Flux-Steel Reaction of CaO-SiO$_2$ and CaO-Al$_2$O$_3$-based Mold Fluxes with High-Al Steel

J. Yang, J. Zhang, O. Ostrovski, C. Zhang, D. Cai

Advanced properties of high-Al steel such as high mechanical strength and formability make it attractive for the applications in the automobile industry. However, when conventional CaO-SiO$_2$-based mold fluxes are used for the continuous casting of such steel, [Al] in the steel reacts with SiO$_2$ in the fluxes. It changes the chemical composition and in-mold performances of mold fluxes, leading to unstable heat transfer and insufficient lubrication for the steel strands. CaO-Al$_2$O$_3$-based mold fluxes with low SiO$_2$ content are under development, expecting to suppress the interfacial reaction between mold fluxes and high-Al steel. In this article, the effects of different CaO-SiO$_2$ and CaO-Al$_2$O$_3$-based mold fluxes on the reaction kinetics were evaluated through both pilot and laboratory tests. It was found that there were significant changes in SiO$_2$ and Al$_2$O$_3$ concentrations in CaO-SiO$_2$-based mold fluxes, indicating a severe reaction between fluxes and high-Al steel. CaO-Al$_2$O$_3$-based mold fluxes showed a better composition stability than CaO-SiO$_2$-based mold fluxes when reacting with high-Al steel. In the lab tests, CaO-Al$_2$O$_3$-based mold fluxes with different CaO/Al$_2$O$_3$ ratios were also evaluated. It showed that the increase of CaO/Al$_2$O$_3$ ratio accelerated the flux-steel reaction according to the change of [Al] concentration in the steel. CaO-Al$_2$O$_3$-based mold fluxes showed promising results when reacting with high-Al steel, but the fluxing agents, e.g. B$_2$O$_3$ and Li$_2$O, may also react with [Al] in steel and cause an additional increment of Al$_2$O$_3$ in mold fluxes, which needs further research in the future.

The variation of flux composition may make the in-mold performances of mold fluxes undesirable and unpredictable in the casting of high-Al steel, increasing the likelihood of sticker breakout and surface defects. CaO-Al$_2$O$_3$-based mold fluxes with low SiO$_2$ content is recently introduced to depress the driving force of reaction [1]. But the increase of Al$_2$O$_3$ and decrease of SiO$_2$ concentrations would raise the liquidus temperature of mold fluxes significantly [10]. Fluxing agents, e.g. B$_2$O$_3$ and Li$_2$O, are normally added to reduce the liquidus temperature of mold fluxes. However, B$_2$O$_3$ is also reactive with [Al] in steel [10] and the use of Li$_2$O is limited in industry due to its high cost.

KEYWORDS: HIGH-AL STEEL – MOLD FLUXES – INTERFACIAL REACTION – KINETICS – THERMODYNAMICS
In this article, the reaction of CaO-SiO$_2$ and CaO-Al$_2$O$_3$-based mold fluxes in the casting of high-Al steels was investigated based on the composition changes of mold fluxes and steel in both pilot and laboratory tests. The aim of this study is to deepen the understanding of the flux behavior in flux-steel reaction, promoting the design of new mold fluxes for the casting of high-Al steel.

**EXPERIMENTAL PROCEDURE**

**Pilot Tests**

Both CaO-SiO$_2$ and CaO-Al$_2$O$_3$-based mold fluxes were investigated in the pilot tests. The compositions of mold fluxes and steels used in the pilot tests are given in Tables 1 and 2, respectively. The concentrations of B$_2$O$_3$ and Li$_2$O in mold fluxes were determined using inductively coupled plasma (ICP) analysis; other components were analyzed using X-ray florescence (XRF). The concentrations of [Al], [Mn] and [Si] in steel were examined using ICP analysis. Two sets of pilot tests were carried out in this study. The first set tested the reaction between CaO-SiO$_2$-based mold fluxes (Fluxes 1 and 2) and high-Al steel. Approximately 150 kg steel was charged in an induction furnace with the protection of non-reactive mold fluxes which were used to avoid oxidation before the introduction of the designed mold fluxes. After the temperature of molten steel was stabilized at 1600 °C, a steel sample was acquired. The composition of this steel is indicated as Steel 1. Then, 4 kg Flux 1 was added on the top of molten steel to replace the non-reactive protection slags. Mold flux samples were taken at 900 and 1800 s after Flux 1 was melted; while the steel sample was acquired at only 1800 s whose composition is defined as Steel 2. Afterward Flux 1 was replaced by Flux 2. It was sampled at 600, 900, 1200, 1500 and 1800s, respectively; while the steel sample was acquired at 1800 s. As [Al] concentration dropped to a low level after the reaction between Flux 1 and Steel 1, an additional experiment was arranged for Flux 2 to react with a new steel with a high Al content whose composition is listed as Steel 3.

