1. Introduction

Non-metallic inclusions in steel refining process can be classified into two types depending on the sources: endogenous and exogenous. Endogenous inclusions are mainly generated during deoxidation process, while exogenous inclusions are caused by slag entrapment, breakdown of refractory materials and reoxidation by air. Recently, ladle glaze has been suspected as one of the major sources of non-metallic inclusions in molten steel during ladle metallurgy.1–11

Ladle glaze is a thin film of molten slag adhered on ladle refractory linings, which is formed during the discharge of molten steel to a tundish. The molten slag film can be frozen when a ladle cool down. When next heat is poured into a glazed ladle, solid glaze can be melted again and even detached from refractory lining due to the strong liquid metal flow during various ladle treatments. In addition, glazed refractories can react continuously with molten steel to generate non-metallic inclusions.

High alumina ladle lining has been widely used in secondary refining process in order to increase liquid steel cleanliness. However there has been lack of study on ladle glaze formation and its influence on melt cleanliness. In our previous study,1) the formation mechanism of ladle glaze on a high alumina refractory composed of large corundum particles and porous spinel matrix was investigated. The chemical reaction between the glazed refractory and Al-deoxidized molten steel and the generation of non-metallic inclusions in Al-deoxidized steel were investigated.

As a sequel of our previous study, the influence of Ca treatment on the chemical reaction between the glazed refractory and Al-deoxidized molten steel has been investigated at 1600°C. The evolutions of chemistry of the glazed refractory and non-metallic inclusions by Ca treatment were determined using SEM, EPMA and EDS analyses. The FactSage thermodynamic software12) was also employed to perform thermo-chemical analyses of the reactions.

2. Experimental

The experimental procedure of the present study is briefly summarized in Fig. 1. As-received refractory was cut into proper size and dipped into liquid slag to form glaze. Various non-metallic inclusions were generated in molten steel. The major inclusions were liquid Ca–Al–Mg–O–S inclusion and its mixtures with solid phase such as CaS, MgO and MgAl2O4. Thermodynamic analysis using the FactSage software was also carried out to understand the chemical reactions of the glazed refractory with molten steel more clearly.

KEY WORDS: ladle glaze; refractory; inclusion; FactSage.
Table 1. Chemical compositions of glazed refractory and initial molten steel (in mass%).

|                | CaO | MgO | Al₂O₃ | SiO₂ |
|----------------|-----|-----|-------|------|
| As-received refractory | 2.4 | 8.6 | 88.2  | 0.8  |
| Molten slag       | 50.0| 7.0 | 33.0  | 10.0 |
| Glaze (non-crystalline) | 35.8| 6.5 | 51.1  | 6.6  |
| Overall Steel Composition: Fe-0.0015C-0.038Al-0.009S-0.008Si-0.066Mn-0.0072O |

prepare the glazed refractory. Then, the glazed refractory was dipped into Al-deoxidized/Ca treated molten steel in order to investigate the chemical reactions and influence of the glazed refractory to the steel cleanliness.

Table 1 shows the chemical compositions of an as-received refractory (a sintered bulk castable from ChoSun refractory company, Korea) and slag used in the present study. The sintered bulk castable was cut into bar-type specimens (1 cm × 3 cm × 10 cm in height) in the experiment. The details of the experimental procedure can be found in the previous study.¹

In order to simulate the glaze formation during slag discharging process, a bar-type refractory sample was dipped into the premelted slag (~30 g) in a MgO crucible for 2 min and then quickly pulled out. This refractory is considered as the glazed refractory in the present study. Fe–Al (2 mass% Al) alloy was added into molten steel in a MgO crucible to simulate Al deoxidation, and Ca (~5 g of Ca wrapped by iron foil) was added 30 s after the Fe–Al addition. Then, about 20 s after the Ca addition, the glazed refractory was dipped into the molten steel (~300 g). The glazed refractory was kept in the liquid steel for 0.5, 1, 3, 5, 10, 15 and 30 min, and then pulled out for furnace cooling at cooling rate of 32°C/min on average. The refractory samples were analyzed later. In the case of a 30 min experiment, the samplings of liquid steel were carried out immediately before Ca addition (0 reaction time) and then after 0.5, 1, 3, 5, 10, 15 and 30 min to investigate the variations of steel and inclusion chemistry. During the entire procedure, the furnace was kept under an Ar gas atmosphere, purified by passing through liquid Mg(ClO₄)₂ at room temperature and Mg chips at 450°C.

