Agglomeration of Non-metallic Inclusions at the Steel/Ar Interface: Model Application

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Abstract:
Inclusion agglomeration is an important element in several industrial problems during steelmaking, such as nozzle clogging. It is also important in the solution of these problems. In parallel work by the authors, a revised Kralchevsky-Paunov model has been established and the performance of this model has been validated against the experimental data from in-situ observations using confocal laser scanning microscopy. In this work, the revised model has been applied to quantitatively evaluate the attractive capillary force for the agglomeration of various inclusions at the interface between Ar and liquid iron/steel. A parametric study of the effects on the capillary force of the inclusion density, contact angle between the inclusion and liquid steel, and the surface tension of the liquid metal are quantitatively investigated. The results show that inclusion density and contact angle have a more marked effect on the capillary force than surface tension of liquid metal. Moreover, the inclusion agglomeration behavior in the liquid iron/steel matrix is discussed. The coagulation coefficient of various inclusions is calculated. Both the calculation results of the attractive capillary force of inclusions at the interface between Ar and liquid iron/steel and coagulation coefficient of inclusions in the liquid iron/steel matrix can offer a close agreement; moreover, the order of magnitude of inclusion agglomeration tendency is suggested. By using the coagulation coefficient, the inclusion collision volume and collision rate are calculated and the effects of inclusion composition, size, and number density are investigated. The evaluation results show that the tendency for affecting inclusion collision is inclusion number density>inclusion size>inclusion composition.

Key words: inclusion; agglomeration; capillary force; coagulation coefficient; collision velocity; steelmaking.
I. INTRODUCTION

Nozzle clogging is a well-known problem for continuous casting industrial practice. In order to understand the mechanism, a huge number of publications are summarized in Refs. [1-4]. Among the mechanisms, inclusion agglomeration is one of major importance. Besides nozzle clogging, inclusion agglomeration can also lead to mechanical defects if the agglomerate remains in the solid steel product [1-2]. However, agglomerated inclusions are generally easily removed during Ar bubbling [5-7]. Previous experimental studies [8-16] reported the in-situ observation of inclusion agglomeration at the steel/Ar interface by confocal laser scanning microscope (CLSM) as a means to understand more deeply inclusion agglomeration behavior during Ar bubbling. Moreover, capillary interaction between inclusions partly immersed at the steel/Ar interface is reported to be one mechanism for agglomeration [8-13]. In order to investigate this mechanism, a theoretical model based on Kralchevsky-Paunov model [17, 18] has been subsequently used by Nakajima and co-workers [10-11] and Jönsson and co-workers [12, 13]. These workers showed good agreement between their experimental data for attractive force of inclusion agglomeration at the steel/Ar and steel/slag interfaces. However, to date, quantitative evaluation of the agglomeration tendency of different inclusions has not been reported.

In the present work, the physical properties including inclusion density, contact angle between inclusions and liquid iron/steel, surface energies of inclusions, interfacial energies between inclusions and liquid iron/steel are used to represent different inclusions. The present capillary force model [19, 20] is applied quantitatively, to evaluate the attractive capillary force for the agglomeration of different inclusions at the interface between Ar and liquid iron/steel. Thereafter, the coagulation coefficient, which can be used to evaluate the inclusion agglomeration tendency in the liquid iron/steel matrix, is calculated, and quantitative comparison of different inclusions is performed. Subsequently, the inclusion collision volume \( W_{ij} \) and collision rate \( N_{ij} \) for inclusion collision in the liquid iron/steel matrix are calculated using the Hamaker constant and coagulation coefficient. Finally, the effects of inclusion composition, size and number density are investigated, and, thus, the contribution to inclusion agglomeration by each factor is considered. The present work aims to offer a better understanding of the mechanisms of inclusion agglomeration at the steel/Ar interface and the liquid steel matrix as well as inclusion elimination for clean steel manufacturing.

II. METHODOLOGY

A. Capillary force model of inclusion at steel/Ar interface

The capillary force model discussed here was originally derived by Kralchevsky et al. [17] and Paunov et al. [18] to present the energy and force balances between two particles floating on the surface of a liquid at room temperature. The capillary interaction energy, \( W \), between two spherical inclusions with a separation distance \( L \), is given by equation (1) [17, 18].

\[
\Delta W = -\pi \gamma \sum_{k=1}^{2} (Q_k h_k - Q_k \infty h_k \infty)(1 + O(q^2 R_k^2))
\]

(1)

where, \( Q_k \) and \( Q_k \infty \) are the effective capillary charges for separation distance \( L \) and infinity respectively. Also, \( h_k \) and \( h_k \infty \) are the height differences of the meniscus when the separation distance is \( L \) and infinity respectively. The subscript \( k \) represents the inclusions 1 and 2 in an inclusion pair. The calculation methods of \( Q_k, Q_k \infty, h_k \) and \( h_k \infty \) can be found elsewhere [10-13]. \( \gamma \) is the surface tension of the liquid iron/steel. \( O(x) \) is the zero function of the approximation.

In addition, \( q \) can be estimated by using the density of the inclusion divided by the density of steel.
\[ q \approx \frac{\rho_{\text{inclusion}}}{\rho_{\text{steel}}} \] is termed the capillary length \([10-13]\). The capillary force, \( F \), at different distances \((L)\) can be calculated as equation (2).

\[
F = \frac{d(\Delta W)}{dL} \tag{2}
\]

where, \( \Delta W \) can be calculated by the contributions from wetting, meniscus surface free energy part and gravity. A simplified model to evaluate the capillary force is suggested \([18]\), as shown in equation (3).

\[
F = 2\pi \gamma \frac{Q_1 Q_2}{L} \left( r_k << L \right) \tag{3}
\]

Where \( Q_1 \) and \( Q_2 \) are effective capillary charges of inclusions 1 and 2 when the distance between two inclusions is \( L \). \( \gamma \) is the surface tension of the liquid iron/steel. Comparison of equations (1), (2) and 3 indicates the implied assumption in equation 3, stated below as equation 4. This assumption was introduced by Paunov et al.\([18]\) for simplification.

