Thermodynamic Evaluation of Formation of Oxide–Sulfide Duplex Inclusions in Steel

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Calcium is widely used for improving the castability of liquid steel, as well as for improvement of steel cleanliness and inclusion modification for better quality steel. Calcium modifies solid alumina inclusions, arising out of deoxidation of liquid steel, into liquid calcium aluminate. Depending upon the steel composition, calcium sulfide (CaS) and/or various forms of calcium aluminates may form. Sulfides are often associated with the oxide phase, which is typically known as oxide–sulfide duplex inclusion. Formation of solid calcium sulfide must be avoided during the ladle treatment of liquid steel, since it is detrimental to the castability of steel. In the present work a thermodynamic model has been developed for predicting the formation of oxide–sulfide duplex inclusions arising out of competitive reactions between [O], [S] and [Ca] in Al-killed steel. The model predictions of the present work were compared with those reported in literature, as well as with the types of inclusions observed in steel samples collected from the plant. Reasonably good agreements amongst them were observed. The results indicated that in order to achieve completely liquid calcium aluminate without forming any sulfides the sulfur content of liquid steel must be sufficiently low. With increasing S content of liquid steel, complete modification of alumina inclusions into liquid calcium aluminate becomes difficult. The maximum sulfur content to avoid formation of CaS depends upon the steel composition, principally aluminum. The sulfide inclusions are often a solid solution of CaS and MnS. Thermodynamic analysis for this system was also carried out. Based on the analysis in the present work, it is possible to predict the influence of sulfide composition on formation of duplex inclusions.

KEY WORDS: steelmaking; calcium treatment; oxide–sulfide inclusions; duplex inclusions.

1. Introduction

Non-metallic inclusions formed during deoxidation of steel are mostly oxides. But mixed oxide–sulfide types (duplex) with or without oxy sulfides are also often encountered. Like solid alumina, solid sulfide (CaS) inclusions are also harmful to the castability of liquid steel.\textsuperscript{1,2}) In addition, sulfide inclusions make steel prone to hydrogen induced cracking. When calcium is added to the liquid steel it can (a) modify oxide inclusions, (b) desulfurise steel, and (c) control shape of sulfide inclusions. However, insufficient calcium addition leads to incomplete modification of alumina inclusions and consequent formation of solid calcium aluminates having high melting points. These are detrimental to the castability of steel. On the other hand, excess calcium addition leads to formation of large number of CaS inclusions, deteriorating castability of steel besides causing erosion of ladle slide gate plate and refractory nozzles during casting.\textsuperscript{1)}

Therefore, successful calcium treatment calls for optimisation of the amount of calcium to be added to the liquid steel. With increasing S content of liquid steel, complete modification of alumina inclusions to liquid calcium aluminate becomes difficult as the liquid window for successful casting becomes narrower.\textsuperscript{21) Steel composition, particularly oxygen and sulfur contents, plays an important role in inclusion modification by calcium treatment. Calcium has strong affinity for both oxygen and sulfur. The standard free energies of formation CaO and CaS are \(-853\) kJ/mol and \(-693\) kJ/mol respectively at 1 873 K.\textsuperscript{3}) Therefore, it is important to consider which reactions are thermodynamically preferred during calcium treatment of steel. The present work aims at development of a thermodynamic model for predicting the formation of oxide–sulfide duplex inclusions arising out of competitive reactions between [O], [S] and [Ca] in Al-killed steel.

Controversy exists in the literature over the choice of thermodynamic data for reaction of calcium dissolved in liquid steel. The value of empirically determined equilibrium constant \((K_{Ca})\) for the reaction CaO(s)=[Ca]+[O] varies from \(10^{-6}\) to \(10^{-10}\), and was observed to be several orders of magnitude larger than those calculated from the reliable thermochemical data \((9.3\times10^{-11}, 4.6\times10^{-11})\).\textsuperscript{4) Large discrepancy is also observed in the data of equilibrium constant \((K_{CaS})\) of reaction CaS(s)=[Ca]+[S]. The measured value of \(K_{CaS}\) \((1.7\times10^{-7})\) was found to be several orders of magnitude larger than those calculated \((3\times10^{-9})\) from the reliable thermochemical data.\textsuperscript{5) These discrepancies have been attributed to the errors involved in experimental measurements viz., (a) chemical analysis of oxygen...
and calcium, (b) emf measurement by an oxygen sensor, and (c) reported values for the Gibbs free energy of formation of CaO. Turkdogan\(^6\) reported, on the basis of theoretical analysis that \( \Delta G^o \) of formation of CaO from its constituent elements to be in error by 10 to 30 kJ/mol. Therefore, he\(^6\) advocated use of only reliable thermochemical data in calculations since experimental measurements of equilibrium [Ca] in liquid iron suffers from large discrepancy.