Chemical and microstructural analyses of the glazed refractories were carried out using an optical microscope, SEM and EPMA (WDS). The chemical composition of the slag was ascertained by the ICP-AES and the XRF analyses. The oxygen and sulfur contents in steel samples were analyzed by LECO spectrometry and CS spectrometry, respectively. The concentrations of other elements were analyzed by ICP-AES. The compositions of non-metallic inclusions (around 20 inclusions in each steel sample) were analyzed by the energy dispersive X-ray spectra (EDS).

3. Results

Table 1 shows the chemical compositions of the as-received refractory, molten slag and glaze formed on the surface of the refractory. The chemical composition of Al-deoxidized/Ca-treated molten steel prior to the chemical reaction with the glazed refractory is also listed in the table. Since the present results for the chemical reaction of the glazed refractory with Al-deoxidized/Ca-treated molten steel are often compared with the previous experimental results¹ with Al-deoxidized molten steel, the following abbreviations are used to distinguish two cases:

(i) Al-deoxidized/Ca-treated molten steel: AlCa-steel
(ii) Al-deoxidized molten steel: Al-steel.

3.1. Glazed Refractory Prior to the Chemical Reaction with Molten Steel

The morphology and chemistry of the as-glazed refractory were presented in detail in the previous study.³ The same glazed refractory was used in the present study. The summary of the glazed refractory is below.

After the chemical reaction of the as-received refractory (which was composed of large dense alumina particles and porous spinel matrix) with the molten slag of 50CaO–7MgO–33Al₂O₃–10SiO₂ in mass% for 2 min (which is determined based on the discharging time of 270 ton ladle), the glaze layer of 150 to 200 μm thickness formed on the surface of the refractory. The glaze layer was composed of liquid oxide phase and small amount of spinel particles. The chemical composition of the liquid phase (36CaO–51Al₂O₃–7SiO₂–6MgO in mass%) in the glaze layer was quite different from the original slag. Thermodynamic analysis showed that the glaze was the reaction product of molten slag and refractory.

3.2. Reaction between the Glazed Refractory and Al-deoxidized/Ca-treated Steel

3.2.1. Molten Steel

Figure 2 shows the variation of overall chemical composition of AlCa-steel in reaction with the glazed refractory. The chemical composition in Fig. 2 is the overall composition of dissolved elements in steel and insoluble inclusions. Al content in molten steel decreased continuously with reaction time. On the contrary, Si content increased rapidly up to 300 mass ppm in early stage of the reaction and became saturated at about 350 mass ppm. The concentrations of Ca and S decreased rapidly with the reaction, and Mn content was almost constant. In comparison with the previous study for Al-steel, Si pick-up rate of AlCa-steel is much higher than that of Al-steel, and final Si content in AlCa-steel ([Si]≈350 mass ppm) is also higher than that in Al-steel ([Si]≈200 mass ppm). In addition, although initial Al content in both steels were similar, final Al content in AlCa-steel (about 250 mass ppm) is much higher than that in Al-steel (about 50 mass ppm). S content decreased rapidly in AlCa-steel, while it was almost constant in Al-steel. The observed difference in two steels results from the addition of Ca. Details of the chemical reaction will be discussed in Sec. 4. According to the equilibrium calculation using FactSage software,¹² the equilibrium soluble oxygen should be about 5 to 10 mass ppm. This means that most of
3.2.2. Glazed Refractory

3.2.2.1. Overview of the Glazed Refractory after Reaction

Figure 3 shows the surface morphology change of the glazed refractory with reaction time. Initial smooth glaze surface is changed to rough surface by chemical reactions with molten AlCa-steel. Although in general the surface configuration of the glazed refractory reacted with AlCa-steel is similar to that reacted with Al-steel, more severe chemical reaction was observed in the present AlCa-steel case. For example, large dense corundum particles (large grey particles) were already observed on the surface of the glazed refractory reacted for 5 min with AlCa-steel, which is similar to the glazed refractory after 30 min reaction with Al-steel.

