Wetting of Solid Al₂O₃ with Molten CaO–Al₂O₃–SiO₂

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The wetting behavior of solid Al₂O₃ with molten CaO–Al₂O₃–SiO₂ was investigated at 1873 K using the sessile drop method. A new model was developed to represent the time dependence of the contact angle, i.e., the spreading behavior of a liquid drop on a solid substrate. The model takes into consideration chemical interactions which continually take place at the interface between the solid Al₂O₃ and molten CaO–Al₂O₃–SiO₂. By applying the model to the experimental results of the present study the equilibrium contact angle between the liquid slag and solid alumina was determined for a number of different slag compositions, and an iso-contact angle diagram was constructed. The equilibrium contact angle was greatly affected by the slag composition, and it was found that the interfacial tension was the major factor governing the equilibrium contact angle. In the region of low SiO₂ content, the slag with higher CaO content exhibits a smaller contact angle, i.e., better wettability with alumina. For slag with a given CaO/SiO₂ ratio, an increase in Al₂O₃ results in a corresponding increase in the contact angle, i.e., decrease in wettability. For a given CaO/Al₂O₃ ratio, the variation of the contact angle with SiO₂ content shows a minimum. The contact angle decreases by increasing the surface roughness of the alumina substrate.

KEY WORDS: contact angle; equilibrium; spreading; rate; CaO–Al₂O₃–SiO₂ slag; alumina; Al₂O₃; substrate; interfacial tension.

1. Introduction

Non-metallic inclusions form mainly by deoxidation in the steelmaking process. Their presence in steel causes a number of problems in steelmaking processes and with steel products, and consequently they must be removed as much as possible before casting. In general the density of steel products, and consequently they must be removed as much as possible before casting. In general the density of steel products, and consequently they must be removed as much as possible before casting. In general the density of steel products, and consequently they must be removed as much as possible before casting. In general the density of steel products, and consequently they must be removed as much as possible before casting. In general the density of steel products, and consequently they must be removed as much as possible before casting.

2. Experimental

The alumina substrate was prepared with the sintered Al₂O₃ (>99.8%) (22×10⁻³ m×20×10⁻³ m×3×10⁻³ m). All substrates were polished to keep the surface roughness identical. The roughness was measured by using a non-contacting surface roughness measuring apparatus (Rodenstock RM600) and the mean center-line roughness (Rₜ) was measured to be 0.553μm. Some substrates were prepared with different surface roughness in order to investigate the effect of the surface roughness of alumina substrate.

Slag samples for the measurement of wetting behavior were prepared by mixing master slags of an appropriate ratio to weigh a total of 0.3×10⁻³ kg. Each sample was pressed to form a small pellet. The master slags were prepared by mixing oxides (Al₂O₃, SiO₂, CaO and MgO) of reagent grade at an appropriate proportion and melted in a graphite crucible using a high frequency induction furnace and the slags were then quenched, ground into powder, and decarburized by heating under the atmosphere at 1273 K for 12 h. The composition of the master slags was confirmed by XRF analysis. The slag compositions investigated in the present study are given in Fig. 1 and also in Table 1.

The apparatus employed to measure the change of the
wetting angle over time is schematically shown in Fig. 2. An alumina substrate (7) was positioned horizontally in the induction furnace (15 kW–20 kHz). A slag pellet was held in a graphite slag holder (5) with a small hole (2×10⁻⁷ m in diameter) at the bottom. The furnace including the substrate and the slag holder with the slag pellet was heated at a rate of 100 K/min up to 1873 K under an inert atmosphere by flowing purified argon gas. The system was held isothermally for 10 min at 1873 K to ensure complete melting of the slag sample. The molten slag was then slowly squeezed out of the slag holder through the hole at the bottom by pressurizing the tube (3) with a bellow connected to the slag holder.