Calcium dissolved in liquid steel reacts with solid alumina to form CaO–Al\(_2\)O\(_3\) inclusion according to the following reaction:

\[
x[\text{Ca}]+(1-2/3 \times x)\text{Al}_2\text{O}_3=\left(\text{CaO}\right)\left(\text{Al}_2\text{O}_3\right)_{1-x}+2/3 \times x[\text{Al}]
\]

where \(0 < x \leq 1 \) ..........................(1)

A detailed analysis of CaO–Al\(_2\)O\(_3\) binary system has established that at 1 723–1 823 K the modification of solid alumina by progressive addition of Ca occurs via solid CaO·6Al\(_2\)O\(_3\) (C\(_6\)A), CaO·2Al\(_2\)O\(_3\) (C\(_2\)A), CaO·Al\(_2\)O\(_3\) (CA) and liquid phase 12CaO·7Al\(_2\)O\(_3\) (C\(_{12}\)A\(_7\)), and finally to a solid phase 3CaO·Al\(_2\)O\(_3\) (C\(_3\)A).

Sulfur remains in dissolved form in liquid steel but during casting and solidification it reacts with manganese to form manganese sulfide inclusions in steel. Thermodynamic calculations indicated that for formation of MnS the value of [Mn]×[S] should be greater than 2 at solidification temperatures in 0.25 mass% C, 1.5 mass% Mn and 0.05 mass% S steel.\(^7\) The value of critical [Mn]×[S] depends on steel composition. For most steels [Mn] and [S] levels are not high enough for the formation of MnS in the bulk liquid. Therefore, MnS inclusion is commonly not found in liquid steel. However, as the steel solidifies, [Mn] and [S] are rejected from the solidifying dendrites, causing an increase in their concentration in the remaining liquid (interdendritic segregation), which finally leads to MnS precipitation in the interdendritic spaces towards the end of solidification. MnS is readily deformable at hot rolling temperatures and thus gets elongated to long stringers, causing anisotropy in mechanical properties of hot rolled steel products.

The degree to which Al\(_2\)O\(_3\) inclusions are modified by calcium treatment depends on the competitive reaction between [O] and [S] with [Ca] in liquid steel. When calcium is added to Al-killed steel, it first converts alumina inclusions to calcium aluminates. If the calcium aluminate that forms is high in CaO content, the inclusion has high sulfide capacity and can absorb significant quantities of sulfur. As the steel cools the solubility of sulfur in the inclusion decreases and CaS precipitates, resulting in a duplex inclusion of CaS or CaS–MnS and calcium aluminate.

CaS has low solubility in the calcium aluminate inclusions. Ozturban and Turkdogan\(^8\) have reported the maximum solubility of CaS in the calcium aluminate melt to about 4.8 mass% at CaO/Al\(_2\)O\(_3\)=1.6 at 1 873 K. Due to low solubility of CaS in liquid CaO·Al\(_2\)O\(_3\), in most of the thermodynamic calculations dealing with formation of oxide–sulfide duplex inclusions in steel, the activity of CaS has been assumed to be 1. However, in steels containing Mn, the activity of CaS may not be 1. CaS is usually found in a solid solution with MnS as a result of which, its activity is lowered. Lu et al.\(^9\) has estimated the activity of CaS and MnS using a regular solution based model. Activity of CaS in the binary CaS–MnS solid solution at 1 823 K was found to vary from 1 to 0.8 up to 0.3 mole fraction of MnS (X\(_{\text{MnS}}\)). Beyond 0.3 and up to 0.6 X\(_{\text{MnS}}\), it remained constant at 0.8. At higher MnS concentrations \( \theta_{\text{CaS}} \) again decreased sharply. A few percent of CaS in solution hardens MnS by solid solution hardening.\(^10\) Therefore, this reaction has technological significance because calcium treatment has also been used to obtain shape control of MnS phases in hot rolled steel.