Figure 4 shows the cross-sectional view of the glazed refractory after reaction with AlCa-steel. Wide SEM images were taken in order to observe the structure of the glazed refractories more objectively. In general, the macroscopic change of the glazed refractories in AlCa-steel is similar to that in Al-steel. The corrosion rate of the glazed refractories was inhomogeneous. Like the case of Al-steel, the corrosion rate is faster in the porous spinel matrix area than dense corundum particle (large grey particle) area. The local surface erosion of the glazed refractories was already observed in 5 min, which is rather faster than the Al-steel case (5 min). Large pits (very rough surface) observed in 10 min sample seem to result from the detachment of large corundum particles after severe corrosion in porous spinel matrix.

The EPMA mapping images of the glazed refractories are shown in Fig. 5. Like Al-steel case, the profiles of Ca and Si can give a clue for the reaction mechanism of glazed refractory with AlCa-steel. The Ca concentration image shows that the diffusion of Ca from the glazed surface toward refractories. The penetration rate and depth of the glaze into porous spinel matrix of refractories are similar to the case of Al-steel. However, the Si mapping results are somewhat different from the Al-steel case. First of all, the concentration of SiO₂ on the glazed refractory surface decreased much faster than the case of Al-steel. Nearly no SiO₂ was detected on the surface after 3 min rather than 10 min for Al-steel. The concentration of SiO₂ in refractory beneath of the glazed surface was also much lower than the case of Al-steel. These results are consistent with the large increase of Si content in molten steel in Fig. 2. The EPMA results tell that two major chemical reactions occurring during the reactions of the glazed refractories with AlCa-steel are (a) chemical reaction of infiltrated liquid glaze oxide with refractory and (b) chemical reaction between liquid glaze oxide and molten steel. This will be discussed in detail in Sec. 4.

3.2.2.2. Glazed Refractory after 1 min Reaction

Figure 6 shows the SEM images of the glazed refractory reacted with AlCa-steel for 1 min. The overview image of the glazed refractory is presented in Fig. 6(a) and the close-up images of several typical areas are presented in Figs. 6(b) to 6(d). The chemical compositions of all phases marked in the figures were quantitatively analyzed by the EPMA (WDS), which are listed in Table 2.

In the glaze layer as shown in Fig. 6(b), many spinel particles (black; spot 3) were observed in liquid Ca–Al–Si–Mg–O matrix (gray; spot 1). The Ca–Al–Si–Mg–O glaze matrix was a non-crystalline phase in a quenched sample, which can be assumed to be liquid state at experimental
condition. The population of spinel particles increased, compared with original glaze layer (see Fig. 3 in the previous study\textsuperscript{1}). The composition of the liquid Ca–Al–Si–Mg–O phase was quite different from that of the original liquid glaze. The concentrations of MgO and SiO\textsubscript{2} were less than 2 mass\% except for certain local area (white area; spot 2). This local area containing about 6 mass\% SiO\textsubscript{2} seems to be formed during cooling of the sample. Thus, the SiO\textsubscript{2} content in the liquid glaze at experimental condition can be about 2 mass\%. Adjacent to a large alumina particle (b area in Fig. 6(a)), the Ca–Al–O compounds (CaAl\textsubscript{4}O\textsubscript{7}) were also detected. Figure 6(c) shows the interface between the glaze layer and porous spinel matrix of refractory. The Ca–Al–Mg–Si–O matrix (spot 6) contained about 2 mass\% SiO\textsubscript{2} and more than 10 mass\% MgO. Large spinel particles (spot 5) can be observed in the spinel matrix. Even in more inner side of the refractory (Fig. 6(d)), spinel particles and the Ca–Al–Mg–Si–O phase were observed. Small secondary precipitations were observed inside the Ca–Al–Mg–Si–O phase (spots 7 and 8), which tells the Ca–Al–Mg–Si–O phase may be in liquid state at 1600°C.