\[
O((qL)\ln(qL)) \approx 0 \tag{4}
\]

In this work, the equation for capillary force has been further modified based on the L'Hôpital's rule \([21]\). The derivation of the capillary force can be found elsewhere \([19, 20]\). The final equation is provided in equation (5).

\[
F = \frac{2\pi \gamma q_1 q_2 (1-q^2 L^2)}{L} \left( r_k << L \right) \tag{5}
\]

### B. Agglomeration rate in steel matrix

The rate of collisions per unit volume, \((N_{ij})\), between two inclusions with \( R_i \) and \( R_j \) has been defined by many workers according to equation (6) \([22-27]\). However the current authors believe that this would be better defined as agglomeration rate, specifically because the turbulent collision cross section defined below includes a coagulation coefficient which describes the tendency for colliding particles to form an agglomerate. This parameter would not be necessary when we are only concerned with the rate of collision. Perhaps the best way to think of \( N_{ij} \) would be as the rate of successful collisions.

\[
N_{ij} = W_{ij}^{TC} n_i n_j \tag{6}
\]

where, \( n_i \) and \( n_j \) are the numbers of colliding inclusions with radii \( R_i \) and \( R_j \), respectively, \( t \) is time. \( W_{ij}^{TC} \) is the total collision volume expressed in \( m^3/s \), which can be calculated using equation (7) \([22-27]\).

\[
W_{ij}^{TC} = W_{ij}^{B} + W_{ij}^{S} + W_{ij}^{T} \tag{7}
\]

where, \( W_{ij}^{B} \) represents Brownian collisions as a result of random movements in the melt; \( W_{ij}^{S} \) represents Stokes collisions due to buoyancy difference; and \( W_{ij}^{T} \) represents turbulent collisions as a result of movement of inclusions together with liquid steel flow. Expressions for each type of collision volume developed elsewhere \([22-27]\), are given as equations (8) to (10).

\[
W_{ij}^{B} = \frac{2kT(r_i + r_j)^2}{3\mu r_j} \tag{8}
\]

\[
W_{ij}^{S} = \frac{2\pi g (\rho_f - \rho_{\text{inc}}) g \mu}{9\mu} |R_i^2 - R_j^2|(R_i + R_j)^2 \tag{9}
\]

\[
W_{ij}^{T} = 1.3\alpha_{tij}\sqrt{\pi \rho_f \varepsilon/\mu (R_i + R_j)^3} \tag{10}
\]
where, $R_i$ and $R_j$ are the radii of inclusion $i$ and $j$ in the colliding pair, $\kappa$ is the Boltzmann constant, $1.3807 \times 10^{-23}$ J/K, $T$ is the temperature, here, 1873 K (1600 °C) is used. $\mu$ is the dynamic viscosity of the liquid steel, $6.92 \times 10^{-3}$ Pa·s. $g$ is the gravitational acceleration. $\varepsilon$ is the turbulent energy dissipation rate, taken as $0.01$ m$^3$/s$^3$ in this calculation. Rushton et al. [28] reported the definition of $\varepsilon$, expressed as equation (11).

$$\varepsilon = \frac{N_p n^3 d_s^5}{M}$$  \hspace{1cm} (11)

where, $n$ is the agitation speed, $\rho$ is the liquid density, $d_s$ is the diameter of the impeller, $M$ is the mass of liquid and $N_p$ is the power number. Higashitani et al. [29] recommended equation (12) for the calculation of turbulent energy dissipation rate, because not all the energy input dissipated in the liquid was contained in the agitated vessel. This revised equation was adopted by Taniguchi et al. [30] for water modeling studies.

$$\varepsilon' = 0.15 \varepsilon$$  \hspace{1cm} (12)

Taniguchi et al. [30] and Ling et al. [31] reported that the coagulation coefficient decreases markedly as turbulent dissipation rate increases from 0.00001 to 0.1 m$^3$/s$^3$. In equation (10), $\rho_f$ is the density of liquid steel, in this work, 7000 kg/m$^3$ is used. $\rho_{inc}$ is the density of different inclusion, the chosen values are listed in Table 1. $\alpha_{i,j}$ is the coagulation coefficient of inclusions in the liquid steel, and its calculation method is described in the following section. In this calculation, $\alpha_{i,j}$ equals the average value of the coagulation coefficients of inclusion $i$ and $j$ ($\alpha_{i,i}$ and $\alpha_{j,j}$), $\alpha_{i,j}=1/2(\alpha_{i,i}+\alpha_{j,j})$. 1.3 in equation (10) is expressed as $\sqrt{8\pi/15}$ in the original equation reported by Saffman and Turner [32]. This constant is based on an assumption that the velocity gradient related to $\varepsilon$ and kinematic viscosity ($v=\mu/\rho_f$) is normally distributed.

### C. Coagulation coefficient of inclusion in steel matrix

For the case of turbulent collisions, the inclusion agglomeration potency in the liquid steel or at a nozzle wall can be related to the coagulation coefficient. The coagulation coefficient can be found using equation (13) [29-33].

$$\alpha = 0.727 [\mu R_i^3 (\rho_f \varepsilon/\mu)^{1/2}/A_{IM}]^{-0.242}$$  \hspace{1cm} (13)

where $\alpha$ is the coagulation coefficient for turbulent collision, $\rho_f$ is the density of liquid steel, $\varepsilon$ is the turbulent energy dissipation rate and $\mu$ is the viscosity of iron/steel melt. Before discussing the coagulation coefficient, it is important to introduce the concept of the Hamaker constant. According to the background of the van der Waals force acting on the particles and interpreting colloidal stability, Hamaker firstly reported that the vdW force could be split into a purely geometrical part associated with a Hamaker constant [34]. For his method, the vdW interaction energy between two macroscopic bodies, and the interactions between all molecular pairs of the two bodies were summed. The equation of vdW energy for the interaction between a spherical and a flat surface separated by a distance ($L$) is shown as equation (14) [35].