From the instant when the molten slag drop touched the alumina substrate, the change of the shape, i.e., the wetting behavior, was continually recorded by using a digital video camera running at 30 frames/sec. Using image capturing software (MIRO DC-20 PLUS®), and image digitizing software (WINDIG®), the change in the height and width of the drop with time was precisely measured.
3. Results

3.1. Spreading Behavior

A typical example of the spreading and wetting behavior of a liquid slag drop on an alumina substrate is shown in Fig. 3. It is seen that the liquid drop spreads out on the substrate with time. In the present study the moment at which the slag drop forms the right angle with the substrate is taken as the zero time. The experimental results of the spreading behavior are shown in Fig. 4. It is obvious that the spreading continues to proceed until the contact angle has reached the limiting value which is the equilibrium contact angle. General observations from the figure can be summarized as follows:

![Fig. 2. Experimental apparatus.](image1)

![Fig. 3. Spreading behavior of slag on an alumina substrate. (slag: A2, T: 1873 K)](image2)

![Fig. 4. Spreading behavior of slag of different compositions (mass%) on Al2O3 substrate at 1873 K.](image3)
1) The contact angle changes very rapidly in the first few seconds, followed by an asymptotic approach to an equilibrium value.

2) The rate of the change in the contact angle depends on the slag composition.

3) The equilibrium contact angle differs with different slag compositions.

A number of factors may be involved in governing the spreading behavior, i.e., the change in the contact angle. These may include the slag viscosity, the surface and interfacial tension, and the surface roughness of the substrate. In addition, any chemical interaction between the slag and the substrate that may occur should also be taken into consideration.

3.2. Chemical Interactions at the Interface

In order to check if any chemical interactions took place at the interface, some specimens (slag/substrate) were rapidly taken out of the heating zone after the experiment and immediately quenched by blowing helium gas. The compositional change across the slag/substrate interface was investigated using electron probe microanalysis (EPMA). The result with the slag A1 (57.7%CaO–42.3%Al2O3) is given in Fig. 5 where the compositional change across the interface is clearly visible. The alumina content in the slag phase increases towards the alumina substrate, but there is also a layer at which the composition stays constant. Considering the atomic percent ratio of Al/Ca being constant at about 2/1 at the layer as shown in Fig. 5, the phase which prevails at the layer should be the compound of CaO · Al2O3. A similar study with different slag compositions has confirmed the formation of other compounds, i.e., CaO · 2Al2O3 with slag B1 and CaO · 6Al2O3 with slag D4.

With slags in a certain compositional range (e.g., Slag E6) no compound formation was observed. In Fig. 6 the results of the observation are represented together with the CaO–Al2O3–SiO2 phase diagram. The formation of a compound layer may be explained by mutual interactions or reactions between the slag and alumina substrate. When molten slag comes into contact with the alumina substrate, alumina in the substrate dissolves into the slag and slag components diffuse into the alumina substrate. Slag composition in the vicinity of the interface continues to change in the direction toward the Al2O3 corner until the composition hits the primary field boundary of the corresponding compound. It is seen in Fig. 6 that in the case of slag B1 (59.4%CaO–5.0%SiO2–35.5%Al2O3) the corresponding compound is CaO · 2Al2O3 and the compound which actually forms is also CaO · 2Al2O3. These observations tend to imply that the formation of a corresponding compound takes place at a relatively fast rate and the dissolution of alumina into the slag occurs in two steps: i.e., formation of a CaO–Al2O3 compound and subsequent dissolution of the compound.

