Investigation of *in-situ* Chemical Reactions of Al$_2$O$_3$–SiC–SiO$_2$–C Refractory and Its Interactions with Slag

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Experiments were carried out to investigate *in-situ* reactions of refractory and its interactions with slag (composition: 45.4%SiO$_2$+36.6%CaO+15.9%Al$_2$O$_3$) using a horizontal furnace by detecting CO and CO$_2$ contents in off gas with an infrared (IR) analyzer. The composition of refractory is 69.4%Al$_2$O$_3$+7.3%SiO$_2$+10.6%SiC+12.7%C. Temperature was from 1 773 to 1 873 K. The samples after high temperature experiments were analyzed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)—Energy Dispersive Spectrometer (EDS). Mullite was detected after refractory samples were maintained at high temperatures. The refractory/slag reaction was evaluated by calculating the carbon removed. Carbon removal process was a two-step reaction, in the beginning the carbon was removed very quickly (fast reaction stage) and both CO and CO$_2$ gases were detected by IR analyzer. Then after around 2 000 s the reaction slowed down and no CO$_2$ gas could be detected (slow reaction stage). The main *in-situ* reaction product was SiC rather than SiO. Slag showed good wetting with the refractory and penetrated into it through pores. Low melting point compounds, anorthite (CaAl$_2$Si$_2$O$_8$) and gehlenite (Ca$_2$Al$_2$SiO$_7$) were detected after heating refractory for 7 200 s while remaining in contact with slag.

KEY WORDS: refractory; slag; reactions.

1. Introduction

Refractory is responsible for significant costs associated with metallurgical processes such as ironmaking, steelmaking, ladle refining and casting etc. Due to its superior thermal shock resistance, alumina–carbon refractory has made up a significant proportion of refractories such as those used as furnace trough materials and nozzles. Fundamental understanding of refractory behavior at high temperatures is therefore very important, this will lead to decreased consumption, reduced downtime and increased product quality. K. Mukai et al. proposed a local corrosion mechanism of carbon–oxide refractory. Slag not only wets the oxides inside refractory but also dissolves them in preference to carbon and results in a carbon rich layer. Metal phase wets and dissolves carbon in preference to the oxides. Once the carbon rich phase disappears, the slag again penetrates into the boundary between metal and refractory to repeat the process. This mechanism explains the corrosion phenomena of refractory around metal–slag–refractory coexistence zone. M. Lee et al. investigated the dissolution kinetics of dense alumina in calcium aluminosilicate based melts under controlled atmosphere Ar–CO–CO$_2$. They suggested the dissolution rate is most likely controlled by mass transfer in slag phase.

Generally, researchers have focused on dissolution phenomena of refractory into slag or metal melt. However, in addition to these phenomena, refractory could be degraded due to *in-situ* reaction in the presence of silica. V. Sahajwalla et al. reported a systematic investigation on *in-situ* reduction kinetics of silica in carbon based materials for refractories. They showed that silica in graphite–silica mixtures for refractories is reduced by carbon, which leads to bulk decarbonization and degradation of refractories.

However, the *in-situ* reaction of actual refractory used in iron and steel making processes is more complicated than silica–carbon system due to the presence of other components such as alumina, silicon carbide etc.

In the present research, a systematic experimental investigation has been carried out to develop the *in-situ* decarbonization mechanisms inside Al$_2$O$_3$–SiO$_2$–C–SiC refractory, which is a common refractory system used for metallurgical processes. Furthermore, the interactions between refractory and slag are also studied to shed light on the dissolution mechanism of the refractory into slag. The influence of temperature and silica content on the reaction system is investigated.

2. Experimental

2.1. Experimental Material

The refractory composition is 69.4% Al$_2$O$_3$, 7.3% SiO$_2$, 10.6% SiC and 12.7% C. The carbon is provided in excess for the reaction with silica. Around 15 g of refractory with above composition was hydraulically pressed under a pressure of 1.7×10$^8$ Pa. The size of the samples is 23×23×10 mm. In order to clarify the effect of silica on *in-situ* reaction of refractory, the refractory sample with greater silica...
content (67.1% Al₂O₃, 10.5% SiO₂, 10.2% SiC, 12.2% C) was also investigated for comparison.