In summary, although the microstructure of the glazed refractory reacted with Al-deoxidized and Ca-treated molten steel.

Fig. 4. SEM images for the glazed refractories after chemical reaction with Al-deoxidized and Ca-treated molten steel.
area was similar to that of (b) area except that more CaAl$_4$O$_7$ particles were observed around a large corundum particle. The microstructure beneath a large corundum particle is shown in Fig. 7(c). Spinel (spot 11), CaAl$_4$O$_7$ (spot 10), CaAl$_{12}$O$_{19}$ (spot 8) and the Ca–Al–Si–O phase (spot 9) were observed. The distinctive layers of CaAl$_{12}$O$_{19}$ and CaAl$_4$O$_7$ were observed around a corundum particle (spot 7). Chemical composition of the Ca–Al–Si–O phase (spot 9) was close to gehlenite (Ca$_2$Al$_2$SiO$_7$). Figure 7(d) shows the refractory area infiltrated by liquid glaze. Fine spinel (spot 14) and CaAl$_4$O$_7$ particles (black; spot 12) were distributed homogeneously in the Ca–Al–Si–O phase (white; spot 13) containing about 2 mass% SiO$_2$. Compared with the previous study for Al-steel, the SiO$_2$ content in the infiltrated liquid Ca–Al–Si–O oxide phase is less, which suggests that the SiO$_2$ content in liquid glaze infiltrating into the refractory had already been depleted by the reaction with AlCa-steel. This is consistent with the chemistry of the glaze layer and molten steel.

3.2.2.4. Glazed Refractory after 30 min Reaction

Figure 8 shows the SEM images of the glazed refractory reacted with molten AlCa-steel for 30 min. Even in the overview image in Fig. 8(a), the Ca–Al–O layer of about 100 μm in thickness was clearly observed around large corundum particles. This Ca–Al–O layer is thicker than the case for Al-steels. Spinel (spot 1), CaAl$_2$O$_4$ (spot 3) and CaAl$_4$O$_7$ (spot 2) particles were abundantly observed in the glazed layer (Fig. 8(b)). Liquid Ca–Al–O phase (the atomic ratio of Ca to Al was about 1 : 2) contained less than 0.5 mass% MgO and SiO$_2$. The distinctive layers of CaAl$_{12}$O$_{17}$ (spot 5) and CaAl$_4$O$_7$ (spot 6) phases were developed around a dense corundum particle (Fig. 8(c)). The matrix was composed of spinel particles and infiltrated Ca–Al–Si–O phase (spot 7) containing less than 2 mass% SiO$_2$. Figure 8(d) shows the relics of a dense corundum particle completely dissolved in the refractory matrix after reacting with infiltrated glaze. Small amount of CaAl$_{12}$O$_{19}$ phase covered by CaAl$_4$O$_7$ (spot 9) was detected in this area.

3.2.3. Non-metallic Inclusions

The variation of non-metallic inclusions in AlCa-steels generated during the reaction with the glazed refractory is summarized in Table 3. More than 20 inclusions were randomly selected from each steel sample and EDS analysis was carried out. SEM images of the typical inclusions are presented in Fig. 9. It should be noted that most of the non-metallic inclusions observed in the present study are spherical, which means they were mostly liquid inclusions or mixed inclusions of liquid and solid. On the contrary, the inclusions observed in the previous study for Al-steel were mostly irregular shapes, which means they were solid inclusions. In addition, most of the inclusions in the present study belonged to the CaO–MgO–Al$_2$O$_3$–CaS system. SiO$_2$ was hardly detected in the inclusions. The inclusions in the previous study for Al-steel were mostly MgAl$_2$O$_4$ and Al$_2$O$_3$.