4. Discussion

4.1. Model Development for Spreading Behavior

As for the spreading of a liquid drop on a solid substrate, a number of models have been proposed, and some relevant to the present study are summarized in the following:

a) Model Proposed by Newman, 2) and Cherry–Holmes 3)

\[
\cos \theta = \cos \theta_{\text{app}} (1 - ae^{-ct}) \quad \cdots \cdots \cdots \cdots \cdots \cdot (1)
\]

where \( a = 1 - \cos \theta_0/\cos \theta_e \), \( c = \pi \mu L \), \( \cos \theta = (\sigma_{SV} - \sigma_{LS})/\sigma_{SV} \), \( \theta_0 = \) contact angle at \( t = 0 \), \( \theta_{\text{app}} = \) equilibrium contact angle.
angle on a rough surface, \( \theta = \) contact angle at \( t \), \( \mu = \) viscosity of the liquid drop, \( \sigma_L = \) surface tension of the liquid drop, \( \sigma_S = \) surface tension of the solid substrate, \( \sigma_{LS} = \) interfacial tension between the solid substrate and the liquid drop, \( L = \) scaling length.

b) Model Proposed by Ogarev et al.\(^4\)

\[
t = \frac{\mu(3V_0 / \pi^{1/3})}{8\sigma_L V_0 \cos \theta_{c, app} \cos \theta} - \exp(mt) 
\]

where \( V_0 = \) volume of the liquid drop.

c) Model Proposed by Schroeder\(^5\)

\[
\cos \theta(t) = \cos \theta_0 + \cos \theta_{c, app} [1 - \exp(-mt^3)] 
\]

where \( m \) is related to surface tension and viscosity of liquid drop and \( b \) is related to the surface roughness of the solid substrate.

In order to confirm the validity of the above models for the present experimental geometry, a cold model experiment was carried out using liquid glycerol and a glass substrate. Figure 7 shows experimental results together with predictions by the various models. It is seen that the Shroeder model results in excellent agreement with the experimental data, but either the Ogarev or Newman–Cherry–Holmes model does not show a good fit with the experimental results.

In order to apply the Schroeder model to the present liquid slag–alumina substrate system, the factor \( b \) in Eq. (3), which is related to the surface roughness of the substrate, must be determined in advance. The relationship between true roughness and the value \( b \) was examined through the cold model experiment using glycerol and glass substrates of various surface roughness and the result is given in Fig. 8. Using this figure the value of \( b \) for the alumina substrate with surface roughness of \( R_a = 0.553 \) \( \mu m \) was found to be 0.5675.

Taking zero time when the contact between the drop and substrate forms the right angle (\( t = 0 \) at \( \theta = 90^\circ \)), which leads to \( \cos \theta_0 = 0 \), the Schroeder model of Eq. (3) is simplified as,

\[
\cos \theta(t) = \cos \theta_{c, app} [1 - \exp(-mt^3)] 
\]

Applicability of the Schroeder model was examined by fitting Eq. (4) to each set of experimental results through regression analysis. Some of the results are given in Fig. 9 and it is seen that the degree of agreement is unacceptably poor. It should be noted that the Schroeder model assumes
Eq. (4) needs to be modified to accommodate the change of due to the compositional change at the interface. Therefore, the value of the contact angle should also change with time due to the compositional change at the interface. Therefore, Eq. (4) needs to be modified to accommodate the change of with time. In order to express the equilibrium contact angle as a function of time, an assumption is now introduced; that is, the interfacial tension between the liquid drop and substrate, and the interfacial tension between the slag and alumina substrate at time vary exponentially with time. This assumption should not be considered unreasonable, since the compositional change due to mass transfer generally follows an exponential pattern with time and the interfacial tension is usually proportional to the materials compositions. With this assumption, together with boundary conditions of at , and at , the following expression can be obtained:

\[
\cos \theta_{\text{app}}(t) = \cos \theta_{\text{app}}^0 - (\cos \theta_{\text{app}}^0 - \cos \theta_{\text{e, app}}) \exp(-kt) \]  \hspace{1cm} (5)
\]
where \( \theta_{\text{app}}(t) \) is the equilibrium contact angle between the initial slag and alumina substrate, \( \theta_{\text{e, app}} \) is the equilibrium contact angle at time, \( \theta_{\text{app}}^0 \) is the apparent contact angle on a perfectly smooth surface, and \( k \) is a constant.

