The Effect of Aluminum Addition on the Evolution of Inclusions in an Aluminum-Killed Calcium-Treated Steel

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Abstract: In the current study, the reduction of CaO-Al2O3 inclusions in steel by the subsequent addition of aluminum is revealed through industrial trials, laboratory experiments, and thermodynamic calculations. During the industrial production of the Al-killed Ca-treated steel, the Al2O3 content in CaO-Al2O3 inclusions increased from 72.05% to 79.83%, after the aluminum addition. In laboratory experiments, the addition of aluminum increased the Al2O3 content, and meanwhile lowered the contents of CaS and CaO in the inclusions. The average diameter of the inclusions decreased and the number density increased after the Al addition in steel, due to the formation of tiny inclusions. Based on the thermodynamic consideration, the transformation of the inclusions was attributed to the re-equilibrium of the reaction between steel and the inclusions after aluminizing. The Al2O3-riched calcium aluminate with a high melting point increased the possibility of the nozzle clogging during the continuous casting process, reducing the effect of the calcium treatment. Therefore, the addition of aluminum after calcium treatment should be avoided as far as possible.

Keywords: inclusion transformation; aluminum addition; calcium-treated steel

1. Introduction

Non-metallic inclusions in steel, such as oxides, sulfides, and nitrides [1–3], are harmful to the continuity of the steel matrix. The stress concentration at the interface between inclusion and steel was detrimental to the strength, toughness, corrosion resistance, and surface finishing performance of steels [4–9]. During the steelmaking process, aluminum was added into the molten steel as a deoxidizer, leading to the formation of a large number of Al2O3 inclusions [8,10], which were seriously harmful to the steel performance [1,11–18] and the castability of the molten steel during the continuous casting process [10,19]. In order to reduce the detrimental effect, the Al2O3 inclusions in the steel must be removed as much as possible and modified into liquid before casting [14,20,21].

Calcium (Ca) treatment was widely used to modify solid Al2O3 to liquid calcium aluminates in the molten steel. With the increase in the calcium content in steel, the transformation route of Al2O3 inclusions was Al2O3 → CaO·Al2O3 → CaO·2Al2O3 → CaO·Al2O3 → 12CaO·7Al2O3 → 3CaO·Al2O3 → CaO + CaS [22–24]. Yang et al. [17] revealed the modification mechanism of magnesium aluminum spinel by calcium treatment. Ren et al. [13] discussed the precipitation and modification of CaS in the calcium treatment process. Zhang et al. [18,21] proposed that there was a “liquid window” for calcium treatment with a minimum and maximum addition amount. Liu et al. [25] proposed the evolution mechanism of inclusions in the calcium treatment process, and discussed the influence of sampling methods, sulfur content in steel, and other factors on the calcium treatment effect. Ye et al. [26] proposed a layer-by-layer reaction model for the modification of Al2O3 by calcium. The precipitated CaS outer layer on the oxide core prevented the modification reaction. Presern et al. [27] and Korusic et al. [28] established a thermodynamic model to
predict the modification of inclusions from solid $\text{Al}_2\text{O}_3$ inclusions to calcium aluminates. Jung et al. [29] predicted the modification of the inclusions by the addition of a CaSi line in the Al-killed steel using Factsage software.

During the industrial production process of H-beam steel in a domestic steel plant, Al pellets were sometimes added into the molten steel after the Ca treatment to adjust the chemical composition of molten steel. The reaction between Al and CaO was also reported. Zheng [30] verified reducing CaO, with liquid aluminum as a reducing agent, under laboratory conditions, and the chemical reaction was $6(\text{CaO}) + 2[\text{Al}] \rightarrow (3\text{CaO·Al}_2\text{O}_3) + 3[\text{Ca}]$. Zhang et al. [31] reported that a weak calcium treatment can modify solid inclusions to full liquid ones in high-titanium steels with a low Al content, while it was hardly suitable for the high Al steel. Guo et al. [32] found that for 20Mn steel, the precipitation temperature of solid calcium aluminate inclusions decreased with the increase in the ratio of calcium to aluminum. When the $w(\text{Ca})/w(\text{Al})$ equaled to 0.10, the liquefaction degree of inclusions was the highest, the liquid fraction temperature range was the largest, and the calcium treatment effect was the best. Li et al. [33] found that aluminizing treatment can greatly improve the corrosion resistance of 430SS and FMA test pieces. However, the effect of aluminum on the calcium aluminate inclusions during the production process of steel has been little-reported.

In the current work, industrial trials, laboratory experiments, and thermodynamic calculations were performed to reveal the evolution mechanism of calcium aluminate inclusions after the aluminum addition.