$$W_{vdw}(L) = -(A_{12}R/6L)$$  \hspace{1cm} (14)

where $R$ is the radius of a sphere body, and $A_{12}$ is the Hamaker constant between body $1$ and $2$, which is originally defined as equation (15).

$$A_{12} = \pi^{2} \lambda_{12} \rho_1 \rho_2$$  \hspace{1cm} (15)

where $\lambda_{12}$ is the coefficient which relates to atom-atom pair potential and polarizability, $\rho_1$ and $\rho_2$ are the number of atoms per unit volume in the two bodies. Hamaker’s method ignores the
influence of the intervening medium between two bodies of interaction. Thereafter, Lifshitz [36] developed a description of the vdw energy with consideration of the dielectric properties of the intervening medium. Subsequently, the calculation methods of Hamaker constant are modified by either experimental observation or the theoretical deviation. Visser reviewed the existing methods [37].

Hamaker constant is originally applied in the field of colloid chemistry [37]. Subsequently, Taniguchi et al. [30] applied this concept to the particle coagulation in liquid iron/steel, and applied a physical model based on the coagulation of Polystyrene-latex particles as well as Al$_2$O$_3$ and silica particles. They considered the particles as rigid spheres, and proposed the Hamaker constant of Al$_2$O$_3$ and silica in liquid iron by ignoring the temperature dependence. Subsequently, Nakajima et al. [38] proposed a method to calculate the Hamaker constant and coagulation coefficient of various inclusion particles in liquid metal, using the physical properties including contact angle and interfacial energy between inclusion and liquid metal at high temperature. Their method is based on the original equations by Frenkel et al. [39], expressed as equations (16) and (17). The present work applied the same method as Nakajima et al. [38] proposed to investigate the agglomeration potency of more kinds of inclusion particles in the steel matrix.

\[ A_{IM} = 24\pi a^2 \cdot \gamma_{IM} \]
\[ \gamma_{IM} = \gamma_I - \gamma_M \cdot \cos \alpha_{IM} \]

where \( A_{IM} \) is the Hamaker constant describing particle dispersion/coagulation phenomena in liquid metal. \( a \) is the distance between anion and cation in a specific inclusion phase. Originally \( a \) is the intermolecular distance in a polymer [40]. The value of \( a \) is reported to be 2.8\times10^{-10} \text{ m} for oxide particles [38]. \( \gamma_I \) is the surface tension of specific inclusion, \( \gamma_M \) is the surface tension of liquid iron/steel melt, \( \gamma_{IM} \) is the interfacial tension between iron/steel melt and inclusion, \( a_{IM} \) is the contact angle between liquid iron/steel and inclusion.

### III. RESULTS AND DISCUSSIONS

#### A. Parametric study on inclusion agglomeration behavior at the steel/Ar interface

In parallel work by the authors [20], the effect of inclusion size on attractive capillary force has been investigated. It was shown that larger inclusions are more strongly attracted. The other parameters including inclusion density, contact angle, surface tension of steel and phases of inclusions in a pair are examined here using the revised model.

#### i) Effect of inclusion density

The effect of inclusion density can be represented as inclusion mass on the attractive capillary force, and the result is shown in Figure 1. The experimental data of attractive capillary force is used to validate the present model calculation results. This data is based on the in-situ observation using a confocal laser scanning microscope. The details can be seen in parallel work by the authors [20]. The experimental conditions of inclusion radius \((R_1=46.9 \text{ \mu m}, R_2=4.7 \text{ \mu m})\) and contact angle \((\alpha_1=\alpha_2=137^\circ)\) are used in the revised capillary force calculation, and the model calculation results can offer a close agreement with the experimental data using same condition. Moreover, the capillary attractive force decreases with about one order magnitude with the decreasing inclusion density from 6500 to 2000 kg/m$^3$. This tendency means that the more dense inclusion is more easily agglomerated, when the surfaces of the inclusions are non-wetted with the liquid steel \((90^\circ<\alpha_i<180^\circ)\). In order to compare with the case of inclusions which are wetted with the liquid steel, the capillary attractive force is plotted as a function of inclusion density, and
two contact angles, 50° and 137°, are used. The results are shown in Figure 1(b). It is found that the attractive capillary force decreases with increasing inclusion density, for the case of 50° contact angle. This means that less dense inclusions are more readily agglomerated, when the surfaces of the inclusions are wetted with the liquid steel.

**Figure 1.** Effect of inclusion density and contact angle on the attractive capillary force. The capillary force as a function of (a) distance between inclusions, and (b) inclusion density.

**ii) Effect of contact angle**

The effect of contact angle on the attractive capillary force is shown in Figure 2. The calculation results offer good agreement with the experimental data reported by the authors [20] with the same contact angle of 137°. For this calculation, the inclusions with the same radius and same density have been considered. The parameters are shown in Figure 2. It is found that there is a transition at a contact angle which is close to 90°. Actually, Kralchevsky et al. [17] reported an approximation can be made according to the original model, as shown in Eq.(18).

\[
F = \frac{dW}{dL} \approx \frac{2\pi r_1 r_2 \sin \phi_1 \sin \phi_2}{L}
\]

(18)

where, \( r_1 \) and \( r_2 \) are capillary meniscus radius, and \( \phi_1 \) and \( \phi_2 \) are the angles according to the slope of the meniscus of liquid metal.