In another experimental series, slag and refractory interactions were studied to establish dissolution behavior of refractory into slag, which is another cause of refractory degradation besides the in-situ reaction of refractory. About 1 g of slag, 45.4% SiO₂, 36.6% CaO, 15.9% Al₂O₃, and the balance of MgO, P₂O₅, S, etc. approximately less than 2.1%, was used for the investigation of interaction between refractory and slag. High purity Argon gas was used as the atmosphere gas.

2.2. Experimental Apparatus and Procedure

The experiments were conducted in a horizontal Super–Kanthal resistance tube furnace as shown in Fig. 1. The refractory or refractory/slag sample was set on an alumina sample supporter in the cold zone of the furnace (under 1173 K). After the furnace was heated up to the desired temperature, the sample was pushed into the hot zone to start the experiment. For most of the experiments, the sample was kept in the hot zone for 7200 s. Argon gas at a flow rate of 1.67 × 10⁻⁵ Nm³/s was maintained throughout the experiments to keep inert atmosphere with oxygen partial pressure under 10⁻¹⁰ Pa to minimize decarbonization of refractory by atmosphere. To assist with fundamental understanding of reactions occurring at high temperature, the gas outlet was connected to an infrared detector for analyzing CO and CO₂ content, which were generated from reactions between oxides and carbon. The temperatures, at which the refractory in-situ or refractory/slag reactions were studied, were 1773, 1823 and 1873 K.

After the experiments, samples were analyzed using XRD and SEM-EDS for determining composition.

3. Experimental Results

When samples were heated to desired high temperatures, CO and CO₂ gas could be detected using IR analyzer. The typical changes of CO and CO₂ gas content with reaction time at temperature of 1823 K are shown in Fig. 2. Where, \( W_{\text{ref}} \) is the initial weight of refractory sample. It is clear that both CO and CO₂ contents in outlet gas increase sharply in the beginning to peak values and then decrease gradually. The evolution of CO₂ gas initiates a little later than CO gas. In Fig. 2, the occurrence of CO₂ peak is at about 600 s, earlier than that for CO peak, which is seen at approximately 900 s.

The reaction rate is evaluated by the carbon removed from the reaction system. Carbon removed can be calculated from the CO and CO₂ concentrations in the off gas, defined in the following Eq. (1).

\[
\alpha = \left( \frac{n_{\text{CO}} + n_{\text{CO}_2}}{N_C} \right)
\]

Where, \( \alpha \) is the fraction of carbon removed at time \( t \), \( n_{\text{CO}} \) and \( n_{\text{CO}_2} \) are moles of CO and CO₂ removed by gas phase until time \( t \), respectively. \( N_C \) is the initial moles of carbon in the sample.

Figure 3 shows the effect of temperature on carbon removal. This figure shows that overall reduction reaction could be separated into three distinct stages. However, the initial stage in the time less than 300 s is considered to be due to the response delay of IR analyzer. In the following section of this paper, only the latter two stages will be discussed corresponding to fast (2nd stage) and slow (3rd stage) stages as indicated by the shapes of the curves beyond the initial stage. The fraction of carbon removed, \( \alpha \), increases with reaction time vigorously until about 2000 s (this is slightly different for various temperatures, shorter at higher temperature), which is called fast stage, and then \( \alpha \) value changes with time more gradually, which is called slow stage. Higher temperature favors a more rapid overall reduction reaction in the fast stage. The fraction of carbon removed in slow stage increases with reaction time more slowly at higher temperature. This is because at higher temperature, the carbon removal fraction at the end of
fast stage is much higher than that at lower temperature. Therefore, the contacting area for reactants in the slow stage is much less at higher temperature than that at lower temperature.

