alpha \)-alumina and molten steel | N·m^-1 | 0.5 |
| Initial supersaturation \( S \) | -     | 100.0  |
| Initial total oxygen in molten steel | ppm | 300    |
| Final free oxygen in molten steel | ppm | 3      |
| Temperature of melt \( T \) | K | 1873   |

Fig. 1. Evolution of total number density of particles: comparison of the DS method with the accurate discrete representation in terms of model NO (N-Nucleation; O-Ostwald ripening).

![Fig. 1](image-url)

Fig. 2. Evolution of mean particle size: comparison of the DS method with the accurate discrete representation in terms of model NO.

![Fig. 2](image-url)
time. The solid curve comes from the accurate discrete model, and the dot curve from the DS model. Comparison of the two curves shows good agreement with each other.

Figure 2 gives the time evolution of mean particle size predicted by using the accurate discrete model and DS technique. In the present study, mean particle size is defined as the ratio of total number of monomers in all particles to total particle number represented by the left \(y\)-axis in Fig. 2. The right \(y\)-axis stands for the mean diameter \(d_m\) of particles corresponding to \(i_m\) in terms of the \(\text{Al}_2\text{O}_3\) molecule diameter of \(4.77826 \times 10^{-10}\) m. Agreement is also attained for the above two approaches.

Although the predicted results from the two numerical approaches are close to each other, differences do exist. The approximate numerical technique, \textit{i.e.}, the DS method, overestimates inclusion growth rate. It is possible to improve accuracy by extending the discrete part (setting larger value for \(M\)) and employing more size groups in the sectional part in the DS method. The following numerical calculations should proceed by means of DS method.

### 4.2. Analysis of Particle Growth Mechanisms during Deoxidation

As discussed above, inclusions in molten steel start to grow after nucleation during deoxidation due to various growth mechanisms, including oxygen diffusion, Ostwald ripening and several collision-coagulation growth approaches. It is certain that different mechanisms play different roles in growth processes. Simulated results from the general nucleation-growth model make growth mechanisms explicit, as shown in Figs. 3(a) through 3(b) and Figs. 4(a) through 4(b), which describe the variation in total number density and mean size of stable \(\text{Al}_2\text{O}_3\) particles in molten steel at different stages within a 0–10 min time range.

Figure 3(b) shows the time evolution of particle growth at the initial deoxidation stage in terms of dimensionless number density of total particles \(N_t\), which is computed by summation of the number density \(N_k\) of every size particle. Curves 1 in Figs. 3(a) and 3(b) show the prediction from the model NO, where the model name NO originates from the first letters of ‘Nucleation’ and ‘Ostwald ripening’. Model NO considers the function of homogeneous nucleation and the contribution of molecular diffusion growth and Ostwald ripening. The impacts of Brownian coagulation, turbulence coagulation, Stokes coagulation and gradient coagulation are evaluated as additional mechanisms and added to the model NO serially, forming model NOB, model NOBT, model NOBTS and model NOBTSG respectively. The corresponding numerical results are represented by serial curves 2–5 in Figs. 3(a) to 3(b), respectively.