By using this simplified equation, the transition contact angle equals to 90° exactly. However, this simplified model will not consider in this work. The attractive capillary force increases with the increasing contact angle from the transition value to 180°. Alternatively, this capillary force decreases with the increasing contact angle from 0° to the transition value. According to the calculation results, the contact angle significantly affects the capillary force, since different inclusions hold the different contact angle data with the liquid steel. For the case of the non-wetted inclusions, the contact angles of solid inclusions are larger than other phase inclusions (semi-liquid and liquid). According to the present calculation results, the attractive force of the solid inclusion will be mainly stronger than that of other phase inclusions, which is the same tendency as the previous experimental data observed by CLSM [8-11]. As a summary, the contact angle can be considered to be a key factor which controls the coagulation or dispersion of inclusions in the liquid steel.
iii) Effect of surface tension of steel

The effect of surface tension of the liquid steel on the attractive capillary force is shown in Figure 3. For this calculation, experimental conditions, previously employed by the authors with inclusion radius \((R_1=46.9 \ \mu m, \ R_2=4.7 \ \mu m)\) and contact angle \((\alpha_1=\alpha_2=137^\circ)\) have been used in Figure 3(a), and the calculation result shows excellent agreement with the experimental data from Ref.[20]. It is found that the attractive capillary force increases slightly with the decreasing surface tension from 1.9 to 1.1 \(J/m^2\), and this conclusion is in agreement regardless of whether the inclusion is wetting or non-wetting with the liquid steel, as seen in Figure 3(b). Since the surface tension of the liquid steel is affected by different steel grades, this conclusion suggests that inclusion agglomeration behavior in different steel grades would not be appreciably different, if the wetting behavior was not markedly changed.

Figure 3. Effect of surface tension of liquid steel on the capillary attractive force. The capillary force as a function of (a) distance between inclusions, and (b) surface of liquid steel.

iv) Effect of different inclusion types in an inclusion pair

In this section, the agglomeration behavior of different types of inclusions with different contact angles are shown. In order to change only one variable, the densities of inclusions 1 and 2 are kept constant. Figure 4(a) shows the model calculation results can be validated by the experimental data with the same conditions. Moreover, Figure 4(b) shows both attractive force
and repulsive force exist when the inclusion types are different. It is seen that a repulsive force exists for solid-liquid inclusion pairs, whereas an attractive force exists for inclusion pairs of the same solid phase. The contact angle for inclusion 1 ($\alpha_1$) is fixed to be 137°, and the change in capillary force as a function of the contact angle for inclusion 2 ($\alpha_2$) is shown in Figure 4(c). It is found that the attractive force increases with increasing $\alpha_2$ from around 90° to 180° and this tendency can be found in inclusion pairs with different sizes. Alternatively, the repulsive force decreases with the increasing $\alpha_2$ till a value which is closed to 90° where it becomes an attractive force. This transition angle can be exactly 90° if using simplified equation (18), described in last section. According to the results in this section, the contact angle data determines the type of the capillary interaction between the inclusions in the liquid steel. Nakajima and Mizoguchi [11] reported a similar conclusion that an attractive force exists between the same kinds inclusions (solid-solid, complex-complex/solid, liquid-liquid) and a repulsive force exists between the different kinds of inclusions (solid-liquid and complex-liquid) according to their experimental observations.

**Figure 4.** The capillary force between the same type inclusions and different types inclusions in an inclusions pair. (a) The model calculation can be validated by the experimental data [20]. The capillary force as a function of (b) distance between inclusions, and (c) contact angle of the second inclusion.

**B. Effect of inclusion composition on inclusion agglomeration behavior at the steel/Ar**
interface

i) Pure Fe

The present capillary force model is used to provide a quantitative evaluation of the agglomeration tendency of different inclusions at a liquid steel/Ar interface. The physical parameters for the calculation were taken from the literature [41-47] and are summarized in Table 1. The attractive capillary force of inclusion agglomeration at the pure iron/Ar interface is listed in Table 1, to compare with the case of inclusion agglomeration in the steel matrix. The range of different value represents the capillary force for inclusions at different distance. A comparison of the attractive capillary force for different inclusions in pure liquid iron is shown in Figure 5(a). In this figure, logarithmic scale of y axis is used to make a clear comparison of various inclusions. The value of $\gamma_{M(I)}$ has been determined by different authors using the contact angle observed in their experiments. Consequently, there have been a range of values reported, despite the fact that the surface tension of the metal should not change with inclusion type. In the present work for theoretical calculations to compare inclusion behavior, it makes more sense to employ a single value for 1.6 J/m$^2$ ($\gamma^{*}_{M(I)}$). This approach is compared in Figure 5(b) with the individual values used by previous authors. [41-47].

Table 1. Physical parameters used for the calculation of the attractive capillary force of inclusions in pure iron [41-47].