The second set of pilot tests investigated the reaction between CaO-Al$_2$O$_3$-based mold fluxes and steel. The steel sample acquired before the introduction of Flux 3 was marked as Steel 4. Flux 3 was then added and sampled at 600, 900, 1200 and 1500 s. Steel composition was acquired at 1500 s, which was marked as Steel 5. Afterward, Fluxes 4 was used to react with Steel 5 and sampled at 600, 900, 1200, 1500 and 1800s, respectively. The final composition of Steel 5 was obtained at 1800 s.

**Laboratory Tests**

The flux-steel reaction between CaO-Al$_2$O$_3$-based mold fluxes and high-Al steel was also carried out in laboratory. CaO-Al$_2$O$_3$-based mold fluxes were prepared by mixing reagent chemicals using an agate mortar. The mixed powders were then melted in a graphite crucible at 1400 °C for 20 minutes. Afterward, the melt was quenched in water, forming a highly porous glass. It was then crushed to coarse grains with an average diameter of ca. 2 mm. The composition of mold fluxes is listed in Table 3; while the composition range of high-Al steel is given in Table 4. The composition measurements used the same way as in pilot tests.
Continuous casting

Tab. 3 – Compositions of Mold Flues in Lab Tests. (mass%)

<table>
<thead>
<tr>
<th>Number</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Li₂O</th>
<th>B₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux 5</td>
<td>6.9</td>
<td>36.3</td>
<td>36.8</td>
<td>1.8</td>
<td>5.9</td>
<td>2.1</td>
<td>9.5</td>
</tr>
<tr>
<td>Flux 6</td>
<td>6.9</td>
<td>17.7</td>
<td>54.1</td>
<td>1.7</td>
<td>5.5</td>
<td>2.1</td>
<td>11.3</td>
</tr>
<tr>
<td>Flux 7</td>
<td>6.9</td>
<td>15.1</td>
<td>57.4</td>
<td>1.8</td>
<td>5.0</td>
<td>2.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Tab. 4 – Composition Range of High-Al Steel in Lab Tests. (mass%)

<table>
<thead>
<tr>
<th>Number</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel 6</td>
<td>0.14-0.20</td>
<td>&lt; 0.15</td>
<td>21-25</td>
<td>1.5-2.5</td>
</tr>
</tbody>
</table>

The flux-steel reaction was carried out in a MoSi₂ resistance furnace as illustrated in Figure 1. A MgO crucible (40 x 35 x 81 mm) was used to accommodate steel sample and mold fluxes (8). An Al₂O₃ protection tube (40 x 35 x 360 mm) was placed above the MgO crucible. The temperature of the sample was measured and calibrated by two thermocouples in the bottom of the furnace. 300 g high-Al steel sample was heated at 1500 °C in the MgO crucible. Highly purified Ar-5H₂ gas was flown into the protection tube with a flow rate of 1 L/min in the heating process. After the temperature was stabilized at 1500 °C for 5 min, a quartz tube (8 x 6 x 1200 mm) was lowered to the crucible through a stainless steel tube (14 x 12 x 700 mm) to acquire steel sample and then quenched into water immediately. Afterward, 30 g coarse grained mold fluxes were added to the MgO crucible through the stainless steel tube. Mold fluxes were assumed to take 1 min to melt completely on molten steel after which zero time was set. Quartz tubes were used to sample liquid steel periodically and then quenched into water. The concentrations of [Al] and [Mn] in acquired steel samples were analyzed using ICP analysis.