During the first 1.0 \(\mu\)s (\(10^{-6}\) s) after the start of nucleation, curves 1–5 in Figs. 3(a) through 3(b) coincide with each other. This implies that diffusion of oxygen and deoxidizer elements to embryos or particles predominates the growth process of particles. In this stage, stable \(\text{Al}_2\text{O}_3\) particles start to form and grow because a mass of nuclei nucleate under the condition of supersaturated \(\text{Al}_2\text{O}_3\) monomers. According to Eq. (11), during the initial stage, the change rate of particle concentration \(\frac{d N_k}{dt}\) mainly depends on the first positive item on the right hand side of Eq. (11), \textit{i.e.}, a particle generation item, which is proportional to monomer concentration and multi-mer concentration. Apparently, initial monomer concentration is quite high. Therefore, a rapid growth rate in number density of stable particles is expected, which is mapped to show a steep ascent curve in Fig. 3(b). Interestingly, the tendency of mean size evolution in Fig. 3(a) keeps step with that in Fig. 3(b).
As shown in Fig. 3(b), the total number of Al2O3 particles attains maximum value at about 1.0 μs, and then gradually decreases while inclusion size increases continuously. According to assumption (8), collision-coagulation growth mechanisms make sense only among stable particles larger than critical size. Hence, Brownian collision may not occur until stable particles appear. After 1.0 μs (10^{-6}s), the function of Brownian collision on particle growth tends to become significant, which results in a bifurcation of the trend lines at point A1 in Fig. 3(b), curve 1 for model NO and curve 2 for model NOB, and the same situation, i.e., a bifurcation point A2, in Fig. 3(a). When the effect of Brownian collision is fully released, the number density of total particles is one order less than that from model NO without Brownian coagulation and the mean size is also much larger than Model NO.

Additionally, curves 2–5 superpose each other from about 1.0 μs (10^{-6}s) to 2.0 s (also see Figs. 4(a) through 4(b)), which indicates that Brownian coagulation between particles in this period is the dominating collision-coagulation mechanism for the growth of Al2O3 particles compared with turbulent collision, Stokes collision, and gradient collision.

The function of turbulent coagulation is quantitatively formulated by Eq. (15a) and is distinctly illustrated in Fig. 5, which is a modification on the basis of Ref. 36. Both collision frequency function and particle concentration determine the change rate of inclusion number density. Although the collision frequency function β^b (Eq. (12)) due to turbulent collision sharply increases with particle size, the impact of turbulent collision on particle growth may not be remarkable until the number of large particles becomes large. The detailed effect of turbulent collision in the present case is illustrated in Fig. 4, which is an extent of Fig. 3 and shows the evolution of number density of total particles and mean particle size in the later stage of deoxidation, i.e., from 0.1 to 600s. Being similar to the critical points A1 and A2 caused by the function of Brownian collision in Fig. 4, the curves in Fig. 5 divide into two branches (curve 2 and curve 3) at points B1 and B2 corresponding to the moment about 2.0 s after nucleation. Curve 3 presents the prediction from model NOBT, which covers simultaneous Brownian and turbulent coagulation. According to the model calculation in which a mean turbulent energy dissipation rate e of 0.01 m^2 s^{-3} was employed, the contribution of turbulent collision to particle growth becomes increasingly significant and creates a joint dynamic force together with Brownian collision from 2.0 s after nucleation with increases of average particle size and increases in concentration of large inclusions. As a result of turbulent coagulation, particle number density is finally less than that of curve 2 by a factor of fifteen, and the mean particle size shown in Fig. 4(a) sharply increases after point B2.

Stokes collisions of particles occur because of the existence of relative movement of particles. In other words, Stokes collision between two particles takes place only when the two particles different in size, which is why the curve describing the relationship between collision frequency function and particle size is ‘Y’ shaped in Fig. 5. In the present simulation case of the Fe-Al-O system, the contribution of Stokes collision is not noticeable until 1.0 min after the starting point as predicted by curve 4 from model NOBTS in Figs. 4(a) to 4(b). The points C1 and C2 in Fig. 4(b) and Fig. 4(a) represent the critical moment from which the Stoke collision begins to take effect.

According to curves 3 through 5 in Fig. 5(a), the increase of mean particle size accelerates during the later stage of deoxidation and the curves reach their peaks, the maximum of mean particle size, at about t=200 s, then gradually descend and tend toward constants. The reason behind the phenomena is the assumption that particles larger than 50 μm are immediately removed from molten steel. The contribution of particle growth due to collision and coagulation exceeds the effect of the removal of those large particles before the peak moment. Thereafter, the impact of particle removal becomes more significant due to the formation of plentiful particles larger than 50 μm so that the integrated effect yields the decrease of mean particle size. When the above two driving forces tend to create balance, the mean particle size tend toward a constant.