Combination of Eq. (5) and the original Shroeder model of Eq. (3) yields,

\[
\cos \theta(t) = \cos \theta_{\text{true}} + \left[ \cos \theta_{\text{e, app}} - \cos \theta_{\text{e, app}}^0 \right] \exp(-kt) \]  \hspace{1cm} (6)
\]

Now, Eq. (6) was applied to the experimental results with different slag compositions, and the various terms \( \theta_{\text{e, app}}, \theta_{\text{true}}, k, m \) were determined through regression for each slag composition. Figure 10 shows typical examples of the fitting of Eq. (6) to the experimental results. It is seen that the new model gives a striking agreement with the experimental results. The solid lines shown in Fig. 4 where experimental data are presented are in fact the results fitting with Eq. (6). These agreements prove that the new model of Eq. (6) correctly represents the spreading behavior of liquid slag on the alumina substrate. Application of the model enables us not only to describe the spreading behavior as a function of time, but also to determine \( \theta_{\text{e, app}} \) which is the equilibrium contact angle to be formed between the alumina substrate and the slag if there were no chemical interactions at the interface. The various terms in Eq. (6), \( \theta_{\text{e, app}}, \theta_{\text{true}}, k, m \), which were determined for each slag composition by regression analysis are included in Table 1.

4.2. Effect of Surface Roughness

If the surface of a solid substrate is perfectly smooth, the adhesion tension \( \alpha \) can be expressed as follows:

\[
\alpha = \sigma_s - \sigma_{Ls} = \sigma_L \cos \theta_{\text{true}} \]  \hspace{1cm} (7)
\]
where \( \theta_{\text{true}} \) is the contact angle on a perfectly smooth surface.

If the surface roughness is considered, Eq. (7) needs to be modified as follows:

\[
r \alpha = r(\sigma_s - \sigma_{Ls}) = r \sigma_L \cos \theta_{\text{app}} \]  \hspace{1cm} (8)
\]
where \( \theta_{\text{app}} \) is the contact angle on a rough surface, \( r \) = Wenzel’s ratio \((=A/A_{\text{app}})\), \( A \) = the actual surface area between the liquid drop and substrate, and \( A_{\text{app}} \) = the apparent surface area between the liquid drop and substrate.

Combination of the above two equations yields,

\[
\cos \theta_{\text{app}} = r \cos \theta_{\text{true}} \]  \hspace{1cm} (9)
\]
It is noted from the above equation that if the true contact angle is less than 90°, then \( q_{\text{true}} > q_{\text{app}} / H_1 \), and the apparent contact angle decreases with increasing the roughness, whereas if the true contact angle is greater than 90°, the opposite is true. If the true contact angle is just 90°, the surface roughness will not exert any effect on the contact angle.

The Wenzel's ratio \( r = A / A_{\text{app}} \) can be evaluated using the following relationship:

\[
\frac{A}{A_{\text{app}}} = \left( \frac{l}{l_0} \right)^2 \quad \text{(10)}
\]

where \( l \) and \( l_0 \) are the actual profile length and the apparent length, respectively.

The actual profile length can be measured by tracing the actual contour of the surface. In the present study the actual profile length was measured using a non-contacting surface roughness measuring apparatus (Rodenstock RM600®). The measured profile length ratios are represented in Table 2, together with the calculated Wenzel's ratios.

The effect of the surface roughness was examined using Slag C2 (54.7%CaO–33.7%Al_2O_3–11.6%SiO_2) and the results are summarized in Fig. 11.

In Fig. 11, it is seen that the spreading behavior differs with different surface roughness, and hence different values of the apparent equilibrium contact angle \( \theta_{\text{true}} \) result. However, the true equilibrium contact angles \( \theta_{\text{true}} \) calculated using Eq. (9) are very much the same for the different surface roughness (see Fig. 12).