RESULTS AND DISCUSSION

Flux-Steel Reaction in Pilot Casting

Figure 2 show the changes of SiO₂, Al₂O₃, MgO, MnO, Na₂O, and B₂O₃ contents during the reaction between Flux 1 and Steel 1. The concentrations of [Mn], [Al] and [Si] before and after the reaction were shown in Table 5. The significant changes of SiO₂ and Al₂O₃ in mold fluxes were observed. SiO₂ content decreased from 42.0 to 2.9 mass% in 1800 s, which was only 7% of the original concentration; while Al₂O₃ content increased from 6.1 to 47.7 mass% during the same time span. It indicates that the rapid reaction between SiO₂ in Flux 1 and [Al] in Steel 1 took place, leading to the accumulation of Al₂O₃ in the mold flux and [Si] in the steel. MgO content increased from 1.8 to 5.8 mass% during the experiment, which mainly came from the refractory. Na₂O content decreased slightly from 7.4 to 5.9 mass%. It might attribute to the evaporation of Na₂O-containing phases at high temperature or the reaction with [Al] in steel. MnO content decreased from 3.3 to 0.8 mass% in the experiment while [Mn] concentration slightly decreased by 0.2 mass%. The decrease of MnO in mold fluxes may be caused by the formation of Mg, MnAl₂O₄ spinel which was reported by Kim et al. (11). This phase is thermodynamically feasible to form when the Al₂O₃ content is high, but SiO₂ is low. Therefore, the flux/steel interface might be a preferred location for the
precipitation of [Mg, Mn]Al2O4 spinel. The decrease of B2O3 content from 3.4 to 0.3 mass% was observed in mold fluxes, which may result from evaporation, or reaction with [Al]. B2O3 is thermodynamically possible to be reduced by [Al] according to the following equation:

\[ \text{B}_2\text{O}_3 + 2[\text{Al}] \rightarrow 2[\text{B}] + \text{Al}_2\text{O}_3 \]  

The composition change of Flux 2 during the reaction with Steel 2 is given in Figure 3. The composition change of Steel 2 is listed in Table 5. During the reaction between Flux 2 and Steel 2, SiO2 content decreased from 43.3 to 17.2 mass% in 1800 s, while Al2O3 content increased from 3.2 to 27.5 mass% due to the severe reaction. The reduction of SiO2 was less intense than that in the reaction between Flux 1 and Steel 1 although the initial SiO2 content was close. It may result from the lower [Al] concentration in Steel 2 as [Al] concentration was proved to strongly affect the reaction rate in Reaction [1] based on the previous investigation on reaction between CaO-SiO2-based mold fluxes and high-Al steel (8). The changes of Na2O and MgO were similar to those in the reaction between Flux 1 and Steel 1. The concentration of MnO sharply increased in the first 600 s and gradually decreased thereafter. It was noticed that the concentration of MnO in mold fluxes and [Mn] in steel both increased after the reaction between Flux 2 and Steel. There are two possible reasons. The increase of MnO may come from the oxidation of [Mn] by SiO2, which is possible when [Al] concentration is low in steel (8). But once MnO content reached a
Continuous casting

threshold, it might be reduced by [Al] again. The second expla-
nation is related to the [Mg, Mn]Al₂O₄ spinel. The extra MnO
may come from the remnant [Mg, Mn]Al₂O₄ spinel formed in
the previous experiment. The remnant disintegrated into Flux 2
since Al₂O₃ content decreased and SiO₂ content increased in the
initial stage of flux pool after the introduction of Flux 2, which
moved the flux composition away from the saturation line of
[Mg, Mn]Al₂O₄ spinel. As a result, MnO content increased in
the initial stage. After 600 s, the accumulation of Al₂O₃ and re-
duction of SiO₂ pushed the composition close to the saturation
line of [Mg, Mn]Al₂O₄ spinel that could initiate the formation of
[Mg, Mn]Al₂O₄ spinel again, causing the minimization of MnO
content in the later stage. But the decrease of MnO was not
severe since the SiO₂ content in Flux 2 was not as low as that
in the reaction between Flux 1 and Steel 1.