<table>
<thead>
<tr>
<th>Inclusion</th>
<th>$\rho_1=\rho_2$ (kg/m$^3$)</th>
<th>$\alpha_1=\alpha_2$ ($^\circ$)</th>
<th>$\rho_f$ (kg/m$^3$)</th>
<th>$\gamma_{M(I)}$ (J/m$^2$)</th>
<th>$\gamma^{*}_{M(I)}$ (J/m$^2$)</th>
<th>$\gamma_1$ (J/m$^2$)</th>
<th>$\gamma_M$ (J/m$^2$)</th>
<th>Attractive capillary force (N)</th>
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<tbody>
<tr>
<td>Ce$\text{O}_2$</td>
<td>6900</td>
<td>105</td>
<td>7000</td>
<td>1.600*</td>
<td>1.600</td>
<td>×</td>
<td>×</td>
<td>3.7E-17-3.7E-16</td>
</tr>
<tr>
<td>Al$\text{O}_3$</td>
<td>3950</td>
<td>137</td>
<td>7000</td>
<td>1.490</td>
<td>1.600</td>
<td>0.750</td>
<td>2.026</td>
<td>2.2E-17-2.2E-16</td>
</tr>
<tr>
<td>Ti$\text{O}_3$</td>
<td>4490</td>
<td>128</td>
<td>7000</td>
<td>1.740</td>
<td>1.600</td>
<td>0.584</td>
<td>1.658</td>
<td>2.1E-17-2.1E-16</td>
</tr>
<tr>
<td>MgO</td>
<td>3580</td>
<td>122</td>
<td>7000</td>
<td>1.717</td>
<td>1.600</td>
<td>0.710</td>
<td>1.616</td>
<td>1.1E-17-1.1E-16</td>
</tr>
<tr>
<td>CaO</td>
<td>3350</td>
<td>121</td>
<td>7000</td>
<td>1.660</td>
<td>1.600</td>
<td>0.621</td>
<td>1.474</td>
<td>9.0E-18-9.0E-17</td>
</tr>
<tr>
<td>CaO-2Al$\text{O}_3$ (CA2)</td>
<td>3617</td>
<td>60.8</td>
<td>7000</td>
<td>1.522</td>
<td>1.600</td>
<td>0.599</td>
<td>1.336</td>
<td>8.4E-18-8.4E-17</td>
</tr>
<tr>
<td>MgAl$\text{O}_4$</td>
<td>3578</td>
<td>110</td>
<td>7000</td>
<td>1.600*</td>
<td>1.600</td>
<td>0.550</td>
<td>1.097</td>
<td>5.5E-18-5.5E-17</td>
</tr>
<tr>
<td>MgO-FeO</td>
<td>3808</td>
<td>99.2</td>
<td>7000</td>
<td>1.447</td>
<td>1.600</td>
<td>0.710</td>
<td>0.940</td>
<td>2.2E-18-2.2E-17</td>
</tr>
<tr>
<td>Al$\text{O}_3$-FeO</td>
<td>3224</td>
<td>105</td>
<td>7000</td>
<td>1.445</td>
<td>1.600</td>
<td>0.750</td>
<td>1.139</td>
<td>1.9E-18-1.9E-17</td>
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<tr>
<td>SiO$_2$</td>
<td>2650</td>
<td>106</td>
<td>7000</td>
<td>1.720</td>
<td>1.600</td>
<td>0.400</td>
<td>0.873</td>
<td>5.3E-19-5.3E-18</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>4230</td>
<td>79.27</td>
<td>7000</td>
<td>1.600</td>
<td>1.600</td>
<td>0.380</td>
<td>0.081</td>
<td>9.3E-20-9.3E-19</td>
</tr>
</tbody>
</table>

\(\gamma^{*}_{M(I)}\) - unified value of surface tension of steel;

× - Not available;

* - Use the unified value since the actual value is not available.

The results in Figure 5(a) and (b) assume that the inclusions in a pair have the same radius of 10 μm. Regardless of the type of the inclusion studied, the attractive capillary forces decrease with an increase in the distance between the inclusions and show little dependency on the choice of $\gamma_{M(I)}$. The relative magnitude of the attractive capillary force is as follows: Ce$\text{O}_2$>Al$\text{O}_3$>Ti$\text{O}_3$>MgO>CaO>MgAl$\text{O}_4$>Al$\text{O}_3$>FeO>MgO-FeO>SiO$_2$>TiO$_2$. The attractive capillary force for Ce$\text{O}_2$, Al$\text{O}_3$ and Ti$\text{O}_3$ inclusions are highest indicating that these inclusions have the strongest tendency to agglomerate at the metal/Ar interface. It is well known that Al$\text{O}_3$ and Ce$\text{O}_2$ cause clogging at the narrow transfer part of the submerged entry nozzle (SEN) during casting [2, 23, 24] and our results are consistent with this practical observation.

Specifically, Ce$\text{O}_2$ holds the higher capillary force than Al$\text{O}_3$ because Ce$\text{O}_2$ is a more dense inclusion. Capillary force is affected markedly by the inclusion density. Similarly, Ti$\text{O}_2$ with a
much lower contact angle shows a capillary force that is almost the same as Al₂O₃ due to the density of Ti₂O₃ being higher. Note that the contact angle between Ce₂O₃/Ti₂O₃ and pure iron is smaller than that between Al₂O₃ and pure iron. This fact leads to a qualitative conclusion that inclusion density offers a more important role in the capillary force than contact angle. MgAl₂O₄ is another type of inclusion which can lead to nozzle clogging; however, the attractive capillary force for MgAl₂O₄ is not as large as that of Al₂O₃. According to the parametric studies, it is noted that the capillary force is affected greatest by inclusion size, inclusion density, and contact angle. Table 1 shows that the density of MgAl₂O₄ is slightly less than that of Al₂O₃, and the contact angle of MgAl₂O₄ is much smaller than that of Al₂O₃. This leads to the difference of attractive capillary force between MgAl₂O₄ and Al₂O₃. The apparent contradiction between this result and practical experience of nozzle clogging, offers insight that the potency of inclusion agglomeration at the steel/slag interface and inclusion agglomeration in the steel matrix or at a refractory surface is not always same. In a previous study, Kang et al. [48] was the first to state that the capillary force can be applied only at the liquid metal surface and the steel/slag interface. This viewpoint is entirely consistent with the present study. The authors suggest that while calculations of the attractive capillary force, such as those employed in the current work, offer a clear prediction of inclusion behavior at the gas/metal interface in a CLSM, and provide insight on particle motion dynamics in liquid steel, they do not offer a good prediction of nozzle clogging or on inclusion agglomeration in the actual bulk steel. A more appropriate parameter, to predict the tendency to clog or agglomerate, is the coagulation coefficient.
**Figure 5.** Comparison of the attractive capillary force of different inclusions in pure iron. (a) The calculation results use actual $\gamma_{M(I)}$ in Table 1; (b) The calculation results use unified $\gamma^*_{M(I)}$ of 1.6 J/m$^2$ in Table 1.