Gradient collision arises in laminar shear layers near walls. Although it shares the same factor (r^+r^-)^3 in Eq. (15d) as turbulent collision from particle-size point of view, gradient collision may almost be ignored during the entire nucleation and growth process of inclusions according to the computation shown in Fig. 4.

In the following text, model NOBTSG will be employed to predict the dynamics of alumina particles.

4.3. Time Evolution of Supersaturation, Critical Size and PSD

The prediction results in Fig. 6 show the history of critical size (critical radius r_c) (Fig. 6(a)), supersaturation S (Fig. 6(b)) during the nucleation and coarsening process. The left y-axis in Fig. 6(a) is the critical number of monomers in a particle and the right one represents the particle critical radius r_c. In a real deoxidation case, when aluminum is added to liquid steel, the reaction between aluminum and oxygen proceeds very quickly under such a high temperature condition. Therefore, as stated above, the supersaturation of [Al2O3] monomers is assumed to be the
maximum value, 100.0, as an initial condition, which means that the critical size of nuclei is expected to be a minimum value, about $4.1 \times 10^{-4} \mu m$, initially corresponding to an assembling of 9 Al$_2$O$_3$ molecules (see Fig. 6(a)). At the initial stage of deoxidation, there is a duration of about 0.2 $\mu s$, when the supersaturation $S$ drops slightly and the critical size increases gradually, because the number of nuclei precipitated is still not so large and the consumption of monomers due to diffusion is accordingly low. Thereafter, the tendency lines of supersaturation $S$ in Fig. 6(b) falls steeply and tends toward the unit because of the dissipation of monomers for the formation of new particles and the growth of existing particles. Meanwhile, the increase of critical size in Fig. 6(a) becomes rapid correspondingly. It should be mentioned here that stable particles could still dissolve into monomers again when their sizes were exceeded by the growing critical size. The prediction results clearly indicate that the nucleation process is quite rapid, only covering an order of ten microseconds in real time.

Prediction of particle size distribution (PSD) of inclusions is an important task for numerical calculation of particle growth. Figure 7 shows alumina inclusion PSD evolution under the condition of a joint action of Ostwald ripening, Brownian collision, turbulent collision, Stokes collision and gradient collision over a broad deoxidation process time range. The lower and upper x-axes denote the number $i(n)$ of alumina monomers in a particle and inclusion diameter $d_i (\mu m)$, respectively. Curves 1–9 in Fig. 7 refer to PSDs of alumina inclusions at a series of moments from 0.01 to 600.0 s. The predicted breadth of inclusion size spectrum has extended to an order of $10^{15}$ monomers, corresponding to about 50 $\mu m$ in diameter. There are two periods in Fig. 7, i.e., 1.0–60.0 s (curve 3–curve 6) and 60.0–120.0 s (curve 6–curve 7), when the change rates of concentration of larger inclusions are huge. Corresponding to the situation in Fig. 4 during the periods of 1.0–60.0 s and 60.0–120.0 s, one may find that it is just due to the function of turbulent collision and Stokes collision that inclusions grow very rapidly.

Figure 8 shows that number densities of inclusions in different size classes change as a function of time. Each curve in Fig. 8 has a peak value, which indicates that concentrations of all inclusion classes initially increase rapidly until they reach a maximum value, and then drop gradually. Smaller inclusions, for instance, those 0.05 $\mu m$ in diameter, tend to dissipate continuously after 0.003 s. One may also find in Fig. 8 that it only takes several minutes for a nucleus to grow into an inclusion as large as several tens of micrometers.

4.4. Comparison of Predicted Total Oxygen and PSD with Experimental Data

In order to evaluate the general nucleation-growth model, a comparison modeling case to calculate the total oxygen changing in molten steel was run based on the same initial conditions as those of Nakanishi and Szekely's experiments.$^{37}$ In this case, initial oxygen concentration in the bath is about 400 ppm. The experimental data cited from literature$^{37}$ are re-plotted as hollow dots and the predicted deoxidation rates are shown as a solid line in Fig. 9, where the vertical axis denotes total oxygen in molten steel. The comparison case indicates that numerical modeling results
in order to evaluate the general model.