The chemistry of major inclusions in the present study was: ‘liquid (Ca–Al–Mg–O–S)’, ‘liquid + solid CaS’, ‘liquid + solid MgO’, ‘liquid + solid spinel’, ‘solid CaS’ and ‘solid Ca–Al–O’. The amount of CaS in liquid phase was normally less than 5 mass% except for liquid inclusions co-existed with solid CaS (about 15 mass% CaS). Sulfide inclusions such as CaS and CaS–Al$_2$S$_3$ were observed mostly in the early stage of the reaction. Solid Ca–Al–O inclusions (CaAl$_2$O$_4$, CaAl$_4$O$_7$ and CaAl$_{12}$O$_{19}$) and CaO inclusion were also observed. The CaO content in the Ca–Al–O inclusions increased gradually with reaction time. In the AlCa-steel sample at 30 min, the inclusions were mostly liquid Ca–Al–Mg–O inclusions containing less than 0.5 wt% CaS. The size of the inclusions is mostly 3–5 μm except solid CaS inclusion of about 1 μm. The origin of the
Table 2. Phase analyses of refractory materials and ladle glaze by EPMA (WDS) technique (in mol%).

| Ca   | Mg  | Al  | Si  | Phase (estimated) |
|------|-----|-----|-----|-------------------|
| 1    | 33.8| 3.0 | 61.8| 1.4 Liquid        |
| 2    | 45.3| 1.9 | 46.3| 6.5 Liquid        |
| 3    | 0.3 | 29.2| 70.5| 0.1 Spinel        |
| 4    | 32.9| 11.6| 52.9| 2.7 Liquid        |
| 5    | 0.2 | 28.9| 70.8| 0.1 Spinel        |
| 6    | 27.7| 15.3| 54.9| 2.1 Liquid        |
| 7    | 29.7| 2.3 | 56.5| 11.5 Liquid       |
| 8    | 30.9| 4.2 | 51.6| 13.3 Liquid       |
| 9    | 0.2 | 29.3| 70.5| 0.0 Spinel        |

Fig. 6 (1 min)

| Ca   | Mg  | Al  | Si  | Phase (estimated) |
|------|-----|-----|-----|-------------------|
| 1    | 34.1| 0.4 | 64.9| 0.6 Ca$_2$O$_3$   |
| 2    | 3.1 | 28.6| 68.2| 0.1 Spinel        |
| 3    | 20.2| 0.3 | 79.3| 0.2 CaAl$_2$O$_4$ |
| 4    | 0.2 | 29.3| 70.5| 0.0 Spinel        |
| 5    | 32.1| 0.4 | 66.8| 0.7 CaAl$_2$O$_4$ |
| 6    | 42.8| 1.3 | 49.7| 6.3 Liquid        |
| 7    | 100 | 0.0 | 100 | Corundum          |
| 8    | 8.3 | 0.3 | 91.1| 0.3 Ca$_3$Al$_2$O$_7$ |
| 9    | 36.7| 1.9 | 35.9| 25.5 Ca$_2$Al$_2$SiO$_7$ |
| 10   | 19.8| 0.4 | 79.1| 0.7 Ca$_2$O$_3$   |
| 11   | 0.5 | 27.7| 70.7| 1.1 Spinel        |
| 12   | 20.0| 0.5 | 78.9| 0.5 CaAl$_2$O$_4$ |
| 13   | 32.2| 0.5 | 65.5| 1.8 CaAl$_2$O$_4$ + Liquid |
| 14   | 0.3 | 29.2| 70.6| 0.0 Spinel        |

