Transient Evolution of Inclusions during Calcium Modification in Linepipe Steels

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The laboratory experiments of Al2O3 inclusions modified by calcium treatment in linepipe steels with the S content of 30 ppm and 310 ppm were performed at 1873 K. Particularly, samples were taken before calcium treatment (1 minute before the calcium addition) and at various times (typically 1 minute, 10 minutes and 30 minutes) after calcium treatment to study the transient inclusions evolution during calcium modification. Traditional modification mechanism of Al2O3 inclusions is that Al2O3 inclusion is directly modified by dissolved calcium or indirectly modified via CaO formed from calcium and oxygen. In the current study, after Ca–Si alloy power addition, CaS outer layer were promptly formed on the angular Al2O3 inclusion. With the reaction of the CaS outer layer and the Al2O3 core or [O], the Al2O3 inclusion was modified to a spherical liquid calcium aluminate. Moreover, the equilibrium curve of Ca–O and Ca–S, the stability diagram of inclusions and equilibrium precipitation of inclusions during solidification in linepipe steels were calculated to study the formation of inclusions.

KEY WORDS: calcium modification; inclusions; transient behavior; thermodynamic calculation; linepipe steels.

1. Introduction

Since the demand of improved steel quality increases year by year, improving cleanliness is always one of the main tasks of steelmakers.1–5) A wide range of operating approaches including deoxidation, calcium treatment, stirring, etc. were applied throughout the steelmaking processes.6) Aluminum is one of the most popular deoxidizers used in linepipe steels. Particularly, the generated Al2O3 inclusions lead to defects such as hydrogen induced cracking7–9) and cause the clogging of submerged entry nozzle during continuous casting due to their high hardness and high melting temperature.10–16) Calcium treatment is employed to modify Al2O3 inclusions.17–27) The addition of calcium in the molten steel could modify oxide inclusions, desulfurization of steel and control shape of sulfide inclusions. However, insufficient or superfluous addition of calcium leads to incomplete or excessive modification of alumina inclusions and the formation of solid calcium alumimates or CaS, which are detrimental to the castability of linepipe steels.8,28,29)

There was a debate about the correct reaction between [Ca] and Al2O3 inclusions. Traditionally, the reactions of Al2O3 inclusions by calcium treatment were proposed as Eqs. (1) and (2).24,25,30,31) The Al2O3 inclusions were directly reduced by dissolved calcium or indirectly reduced via CaO formed from [Ca] and [O]. On the other hand, it is also reported that CaS inclusions are generated as transient phase immediately upon calcium addition, then decrease to disappearing.17,21,22) Firstly, the [S] reacts with [Ca] to form CaS in the molten steel. Whereafter, CaS modified Al2O3 to calcium aluminites.

\[ [\text{Ca}] + (x/3) \text{Al}_2\text{O}_3 \rightarrow \text{CaO}[(x-1)/3] \text{Al}_2\text{O}_3 + 2/3[\text{Al}] \] (1)

\[ x\text{Al}_2\text{O}_3 + y\text{CaO} \rightarrow x\text{CaO}y\text{Al}_2\text{O}_3 \] (2)

In the current study, laboratory experiments of modification by calcium treatment in linepipe steels were performed. The characteristics of inclusions in samples taken at various times during calcium modification were investigated to study the transient inclusions evolution. The modification mechanism of inclusions in linepipe steels was also discussed by thermodynamic calculation.

2. Experimental Procedure

Approximately 150 grams of linepipe steels before calcium treatment were melted in a MgO crucible (40 mm in inner diameter and 130 mm in depth) at 1600°C in a Si–Mo high temperature tube furnace. The schematic of the experimental furnace is shown in Fig. 1. Two sets of experiments (No.1 and No.2) were performed in the current study. As shown in Fig. 2, after the temperature reached 1600°C, no FeS was added to the molten steel in experiment No.1, while 0.1 g analytically pure grade FeS (>70%) was added to the molten steel in No.2 experiment. Ten minutes later, the first sample before calcium treatment was taken by a quartz tube and quenched into water. Then, 0.5 g Si–Ca alloy powder...
(32% Si + 65% Ca), packed in an iron foil in order to prevent the gasification and the reoxidation of pure Ca, was added into the melt immediately. The other three samples were taken at 1 minute, 10 minutes and 30 minutes after Ca-Si addition and were quenched in water.