The formation and growth of alumina inclusions in a Fe–Al–O system was illustratively computed using aluminum. Their results are compared with the predicted kinetics of total oxygen in Al-killed molten steel is quite reasonable. This manifests the potential of the general nucleation-growth model.

The predicted results demonstrate that one or more of the above growth mechanism approaches together take effect and dominate the growth of inclusions at different molten steel deoxidation stages. At the initial stage, oxygen diffusion and the Ostwald ripening process essentially determine the evolution of particles. At the moment of about 1.0 μs after the start of nucleation, Brownian collision between particles starts to affect the growth course as a joint thruster and gradually becomes the main power. The function of turbulent collision is not significant until 2.0 s after the reference start, when mean particle size reaches some 0.4 μm in diameter. Yet another joint driving force is sequential Stokes coagulation, which is effective in the case of the occurrence of larger particles about 1.0 min after nucleation. On the other hand, the contribution of gradient collision may be ignored during the entire process of particle evolution in the Fe–Al–O system.

Fig. 9. Evolution of total oxygen in Al-killed steel: Comparison of predicted value with experimental data.

Fig. 10. PSD evolution in Al-killed steel: Comparison of predicted results with experimental data.

5. Concluding Remarks

Based on thermodynamics, the classical theory of homogeneous nucleation and theories of diffusion growth and collision-coagulation growth of particles, a general model termed the general nucleation-growth model was developed to describe the molten steel deoxidation process. The model involves the entire process from homogeneous nucleation to Ostwald ripening and various collision-coagulation mechanisms, including Brownian coagulation, turbulent coagulation, Stokes coagulation and gradient coagulation. As a function of the model, the evolution of particle size distribution may be predicted without an initial size distribution of inclusions in steel. The formation and growth of alumina inclusions in a Fe–Al–O system was illustratively computed in order to evaluate the general model.

An approximate numerical approach based on discrete-sectional representation and Particle-Size-Grouping method, namely DS method, was employed to solve the enormous computation load, which comes from the rapid extension of size distribution breadth of particles. Numerical practices indicate that the approximate technique is quite effective for CPU time cutting and the accuracy is acceptable. However, it is still necessary to determine the breadth of the discrete regime and the number of size groups in order to find a balance between time saving and solution accuracy.

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When aluminum is used to deoxidate molten steel, the smallest alumina nucleus is only assembled by 9 Al2O3 monomers under present conditions. Numerical prediction shows that inclusion nucleation is a rapid process, in which the supersaturation of monomers slightly drops at first and then dramatically decreases. The nucleation process in a Fe–Al–O melt system covers only several tens of microseconds in a large measure according to the calculated variation of supersaturation. Furthermore, the growth of alumina inclusions also proceeds very rapidly. It takes only several hundred seconds for a nucleus of several tens of nanometers to grow into an inclusion as large as several tens of micrometers. In the comparison cases, the calculated evolution rate of alumina inclusion growth is lower than experimental data, however the general trend of changing the size and size distribution agrees with each other, and the predicted kinetics of total oxygen in Al-killed molten steel is reasonable and acceptable. This manifests the potential of the general nucleation-growth model.