Fig. 7 (5 mins)

| Ca   | Mg  | Al  | Si  | Phase (estimated) |
|------|-----|-----|-----|-------------------|
| 1    | 0.3 | 29.3| 70.4| 0.0 Spinel        |
| 2    | 33.1| 1.0 | 65.5| 0.4 CaAl$_2$O$_4$ |
| 3    | 20.0| 0.2 | 79.6| 0.2 CaAl$_2$O$_4$ |
| 4    | 100.0| 0.0 | 100.0| Corundum          |
| 5    | 8.2 | 0.7 | 90.1| 1.1 Ca$_3$Al$_2$O$_7$ |
| 6    | 17.5| 0.5 | 81.4| 0.6 Ca$_2$O$_3$   |
| 7    | 32.0| 2.1 | 64.7| 1.3 CaAl$_2$O$_4$ + Liquid |
| 8    | 0.3 | 29.4| 70.3| 0.0 Spinel        |
| 9    | 20.0| 0.4 | 79.2| 0.5 CaAl$_2$O$_4$ |
| 10   | 0.2 | 28.2| 71.6| 0.0 Spinel        |
| 11   | 30.1| 2.0 | 38.3| 29.6 Liquid       |

Fig. 8 (30 mins)

**Fig. 7.** SEM images of the glazed refractory after chemical reaction with Al-deoxidized and Ca-treated molten steel (5 min reaction). (a) Overview image, (b) glaze area, (c) and (d) glaze-infiltrated refractory area.

**Fig. 8.** SEM images of the glazed refractory after chemical reaction with Al-deoxidized and Ca-treated molten steel (30 min reaction). (a) Overview image, (b) glaze area, (c) and (d) glaze-infiltrated refractory area.
4. Discussion

The FactSage thermochemical software\(^{12}\) with recent FToxid database\(^{13-15}\) and FTmisc liquid Fe database\(^{16}\) was used for the thermodynamic analysis to understand the chemical reactions between the glazed refractory and AlCa-steel at 1600°C. The following three reactions are involved in the present experiment.

(i) Chemical reaction between glaze and molten steel.
(ii) Chemical reaction between glaze and refractory on the refractory surface.
(iii) Infiltration of glaze into porous spinel matrix of the refractory.

4.1. Molten Steel

As molten steel directly contacted with glaze in the experiment, the chemistry of molten steel could be mainly influenced by glaze and vice versa. Figure 10 shows the thermodynamic calculation for the reaction between glaze and AlCa-steel at 1600°C. As pointed out in the previous study,\(^{11}\) the amounts of glaze and molten steel participated in the experiment were about 3 and 300 g, respectively. Thus, in order to understand the influence of glaze on the chemical composition of AlCa-steel, 100 g of steel was let to react with increasing amount of glaze up to 1 g in the

| Inclusion type | Time (Min.) | 0.5 | 1  | 3  | 5  | 10 | 15 | 30 |
|---------------|-------------|-----|----|----|----|----|----|----|
| Liquid        | Ca-Mg-Al-O  | 6   | 2  | 8  | 3  | 3  | 3  | 19 |
|               | Ca-Mg-Al-O-S| 1   | 1  | 2  | 5  | 7  | 7  | 13 |
| Liquid + Solid| Ca-Mg-Al-S-O+CaS | 3 | 2  | 7  | 9  | 7  | 13 | 13 |
|               | Ca-Mg-Al-O+MgO | 2 | 5  | 2  | 2  | 2  | 2  | 2  |
|               | Ca-Mg-Al-O+Spinel | 2 |     |    |    |    |    |    |
| Solid Ca oxide and sulfide | CaS | 0   | 4  | 1  | 3  | 1  |    |    |
|               | CaS-Fe2S3 | 2   | 2  | 2  | 2  | 2  | 2  | 2  |
| Solid Ca-Al-O compounds | CA |     |     | 1  | 1  | 1  | 1  | 1  |
|               | CA2       | 1   | 1  | 1  | 1  | 1  | 1  | 1  |
|               | CA6       | 1   | 1  | 1  | 1  | 1  | 1  | 1  |

Fig. 9. Typical non-metallic inclusions observed in the molten steel after reaction with the glazed refractory. (a) Liquid Ca-Mg-Al-O: 0.5 min, (b) spinel+liquid Ca-Mg-Al-O: 0.5 min, (c) CaS: 1 min, (d) MgO+liquid Ca-Mg-Al-O: 1 min, (e) CaS+Ca-Mg-Al-O-S: 15 min, and (f) Ca-Mg-Al-O: 30 min.