**ii) Medium carbon steel**

The same methodology has been applied for inclusion agglomeration in medium carbon steel. Comparison of the attractive capillary forces of inclusions at medium carbon steel/Ar interface is shown in **Figure 6**. The physical parameters used for the calculations are obtained from literature [38, 41-46, 49-52] and listed in **Table 2**. The attractive capillary force of inclusion agglomeration at the steel/Ar interface is also listed in Table 2, and the range of different values represents the capillary force for inclusions move towards each other at different distances. The order of attractive capillary force values for different inclusions followed the trend, which is $\text{Ti}_2\text{O}_3$$>\text{MgO}>\text{CaO}$$>\text{TiO}_2$$>\text{SiO}_2$. Furthermore, the agglomeration tendency of different inclusions in medium carbon steel was similar to that in pure iron. This is most likely due to a minor change between the physical properties of pure iron and medium carbon steels that affects the capillary force.

**Table 2.** Physical parameters used for the calculation of the attractive capillary force and the coagulation coefficient of inclusions in medium carbon steels [38, 41-46, 49-52].

<table>
<thead>
<tr>
<th>Inclusion</th>
<th>$\rho_1 - \rho_2$ (kg/m$^3$)</th>
<th>$\alpha_1 = \alpha_2$ (°)</th>
<th>$\rho_{\text{steel}}$ (kg/m$^3$)</th>
<th>$\gamma_M$ (J/m$^2$)</th>
<th>$\gamma^*_{M(I)}$ (J/m$^2$)</th>
<th>$\gamma_I$ (J/m$^2$)</th>
<th>$\gamma_{IM}$ (J/m$^2$)</th>
<th>Attractive capillary force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ti}_2\text{O}_3$</td>
<td>4490</td>
<td>143.75</td>
<td>7000</td>
<td>1.560</td>
<td>1.500</td>
<td>0.584</td>
<td>1.842</td>
<td>3.3E-17~3.3E-16</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>4230</td>
<td>96.87</td>
<td>7000</td>
<td>1.560</td>
<td>1.500</td>
<td>0.380</td>
<td>0.565</td>
<td>3.3E-18~3.3E-17</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>3580</td>
<td>118</td>
<td>7000</td>
<td>1.360</td>
<td>1.500</td>
<td>0.710</td>
<td>1.347</td>
<td>1.0E-17~1.0E-16</td>
</tr>
<tr>
<td>CaO</td>
<td>3350</td>
<td>108</td>
<td>7000</td>
<td>1.340</td>
<td>1.500</td>
<td>0.621</td>
<td>1.034</td>
<td>4.0E-18~4.0E-17</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2650</td>
<td>97</td>
<td>7000</td>
<td>1.467</td>
<td>1.500</td>
<td>0.400</td>
<td>0.578</td>
<td>8.3E-20~8.3E-19</td>
</tr>
</tbody>
</table>

**Figure 6.** Comparison of the attractive capillary force of different inclusions at medium carbon steel/Ar interface.

**C. Effect of inclusion composition on inclusion agglomeration behavior in the steel matrix**
In the steel matrix, the interface curvature effects are excluded. Inclusion collision was driven by the steel flow. Subsequently, the inclusion agglomeration was caused by van der Waals force, thereafter capillary forces and finally adhesion force of solid phase sintering [53-55]. Specifically, van der Waals force is represented by the Hamaker constant, which is calculated in this work. Previous studies [53, 55] also proposed a liquid bridge force because the inclusion is not completely wet by the liquid steel. However, such a liquid bridge force requires the existence of a void at the particle-particle neck. The current authors struggled to see how such voids would be significant in actual bulk steel.

In the present work, the coagulation coefficient is used to show inclusion agglomeration potency in the liquid steel matrix. Actually, the concept of coagulation coefficient has been used for computational fluid dynamics (CFD) simulation of inclusion agglomeration; however, the values were set to a constant value of 1.0 for the sake of convenience in a CFD study [56]. The present method correlates the coagulation coefficient, the Hamaker constant and the physical properties of the inclusions and the liquid metal. Thus, the effects of inclusion composition and size on the coagulation coefficient can be discussed quantitatively. Moreover, the accuracy of this calculation method has been tested. The coagulation coefficient has been calculated to be around 0.15 to 0.9 for Al₂O₃ inclusions with radii between 2 to 20 μm in pure iron melts, using this method. This data can fit the previous results reported by Nakanishi and Szekely [23] and Zhang et al. [24]. The value in Ref.[23] is reported to vary between 0.27 and 0.63 for the Al₂O₃ inclusion with a radius ranging from 1 to 16 μm, according to the experimental and calculation results obtained from the Al deoxidation process in the ASEA-SKF furnace. The data in Ref.[24] are reported to 0.18 for Al₂O₃ inclusion with a radius of 25 μm belonging to size range between 1 and 70 μm.

**Figure 7.** Comparison of coagulation coefficients of various inclusions with 10 μm of radii.

Figure 7 compares the coagulation coefficients of different inclusion types with a radius of 10 μm. The coagulation coefficient of Ce₂O₃ is not presented here due to the lack of γᵢ in the open literature. It can be seen that the order of the coagulation coefficients for different inclusions offers a close agreement with the order of attractive capillary force. The only exception is the coagulation coefficient of Al₂O₃ provides a markedly higher value than that of Ti₂O₃, whereas,
the capillary force of these two inclusions is slightly different. This discrepancy is due to the fact that the coagulation coefficient is depended on the contact angle, and the capillary force is mainly affected by inclusion density. It is seen that Al₂O₃ inclusions have the highest potency for coagulation, and TiO₂ inclusions have the highest potency to disperse. This result is supported by experimental evidence reported by Xuan et al. [57]. They reported that Al₂O₃ inclusion in the reference steel is easily agglomerated than Ti-oxide in the steel with TiO₂ addition.

By using the same methodology, the coagulation coefficients for oxide inclusions in medium carbon steel are calculated and the results are shown in Figure 8. The order of coagulation coefficient values offers close agreement with that of capillary force. The discrepancy is that the coagulation coefficient of TiO₂ and SiO₂ gets a close agreement; however, the capillary force of TiO₂ is much larger than that of SiO₂ because of the much higher density. In addition, the coagulation coefficient of different inclusions in medium carbon steel was similar to that in pure iron, due to a minor change between the physical properties of pure iron and medium carbon steels.