The compositions of original linepipe steels and the two last samples of experiments were analyzed and listed in Table 1. Compared with the previous results measured using spark source atomic emission spectrometry, the steel compositions were remeasured by more accurate methods. The S contents in the steel of experiment No.1 and No.2 are 30 ppm and 310 ppm, respectively. The calcium content increases from 6 ppm to 13 ppm and 14 ppm by addition of Si-Ca power. The dissolved aluminum and calcium contents of steel were analyzed by inductively coupled plasma emission spectrometry (ICP). The silicon and manganese content of steel was analyzed by an optical emission spectrometry. The sulphur content of steel was analyzed by the infrared absorption method after combustion in an induction furnace using a sulphur analyzer. The total oxygen was analyzed using a Leco analyzer.

After the samples were mounted and polished, the 2-dimensional morphologies and the compositions of inclusions in steel samples were analyzed using SEM-EDS. In order to reveal their three-dimensional morphologies, inclusions were partially extracted from steel samples by the method of non-aqueous solution electrolysis reported by Fang in 1986. The schematic of non-aqueous solution electrolysis device is shown in Fig. 3. The electrolyte was composed of 89% methanol + 5% + glycerine + 5% triethanolamine + 1% tetramethylene ammonium chloride. The extraction was performed under argon atmosphere to avoid oxidation of the steel. During the electrolysis, the steel sample was used as the anode (cylinder, 5 mm in diameter), and a thin stainless steel tube was used as the cathode (100 mm high, 60 mm in diameter). After electrolysis, inclusions on the surface of the anode sample were partially extracted from steel samples. At least 20 typical inclusions were examined in each sample using SEM-EDS.

### Table 1. Measured composition of linepipe steels samples (wt%).

<table>
<thead>
<tr>
<th>No</th>
<th>Time</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>Al</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Original linepipe steels</td>
<td>0.0643</td>
<td>0.233</td>
<td>1.600</td>
<td>0.0030</td>
<td>0.041</td>
<td>0.0006</td>
<td>0.0014</td>
</tr>
<tr>
<td>II</td>
<td>30 min after Ca treatment of experiment No.1</td>
<td>0.0690</td>
<td>0.393</td>
<td>1.571</td>
<td>0.0033</td>
<td>0.040</td>
<td>0.0013</td>
<td>0.0068</td>
</tr>
<tr>
<td>III</td>
<td>30 min after Ca treatment of experiment No.2</td>
<td>0.0700</td>
<td>0.405</td>
<td>1.574</td>
<td>0.0310</td>
<td>0.044</td>
<td>0.0014</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

### Fig. 1. Schematic of experimental furnace.

### Fig. 2. Experimental procedure and heat pattern of the present experiments.

### Fig. 3. Schematic of non-aqueous solution electrolysis to extract inclusions from steel.

### 3. Results and Discussions

The original sulphur content was 30 ppm in experiment No.1 with adding no FeS. The morphologies and compositions of typical inclusions observed in experiment No.1 are shown in Fig. 4. Inclusions were mainly angular Al₂O₃ before adding Ca-Si alloy (Fig. 4(a)). One minute after Ca addition, inclusions were modified to nearly spherical Al₂O₃–CaS–CaO (Fig. 4(b)) and the average content of...
CaS in inclusions increased to 35% immediately. The subscript of (CaO) implies that the inclusions contained a small amount of CaO. There was only approximately 5% CaO in inclusions. Ten minutes later, the inclusions evolved to Al₂O₃–CaO(–CaS) as the CaS content in inclusions decreased to approximately 10% and CaO content increased to 30%. The shape of inclusions trended to more spherical (Fig. 4(c)). Thirty minutes after Ca treatment, the CaS in inclusions disappeared and CaO content slightly declined. Most of inclusions were spherical calcium aluminates (Fig. 4(d)).