4.3. Equilibrium Contact Angles

In order to obtain the true equilibrium contact angle \( \theta_{\text{true}} \) for all slag compositions examined in the present study, the Wenzel's equation of Eq. (9) should be applied to the values of \( \theta_{\text{true}} \) in Table 1 since the values of \( \theta_{\text{true}} \) in Table 1 obtained by fitting the spreading model of Eq. (6) to the experimental data contains the surface roughness. The true equilibrium contact angles so obtained are presented in Fig. 13. Iso-angle lines are also constructed in the figure. It is seen that the equilibrium contact angle varies with slag composition to a large extent. Several important trends can be identified from Fig. 13:

1) In the region of low SiO_2 content, the slag with higher CaO content exhibits a smaller contact angle, i.e., better wettability with alumina.
2) For the slag with a given CaO/SiO_2 ratio, an increase in Al_2O_3 results in an increase in the contact angle, i.e., decrease in wettability.
3) For a given CaO/Al_2O_3 ratio, the variation of the contact angle with SiO_2 content shows a minimum.

In order to determine factors governing the equilibrium contact angle, it is attempted to compare the variation of the contact angle with that of the interfacial tension of the system of liquid CaO–Al_2O_3–SiO_2/solid Al_2O_3 at 1873 K. However, there is no report on the interfacial tension of the above system, and hence it was evaluated by using the Young's equation:

\[
\cos \theta_{\text{SI}} = \frac{\sigma_{\text{SI}} - \sigma_{\text{SI}}}{} \quad \text{(11)}
\]

where \( \theta_{\text{SI}} \) is the contact angle between the slag and substrate.

The interfacial tension between the slag and the alumina
substrate ($\sigma_{ss}$) can be calculated using the above equation, provided that the equilibrium contact angle ($\theta_{eq}$), the surface tensions of the alumina substrate ($\sigma_s$) and the slag ($\sigma_l$) be known. These values can readily be obtained: $\sigma_{ss}$ has already been determined in the present study (see Fig. 13), $\sigma_s$ by applying Nakajima’s suggestion,$^8$ and by employing the model developed by the present authors.$^9$ Figure 14 shows the result of evaluation of the interfacial tension between the liquid CaO–Al$_2$O$_3$–SiO$_2$ slag and the solid Al$_2$O$_3$ at 1873 K. Upon comparison of Fig. 13 with Fig. 14, it can immediately be noticed that the equilibrium contact angle is closely related to the interfacial tension; i.e., the higher the interfacial tension, the larger the contact angle.

Figure 15 shows the iso-viscosity diagram of the CaO–SiO$_2$–Al$_2$O$_3$ slag system at 1873 K.$^{10}$ This diagram shows that a basic property which governs the viscosity may exert a certain degree of influence on the equilibrium contact angle; but it is not the major factor.

In summary, it can now be concluded that interfacial tension is the major factor which governs the equilibrium contact angle, i.e., the wettability.

5. Conclusions

The wetting behavior of molten CaO–Al$_2$O$_3$–SiO$_2$ with solid Al$_2$O$_3$ was investigated at 1873 K using the sessile drop method in which a liquid slag drop was allowed to spread on an alumina substrate. A new model was developed which successfully represents the time dependence of the contact angle, in other words, the spreading behavior, of a liquid drop on a solid substrate. The model takes into consideration chemical interactions which continually take place at the interface between the solid Al$_2$O$_3$ and molten CaO–Al$_2$O$_3$–SiO$_2$. From the experimental results and the model the equilibrium contact angle was determined for a number of different slag compositions, with which an iso-contact angle diagram was constructed. The following are a summary of the findings:

1) Interfacial tension was the major factor governing the equilibrium contact angle.

2) In the region of low SiO$_2$ content, the slag with higher CaO content exhibits smaller contact angle, i.e., better wettability with alumina.

3) For the slag with a given CaO/SiO$_2$ ratio, an increase in Al$_2$O$_3$ results in an increase in the contact angle, i.e., decrease in wettability.

4) For a given CaO/Al$_2$O$_3$ ratio, the variation of the contact angle with SiO$_2$ content shows a minimum.

5) The contact angle decreases with increasing the surface roughness of the alumina substrate.

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