2. Experimental Procedure

2.1. Industrial Trials

Two heats of industrial trials were carried out to present the effect of aluminizing after Ca treatment on inclusions. The production route of the Al-killed Ca-treated steel with a composition listed in Table 1 was “130 ton basic oxygen furnace (BOF) → ladle furnace (LF) refining → continuous casting (CC)”. The deoxidation of molten steel with aluminum was conducted during the tapping of BOF. As illustrated in Figure 1, in order to avoid the nozzle clogging during the CC process, Ca treatment was performed by adding 100 m of calcium wire (98% Ca) at 35 min of the LF refining to modify the inclusions. Two minutes later, approximately 10 kg of aluminum pellets was added in Heat 1, while there was no addition of aluminum after the Ca treatment in Heat 2. Steel samples were taken at 2 min, 36 min, 43 min, and 51 min of the LF refining, respectively.

2.2. Laboratory Experiments

To further reveal the effect of the aluminum content on the evolution of the inclusions after Ca treatment, three heats of laboratory experiments on the modification of calcium aluminate inclusions by aluminum were performed. The steel matrix is the cast billet with the same chemical composition as the aluminum-killed calcium-treated steel used in the industrial trials. Calcium treatment was carried out first, and the calcium content in the steel matrix after treatment was 73 ppm. Three samples were taken from the same steel matrix next to each other, marked as Steel 0. It was assumed that the composition, size, and quantity of the inclusions in Steel 0 were the same. The experiment was carried out using a tubular silicon-molybdenum heating. The molten steel was heated to 1873 K at an argon gas flow rate of 1.5 L·min$^{-1}$. The melt was kept at 1873 K for 30 min to make the steel composition uniform. Then, various amounts of Al pellets (99.999% Al) wrapped in the iron foil were inserted into the liquid steel, marked as Steels 1–3. Samples were taken using quartz tubes at 2 min before the aluminum addition, as well as 1 min, 3 min, and 5 min
after the aluminum addition. In order to prevent the transformation and precipitation of the inclusions in the steel during the cooling and solidification processes, the obtained steel sample was immediately quenched in the cold water. The experimental process is shown in Figure 2. The amounts of the cast billet and Al pellets added in the experiment are shown in Table 2.

| No. | Cast Billet | Al Pellets |
|-----|-------------|------------|
| Steel 0 | --          | --         |
| Steel 1 | 823        | 0.6        |
| Steel 2 | 825        | 1.4        |
| Steel 3 | 823        | 2.2        |

2.3. Sample Analysis

The contents of total calcium (T.Ca) and total aluminum (T.Al) were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES). The content of the total oxygen (T.O) was measured by the Oxygen, Nitrogen, and Hydrogen Analyzer ONH836 Series. The dissolved calcium ([Ca]), dissolved aluminum ([Al]), and dissolved oxygen ([O]) were calculated using FactSage 7.0 (Developed by McGill University and École Polytechnique de Montréal) with the databases of FToxid, FactPS, and FTmisc. The composition, size, number, and morphology of the inclusions in the steel were quantitatively analyzed using an automatic scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The accelerating voltage of the SEM was set as 15 kV, and the minimum diameter of the detected inclusions was set as 2.0 μm. The scanning area of each sample was larger than 20 mm² to obtain a sufficient number of inclusions.
3. Industrial Trials on the Comparison of Inclusions in Steel with and without Al Addition after Ca Treatment

The evolution of the average composition of inclusions during the industrial trials is shown in Figure 3. In Heat 1, the Al2O3 content in the inclusions firstly decreased due to the calcium treatment. After the addition of Al, the Al2O3 content in the inclusions increased from 72.05% to 79.83%, and the CaS content decreased from 15.18% to 7.52%. Meanwhile, the CaO content of the inclusions changed little with the addition of Al. In Heat 2 without the Al addition, the Al2O3 in the inclusions decreased after the calcium treatment. Then, the composition of the inclusions changed little during the refining process. The CaS content in the inclusions first increased then decreased since CaS was the transient product after the calcium treatment.

Figure 3. Evolution of the average composition of the inclusions in the industrial trials: (a) Heat 1 and (b) Heat 2.