Composition evolution of inclusions in the experiment No.1 is shown in Fig. 5. After the addition of Ca–Si alloy, the CaS content first increased, then decreased to disappearing, implying that CaS was immediately generated as a transitional product after Ca treatment, and disappeared with

![Fig. 4. Morphologies and compositions of typical inclusions observed in experiment No.1 (adding no FeS).](image)

![Fig. 5. Evolution of Al₂O₃, CaO and CaS content of inclusions in experiment No.1 (adding no FeS).](image)
reaction of CaS and Al\textsubscript{2}O\textsubscript{3}. Al\textsubscript{2}O\textsubscript{3} content promptly dropped to 37% after the addition of Ca–Si alloy, then rose up to approximately 78%. The CaO content increased gradually during calcium modification process. From the above, the evolution trajectory of inclusions during calcium treatment in the molten linepipe steels with 30 ppm S was Al\textsubscript{2}O\textsubscript{3} → Al\textsubscript{2}O\textsubscript{3}–CaS(–CaO) → Al\textsubscript{2}O\textsubscript{3}–CaO(–CaS) → Al\textsubscript{2}O\textsubscript{3}–CaO.

In the experiment No.2, the sulphur content increased to 310 ppm by adding FeS. The original inclusions were mainly angular Al\textsubscript{2}O\textsubscript{3} (Fig. 6(a)). After adding Ca–Si alloy, Al\textsubscript{2}O\textsubscript{3} inclusions were promptly modified to nearly spherical Al\textsubscript{2}O\textsubscript{3}–CaS in Fig. 6(b). As refining reactions continued, CaO content increased at the cost of decreasing of CaS in Figs. 6(c) and 6(d). The inclusions were modified to liquid ones and the shape of inclusions changed to spherical.

Fig. 6. Morphologies and compositions of typical inclusions observed in experiment No.2 (adding FeS).

Fig. 7. Evolution of Al\textsubscript{2}O\textsubscript{3}, CaO and CaS content of inclusions in experiment No.2 (adding FeS).
Figure 7 is composition evolution of inclusions in experiment No.2 with 310 ppm S content. The CaS formed promptly after addition of Ca–Si alloy. There was hardly any CaO produced in inclusions. Whereafter, CaO continuously generated and CaS content gradually decreased. The decreasing rate of CaS in steel of the experiment No 2 was slower than that of the experiment No.1 (Fig. 5). Thirty minutes after addition Ca–Si alloy, there was still approximately 15% content of CaS. The transient evolution trajectory of inclusions during calcium treatment in the molten linepipe steels with 310 ppm S was $\text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3–\text{CaS} \rightarrow \text{Al}_2\text{O}_3–\text{CaS}–\text{CaO} \rightarrow \text{Al}_2\text{O}_3–\text{CaO}–\text{CaS}$.

Figure 8 is elemental mapping of typical inclusions after addition of Ca–Si alloy in experiment No.1 (S = 30 ppm). A partially extracted inclusion at 1 min after calcium treatment is shown in Fig. 8(a). The CaS phase was generated on a $\text{Al}_2\text{O}_3$ core phase in the inclusion. Figure 8(b) is an inclusion on polished surface of the sample without erosion at 1 min after Ca–Si alloy addition. The inclusion is composed of an $\text{Al}_2\text{O}_3$ core phase and a CaS outer layer phase. It is demonstrated that calcium promptly reacts with sulphur to generate CaS on the surface of the $\text{Al}_2\text{O}_3$ inclusion after addition of Ca–Si alloy in the molten steel. Figures 8(c) and 8(d) are respectively an inclusion partially extracted and an inclusion without erosion on polished surface at 30 min after Ca–Si alloy addition. The Al, Ca and O element distribution of the inclusions are homogeneous. Simultaneously, there is almost no S element in the inclusions, illustrating CaS reacts with oxygen or $\text{Al}_2\text{O}_3$ to produce liquid calcium aluminates at 30 min after calcium treatment.