<table>
<thead>
<tr>
<th>Inclusion/medium carbon steel</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>[38]</td>
</tr>
<tr>
<td>CaO</td>
<td>This work</td>
</tr>
<tr>
<td>MgO</td>
<td>This work</td>
</tr>
<tr>
<td>SiO₂</td>
<td>This work</td>
</tr>
<tr>
<td>R₁=R₂=10 μm</td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Comparison of coagulation coefficient of different inclusions in medium carbon steel.

D. Effect of inclusion size and number density on collision behavior of inclusions in the steel matrix

In the actual steelmaking process, a high number density of inclusions in the liquid steel exists. The higher number density can increase the collision frequency between inclusions of various size. The total collision rate of inclusions in the steel matrix can be evaluated as equation (6). For this equation, the inclusions are assumed as solid, spherical, and uniformly distributed in the steel bath [27, 58]. For this calculation, first the collision volume, W_{ij}^{TC}, is calculated employing equations (7) to (10). The total collision volume is evaluated by summing the three contributions from Brownian collision (W_{ij}^{B}), Stokes collision (W_{ij}^{S}) and turbulent collision (W_{ij}^{T}) [22-27].

Brownian collision means the inclusions coagulate each other because of Brownian motion [58]. Stokes collision represents the inclusion rise with a velocity in Stokes regime and the bigger inclusions have larger rising velocity. Thus, the faster larger inclusions catch up, and collide with, the smaller slower inclusions [27]. Turbulent collision refers to the movement of inclusions
due to turbulent eddies. Sheng et al. [59] state that turbulent collision is often the most important mechanism of inclusion agglomeration. For the present calculation, the coagulation coefficient, $\alpha_{ij}$, is used. The radius of inclusion $i$ is kept constant to be 10 $\mu$m, and that of inclusion $j$ varies from 2 to 20 $\mu$m. The values of $\alpha_{ij}$ with different inclusion radii are listed in Table 3.

Table 3. Coagulation coefficients of Al$_2$O$_3$, CA2 and TiO$_2$ inclusions with different sizes.

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$-Al$_2$O$_3$ ($r_i = 10 \mu$m)</th>
<th>CA2-CA2 ($r_i = 10 \mu$m)</th>
<th>TiO$_2$-TiO$_2$ ($r_i = 10 \mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_j$ ($\mu$m)</td>
<td>$\alpha_{T,j}$</td>
<td>$r_j$ ($\mu$m) $\alpha_{T,j}$</td>
<td>$r_j$ ($\mu$m) $\alpha_{T,j}$</td>
</tr>
<tr>
<td>2</td>
<td>0.875</td>
<td>2</td>
<td>0.791</td>
</tr>
<tr>
<td>5</td>
<td>0.450</td>
<td>5</td>
<td>0.407</td>
</tr>
<tr>
<td>10</td>
<td>0.272</td>
<td>10</td>
<td>0.246</td>
</tr>
<tr>
<td>15</td>
<td>0.203</td>
<td>15</td>
<td>0.183</td>
</tr>
<tr>
<td>20</td>
<td>0.165</td>
<td>20</td>
<td>0.149</td>
</tr>
</tbody>
</table>

The collision volumes due to Brownian collision, Stokes collision, and turbulent collision are plotted in Figure 9. Three types of inclusions, Al$_2$O$_3$, CaO-2Al$_2$O$_3$ (CA2) and TiO$_2$, are considered. It is found that Brownian collision volume ($W_{ij}^B$) decreases slightly when the inclusion radius increases up to around 7.5 $\mu$m and remains constant, because the effect of inclusion size is only considered to calculate Brownian collision volume using equation (8). The value of $W_{ij}^B$ is around 1E-17 m$^3$/s, which is several orders of magnitude lower than $W_{ij}^S$ and $W_{ij}^T$. The contribution of $W_{ij}^B$ to total collision volume can be ignored for all practical steelmaking conditions.

The value of Stokes collision volume ($W_{ij}^S$) firstly decreases when the radius of inclusion $j$ increases from 2 to 10 $\mu$m. Thereafter it increases. The minimum value of $W_{ij}^S$ is approximately 2E-16 m$^3$/s in Figure 9 when $R_j$ equals 9.99 and 10.01 $\mu$m ($R_i=10 \mu$m). $W_{ij}^S$ should equal to zero when $R_i$ and $R_j$ are same ($R_i=R_j$), according to equation (9). This value becomes larger when there is a significant difference between sizes of inclusions. Moreover, it is observed that the sequence of $W_{ij}^S$ is CA2$>$Al$_2$O$_3$$>$TiO$_2$. This is due to the fact that $W_{ij}^S$ is only affected by the inclusion density, and the order of densities of inclusions is $\rho_{CA2}$$>$ $\rho_{Al_2O_3}$$>$ $\rho_{TiO_2}$. Again, for inclusion sizes relevant to steelmaking, Stokes collisions can be regarded as negligible. For the case of turbulent collision volume, the value of $W_{ij}^T$ increases as the inclusion size increases. Moreover, the order of $W_{ij}^T$ for different inclusions is Al$_2$O$_3$$>$CA2$>$TiO$_2$. Considering equation (10), $W_{ij}^T$ is influenced by the coagulation coefficient of different inclusions. The order of $\alpha_i$ is also Al$_2$O$_3$$>$CA2$>$TiO$_2$, which can be observed in Figure 7. Our finding is consistent with equation (10). In summary, the total collision volume is dominantly influenced by Stokes and turbulent collision. Moreover, turbulent collision pays more important role than Stokes collision since the size of real inclusions can even ignore stokes collisions. The effect of Brownian collision can be entirely neglected. This study indicates that the order of collision volumes affecting inclusion agglomeration in the liquid steel matrix is Turbulent collision$>$Stokes collision$>$Brownian collision, when inclusion sizes in a pair are not different from each other.
Figure 9. Effect of inclusion radius and composition on the collision volume of Al$_2$O$_3$, CA2 and TiO$_2$ inclusions.