Figure 4 is the average size change of the inclusions in the industrial trials. The calcium treatment led to an increase in the average size of the inclusions. After the addition of Al in Heat 1, the size of the inclusions first increased and then decreased due to the growth and floating of the inclusions, and the maximum size was 4.21 μm. In Heat 2, the size of the inclusions was reduced from 4.16 μm to 2.42 μm due to the faster floating of the larger inclusions. Figure 5 is the change of inclusion number density in the industrial trials. In Heat 1, the number density of the inclusions significantly increased from 15.34 #/mm² to 29.29 #/mm² due to a large number of small-sized Al2O3 inclusions that were generated. The number density of the inclusions changed little in Heat 2 without Al addition.

Figure 4. Evolution of the average diameter of the inclusions in the industrial trials.
#/mm² to 29.29 #/mm² due to a large number of small-sized Al₂O₃ inclusions that were generated. The number density of the inclusions changed little in Heat 2 without Al addition.

Figure 4. Evolution of the average diameter of the inclusions in the industrial trials.

Figure 5. Evolution of the number density of the inclusions in the industrial trials.

4. Effect of Al Content on the Inclusions after Ca Treatment

The effect of Al content on the inclusions after Ca treatment was revealed by laboratory experiments. The analyzed aluminum, calcium, and oxygen contents in the steel samples taken at 3 min after the addition of Al of each heat are listed in Table 3. With the increase of the [Al] content in steel, both the measured T.Ca content and the calculated [Ca] content decreased, while the oxygen content was almost unchanged, and the T.O content was kept at 24–27 ppm.

Table 3. Composition of different steel samples (mass%).

| No. | T.O [O] | T.Al [Al] | T.Ca [Ca] | T.Al [Al] | T.Ca [Ca] |
|-----|---------|-----------|-----------|-----------|-----------|
| Steel 0 | 0.0027 | 0.0006 | 0.0650 | 0.0639 | 0.0073 | 0.0012 |
| Steel 1 | 0.0026 | 0.0004 | 0.1300 | 0.1284 | 0.0039 | 0.0005 |
| Steel 2 | 0.0024 | 0.0004 | 0.2100 | 0.2085 | 0.0036 | 0.0004 |
| Steel 3 | 0.0026 | 0.0005 | 0.3100 | 0.3084 | 0.0033 | 0.0003 |

Figure 6 is the typical morphology of inclusions in steel at various [Al] contents. Before the Al addition, the inclusions were mainly liquid calcium aluminates with a uniform composition. After the Al addition in steel, the typical inclusions were still mainly calcium aluminate, however, containing a calcium aluminate core and the outer layer of Al₂O₃, the thickness of which increased with the increase of [Al] content.

Figure 7 shows the average composition evolution of inclusions during the laboratory experiments. The composition of inclusions changed little after the Al addition. Time had little effect on the change of the inclusion composition. Since the sulfur content in molten steel was 34 ppm, a large amount of CaS inclusions were generated in the molten steel during the calcium treatment. Then, the content of CaS in the inclusions decreased with a higher [Al] content. The CaO content in inclusions showed a slight decrease in the tendency. With the increase in the [Al] content from 639 ppm to 1284 ppm, 2085 ppm, and 3084 ppm, the Al₂O₃ content in the inclusions increased from 14.07% to 45.61%, 56.21%, and 62.65%, respectively. Figure 8 shows the content of Al₂O₃ inclusions 3 min after the aluminum addition with various [Al] contents during the laboratory experiments. Since the inclusion composition was almost unchanged after aluminum addition for three minutes, aluminum addition for three minutes was selected for analysis below. With the increase of Al in steel, the Al₂O₃ content in the inclusions increased.
aluminate, however, containing a calcium aluminate core and the outer layer of Al$_2$O$_3$, the thickness of which increased with the increase of [Al] content.

Figure 6. Element mapping of typical inclusions with various [Al] contents: (a) 639 ppm, (b) 1284 ppm, (c) 2085 ppm, and (d) 3084 ppm.

Figure 7 shows the average composition evolution of inclusions during the laboratory experiments. The composition of inclusions changed little after the Al addition. Time had little effect on the change of the inclusion composition. Since the sulfur content in molten steel was 34 ppm, a large amount of CaS inclusions were generated in the molten steel during the calcium treatment. Then, the content of CaS in the inclusions decreased with a higher [Al] content. The CaO content in inclusions showed a slight decrease in the tendency. With the increase in the [Al] content from 639 ppm to 1284 ppm, 2085 ppm, and 3084 ppm, the Al$_2$O$_3$ content in the inclusions increased from 14.07% to 45.61%, 56.21%, and 62.65%, respectively. Figure 8 shows the content of Al$_2$O$_3$ inclusions 3 min after the aluminum addition with various [Al] contents during the laboratory experiments. Since the inclusion composition was almost unchanged after aluminum addition for three minutes, aluminum addition for three minutes was selected for analysis below. With the increase of Al in steel, the Al$_2$O$_3$ content in the inclusions increased.