4. Thermodynamic Calculation

Figure 9 is the calculated liquidus projection of the $\text{Al}_2\text{O}_3$–CaO–CaS system using Factsage 6.4 with the FactPS and FToxid databases. The melting temperature of $\text{Al}_2\text{O}_3$, CaO and CaS are more than 2000°C. According to the present thermodynamic prediction, the minimum ternary eutectic temperature is calculated to be 1496°C at the boundary line of $3\text{CaO}•\text{Al}_2\text{O}_3$ and CaO–$\text{Al}_2\text{O}_3$. A higher content of CaO or $\text{Al}_2\text{O}_3$ in inclusions could increase the melting temperature of inclusions, illustrating that excessive or
insufficient addition of Ca alloy is detrimental to the formation of liquid calcium aluminates inclusions. Simultaneously, the CaS content could be controlled to less than 8% to avoid the generation of harmful solid inclusions.

**Figure 10(a)** is the effect of sulphur content on the equilibrium of oxygen and calcium contents in linepipe steels at 1 873 K using Factsage 6.4 with the FactPS and FToxid and FTmisc databases. The stability oxide phase evaluates from CaO·6Al2O3 to CaO·2Al2O3 to liquid to CaO. The equilibrated oxygen is maintained approximately 5 ppm. With sulphur content increases from 0 ppm to 300 ppm, there is a little variation of the oxygen content in a high Ca content (>10 ppm) due to the transformation of stability oxide, indicating that the relationship of the equilibrated oxygen content and the calcium content could hardly be influenced by S content, since the interaction between O and S is much smaller than that between Ca and O.36) The effect of oxygen content on the equilibrium of sulphur and calcium contents in linepipe steels at 1 873 K is shown in Fig. 10(b). The O content has a huge influence on the equilibrium relationship between sulphur and calcium contents in molten steel. A higher content of Ca favors to desulphuration of linepipe steels. As the dissolved oxygen increases, the desulphurization ability of calcium is weakened obviously. There are some inflection points on the curves with [O] = 10 and 50 ppm, since the transformed trajectory of oxide phase is CaO·6Al2O3 → CaO·2Al2O3 → liquid → CaO with an increasing of Ca content.

The calculated stability diagram of inclusions in Fe-0.064 mass pct C-0.23 mass pct Si –1.6 mass pct Mn–Al–Ca–O–S melt at 1 873 K using Factsage 6.4 with the FactPS and FToxid and FTmisc databases is shown in **Fig. 11.** After calcium treatment, inclusions produced in linepipe steels are mainly harmful Al2O3. When S content in linepipe steels is 30 ppm (Fig. 11(a)), various kinds of calcium aluminates are generated after addition of calcium. There is a liquid region with low melting temperature. However, when the calcium content in the steel exceeds an appropriate value, CaS with high melting temperature could be generated, which are also detrimental to steel products. With the S content in linepipe steels increases to 300 ppm in Fig. 11(b), the stability region of CaS enlarges at the cost of the narrowing of the stability region of 2CaO·SiO2. With the steel compositions of the experiment No.1 and No.2, liquid inclusions are stably generated in Figs. 11(a) and 11(b), respectively. However, the transient formation of CaS after calcium modification could hardly be predicted using calculated stability diagram, since stability diagram reflected the formation of inclusions after the equilibrium of reactions.

Since the solidification was relatively rapid during the process of samples quenched in water, it was believed that inclusions formed in liquid steel should be mostly maintained without significant transformation during the solidification. Equilibrium precipitation of inclusions during solidification for linepipe steels is calculated using Factsage 6.4 with the FactPS and FToxid and FStel databases in **Fig. 12.** When the S content in the steel was 10 ppm (Fig. 12(a)), inclusions were liquid in the molten steel at 1 600°C. During
solidification of the steel, the transformed trajectory of oxide inclusions is liquid inclusion $\rightarrow$ CaO·Al$_2$O$_3$ $\rightarrow$ CaO·2Al$_2$O$_3$ $\rightarrow$ CaO·6Al$_2$O$_3$. Simultaneously, CaS starts to be precipitated from mushy zone temperature and the amount of the formed CaS is 0.0022%. With Ca content reaches 30 ppm (Fig. 12(b)), the liquid inclusions are transformed to calcium aluminate first, then to Al$_2$O$_3$. The amount of the formed CaS inclusions increases to 0.0028% and the precipitation temperature of CaS inclusions ranges from 1,500°C to 1,350°C. After the temperature reaches approximately 1,310°C, plenty of MnS starts to be produced. When S content in linepipe steels changes to 100 ppm (Fig. 12(c)), the amounts of the formed oxide and CaS could hardly be changed, while the amount of the generated MnS inclusions increases. There Moreover, the transform temperature of the oxide inclusions and precipitation temperature of MnS rise up. When S content is less than 100 ppm, there is no CaS formed in the molten linepipe steels and CaS could precipitated during solidification. After the S content is added to 300 ppm in Fig. 12(d), a small amount of CaS could be generated together with liquid inclusions in molten steel at 1,600°C. The transform temperatures of inclusions continue to increase. The amount of inclusions could hardly change except for the increasing of MnS content.

