1. Introduction

The development of manufacturing technology for highly-refined steel is essential because non-metallic inclusions result in various types of damages to steel products, such as surface or internal defects in steel products and decreases in strength or fatigue properties.1) SiO₂ is a common primary non-metallic inclusion generated during the steelmaking process. SiO₂ inclusions are formed when Si is added to deoxidize molten iron or steel. Additionally, SiO₂ is one of the principal components of the mold flux, which is a synthesized slag containing oxides, including SiO₂, CaO, and Al₂O₃. The synthesized slag plays an important role in the continuous casting process, such as preventing the oxidation of molten steel surface, trapping of inclusions floating from molten steel, along with heat transfer, lubrication, and buffering between the mold and molten steel.2–4) Therefore, the efficient removal of SiO₂ inclusions or SiO₂ slag is essential for obtaining highly refined steel.

To remove and control the inclusions or slags, it is crucial to understand the wetting behavior between them and molten iron or steel. For example, a large interfacial tension between molten steel and molten slag results in a large restoring force that flattens the interface, preventing the emulsion of small droplets of molten slag into the molten steel.5,6) Conversely, when the interfacial tension is low, the interface becomes unstable and the molten steel and molten slag mix easily, promoting chemical reactions.5) Additionally, the interfacial energy between the molten steel and inclusion is essential for estimating the inclusion particle growth, similar to the Ostwald ripening model.7) Tanaka et al., Sun et al., and Riboud et al. reported the wettability between molten Fe–Al alloys and synthesized slag. Tanaka et al. investigated the wettability between...
molten Fe–Al alloys with 0.007–0.048 mass% Al content and molten SiO2–CaO–Al2O3 slags with 36.0 mass% or 40.0 mass% SiO2 content, and reported the dynamic change in Al composition from low Al composition to high and SiO2–CaO–Al2O3 slag when the mass transfer accompanying the redox reaction between the Al present in the Fe–Al alloy and the SiO2 component of the synthesized slag. 8) Riboud et al. reported a significant decrease in the interfacial tension between seven molten Fe–Al alloys with 0.0002–0.0172 mass% Al content and SiO2–CaO–Al2O3 synthesized slag, and reported a redox reaction between the Al present in the Fe–Al alloy and the SiO2 component of the synthesized slag. 9) Sun et al. evaluated the interfacial tension between seven molten Fe–Al alloys with 0.0002–0.0172 mass% Al content and SiO2–CaO–Al2O3 synthesized slag, and reported a redox reaction between the Al present in the Fe–Al alloy and the SiO2 component of the synthesized slag. 10) 

The aim of this study is to investigate the wettability (i.e., the contact angle and the interfacial energy) between molten Fe–Al alloys with 0.03, 0.3, and 0.3 mass% Al compositions and oxide substrates with 0.002, 0.32, and 1 SiO2 activities, respectively using the sessile drop method, to elucidate the effect of interfacial reactions on the wettability, and to evaluate the entrapment of refining slags.

2. Experimental

2.1. Materials

Wetting tests were conducted using Fe–Al alloys with different Al compositions (Nippon Steel, Tokyo Japan) and oxide substrates, viz. Y2O3 + Y2SiO3, Y2SiO3 + Y2Si2O7, and Y2Si2O7 + SiO2, with different SiO2 activities. The Al contents of the alloys were set to 0.03, 0.3, and 3 mass%. The chemical compositions of the alloys are listed in Table 1. The activity of SiO2 (aSiO2) was set to 0.002 for Y2SiO5, 0.32 for Y2Si2O7, and 1 for Y2Si2O7 + SiO2. The oxide substrates were fabricated by sintering with the following procedure.

Jacobson measured the vapor pressure of SiO(g) in Ta + Y2O3 + Y2O3–SiO2 and Mo + Y2O3–SiO2 mixtures by Knudsen effusion mass spectrometry (KEMS) and evaluated the Y2O3 and SiO2 activities related to pure substances at 1923 K in the Y2O3–SiO2 system (Fig.1). 11–15) Oxide substrates with various SiO2 activities were fabricated at 1923 K with different SiO2 activities, with different Al compositions, as mentioned above. However, no reports are present on the systematic investigation of the effects of change in Al composition from low Al composition to high, and change in Al composition from low Al composition to high on the interfacial reaction and interfacial tension.