To evaluate the composition variation of inclusions, the mass fractions of CaO, CaS, Al$_2$O$_3$, and MgO were normalized and plotted into CaO–Al$_2$O$_3$–MgO and CaO–CaS–Al$_2$O$_3$ ternary diagrams. Figure 9 is the composition distribution of inclusions 3 min after the aluminum addition under various [Al] contents. The size of the points represent the diameter of the inclusions. The average composition of the inclusions was marked by a red star in each figure. The solid line was the liquidus of inclusions at 1873 K. The initial composition of inclusions was mainly CaO–Al$_2$O$_3$ in the liquid region before the Al addition. The CaS in the inclusions reached 53.85% due to the high sulfur content of 34 ppm. After the Al addition, a large number of small inclusions were immediately produced, and the CaS and CaO in inclusions nearly disappeared. The average composition of inclusions gradually shifted to the Al$_2$O$_3$ direction. With the increase in the [Al] content, the average composition of the inclusions gradually moved out of the liquid zone of the MgO–Al$_2$O$_3$–CaO diagram, indicating the formation of calcium aluminate with a high melting point.
Figure 7. Evolution of the average composition of inclusions in the heat with various [Al] contents: (a) 1284 ppm, (b) 2085 ppm, and (c) 3084 ppm.
Figure 8. Evolution of the content of Al$_2$O$_3$ inclusions 3 min after the aluminum addition with various [Al] contents.

Figure 9. Composition distribution of inclusions with various [Al] contents: (a) 639 ppm, (b) 1284 ppm, (c) 2085 ppm, and (d) 3084 ppm.

Figure 10 is the variation of the inclusions average diameters under different [Al] contents. The average size of inclusions in the initial steel was 3.75 µm. The addition of Al promoted the modification of the liquid calcium aluminate and the formation of small Al$_2$O$_3$ inclusions, resulting in the decrease in the average diameter of the inclusions. With the increase in the [Al] content, the size of the inclusions first decreased due to the formation of small Al$_2$O$_3$ inclusions, and then increased due to the aggregation and growth of inclusions. At 5 min after the aluminum addition, the average value of the average diameter of inclusions in the three laboratory experiments was 3.3 µm. It was concluded that the Al addition reduced the average diameter of the inclusions.
The metal inclusion density in steel before Al addition was 4.03 #/mm². After the addition of Al, a large number of Al₂O₃ inclusions were generated. With the increase in the [Al] content, the size of the inclusions first decreased due to the formation of small Al₂O₃ inclusions, and then increased due to the aggregation and growth of inclusions. The maximum content and the progress of the reaction, the number density of the inclusions showed a sharp increase trend, due to the aggregation and growth of inclusions. The maximum number density of inclusions reached 32.86 #/mm² at the [Al] content of 2085 ppm.

Figure 10. Evolution of the average diameter of inclusions under various [Al] contents.

Figure 11 shows the evolution of the number density of the inclusions. The number density of the inclusions in steel before the Al addition was 4.03 #/mm². After the addition of Al, a large number of Al₂O₃ inclusions were generated. With the increase in the [Al] content and the progress of the reaction, the number density of the inclusions showed a sharp increase trend, due to the aggregation and growth of inclusions. The maximum number density of inclusions reached 32.86 #/mm² at the [Al] content of 2085 ppm.

5. Evolution Mechanism of Inclusions after Al Addition

In order to further determine the evolution mechanism of the CaO–Al₂O₃ complex inclusions, thermodynamic calculations were carried out. Figure 12 shows the calculated stability diagram of the Al–Ca–O system in the molten steel at 1873 K. The equilibrium constant logK of reactions and interaction activity coefficients were from different literatures [34]. The activity of oxide products was assumed to be unified. To avoid the nozzle clogging during the continuous casting process, the [Ca] and [Al] contents of steel should be controlled within the Liquid 1 or Liquid 2 region. Among the various Al–Ca–O inclusions, only Al₂O₃·3CaO and 7Al₂O₃·12CaO inclusions were in a liquid state at 1873 K. Current steel compositions were plotted in the diagram. As the [Al] content increased from 639 ppm
to 3084 ppm, the composition of inclusions changed from liquid calcium aluminate to solid \( \text{Al}_2\text{O}_3\cdot\text{CaO}, 2\text{Al}_2\text{O}_3\cdot\text{CaO}, \) and \( 6\text{Al}_2\text{O}_3\cdot\text{CaO} \) in turn. It was indicated that the \( \text{CaO} \) in the liquid calcium aluminate was reduced by the aluminum in the steel, which agreed with experimental results.