The S content is controlled to less than 30 ppm to avoid the formation of stringer shaped MnS inclusions in linepipe
steel. Therefore, modification mechanism of inclusions during calcium treatment in the molten linepipe steels is illustrated in Fig. 13. In step 1, the angular Al₂O₃ inclusion is generated during deoxidation. After addition of Ca–Si alloy in step 2, the [Ca] immediately reacted with [S] by reaction (3). A CaS outer layer is promptly formed on the Al₂O₃ core and the CaS layer by reaction (4) due to thermodynamics. A layer of xCaO·yAl₂O₃ is generated between the Al₂O₃ core and the CaS layer. The produced sulphur enters back to the molten steel from the inclusion. Gradually, more and more xCaO·yAl₂O₃ is generated outside of the Al₂O₃ inclusion, with the core of the Al₂O₃ inclusion and the CaS phase reduce to disappearing. Eventually, the Al₂O₃ inclusion is fully modified to a spherical liquid calcium aluminate as shown in step 4. CaS is immediately generated after Ca treatment as a transitional product and disappears as the reaction progress, which is proved by the fact that the CaS content in the inclusions sharply increases first then reduces to disappearing after calcium treatment.

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

\[
    \text{CaS} + \text{Al}_2\text{O}_3 + \text{[O]} = x\text{CaO} \cdot y\text{Al}_2\text{O}_3 + \text{[S]} \quad \text{.......................... (4)}
\]

5. Conclusions

In the current study, laboratory experiments and thermodynamic calculation were performed to investigate the transient inclusions evolution during calcium modification in linepipe steels. The following conclusions were obtained:

1) The evolution trajectory of inclusions during calcium treatment process in the molten linepipe steels with 30 ppm and 310 ppm S are Al₂O₃ → Al₂O₃–CaS → Al₂O₃–CaS (–CaO) → Al₂O₃–CaO–CaS → Al₂O₃–CaO, respectively. The shape of inclusion changes from angular to nearly spherical to spherical. The decreasing rate of CaO and the increasing rate of CaS in linepipe steels with 310 ppm S are slower than that in the steel with 30 ppm S.

2) CaS is immediately generated after Ca treatment as a transitional product and disappeared as the reaction progress, which could hardly be predicted by calculated stability diagrams of inclusions in the molten linepipe steels.

3) The relationship of the equilibrated oxygen content and the calcium content could hardly be influenced by S content. As the oxygen content increases, the desulphurization ability of calcium is weakened obviously. With S content increases from 30 ppm to 300 ppm, precipitation temperature of MnS rises from mushy zone temperature to liquid steel temperature, and the amount of inclusions could hardly change except for the increasing of MnS content.

4) Modification mechanism of inclusions during calcium treatment in the molten linepipe steels includes four steps: 1) the angular shape Al₂O₃ inclusion is generated during deoxidation of steel; 2) CaS outer layer is promptly formed on the Al₂O₃ inclusion after addition of Ca–Si alloy; 3) A xCaO·yAl₂O₃ layer is generated between the Al₂O₃ core and the CaS layer by reaction between CaS and Al₂O₃ or [O]; 4) The Al₂O₃ inclusion is fully modified to a spherical liquid calcium aluminate.

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