Fig. 10. Calculated chemical compositions of Al-deoxidized and Ca-treated molten steel in the reaction with the glazed refractory at 1600°C.
FactSage calculation. The increasing amount of glaze can be considered as the increase of reaction time, although it may be not liner function with reaction time. The composition of glaze (51Al2O3–36CaO–7SiO2–6MgO in mass%) used in the present calculations was taken from Table 1, which was determined in the previous study.1) The chemical composition of steel except Ca was set to be the same as experimental conditions in Table 1. In the case of Ca, it was hard to estimate actual Ca amount effectively molten in steel for the chemical reaction with glazed refractory. Although total Ca content in molten steel at 0.5 min was just about 70 mass ppm, Si content in molten steel was already changed from 80 to 180 mass ppm, which means a lot of Ca had been already consumed to reduce SiO2 in glaze. In the present thermodynamic calculation, initial Ca content in molten steel was determined to be 0.05 mass% which can closely reproduce the final Al, Si and S contents in the molten steel at 30 min.

According to the thermodynamic calculations in Fig. 10, [Si] increases continuously with the reaction time, and [Al] can have maximum in the early stage and then decrease monotonically. The increase of [Al] in the early stage is due to the reduction of Al2O3 in glaze to [Al] by the highly concentrated Ca in molten steel: Al2O3 + 3[Ca] = 2[Al] + 3CaO, which can actually be observed in experimental result in Fig. 2. This reaction is only possible when [Ca] in molten steel is high enough. No significant change of [Mn] is calculated. The soluble [S] is calculated to be about 10 mass ppm in the early stage due to the formation of CaS inclusions and then it can increase back to above 40 mass ppm. This happens because the Ca is being used to reduce SiO2 in glaze to produce [Si] in molten steel. This is consistent with the results of inclusion observation.

The reduction of SiO2 in glaze can occur by the reaction with [Ca] and [Al] simultaneously:

\[
\text{SiO}_2 \text{(glaze)} + 2[\text{Ca}] = [\text{Si}] + 2\text{CaO} \text{(glaze)} \quad \text{(1)}
\]

\[
3\text{SiO}_2 \text{(glaze)} + 4[\text{Al}] = 3[\text{Si}] + 2\text{Al}_2\text{O}_3 \text{(glaze)} \quad \text{(2)}
\]

Although the amount of Si pick-up in AlCa-steel is higher than that in Al-steel, the [Al] in AlCa-steel remained much higher than that in Al-steel. This means a considerable amount of SiO2 was reduced by [Ca].

The differences between total oxygen and sulfur in Fig. 2 and calculated [O] and [S] in Fig. 9 can be considered as oxygen and sulfur associated with non-metallic inclusions.

4.2. Lade Glaze and Its Infiltration into Refractory

In general, the characteristics of the ladle glaze in the present AlCa-steel are similar to those of the previous Al-steel1) except the rapid reduction of SiO2 content in glaze with reaction time. As discussed in the previous study, the glazed layer is believed to be liquid state in the experimental condition at 1 600°C. The liquid glaze should also be co-saturated with CaAl2O4 and spinel by continuous reaction with original refractory materials.

The infiltration of the glaze into refractory in the present study is similar to the results of previous study.1) Liquid glaze can easily diffuse into porous spinel matrix region of the refractory. The infiltrated Ca–Al2O3 rich liquid glaze can react with solid corundum particle to produce the distinctive layer of CaAl2O19 and CaAl2O4. Because the CaO content in liquid glaze in AlCa-steel is higher than that in Al-steel at given reaction time, the stronger chemical reaction between infiltrated glaze and corundum particle can occur to produce the more well-developed Ca–Al–O layers around large corundum particles inside of the refractory.