![Calculated stability diagram of the Al–Ca–O system in steel at 1873 K.](example.png)

**Figure 12.** Calculated stability diagram of the Al–Ca–O system in steel at 1873 K.

At the steelmaking temperature, only the two calcium aluminates of \( 12\text{CaO}\cdot7\text{Al}_2\text{O}_3 \) and \( 3\text{CaO}\cdot\text{Al}_2\text{O}_3 \) were liquid in the calcium treatment process, so there was an appropriate range for the amount of calcium added, that was the “liquid window”. The variation of the inclusion of the “liquid window” with the [Al] content under different T.O contents was calculated by FactSage 7.0 with FToxid, FactPS, and FTmisc databases and shown in Figure 13. With the increase in the [Al] content, the maximum [Ca] content required to generated liquid inclusions decreased, while the minimum required [Ca] content first decreased and then kept constant. When the content of T.O was 24 ppm, 26 ppm, and 27 ppm, the height of the “liquid window” narrowed. Only inclusions in steel at the [Al] content of 639 ppm were in the liquid region, and solid calcium aluminates with a high melting point were formed in the other three cases. Under the condition of initial steel composition (Steel 0), liquid inclusions would be formed when the [Ca] content was 12–25 ppm, which was considered to be beneficial to the castability of molten steel during the continuous casting.

On the basis of the above analysis, the modification mechanism of \( \text{CaO–Al}_2\text{O}_3 \) inclusions by the Al addition was proposed, as illustrated in Figure 14. Inclusions in steel were spherical liquid \( \text{CaO–Al}_2\text{O}_3 \) before the addition of Al. After the addition of Al, the \( \text{Al}_2\text{O}_3 \) started to form on the surface of the \( \text{CaO–Al}_2\text{O}_3 \) inclusions by the reaction of Equation (1). During the modification, inclusions transformed to those consisted of an unreacted \( \text{CaO–Al}_2\text{O}_3 \) core and an \( \text{Al}_2\text{O}_3 \) outer layer. Finally, liquid \( \text{CaO–Al}_2\text{O}_3 \) inclusions were modified to solid \( \text{Al}_2\text{O}_3 \)-riched \( \text{CaO–Al}_2\text{O}_3 \). The modification process could be finished within several minutes. The higher the [Al] content in steel, the larger the \( \text{Al}_2\text{O}_3 \) content in the inclusions.

\[
2\text{[Al]} + x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \rightarrow 3\text{[Ca]} + (x - 3)\text{CaO} \cdot (y + 1)\text{Al}_2\text{O}_3 \tag{1}\]
Figure 13. Variation of the inclusion “liquid window” with Al content under various T.O contents: (a) 24 ppm, (b) 26 ppm, and (c) 27 ppm.
Figure 13. Variation of the inclusion “liquid window” with Al content.

Figure 14. Modification mechanism of the CaO–Al2O3 inclusions by the addition of Al.

6. Conclusions

The influence of Al addition on the evolution of the inclusions in the Al-killed Ca-treated steel was investigated by industrial trials, laboratory experiments, and thermodynamics analysis. The following conclusions were obtained:

(1) During the industrial production process of the Al-killed Ca-treated steel, the Al2O3 content in CaO–Al2O3 inclusions increased from 72.05% to 79.83% after the aluminum addition. In laboratory experiments, with the increase of the [Al] content from 639 ppm to 1284 ppm, 2085 ppm, and 3084 ppm, the Al2O3 content in the inclusions increased from 14.07% to 45.61%, 56.21%, and 62.65%, respectively.

(2) The addition of Al promoted the modification of liquid calcium aluminates and the formation of small Al2O3 inclusions, resulting in the decrease in the average diameter and the increase in the number density of the inclusions. At 5 min after aluminum addition, the average value of the average diameter of inclusions in the laboratory experiments was 3.3 μm.

(3) As the content of T.O increased from 24 ppm to 27 ppm, the height of the “liquid window” remained unchanged. Under the initial steel composition, liquid inclusions could be formed when the Ca content was 12–25 ppm, which was conducive to the castability of molten steel during the continuous casting.

(4) The CaO in the liquid calcium aluminate was reduced by the aluminum in steel as the reaction of 2[Al] + xCaO·yAl2O3 → 3[Ca] + (x − 3)CaO·(y + 1)Al2O3. The higher the [Al] content in steel, the larger the Al2O3 content in the inclusions. The thermodynamic calculations were consistent with the experimental results.

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