Table 2. Mixture ratio of reagents for sintering substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Composition</th>
<th>mass%</th>
<th>mol%</th>
<th>vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y2O3 + Y2SiO3</td>
<td>Y2O3</td>
<td>44.1</td>
<td>50.0</td>
<td>41.8</td>
</tr>
<tr>
<td>(aSiO2 = 0.002)</td>
<td>Y2SiO3</td>
<td>55.9</td>
<td>50.0</td>
<td>58.2</td>
</tr>
<tr>
<td>Y2SiO3 + Y2Si2O7</td>
<td>Y2SiO3</td>
<td>52.4</td>
<td>57.1</td>
<td>50.0</td>
</tr>
<tr>
<td>(aSiO2 = 0.32)</td>
<td>Y2Si2O7</td>
<td>47.6</td>
<td>42.9</td>
<td>50.0</td>
</tr>
<tr>
<td>Y2Si2O7 + SiO2</td>
<td>Y2Si2O7</td>
<td>85.2</td>
<td>50.0</td>
<td>75.9</td>
</tr>
<tr>
<td>(aSiO2 = 1)</td>
<td>SiO2</td>
<td>14.8</td>
<td>50.0</td>
<td>24.1</td>
</tr>
</tbody>
</table>

2.2. Methods

Materials

Two types of reagents (mixture ratio is listed in Table 2) were weighed, and the reagents and ZrO2 balls were charged into a polyethylene pot (500 mL). 11–15) The weight ratio of the reagents to ZrO2 balls was 1:1. Then, ethanol was poured into the pot until the reagents and balls were soaked. After 24 h ball milling, ethanol was dried using a rotary evaporator (R-3, BUCHI, Flawil, Switzerland). The samples were regulated using a 335/367 mesh screen. Subsequently, uniaxial pressing was employed for 30 s, and the pressure was set at 2 kN. Then, cold isostatic pressing (CPA-50-300, Sansho Industry, Osaka, Japan) was performed for 3 min, and the pressure was set at 300 MPa. The molds were sintered in ambient air inside a muffle furnace. The furnace was heated to 1903 K at 15 K/min and the temperature was maintained at 1903 K for 2 h, after which the furnace was switched off and cooled to room temperature. Figure 2 shows the phase diagram of Y2O3–SiO2 system. 16) The oxides, Y2O3 + Y2SiO3 (aSiO2 = 0.002), Y2SiO3 + Y2Si2O7 (aSiO2 = 0.32), Y2Si2O7 + SiO2 (aSiO2 = 1), and Y2O3 + Y2SiO3 reagent (Nippon Yttrium, Fukuoka, Japan), Y2SiO3 reagent (Nippon Yttrium, Fukuoka, Japan), and SiO2 reagent (>99.9%, mean size: 2.2 μm, Admatechs, Aichi, Japan) that were prepared according to this research.

First, the slurry was prepared by ball milling for 24 h. Two types of reagents (mixture ratio is listed in Table 2) were weighed, and the reagents and ZrO2 balls were charged in a polyethylene pot (500 mL). 11–15) The weight ratio of the reagents to ZrO2 balls was 1:1. Then, ethanol was poured into the pot until the reagents and balls were soaked. After 24 h ball milling, ethanol was dried using a rotary evaporator (R-3, BUCHI, Flawil, Switzerland). The samples were regulated using a 335/367 mesh screen. Subsequently, uniaxial pressing was employed for 30 s, and the pressure was set at 2 kN. Then, cold isostatic pressing (CPA-50-300, Sansho Industry, Osaka, Japan) was performed for 3 min, and the pressure was set at 300 MPa. The molds were sintered in ambient air inside a muffle furnace. The furnace was heated to 1903 K at 15 K/min and the temperature was maintained at 1903 K for 2 h, after which the furnace was switched off and cooled to room temperature. Figure 2 shows the phase diagram of Y2O3–SiO2 system. 16) The oxides, Y2O3 + Y2SiO3 (aSiO2 = 0.002), Y2SiO3 + Y2Si2O7 (aSiO2 = 0.32), Y2Si2O7 + SiO2 (aSiO2 = 1), and Y2O3 + Y2SiO3 reagent (Nippon Yttrium, Fukuoka, Japan), Y2SiO3 reagent (Nippon Yttrium, Fukuoka, Japan), and SiO2 reagent (>99.9%, mean size: 2.2 μm, Admatechs, Aichi, Japan) that were prepared according to this research.