Nomenclatures

- \( a_M \): Activity of M in the Fe–M–O melt system
- \( a_O \): Activity of O in the Fe–M–O melt system
- \( a_{M,O} \): Activity of the associated compound M₃O₉
- \( A_i \): Surface area of an i-size particle (m²)
- \( C_{M,O} \): Concentration of [M₃O₉] monomers in a supersaturation state
- \( C_{M,O} \): Concentration of [M₃O₉] monomers in a supersaturation state
- \( du/dy \): Velocity gradient (m/s)
- \( D_M \): Diffusion coefficient of monomers in molten steel (m²·s⁻¹)
- \( D_O \): Diffusion coefficient of oxygen in molten steel (m²·s⁻¹)
\( g \): Gravitational acceleration (m·s\(^{-2}\))

\( \Delta G \): Total Gibbs energy change for the formation of nuclei (J)

\( \Delta G_m \): Bulk Gibbs energy per mol (J·mol\(^{-1}\))

\( h_q \): Volumetric threshold of section \( q \), positive integer, number of monomers included in a particle

\( k_0 \): Rate constant of reaction \((i) + (j) \rightarrow (i+j)\)

\( k_{Bn} \): Boltzmann constant (J·K\(^{-1}\))

\( M \)-mer: Largest particle in the discrete regime in the DS method

\( n_i \): Number density of monomers (n·m\(^{-3}\))

\( n_{1e} \): Equilibrium number density of alumina monomers (n·m\(^{-3}\))

\( n_{iV} \): Number density of i-size particles (n·m\(^{-3}\))

\( n_{iN} \): Number density of total inclusions (n·m\(^{-3}\))

\( N_{iV} \): Avogadro number (mol\(^{-1}\))

\( N_p \): Dimensionless number density of particle \( k \)

\( N_q \): Dimensionless number density of section \( q \)

\( N_t \): Dimensionless number density of total inclusions

\( r_{cV} \): Critical radius of particles (m)

\( r_i \): Radius of a monomer (m)

\( r_i \): Radius of a k-size particle (m)

\( r_q \): Equivalent particle radius of \( q \) section in the sectional regime in the DS method (m)

\( r_{qV} \): Threshold radius of section \( q \) (m)

\( R \): Gas law constant (J·K\(^{-1}\)·mol\(^{-1}\))

\( R_i \): Volume ratio between two neighboring size sections in approximation calculation

\( S \): Supersaturation of system equal to dimensionless number density of monomers

\( t \): Time (s)

\( T \): Absolute temperature (K)

\( v_t \): Monomer volume (m\(^3\))

\( V_{1e} \): Volumetric dividing point between the discrete part and the sectional part (m\(^3\))

\( V_{iV} \): Molar volume of particle (m\(^3\)·mol\(^{-1}\))

\( V_q \): Equivalent particle volume of section \( q \) in the sectional regime in the DS method (m\(^3\))

\( V_{qV} \): Threshold volume of section \( q \) (m\(^3\))

\( V_{iq} \): Volume of the \( i \)-th particle in section \( q \) (m\(^3\))

\( \alpha_i \): Number of monomers dissociating from unit area of a k-size particle in unit time (m\(^{-2}\)·s\(^{-1}\))

\( \alpha_l \): Turbulent conglomeration coefficient

\( \beta_i \): Rate constant of the reaction \((i) + (j) \rightarrow (i+j)\) (m\(^3\)·s\(^{-1}\))

\( \beta_c \): Total collision frequency function

\( \beta_q \): Collision frequency function of Brownian collisions

\( \beta_q^B \): Collision frequency function of Stokes collisions

\( \beta_q^T \): Collision frequency function of Turbulent collisions

\( \beta_q^G \): Collision frequency function of Gradient collisions in laminar shear zone

\( \delta_l \): Dirac delta function

\( \epsilon \): Dissipation rate of turbulence energy (m\(^2\)·s\(^{-3}\))

\( \theta \): Dimensionless time

\( \mu_l \): Molecular viscosity (kg·m\(^{-1}\)·s\(^{-1}\))

\( \nu_k \): Kinematic viscosity (m\(^2\)·s\(^{-1}\))

\( \xi_i, \xi_j, \xi_k, \xi_l \): Correction factors according to the mass conservation law

\( \rho_i \): Density of liquid phase (molten steel) (kg·m\(^{-3}\))

\( \rho_{iV} \): Density of particle (kg·m\(^{-3}\))

\( \sigma \): Interfacial tension (N·m\(^{-1}\))

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