4.3. Non-metallic Inclusions

The chemistry of inclusions in the present study is much complex than that in the previous study with Al-steel.1) In the present study, the glazed refractory was inserted into Al-deoxidized steel firstly. Then, Ca treatment was performed. Thus, in order to understand the evolution of inclusion, we have to consider the inclusion exist before Ca treatment. According to the previous study with Al-steel, Al2O3 and MgAl2O4 inclusions can be expected to exist in Al-deoxidized molten steel by the reaction with glazed refractory before Ca treatment. Then, Ca treatment could produce solid CaS, and modify the existing Al2O3 and MgAl2O4 to ‘Ca–Al–O’ inclusion and ‘Ca–Mg–Al–O–(S)’ inclusion, respectively:

\[
\text{Ca} + S = \text{CaS} \quad \text{(3)}
\]

\[
\text{xCa} + \text{xO} + \text{yAl}_2\text{O}_3 = \text{xCaO} \cdot \text{yAl}_2\text{O}_3 \quad \text{(4)}
\]

\[
\text{xCa} + \text{yMgAl}_2\text{O}_4 + 2z\text{Al} + (x + 3z)O = \text{xCaO} \cdot \text{yMgO} \cdot (y + z)\text{Al}_2\text{O}_3 \quad \text{(5)}
\]

According to our previous study,1) Al2O3 inclusions were produced as deoxidation products and MgAl2O4 inclusions were generated from ladle glaze. MgAl2O4 inclusions became dominant with reaction time. Therefore, we can expect that the reaction producing ‘liquid Ca–Mg–Al–O’ inclusion becomes more pronounced with reaction time in the present AlCa-steel. Of course, the liquid inclusion can easily dissolve S to become ‘liquid Ca–Mg–Al–O–S’ inclusion and also combine with solid CaS inclusion to form ‘Ca–Mg–Al–O–S+CaS’ inclusion. In addition, the Ca–Mg–Al–O inclusion can combine with MgAl2O4 inclusion to form ‘Ca–Mg–Al–O+MgAl2O4’ inclusion or ‘Ca–Mg–Al–O+MgO’ inclusion.

This is very important observation to understand the origin of spinel type inclusions frequently reported in molten steels in ladle especially with high-alumina refractories. Liquid ‘Ca–Mg–Al–O’ inclusions containing MgAl2O4 particle or solid MgAl2O4 inclusions are often reported in the secondary steelmaking process. Although it can be postulated that MgAl2O4 inclusion is formed directly by the reaction of Mg+O+Al2O3=MgAl2O4, the results of present study and previous study1) can support the postulation that MgAl2O4 inclusions in molten steel can be originated by the detachment of pre-formed MgAl2O4 particles in ladle glaze. More studies are required to fully understand the influence of ladle glaze on steel cleanliness.

5. Summary

The influence of a high alumina refractory, glazed by the typical CaO–MgO–Al2O3–SiO2 ladle slag, on the generation of non-metallic inclusions in Al-deoxidized and Ca-treated molten steel was investigated at 1 600°C.
In general, the chemical reactions of the glazed refractory in AlCa-steel were similar to those in Al-steel. However, much faster reduction of SiO₂ in the glaze and more severe corrosion of the glazed refractory were observed in AlCa-steel. The majority of non-metallic inclusions observed in molten steel were liquid Ca–Al–Mg–O–S inclusion, and its mixtures with solid CaS, MgO and spinel. The observed liquid inclusions containing MgAl₂O₄ particle supports that the spinel type inclusions often observed in the secondary steelmaking can be originated from ladle glaze.

Acknowledgment
The authors wish to express their appreciation to POSCO for providing financial support which enabled this study to be successfully carried out. Chosun Refractory Inc. is also appreciated for providing the refractory materials.

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