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and $Y_2SiO_3 + SiO_2$ ($a_{SiO_2} = 1$), substrates are all present the two-phase coexistence region of the mixtures at a sintering temperature of 1903 K (1630°C). Therefore, because the reagents were crushed and mixed by ball milling, each reagent was considered to be uniformly dispersed in the obtained substrate. The relative densities of the resultant substrates were measured using the Archimedes’ method. Photographs of the substrates and their relative densities are presented in Fig. 3.

The formation reactions of $SiO_2$ and $Y_2O_3$ are given by Eqs. (1) and (2), respectively.

$$2Y(s) + \frac{3}{2}O_2(g) = Y_2O_3(s) \quad (1)$$

$$Si(l) + O_2(g) = SiO_2(s) \quad (2)$$

The Gibbs free energies for the formation of Eqs. (1) and (2) were −1370 and −577 kJ·mol$^{-1}$ (at 1873 K), respectively.$^{17)$ Here, the free energy of Eq. (1) was extrapolated from the value between 298 and 1799 K. It is recognized that $Y_2O_3$ is more stable than $SiO_2$ owing to the smaller Gibbs free energy of formation for $Y_2O_3$ than that of $SiO_2$. Therefore, in this study, it was assumed that chemical reactions occur between the molten alloy and $SiO_2$ content of the substrate.

The alloys were cut into small pieces using a diamond saw (Isomet4000, BUEHLER, Lake Bluff, IL, USA). Each metallic sample (2 g) was weighed and immersed in a H$_2$O:HCl (1:1) aqueous solution for 10 s immediately before performing the wetting test to remove any surface oxide layer.

One surface of each oxide substrate was polished using a 35-µm diamond disc and diamond pastes with decreasing grain sizes (9, 6, and 1 µm) with an automatic polisher (AutoMet250, BUEHLER, Lake Bluff, IL, USA). The substrates were polished using 0.025 µm colloidal silica. Each substrate was washed sequentially by ultrasonic cleaning in soap water, ultrapure water, 2-propanol, and acetone for 15 min, immediately before the wetting test.

The mean roughness (Ra) was estimated using a surface roughness measurement equipment (SURFCOM 1500DX-3DF, Tokyo Seimitsu, Tokyo, Japan); the mean roughness values of the $Y_2O_3 + Y_2SiO_3$, $Y_2SiO_3 + Y_2Si_2O_5$, and $Y_2SiO_3 + SiO_2$ substrates were 0.099, 0.109, and 0.052 µm, respectively. Previously, Ogino et al. reported that surface roughness below 30 µm does not influence the contact angle of the Fe/Al$_2$O$_3$ wetting couple.$^{18)$ Thus, the low surface roughness of the substrates in this study was assumed to have no influence on the contact angle.
2.2. Wetting Tests

The experimental wetting furnace consisted of a graphite stage, graphite heating elements, and sapphire windows (Fig. 4). Wetting tests were performed by dropping the molten metal onto the oxide substrate. Illustrations of the molten metal before and after it was pushed out of the crucible and onto the substrate are shown in Fig. 5. The substrate was positioned horizontally on a graphite stage, and 2 g of the metallic sample was placed in an alumina crucible just above the substrate. An alumina crucible was placed inside the graphite crucible. The furnace was evacuated from ambient atmosphere to 30 Pa and filled with Ar gas at 1 atm; this procedure was repeated three times. Ar gas was passed through the silica gel and P2O5 reagent to remove the H2O present in the gas. The furnace was heated to 1873 K at 15 K/min with an Ar gas flow rate of 0.5 L/min. The metal was pushed out of the crucible and onto the substrate using an alumina push stick above the alumina crucible. The metal and substrate couple was maintained at 1873 K for 1 h, after which the furnace was switched off and cooled to room temperature. A digital camera was used to capture images through the sapphire window, and images were captured when the temperature of the coupled sample was maintained at 1873 K. Before the wetting tests, the oxygen partial pressure of the Ar gas was estimated as 10^{-12} atm using a ZrO2 oxygen sensor, which was based on the redox reaction of Ni.