Most of the sulfur in steel can be in the form of calcium sulfide in low sulfur steel (S<0.005 mass%). On the other hand if the sulfur content of the steel is high (S>0.03 mass%), there will be numerous MnS-rich sulfide inclusions containing some CaS.\(^11\) High sulfur content is desirable in steels requiring good machinability. Sulfur levels in those steels are commonly in the range of 0.020–0.050 mass%. Unlike MnS, most of the sulfides (CaS, TeS, CeS) are nearly non-deformable during rolling.\(^10\)–\(^12\) Mostly, these inclusions are quite tiny, less than 5 \( \mu \)m in size. However, depending on the steelmaking practice, even bigger inclusions may be found.

Present work involved:

1. development of a thermodynamic model for formation of oxide–sulfide duplex inclusion in Al-killed steel.
2. characterization of inclusions in samples of Ca-treated Al-killed steel using SEM-EDS.
3. validation of results of thermodynamic calculations with data reported in literature as well as inclusion characteristics observed during SEM-EDS examination of steel samples.

2. Theoretical Analysis

2.1. Formation of Duplex Inclusion with Pure CaS as Sulfide Phase

Amongst all calcium aluminates, C\(_{12}\)A\(_7\) has the lowest melting point. Therefore, at the casting temperature (~1 823 K) the targeted inclusion must be around the composition of C\(_{12}\)A\(_7\) in liquid steel to ensure good castability. In actual practice it has been observed that full modification of alumina (i.e., formation of liquid inclusion) requires Al\(_2\)O\(_3\) mass% less than 58 mass% but more than 43 mass% (i.e. mixture of CA+C\(_{12}\)A\(_7\) or C\(_{12}\)A\(_7\)+C\(_{3}\)A) in the inclusion at 1 823 K.\(^13\) Therefore, the quantity of Ca that should be added depends on concentration of alumina inclusions in steel.

Total oxygen content of steel gives fairly good idea about the concentration of oxide inclusions in low sulfur steels. Therefore, the degree of inclusion modification can be monitored by measuring total oxygen content and total Ca content of steel. Based on stoichiometry of various compounds in CaO–Al\(_2\)O\(_3\) system, values of [Ca]\(_{\text{tot}}\)/[O]\(_{\text{tot}}\) have been calculated for each compound. From the values of [Ca]\(_{\text{tot}}\)/[O]\(_{\text{tot}}\), variation of [Ca]\(_{\text{tot}}\) with [O]\(_{\text{tot}}\) of steel was deduced for various calcium aluminates, as shown in Fig.1. Similar plots have also been reported by other investigators,\(^14\)\(^15\) where reasonable agreement between the observed inclusion characteristics and the predictions have been demonstrated. Plots presented in Fig. 1 can be used to...
get an approximate idea of the type of oxide inclusion present in steel without microscopic examination. This is because, quantity wise very little Ca and O will be dissolved in liquid steel and, by and large, almost all Ca and O will be present in inclusions.

Normally, the ratio \([\text{[Ca]}_{\text{total}}]/\text{[O]}_{\text{total}}\geq 0.6\) is considered satisfactory with respect to castability.\(^{13}\) If the ratio \([\text{[Ca]}_{\text{total}}]/\text{[O]}_{\text{total}}\) is just larger than 0.6, inclusions will be a mixture of solid phase CA and liquid phase \((\text{CaO})_{0.57}(\text{Al}_2\text{O}_3)_{0.43}\) at casting temperature \(\approx 1823\) K.\(^{13}\) This may be sufficient to ensure good castability and full liquefaction of inclusion may not be required. Full liquefaction of inclusion would require \([\text{[Ca]}_{\text{total}}]/\text{[O]}_{\text{total}}\) ratio would give a realistic picture of inclusion modification. But calcium can also react with dissolved sulfur to form solid CaS. For this case, \([\text{[Ca]}_{\text{total}}]/\text{[O]}_{\text{total}}\) may not provide the true picture of inclusion modification.\(^{13}\)

In the above stochiometric analysis it is assumed that all Ca is bound only to oxygen in the inclusions. Only in this case \((\text{[Ca]}_{\text{total}})/\text{[O]}_{\text{total}}\) ratio would give a realistic picture of inclusion modification. But calcium can also react with dissolved sulfur to form solid CaS. For this case, \((\text{[Ca]}_{\text{total}})/\text{[O]}_{\text{total}}\) may not provide the true picture of inclusion modification. Precipitation of CaS along with calcium aluminates needs to be considered to describe the types of inclusions formed during calcium treatment realistically.