For the present refractory composition, carbon is excess to silica for complete reaction. The maximum complete carbon removal fraction for the refractory composition 69.4%Al2O3+7.3%SiO2+10.6%SiC+12.7%C is 34.5%, this corresponds to the carbon removal fraction for silica completely reacting with carbon to form only SiC according to reaction (2). Take results at 1873 K as example, the reduction reaction is almost finished and the final α value is around 32%, only a little smaller than 34.5%, which implies a small part of silica reacts with carbon to form SiO (reaction (3)). The possible maximum carbon removal fraction is 11.5% for its reaction with silica to form only SiO according to reaction (3).

\[
\text{SiO}_2(s \text{ or } l) + 3C(s) = \text{SiC}(s) + 2\text{CO}(g) \quad \text{(2)}
\]

\[
\text{SiO}_2(s \text{ or } l) + C(s) = \text{SiO}(g) + \text{CO}(g) \quad \text{(3)}
\]

Figure 4 shows dependence of α on reaction time for the samples with different silica content. There is more gas produced for the samples with greater silica content. This proves that the reaction of the refractory is due to the interaction between silicon oxide and carbon.

Figure 5 shows the dependence of α on reaction time under the conditions with and without slag on the surface of refractory sample. It shows that the overall reduction reaction rate does not change significantly due to slag addition.

4. Discussion

4.1. In-situ Reactions of Refractory

The experimental results show that the in-situ reaction of refractory is a two-step process. In the fast stage, the carbon removal fraction increases with reaction time sharply and then in the slow stage, the carbon removed from the refractory slows down. Refer to Figs. 2 and 3, CO2 gas can be detected by IR almost during fast stage, while no CO2 gas is present in slow stage, which suggests the different reaction mechanisms in these two stages and the reaction may proceed via gas intermediates as follows.

\[
\{O\}(s,l) + \text{CO}(g) = \text{CO}_2(g) \quad \text{(4)}
\]

\[
C(s) + \text{CO}_2(g) = 2\text{CO}(g) \quad \text{(5)}
\]

Where, \{O\} is the oxygen in the refractory. In the fast stage, solid–solid reactions (2) and (3) are predominant, contacting area between gas phase and solid phase is less and therefore it is hard to get equilibrium for reaction (5). This results in the detection of CO2 gas in the off-gas. While in the slow stage, there is greater level of gas generation and the contact area between gas phase and solid phase is predominant rather than solid–solid contact, the occurrence of reaction (5) is easier and CO2 is hardly detected in off-gas. In order to confirm this, one of the refractory samples was reheated after being kept at high temperature for 7200 s. As shown in Fig. 6, even though the in-situ reaction of refractory is mostly finished after being heated at 1823 K for 7200 s, when this sample was heated to 1823 K again, CO2 gas could be detected in the beginning until the end of fast reaction stage as can be seen upon comparison of Fig. 6 and Fig. 7. This shows that when there is no gas intermediates inside refractory, even though the refractory sample is more porous and less solid–solid particle contact area is available, the overall reaction still starts from
solid–solid process. It is possible to deduce that the shift from fast reaction stage to slow reaction stage corresponds to the change of predominant reduction mechanism from solid–solid reaction to gas–solid reaction.

The blank refractory samples without slag contacting after reactions were analyzed using XRD technique, mullite was identified (Fig. 8). There is more alumina than silica in the samples, silica can react with alumina according to reaction (6) to form mullite.

\[
\text{2SiO}_2(s, l) + 3\text{Al}_2\text{O}_3(s) = \text{Al}_6\text{Si}_2\text{O}_13(s) \\
\Delta G^\circ = 17563.6 - 26.02T \text{ J/mol} \tag{6}
\]

Formed mullite reacts with carbon to produce CO and CO\(_2\) gas. There are two possible reactions between mullite and carbon at the temperature above 1673 K under argon atmosphere.