2.3. Characterization

Contact angles between the molten Fe–Al alloy and oxide substrate were determined using the curve-fitting method. The surface and interfacial tensions are balanced in the triple phase of liquid, solid, and gas; their relationship is given by the Young’s Eq. (3):

\[ \sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta \] .................. (3)

where \( \sigma_{SV} \) is the surface tension of the oxide, \( \sigma_{SL} \) is the interfacial tension between the molten metal and oxide, \( \sigma_{LV} \) is the surface tension of the molten metal, and \( \theta \) is the contact angle between the molten metal and the oxide. The interfacial energies between the molten Fe-based metals and nonmetallic inclusion-type oxides were calculated using Eq. (3); the contact angles during 60 s after dropping the molten material onto the substrate were used to evaluate the wetting behavior before and after the organization of the interface.

After the wetting tests, soluble Al and Si in the metal samples were identified using inductively coupled plasma optical emission spectrometry (ICP–OES; iCAP 6500, Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussion

3.1. Wetting Behavior

Photographs of the wetting couple during wetting tests are shown in Figs. 6 to 8. The time change in the contact angle for each wetting couple is shown in Fig. 9. Although the contact angle of Fe–0.3Al with the Y2Si2O7 substrate (\( \alpha_{SiO2} = 1 \)) decreased over time and during 60 s after the molten alloy was dropped, other contact angles were almost stable during the same period. The decrease in the contact angle of Fe–0.3 Al against the Y2SiO3 + SiO2 substrate (\( \alpha_{SiO2} = 1 \)) was 20°, and the contact angle was smaller than 90°. This indicates that the wettability of the couple improved over 60 s. Conversely, the decreases in other couple contact angles ranged from 0° to 7°, and the wettabilities deteriorated over time during the same period because the contact angles were larger than 90°.

During the observation period of 60 min, the contact angle of molten Fe–0.03Al was almost stable against each oxide substrate, and the metal was not covered with an oxide layer during the wetting tests. In contrast, the molten Fe–0.3Al and Fe–3Al alloys on each oxide substrate were either covered with an oxide layer or oxidized. The contact angles of Fe–0.3Al and Fe–3Al alloys on each oxide substrate were either covered with an oxide layer or oxidized. The contact angles of Fe–0.3Al and Fe–3Al on the Y2O3 + Y2SiO4 substrate (\( \alpha_{SiO2} = 0.002 \)) did not reach approximately 90° after 60 min (Fig. 6), whereas that of Fe–0.3Al on the Y2SiO3 + Y2Si2O7 substrate (\( \alpha_{SiO2} = 0.32 \)) reached approximately 90° after 20 min, and the wettability improved (Fig. 7). The effect of Fe–3Al on the Y2SiO3 + Y2Si2O7 substrate (\( \alpha_{SiO2} = 0.32 \)) after 5 min, and the wettability improved (Fig. 7). In addition, the contact angle of Fe–0.3Al on the Y2SiO3 + SiO2 substrate (\( \alpha_{SiO2} = 1 \)) reached an angle smaller than 90° after 30 s, and
the wetting behavior improved (Fig. 8).

### 3.2. Evaluation of Interfacial Energy

The interfacial energies between the molten metals with various Al contents and the substrates with various SiO₂ activities was evaluated using the Young’s Eq. (3), focusing on the initial wetting characteristics. The wetting behavior during 60 s after dropping the molten alloy onto the substrate was studied to evaluate the wetting behavior before and after the organization of the interface.

First, the surface tension of molten Fe–Al alloys was evaluated. From the Keene report, the surface tension of the molten Fe–Al alloy was obtained as a function of Al content using the following equation:  

\[
\sigma_{\text{Fe-Fe at% Al}} = -18 - \frac{18}{\text{at% Al}}
\]

(4)

where \(\sigma_{\text{Fe-Fe at% Al}}\) and \(\sigma_{\text{Fe}}\) are the surface tensions of the molten Fe–Al alloy and molten Fe, respectively. The value of \(\sigma_{\text{Fe}}\) was calculated using Eq. (5) based on the report of Takiuchi et al.:

\[
\sigma_{\text{Fe}} = 1900 - 327 \ln (1 + 96dO)
\]

(5)