The effects of inclusion radius and number density on collision rate are illustrated in Figure 10 and Figure 11, respectively. Three types of inclusions, Al$_2$O$_3$, CA2 and TiO$_2$ are plotted. For this calculation, the number density of inclusion i and j are considered to be the same for simplicity ($n_i=n_j$). It is found that the collision rate, $N_{ij}$, increases with increasing radius of inclusion j ($R_j$) when $R_i$ is fixed. Furthermore, $N_{ij}$ is observed to be larger when the number density of inclusions is higher. In addition, there is an inflection point in Figure 10 when $R_i$ and $R_j$ equal to 10 μm. This is because $W_{ij}^S$ gets zero when $R_i$ equals to $r_j$ ($R_i=R_j=10$ μm). In combination of Figure 10 and Figure 11, it is found that the order of effect of inclusion composition on the total collision rate is Al$_2$O$_3$>CA2>TiO$_2$. However, it is noted that the contribution of effect of inclusion composition is much smaller, compared with the effects of inclusion radius and inclusion number density on collision rate. Moreover, the inclusion number density plays more markedly role on collision rate, compared with inclusion radius. For instance, $N_{ij}$ increases from 1E-7 to 1E-5 m$^3$s$^{-1}$ when $R_j$ increases from 2 to 40 μm. However, $N_{ij}$ increases from 1E-8 to 1E-3 m$^3$s$^{-1}$ when the number density ($n_i=n_j$) increases from 1000 to 20000 m$^{-3}$. Even if the inclusion radius cannot be compared with its number density directly, a qualitative conclusion can be obtained that the order of affecting factors on the inclusion collision rate is inclusion number density>inclusion size>inclusion composition. More experimental work aimed to validate this calculation result is considered in the future work by the authors by using CLSM.
**Figure 10.** Effect of inclusion radius on the collision rate of Al₂O₃, CA2 and TiO₂ inclusions.

**Figure 11.** Effect of inclusion number density on the collision rate, Al₂O₃, CA2 and TiO₂ inclusions.

**E. Consideration on future work and industrial practice**

Based on the present theoretical studies of inclusion agglomeration, several research aspects are considered as follows.

i) **Effect of steel flow on inclusion agglomeration**

In a separate work by the authors [20], agglomeration of inclusions is observed at the stagnant steel/Ar interface when the steel is completely melted. However, steel flow also occurs for a short period during incipient melting of the surface of steel matrix. It is found that the steel flow
can strongly push inclusions together within several seconds from long distance. In a previous study, it is reported that liquid oxide inclusions, which cannot be attracted by themselves, can occasionally be forced together by an external steel force [48]. In the actual steelmaking process, steel flow is inevitable, and hence, inclusion collision and agglomeration is strongly driven by turbulence in the liquid steel, such as ladle stirring and continuous casting. The discussion in the last section shows that inclusion number density has a higher effect than inclusion size and inclusion composition on its collision rate. If considering the actual steel flow, the effect of inclusion number density can be enhanced, since the collision frequency can be increased if the steel flow is marked.

**ii) Nozzle clogging**

It is well known that inclusion agglomeration is an important reason to induce clogging of submerged entry nozzle (SEN). Previous studies [60, 61] reported that re-oxidation deteriorates the castability of Al-deoxidized Ti-bearing ultra-low carbon steels primarily due to the formation of Ti-bearing inclusions. These inclusions promote large-scale melt freezing inside the nozzle deposits. This finding is based on industrial scale experiments. Actually, the phase and morphology of inclusions in the clogged SEN were in reasonably agreement with those observed in the in-situ experiments in a parallel work by the authors [20]. The authors hope some results and ideas in this work are expected to give a better understanding of the mechanism of nozzle clogging for Al deoxidized Ti-alloyed IF steel production.

**IV. CONCLUSIONS**

Theoretical studies of inclusion agglomeration at the liquid steel/Ar interface and in the liquid steel matrix have been performed in this work. The following conclusions can be drawn.

1. The order of capillary force of different inclusions at the pure iron/Ar interface is Ce2O3＞Al2O3＞Ti2O3＞MgO＞CaO＞MgAl2O4＞Al2O3·FeO＞MgO·FeO＞SiO2＞TiO2, and this order at the medium carbon steel/Ar interface of differs an agreement result, which is Ti2O3＞MgO＞CaO＞TiO2＞SiO2. Note that the order of coagulation coefficient of various inclusions in the steel matrix offers a close agreement with that of attractive capillary force at the steel/Ar interface in the present work. The discrepancy is because the coagulation coefficient is affected by contact angle whereas inclusion density is a dominant factor for capillary force.

2. Parametric studies of the revised capillary force model show that the inclusion mass density and contact angle have a remarkable effect on the capillary force. Specifically, the inclusion density plays a more dominant role on affecting the capillary force than contact angle and inclusion size. However, the effects of surface tension on this force are much weaker.

3. Based on the calculation results by the collision volume and collision rate of inclusion in the steel matrix, the tendency for affecting inclusion collision is inclusion number density＞inclusion size＞inclusion composition.

4. The calculations of the attractive capillary force can offer a clear prediction of inclusion behavior at the gas/metal interface, and provide insight on particle dynamics in liquid steel. The capillary force calculation associated with the in-situ observation experiments can offer good agreement with the industrial nozzle clogging for Al2O3 inclusions. However, the results do not always offer a good prediction of nozzle clogging or on specific kinds of inclusion agglomeration in the bulk steel. A more appropriate parameter, to predict the tendency to clog or agglomerate, is the coagulation coefficient.
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REFERENCE