\[
\text{Al}_6\text{Si}_2\text{O}_{13}(s) + 6\text{C}(s) = 3\text{Al}_2\text{O}_3(s) + 2\text{SiC}(s) + 4\text{CO}(g) \\
\Delta G^\circ = 1158030 - 613.52T \text{ J/mol} \tag{7}
\]

\[
\text{Al}_6\text{Si}_2\text{O}_{13}(s) + 2\text{C}(s) = 3\text{Al}_2\text{O}_3(s) + 2\text{SiO}(g) + 2\text{CO}(g) \\
\Delta G^\circ = 1313110 - 631.36T \text{ J/mol} \tag{8}
\]

In order to confirm the main reaction, thermodynamic calculation was conducted using FACT database. The calculation is started from 0.5 mol mullite and 1 mol C. As shown in Fig. 9, SiC is the main product compared with SiO at high temperatures, which is consistent with experimental results (Fig. 3). However, higher temperature favors SiO formation slightly. Both mullite and silica react with carbon to form SiC mainly.

### 4.2. Slag Penetration into the Refractory

When refractory sample with slag on the surface was heated to high temperature, because slag is wettable to the refractory, it spread on refractory surface shortly after melting and penetrated into refractory through pores.

According to the results of XRD shown in Fig. 10, the...
After experiments with slag on surface are mixtures of corundum and silicon carbide, mullite, anorthite and gehlenite. Anorthite can be formed according to reaction (9) since this reaction is favorable at high temperature.

$$\text{CaO(s,l)} + 2\text{SiO}_2(s,l) + \text{Al}_2\text{O}_3(s) = \text{CaAl}_2\text{Si}_2\text{O}_8(s,l)$$

The melting point of anorthite is 1828 K, which is lower than or similar to temperatures in iron or steel making processes. The formation of anorthite leads to the softening and thereafter the degradation of the refractory.

However, slag addition has almost no effect on carbon removal, this can be explained as follows. The slag main composition is 45.4% SiO$_2$, 36.6% CaO, and 15.9% Al$_2$O$_3$. In order to form anorthite for all CaO, only a little amount of silica from refractory is necessary. Furthermore, the weight of slag added is around several percent that of refractory, therefore the amount of silica and mullite available for the reaction with carbon does not change significantly. However, it is possible that anorthite reacts with carbon as shown in reaction (10).

$$11\text{CaAl}_2\text{Si}_2\text{O}_8(s,l) + 51\text{C}(s) = 5\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_8(l) + \text{CaAl}_2\text{O}_4(s) + 17\text{SiC}(s) + 34\text{CO}(g)$$

Gehlenite has a melting point of 1600 K, much lower than that of anorthite. The formation of gehlenite could lead to significant damage to the refractory life.

Figure 11 shows the SEM mapping and EDS results of refractory sample contacting with slag after experiment at 1823 K, for 7200 s. The existence of alumina and mullite can be confirmed from this figure. At some large block area, only Al and O are detected but not Si, this implies the existence of alumina. On the other hand, where Si can be detected, both Al and O can be detected, which shows the existence of mullite. Calcium seems to be distributed along the inside surfaces of pores, which is the result of slag penetration into the refractory.

5. Conclusions

The in-situ reaction of Al$_2$O$_3$–SiO$_2$–SiC–C refractory and its penetration behavior by slag have been investigated in the temperature range from 1773 to 1873 K under argon atmosphere. The results can be summarized as follows.

(1) Carbon removal process from the refractory is a two-step one. The fraction of carbon removed increases with reaction time vigorously at first (fast stage) and then changes slowly (slow stage). The carbon removal fraction in the first stage increases more rapidly with increasing temperature.

(2) For the present refractory composition, mullite is formed after heating to high temperature. The main reaction product is SiC rather than SiO.

(3) Slag is wettable to the refractory and penetrates into it through pores. When slag contacts with refractory at high temperature, low melting point compounds, anorthite and gehlenite can be formed, these low melting point compounds could lead to significant damage to the refractory.

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