Fig. 6. Sessile drop images of the molten (a) Fe–0.03Al, (b) Fe–0.3Al, and (c) Fe–3Al and Y₂O₃ + Y₂SiO₅ (aSiO₂ = 0.002) substrate wetting couple. (Online version in color.)
where $a_O$ is the activity of oxygen relative to the 1 mass% standard state in molten Fe and it was calculated using Eqs. (6) and (7):

\[
\frac{1}{2} O_2 \rightarrow [O] \quad \text{........................................ (6)}
\]

\[
\log a_O = \frac{5836}{T} + 0.354 \quad \text{.................. (7)}
\]

where $P_{O_2}$ is the oxygen partial pressure. Using Eqs. (6) and (7), and $P_{O_2} = 10^{-12}$ atm, which corresponds to the oxygen partial pressure in the furnace at 1873 K, $a_O$ was estimated as $2.94 \times 10^{-3}$. Accordingly, the surface tension of molten Fe was calculated to be 1818 mN·m⁻¹ from Eq. (5). In addition, the atomic percentage of Al in each alloy was calculated from Table 1, where the Fe component was considered as the background of the compositions: 0.0742 at% for Fe–0.03Al, 0.654 at% for Fe–0.3Al, and 6.03 at% for Fe–3Al. Based on the above results, the surface tensions of the molten Fe–Al alloys were estimated to be 1817 mN·m⁻¹ for Fe–0.03Al, 1806 mN·m⁻¹ for Fe–0.3Al, and 1709 mN·m⁻¹ for Fe–3Al alloys.

Fig. 7. Sessile drop images of the molten (a) Fe–0.03Al, (b) Fe–0.3Al, and (c) Fe–3Al and $Y_2SiO_3 + Y_2Si_2O_7$ (aSiO$_2$ = 0.32) substrate wetting couple. (Online version in color.)
The surface tensions of the substrates were estimated using Eq. (8), because these values were not reported previously.

$$\sigma_{\text{sub}} = \sum \sigma_i \times V_i$$ .............................(8)

where $\sigma_{\text{sub}}$, $\sigma_i$, and $V_i$ are the surface tension of the substrate (i.e., $Y_2O_3 + Y_2SiO_5$, $Y_2SiO_5 + Y_2Si2O_7$, or $Y_2Si2O_7 + SiO_2$ substrate), surface tension of the oxide that is a component of the experimental substrates (i.e., $Y_2O_3$, $Y_2SiO_5$, $Y_2Si2O_7$, and $SiO_2$), and volume ratio of the oxides that constitute the substrate (Table 2), respectively. Based on the reports of Triantafyllou et al. and Bruce, the surface tensions of $Y_2O_3$ ($\sigma_{Y_2O_3}$) and $SiO_2$ ($\sigma_{SiO_2}$) solids were calculated as 1 546 mN·m$^{-1}$ and 563.5 mN·m$^{-1}$, respectively. 22,23) As the surface tensions of $Y_2SiO_5$ and $Y_2Si2O_7$ could not be found in academic research databases, they were estimated by extending the estimation model of the surface tension of liquid metals expressed using the following equation based on the report of Tanaka et al.24)

$$\sigma = \frac{\Delta H_{\text{Vap}}}{Z_{\text{Surface}}} \left( \frac{\Delta H_{\text{Fus}}}{V} \right) \frac{1}{N_0}$$ ..............................(9)

where $Z_{\text{Surface}}$, $Z_{\text{Bulk}}$, $\Delta H_{\text{Vap}}$, $V$, and $N_0$ are the coordination number on the surface, coordination number in the bulk, enthalpy of vaporization of $x$, molar volume of $x$, and Avogadro’s number, respectively. Equation (9) was used to estimate the surface tension of the solid interfaces; thus, $\Delta H_{\text{Vap}}$ was replaced with the enthalpy of fusion ($\Delta H_{\text{Fus}}$). Additionally, as the substrate was assumed to be sufficiently densified, value of the term corresponding to coordination number in Eq. (9) was assumed to be 1. Therefore, Eq. (9) was rewritten as Eq. (10), and was used to estimate the surface tension of the oxides.

$$\sigma = \frac{\Delta H_{\text{Fus}}}{Y_x N_0}$$ ..............................(10)