Thermodynamic behavior of \(\text{Al}–\text{Ca}–\text{O}–\text{S}\) system governing the formation of duplex inclusions in liquid steel can be described by considering the following sets of chemical reactions.

\[
\begin{align*}
2[\text{Al}]+3[\text{O}] &= \text{Al}_2\text{O}_3(s) \\ [\text{Ca}] + [\text{O}] &= \text{CaO}(s) \\ [\text{Ca}] + [\text{S}] &= \text{CaS}(s) \\ (\text{CaO}) + (\text{Al}_2\text{O}_3) &= (\text{CaO} \cdot \text{Al}_2\text{O}_3) \\ 12(\text{CaO})+7(\text{Al}_2\text{O}_3) &= (12\text{CaO} \cdot 7\text{Al}_2\text{O}_3)
\end{align*}
\]

Rearrangement of Eqs. (2)–(6) yields the following reaction.

\[
\frac{4}{5}(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3) + 2[\text{Al}] + 3[\text{S}]
\]

\[
= \frac{33}{5}(\text{CaO} \cdot \text{Al}_2\text{O}_3) + 3(\text{CaS})
\]

In order to form exclusively liquid \(\text{C}_{12}\text{A}_7\) inclusion, the Al and S contents of liquid steel must be less than those for the equilibrium of reaction (7). The merit of considering Eq. (7) is that it only depends on \([\text{Al}]\) and \([\text{S}]\) contents and not on the \([\text{Ca}]\) content. Therefore, the discrepancy associated with the thermodynamic data of \([\text{Ca}]\) already discussed in the previous section, gets eliminated due to cancellation effect while deriving the Eq. (7). Applicability of Eq. (7) is also consistent with the fact that during formation of CaS, highly modified form of calcium aluminates get transformed into the lower modification of calcium aluminates.\(^{12}\)

Equilibrium constant of reaction (7) is given by:

\[
K_6 = \frac{(a_{\text{CaO} \cdot \text{Al}_2\text{O}_3})^{1.5}(a_{\text{CaS}})^3}{(a_{12\text{CaO} \cdot 7\text{Al}_2\text{O}_3})^{1.8}(h_{\text{Al}})^1(h_{\text{S}})^1}
\]

where \(a_i\) is the activity of \(i\) (where \(i = \text{CaO} \cdot \text{Al}_2\text{O}_3, 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3\) or CaS) with respect to the pure standard state, and \(h_i\) (\(i = \text{Al}\) and \(S\)) is the activity for the 1 wt% standard state.

The activities of \(\text{Ca}\) and \(\text{C}_{12}\text{A}_7\) have been considered to be 1 in the present work, though the activity of liquid \(\text{C}_{12}\text{A}_7\) has been reported to vary from 0.8 to 1.\(^{14}\) Equilibrium constant for reaction (7) has been determined from the free energy data of reactions (2)–(6) collected from various standard data sources.\(^{16–20}\)

Table 1 presents the free energy data of various reactions considered in the present work. For this, thermodynamic data were collected from different sources.\(^{16–20}\) Then they were carefully analyzed. Wherever significant discrepancies were found, special attention and scrutiny were carried out in the present investigation, and the data which were considered to be most reliable were accepted and reported in Table 1. In Table 1, more than one source has been noted for some reactions. The reason is that the values have been arrived at by combining component reaction data from different sources. An example is \(\Delta G^\circ\) for the reaction:

\[
[Mn] + [S] = \text{MnS(s)}
\]

for which \(\Delta G^\circ\) for formation of MnS from pure Mn and S were taken from source 1 (Kubaschewski et al.\(^{19}\)), free energies of dissolution of Mn and S, \(i.e.\)

\[
\text{Mn(s)} = [\text{Mn}]_{1\text{mass}\%}
\]

\[
1/2 \text{S}_2(g) = [\text{S}]_{1\text{mass}\%}
\]

were respectively taken from sources 2\(^{8}\) and 3.\(^{16}\)