Fig. 3 – Concentrations of SiO₂, Al₂O₃, MgO, Na₂O, and MnO in mold fluxes during the reaction between Steel 2 and Flux 2.

The composition change of Flux 2 in the reaction with Steel 3
is indicated in Figure 4; while the composition change of Steel
3 is listed in Table 5. SiO₂ content decreased from 43.3 to 1.2
mass% during the experiment; while Al₂O₃ concentration incre-
ased from 3.2 to 52.1 mass% in the meantime. The increment
of Al₂O₃ and the decrement of SiO₂ were both more obvious
than those in the reaction between Flux 2 and Steel 2. It reve-
aled that a high concentration of [Al] in steel could accelerate
Reaction 1. A higher [Al] concentration would facilitate the ac-
cumulation of Al₂O₃ and the reduction of SiO₂ in mold fluxes.

Fig. 4 – Concentrations of SiO₂, Al₂O₃, MgO, Na₂O, and MnO in mold fluxes during the reaction between Steel 3 and Flux 2.
In the 2nd set of experiments, two CaO-Al\(_2\)O\(_3\)-based mold fluxes were used to react with high-Al steel. Flux 3 was used to react with Steel 4. The composition change of Flux 3 in the reaction with Steel 4 is indicated in Figure 5, and the composition change of Steel 4 is listed in Table 5. The initial concentration of SiO\(_2\) in the flux was 15.3 mass\%, which was much lower than those in Fluxes 1 and 2. This concentration decreased to 2 mass\% after 1500 s; while Al\(_2\)O\(_3\) content increased from 16.9 to 40.0 mass\%. In the meantime, [Si] concentration increased from 0.10 to 0.36 mass\%, and [Al] concentration dropped from 1.79 to 1.62 mass\%. It seems that 15.3 mass\% SiO\(_2\) in the initial composition of Flux 3 did not obviously retard Reaction 1. Considering the increment of Al\(_2\)O\(_3\) in the mold fluxes, the reductions of Na\(_2\)O and B\(_2\)O\(_3\) were more likely from the reaction instead of evaporation.

![Fig. 5](image)

Fig. 5 – Concentrations of SiO\(_2\), Al\(_2\)O\(_3\), B\(_2\)O\(_3\), MgO, Na\(_2\)O, MnO, and B\(_2\)O\(_3\) in mold fluxes during the reaction between Steel 4 and Flux 3.

The composition change of Flux 4 in the reaction with Steel 5 is given Figure 6, and the composition change of Steel 5 is listed in Table 5. Flux 4 is based on CaO-Al\(_2\)O\(_3\) flux system where the initial concentration of SiO\(_2\) was as low as 8.1 mass\% and CaO/Al\(_2\)O\(_3\) ratio was 1. SiO\(_2\) content only decreased from 8.1 to 5.6 mass\% throughout the experiment, which means only 30\% of SiO\(_2\) was reduced. It was much smaller than the decline of SiO\(_2\) content in the previous experiments. Al\(_2\)O\(_3\) content increased from 28.8 to 42.4 mass\% in 1800 s, which was also relatively insignificant compared with those in the previous experiments. The major source of the Al\(_2\)O\(_3\) accumulation presented in Figure 6 was likely to stem from the reduction of B\(_2\)O\(_3\) whose concentration dropped from 15.8 to 5.4 mass\% during the experiment. Aside from the contribution to the increase of Al\(_2\)O\(_3\), the abrupt increase of MnO could attribute to the reaction between [Mn] and B\(_2\)O\(_3\).