Based on the report of Mao et al., the enthalpies of fusion for $Y_2SiO_5$ ($\Delta H_{\text{Fus}_{Y_2SiO_5}}$) and $Y_2Si2O_7$ ($\Delta H_{\text{Fus}_{Y_2Si2O_7}}$) were considered to be $\Delta H_{\text{Fus}_{Y_2SiO_5}} = 186.5$ kJ·mol$^{-1}$ and $\Delta H_{\text{Fus}_{Y_2Si2O_7}} = 142.6$ kJ·mol$^{-1}$.25) The molar volumes were calculated as 64.4 cm$^3$·mol$^{-1}$ for $Y_2SiO_5$ and 85.6 cm$^3$·mol$^{-1}$ for $Y_2Si2O_7$ from the density of the oxides.14)

Therefore, the surface tensions of $Y_2SiO_5$ ($\sigma_{Y_2SiO_5}$) and $Y_2Si2O_7$ ($\sigma_{Y_2Si2O_7}$) solids were evaluated as 1 374 mN·m$^{-1}$ and 869 mN·m$^{-1}$, respectively, using Eq. (10). The surface tensions of the experimental substrates were estimated to be 1 446 mN·m$^{-1}$ for the $Y_2O_3 + Y_2SiO_3$ substrate ($\alpha_{SiO_2} = 0.002$), 1 122 mN·m$^{-1}$ for the $Y_2SiO_5 + Y_2Si2O_7$ substrate ($\alpha_{SiO_2} = 0.32$), and 795 mN·m$^{-1}$ for the $Y_2Si2O_7 + SiO_2$ substrate ($\alpha_{SiO_2} = 1$) based on Eq. (8), surface tensions of
the solids, and the volume ratios listed in Table 2.

Figure 10 shows the interfacial energies between the molten Fe–Al alloys and oxide substrates with various SiO₂ activities evaluated based on Young’s equation (Eq. (3)), contact angles (Fig. 9), surface tensions of the molten alloys, and the surface tensions of the substrates. The interfacial energy between the molten Fe–0.3Al alloy and the Y₂Si₂O₇ + SiO₂ substrate (aSiO₂ = 1) decreased over time for 60 s, although the interfacial energies in other cases were almost stable. The decrease in interfacial tension was 628 mN·m⁻¹, while the decrease in the latter interfacial tension ranged from 4 to 195 mN·m⁻¹.

3.3. Interfacial Reaction

Owing to the organization of the interface between the molten alloy and the substrate, it is assumed that interfacial reactions occur. Thus, the interfacial energy, in turn, the contact angle changes over time. In this section, the interfacial reactions between molten alloys with various Al compositions and substrates with various SiO₂ activities are considered based on the change in shape of the alloys (Figs. 6 to 8) and the results of ICP–OES analysis (Table 3).

Tanaka et al. reported a kinetic model of mass transfer and chemical reactions at a molten Fe–Al alloy–liquid slag interface. The model described that the interfacial reaction occurred on the basis of the following reaction (Eq. (11)).5,26)

\[
4Al + 3SiO_{2\text{slag}} \rightarrow 2Al_2O_{3\text{slag}} + 3Si \quad \ldots \ldots \quad (11)
\]

Equation (11) was considered to comprise the SiO₂ decomposition and dissolution reaction and the Al₂O₃ formation reaction.
In this study, interfacial tension and contact angle were ascribed to the aSiO$_2$ reaction was considered to have occurred. In Fe–0.03 Al substrate, and the redox reaction (Eq. (11)) would occur in the Fe–0.3Al and Fe–3Al alloys on each substrate was not covered with an oxide layer, and the wettability was poor over 60 min, it was recognized that the occurrence of redox reaction (Eq. (11)) would be low.

In the above results, only the interfacial reaction between the Al present in the molten Fe–Al alloy and the SiO$_2$ content in the oxide substrate was assumed. Furthermore, we also considered the interfacial reaction between the molten alloy and Y$_2$O$_3$ content in the substrate. The Fe–0.03Al alloy on each substrate was not covered with an oxide layer, whereas the Fe–0.3Al and Fe–3Al alloys were covered with an oxide layer (Figs. 6 and 8). This indicates that the Al present in the Fe–Al alloy induces oxidization of the alloy. The higher the Al content in the alloy, the greater the driving force for the progress of the redox reaction (Eq. (11)). Consequently, the higher the Al content in the molten alloy/substrate couple, the more likely is the formation of FeAl$_2$O$_4$ (hercynite), which is obtained from the reaction between iron oxide and Al$_2$O$_3$ generated from the reaction with oxygen atoms at the molten alloy/substrate interface.