Considering the above, following relationship between \([\text{Al}]\) and \([\text{S}]\) content of liquid steel at equilibrium with liquid \(\text{C}_{12}\text{A}_7\), solid CA and CaS inclusions at 1823 K has been derived assuming the Henrian activity coefficients of \([\text{Al}]\) and \([\text{S}]\) to be equal to 1:
Fig. 2. Comparison of present prediction with that of Geldenhuis et al.\textsuperscript{13}) ($a\textsubscript{CaS} = 1$).

\[
[mass\%Al]^2 \times [mass\%S]^3 = 2.05 \times 10^{-9} (a\textsubscript{CaS})
\]  
Assuming $a\textsubscript{CaS}$ to be equal to 1:

\[
[mass\%Al]^2 \times [mass\%S]^3 = 2.05 \times 10^{-9}
\]  

Geldenhuis et al.\textsuperscript{13}) have reported the variation of $[mass\%Al]^2 \times [mass\%S]^3$ (SAL) with mass%$Al_2O_3$ content of calcium aluminates. However, they have not reported the details of their calculation procedure. They\textsuperscript{13}) reported the value of SAL obtained in the present work was found to be about 2.5 times lower than that of Geldenhuis et al.\textsuperscript{13}) Figure 2 compares the predictions of present work with those of Geldenhuis et al.\textsuperscript{13}) The differences are likely to be due to some difference in assumed compositions of inclusions in the two studies (viz., 48 mass% CaO in the present work and 42 mass% in theirs). Since mass% CaO has been assumed as higher for the present work, the inclusion has higher activity of CaO, hence, more desulfurization of the melt.

Larsen and Fruehan\textsuperscript{14}) considered equilibrium similar to the present work where $a\textsubscript{CaS} = 0.75$ had been assumed in the calculations. In the present work, calculations have been carried out for the same value of $a\textsubscript{CaS}$ and results of present calculation have been compared with those of Larsen and Fruehan\textsuperscript{14}) in Fig. 3. It is evident from the figure that results of present calculation matched quite well with those of Larsen and Fruehan\textsuperscript{14}) at 1 773 K, whereas, some difference was observed for 1 823°C.

From Fig. 3 it is clear that in order to obtain exclusively liquid $C_{12}A_7$ inclusions without forming any solid (CA or CaS) inclusions at a given temperature, the composition of steel must lie below the line. Since $C_{12}A_7$ is liquid at 1 823 K, it is possible to form liquid inclusion slightly above the line as its activity is less than 1. If Ca is injected into the liquid steel having composition above the line, the alumina would be converted to CA along with CaS. If S content of steel is high, the calcium would first react with S until the sulfur content goes below the line before liquid oxide inclusions will form. Clearly, higher S content delays the formation of liquid inclusions.

The line for 1 823 K is relevant for the nozzle clogging during casting. At 1 823 K, liquid steel has started solidifying with consequent segregation and enrichment of solute concentrations in the liquid portion. Since the present analysis does not consider this effect, the predictions for 1823 K would be applicable only approximately to real situation in the plant. Furthermore, concentration of dissolved Al and S in liquid steel will increase during solidification due to segregation, causing sulfide and alumina rich inclusions to possibly form in the last liquid to solidify even though these do not form at 1 823 K.

If the value of the product $[mass\%Al]^2 \times [mass\%S]^3$ is larger than the equilibrium value calculated for the reaction (7), modification of inclusions will not be successful and solid CaS rather than the liquid inclusion will form. Hence, this equilibrium relationship defines steel composition range that will allow successful inclusion modification. Assuming $a\textsubscript{CaS} = 1$, the limiting value of sulfur content of steel to avoid CaS precipitation before a liquid CaO · $Al_2O_3$ inclusion forms can be obtained when the product of $[mass\%Al]^2 \times [mass\%S]^3$ in steel is less than 2.05 \times 10^{-9} at 1 823 K. Larsen and Fruehan\textsuperscript{14}) assumed $a\textsubscript{CaS} = 0.75$. For this, Figs. 4 and 5 have been presented.
[mass%S]×[mass%Al] with [mass%Al] for different sulfur content of steel is shown in Fig. 4. The maximum allowable sulfur content is determined for various [mass%Al] contents of liquid steel, as shown in Fig. 5. It is evident from the figure that for a steel containing 0.03 mass% Al, the maximum allowable S level should be below 0.01 mass% at 1823 K (Figs. 4 and 5).