According to the results, a low concentration of SiO\(_2\) (< 8 mass\%) could kinetically benefit the restraint on the accumulation of Al\(_2\)O\(_3\). The low addition of SiO\(_2\) requires a large amount of fluxing agent, e.g. B\(_2\)O\(_3\), to decrease the liquidus temperature and adjust other properties. However, the reduction of B\(_2\)O\(_3\) introduced an additional increment of Al\(_2\)O\(_3\) in mold fluxes. Therefore, the balance between the reaction rate and melting property could be a critical factor in the design of CaO-Al\(_2\)O\(_3\)-based mold fluxes.
Continuous casting

**Flux-Steel Reaction in Laboratory Tests**

Three types of CaO-Al₂O₃-based mold fluxes (Fluxes 5, 6, and 7) were studied based on the reaction between these mold fluxes and a high-Al steel (Steel 6). Different CaO/Al₂O₃ ratios were applied to the studied mold fluxes. The changes of [Al] content in steel are compared in Figure 7(a). In Flux 5, [Al] content decreased from 1.65 to 0.53 mass% in 1200 s and 0.37 mass% in 3600 s. In Flux 6, [Al] content decreased from 1.49 to 0.06 mass% in 3600 s. In Flux 7, [Al] content decreased from 1.74 to 0.63 mass% in the first 11 minutes, but no further sample acquisition was made due to a lab incident. It seems that reaction was most intense in first 1200 s. As [Al] concentration should be very low due to the strong affinity of Al and O, the flux of [Al] in steel/flux interface could be written as follows (8):

\[
-k_{Al} \frac{A_{p_{steel}}}{W_{steel}} t = \ln \left( \frac{[Al]_t}{[Al]_0} \right)
\]

where [Al]%₀ and [Al]%ₜ are [Al] concentration at time t and zero, kₐl is the mass transfer coefficient of [Al] (m/s), A is the cross-section area (m²), psteel is the density of steel (g/m³) calculated according to reference (12), Wsteel is the total weight of steel (g), t is reaction time (s). The relationship between \(-\ln([Al]/[Al]₀)\) and t is plotted in Figure 12(b). As \(k_{Al}\) is proportional to the slope of the curve, it is indicated that the decrease of CaO/Al₂O₃ ratio decelerated the oxidation rate of [Al]. Besides, the oxidation of [Al] became rather slower as experiment proceeded in the reaction with the \(k_{Al}\) decreasing up to 6.8x10⁻⁶ m/s when CaO/Al₂O₃ ratio = 1; while it kept relatively constant after 1 min with the \(k_{Al} = 4.0x10^{-5}\) m/s during the experiment when CaO/Al₂O₃ ratio = 3. The oxidation rate of [Al] was also relatively constant in the first 660 s with the \(k_{Al} = 5.7 \times 10^{-5}\) m/s when CaO/Al₂O₃ ratio = 4.

![Fig. 6](image)

*Fig. 6 – Concentrations of SiO₂, Al₂O₃, B₂O₃, MgO, Na₂O, MnO, and B₂O₃ in mold fluxes during the reaction between Steel 5 and Flux 4.*

![Fig. 7](image)

*Fig. 7 – Concentration change of Al in steel during the reaction between Steel 6 and Flux 5/Flux 6/Flux 7.*
The [Al] losses in the liquid steel was higher in the lab experiments compared with those in pilot tests due to the ratio of mold fluxes to steel was much higher in lab experiments. The change of [Al] concentration in lab and pilot tests may not be comparable in value but their tendency should be similar.

CONCLUSIONS
1. CaO-SiO$_2$-based mold fluxes showed a severe reaction when casting high-Al steel, which resulted in a significant increase of Al$_2$O$_3$ content and a decrease of SiO$_2$ content during experiments. It makes the in-mold performance undesirable and unpredictable;
2. CaO-Al$_2$O$_3$-based mold fluxes showed better a stability in composition when casting high-Al steel. The changes of Al$_2$O$_3$ and SiO$_2$ contents were not as severe as those in CaO-SiO$_2$-based mold fluxes. However, the variation of B$_2$O$_3$ may also affect the melting property of mold fluxes;
3. The increase of CaO/Al$_2$O$_3$ ratio could accelerate the reaction between high-Al steel and CaO-Al$_2$O$_3$-based mold fluxes based on the variation of [Al] content in liquid steel.

ACKNOWLEDGEMENT CONCLUSIONS
Financial supports by Baosteel-Australia Joint Research & Development Centre (BAJC) and Australian Research Council Industrial Transformation Research Hub are greatly acknowledged.

REFERENCES