The model consists of the following phenomena: i) silica decomposition and oxygen absorption at the interface as shown in Eq. (12); ii) reactions between Al and oxygen at the interface as shown in Eq. (13); and iii) diffusion of Al$_2$O$_3$ into the slag bulk and oxygen desorption into the steel bulk. Tanaka et al. reported that the changes in interfacial tension and contact angle were ascribed to the excess absorption of oxygen at the interface. In this study, the interfacial energy, and in turn the changes in contact angle, were considered from the viewpoint of the decrease in interfacial energy owing to mass transfer at the molten alloy/substrate interface based on this model.

As the Fe–0.03Al alloy on each substrate was not covered with an oxide layer (Figs. 6 to 8) and, from the ICP–OES analysis, the Si content in the Fe–0.03Al alloy was found to be larger than those in the Fe–0.3Al and Fe–3Al alloys with the same substrate, mainly the SiO$_2$ decomposition reaction was considered to have occurred. In Fe–0.03 Al alloy and each substrate wetting couple, the influences of Al$_2$O$_3$ formation and diffusion reaction on the decrease in the interfacial energy would be small owing to the small initial Al content. Therefore, the decrease in interfacial energy, and the subsequent decrease in contact angle, would not be observed over 60 min.

In Fe–0.3Al and Fe–3Al alloys with $a_{SiO_2} = 0.32$ and $a_{SiO_2} = 1$ substrate couples, redox reaction (Eq. (11)) would occur on account of Eqs. (12) and (13). In the couples, the contact angles decreased and reached a value that is slightly higher or smaller than 90° during 60 min in the later part of the wetting tests, as mentioned in Section 3.1; this could be attributed to the decrease in interfacial energy owing to mass transfer during the interfacial reaction. In addition, decrease in the Al composition and increase in the Si composition for the couples were identified from the ICP–OES analysis, which also indicated the occurrence of a redox reaction.

These results indicate that the SiO$_2$ decomposition reaction (Eq. (12)) occurs in the Fe–0.03Al alloy on each substrate, and the redox reaction (Eq. (11)) would occur in the Fe–0.3Al and the Fe–3Al with $a_{SiO_2} = 0.32$ and $a_{SiO_2} = 1$ substrates. This result is consistent with that reported by Tanaka et al., which indicated the occurrence of the SiO$_2$ decomposition reaction (Eq. (12)) between the molten Fe alloy with small Al content (Fe–0.007Al) and molten slag, along with the occurrence of redox reaction (Eq. (11)) between the molten Fe alloy with large Al content (Fe–0.0042) and molten slag.

Conversely, the interfacial reactions between the molten Fe–0.3Al and Fe–3Al alloys and the Fe–0.002 substrate were not classified as objective reactions. As small amount of Si was produced and no decrease was observed in the Al content compared to the initial value in the ICP–OES analysis (Table 3), it was established that the occurrence of the Al$_2$O$_3$ formation reaction (Eq. (13)) would dominate over the SiO$_2$ dissolution reaction (Eq. (12)). This could be attributed to the low SiO$_2$ activity (0.002), where the SiO$_2$ dissolution reaction would be slow and the Al$_2$O$_3$ formation reaction would occur immediately after the dissolution reaction. Additionally, as the contact angle was larger than 90° and the wettability was poor over 60 min, it was recognized that the occurrence of redox reaction (Eq. (11)) would be low.

### Table 3. Results of ICP–OES analysis.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Alloys</th>
<th>Al (mass%)</th>
<th>Si (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$ + Y$_2$SiO$<em>5$ ($a</em>{SiO_2} = 0.002$)</td>
<td>Fe-0.03Al</td>
<td>0.014</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>Fe-0.3Al</td>
<td>0.52</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>Fe-3Al</td>
<td>3.07</td>
<td>0.23</td>
</tr>
<tr>
<td>Y$_2$SiO$_3$ + Y$_2$Si$_2$O$<em>5$ ($a</em>{SiO_2} = 0.32$)</td>
<td>Fe-0.03Al</td>
<td>0.002</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>Fe-0.3Al</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Fe-3Al</td>
<td>2.74</td>
<td>0.13</td>
</tr>
<tr>
<td>Y$_2$SiO$_3$ + SiO$<em>2$ ($a</em>{SiO_2} = 1$)</td>
<td>Fe-0.03Al</td>
<td>0.003</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>Fe-0.3Al</td>
<td>0.13</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Based on the above results, the FeAl$_2$O$_4$ formation reaction seems to be the predominant oxide formation reaction that could occur at the molten alloy/substrate interface, in addition to the redox reaction (Eq. (11)). In fact, further analysis using scanning electron microscopy with energy dispersive spectroscopy or electron probe micro analyzer is necessary.

3.4. Entrapment of Refining Slag

Oxide inclusions in the steel products can be primarily attributed to several factors including "entrapment of secondary refining slag", "deoxidation products", "refractory particles", and "contamination in molten steel". In general, the higher the interfacial tension between the molten slag and molten steel, the harder it is for the slag to be entrapped and the more advantageous it is for the production of highly refined steel. For example, considering the energy balance between the inertial force in the slag entrainment, buoyant force, and interfacial tension at the slag/molten steel interface, the critical flow velocity of entrainment, $V_{cr}$, is given by Eq. (19), which indicates that $V_{cr}$ increases with the increasing interfacial tension and density difference; consequently, the entrapment of the slag droplet will be reduced.

$$V_{cr} = \frac{48g\sigma_\alpha}{\rho_{m} - \rho_{s}}$$  

where $g$, $\rho_{m}$, and $\rho_{s}$ are the gravitational acceleration, density of the molten steel, and density of the slag, respectively. In this section, SiO$_2$ slag entrapment, which can be attributed to the formation of SiO$_2$ inclusion, is considered based on this experimental results.

Figure 12 shows the interfacial tension of each molten alloy after 5 s and 60 s the molten alloy was dropped onto the substrate. After both 5 and 60 s, the interfacial tension of the molten Fe–0.03Al alloy reached the maximum value at an SiO$_2$ activity of 0.32. The interfacial tensions of the molten Fe–0.3Al alloy decreased convexly with an increase in the SiO$_2$ activity, and the interfacial tension of the molten Fe–3Al alloy also decreased with an increase in SiO$_2$ activity. Because the Al concentration of the common killed steel is above 0.005 mass%, and the Al concentration range, where the equilibrium concentration of oxygen is minimized in equilibrium with the Al content, is between $10^{-1}$ to $10^0$ mass%, the interfacial tensions of molten Fe–0.03Al and molten Fe–0.3 Al were considered (Fig. 12). The interfacial tension plot for the molten Fe–0.03Al alloy suggested that the SiO$_2$ slag inclusions would be less entrapped in molten steel with a low Al content in the medium SiO$_2$ activity range, that is, slag with medium SiO$_2$ content. The interfacial tension plot of the molten Fe–0.3Al alloy suggested that they would be less entrapped in molten steel with a high Al content in the small SiO$_2$ activity range, that is, the slag with low SiO$_2$ content.

4. Conclusion

Oxide substrates with SiO$_2$ activities of 0.002, 0.32, and 1 were fabricated, and the wettability between the substrates and molten Fe–Al alloys with 0.03, 0.3, and 3 mass% Al contents was investigated in an Ar atmosphere at 1873 K. The contact angles and interfacial energies were evaluated. The major findings are summarized below.

(1) $Y_2$O$_3$ matrix oxide substrates with SiO$_2$ activities of 0.002, 0.32, and 1 were fabricated.

(2) The contact angle immediately after the interface was organized was above 90°, and the wettability was poor in most molten alloy/oxide substrate couples. The decrease in the interfacial energy and contact angle at 60 s after the organization of the interface was the highest for the molten Fe–0.3Al alloy/$Y_2Si_2O_7 + SiO_2$ substrate ($a_{SiO_2} = 1$).

(3) The interfacial reaction between the molten Fe–Al alloy and the oxide substrate with SiO$_2$ component was accounted for by the redox reaction model between the Al present in the molten Fe–Al alloy and the SiO$_2$ content in the substrate.

(4) The change in interfacial tension of the molten
Fe–Al alloy with SiO₂ activity suggests that slag inclusions are less entrapped for low-Al-concentration molten steel with medium SiO₂ activity slag, and also for high-Al-concentration molten steel with low SiO₂ activity slag.

REFERENCES