2.2. Formation of Duplex Inclusion with CaS–MnS Sulfide Phase

Activity of CaS in CaS–MnS solid solution was determined from the regular solution based model reported by Lu et al.9) Details of the model are as follows:

\[ \Omega = 2RT_c \] ..........................(14)

Where \( \Omega \) is a parameter related to the interaction energies in the solution and \( T_c \) is critical temperature at the miscibility gap. For CaS–MnS solid solution \( T_c = 1403 \) K.9)

Activities of CaS and MnS in CaS–MnS solid solution can be estimated from the following correlations.

\[ X_{\text{CaS}} + X_{\text{MnS}} = 1 \] ..........................(15)

\[ \ln \left( \frac{a_{\text{CaS}}}{X_{\text{CaS}}} \right) = \frac{\Omega}{RT} (1 - X_{\text{MnS}}) \] ..........................(16)

From Eqs. (15) and (16), activity of CaS, and from Eqs. (15) and (17), activity MnS in CaS–MnS solid solution has been estimated for different values of \( X_{\text{CaS}} \). Variation of activities of CaS and MnS with \( X_{\text{CaS}} \) at 1823 K is shown in Fig. 6. Variation of SAL (mass[%Al]×[mass%S]) with activity of CaS is shown in Fig. 7. There is a gradual increase in the value of SAL with \( a_{\text{CaS}} \), and finally it attained the value of 2.05×10^{-9} when \( a_{\text{CaS}} \) becomes unity.

3. Experimental Results and Discussions

In order to test the applicability of the above theoretical analysis, samples of calcium treated Al-killed steel were collected from the LD-1 shop of Tata Steel, which only occasionally makes this grade of steel for manufacture of the steel wires for various applications. Due to this reason, only four samples could be collected. Chemical composition of the steel samples is presented in Table 2. Characteristics of inclusions in steel samples were examined using energy dispersive spectroscopy (EDS) fitted with a JEOL make scanning electron microscope (SEM).

Most of the inclusions in steel samples were found to be quite small in size (<6 μm). Mostly, inclusions had a cal-
Calcium aluminate core surrounded with a sulfide ring of CaS–MnS or CaS. A typical oxide–sulfide duplex inclusion observed in liquid steel sample after calcium treatment is shown in Fig. 8. X-ray map of the constituent elements of the same is also shown in Fig. 8. Chemical compositions of inclusions were determined from the EDS. These are noted in Tables 3 and 4. Detailed compositions of some of the inclusions observed in samples of the 4 heats (Fig. 9) have been included in an additional table (Table 4). Data of only few representative samples have been presented as illustration. Otherwise the Table will be too long. Our SEM-EDS does not give the accurate value of oxygen that is why it has not been shown against the elemental analysis of each inclusion (Table 4). Inclusion compositions have been deter-
mined from elemental analysis based on the stoichiometry of each compound.

Types of calcium aluminates in the core of duplex inclusions were identified from the ratio of mole percentages of CaO and Al2O3 in those inclusions (Tables 3 and 4). In all duplex inclusions, lower modification of calcium aluminates (CA2 and CA6) were also observed in addition to CA and C12A7. Corresponding to the average mole fraction of CaS/0.7, observed during inclusion characterization, the activity of CaS was found to be equal to 0.8. Substituting this value of $a_{CaS}$ in Eq. (12) relationship between [mass%S] and [mass%Al] content of steel was determined for 1 773 and 1 823 K temperatures as shown in Fig. 9.

Theoretical predictions for these temperatures were compared with plant data (Fig. 9). Plant data were close to 1 823 K line and mostly below it, indicating that inclusions listed in Table 4 seem to have originated at relatively lower temperatures (subsequent to the ladle treatment). From the results of prediction it is also evident that in order to obtain full modification of alumina into liquid calcium aluminate in Al-killed steel and to avoid formation of sulfide, the sulfur content should be quite low. For example, for a steel containing 0.04% Al at 1 823 K, the sulfur content must be below 0.008 mass%. Casting temperature is another important parameter. The higher the temperature, the easier it is to form liquid C12A7 inclusions. For 0.04 mass% Al in steel at 1 873 K the sulfur content needs to be 0.014 mass%, whereas, at 1 823 and 1 773 K the sulfur content should be below 0.01 mass% and 0.00 mass% respectively for the same steel.

Ideally, for complete liquefaction most of the inclusions should be of C12A7. In practice, inclusions should be at least CA/C12A7. However, presence of C12A7 in only one case (Table 4) essentially reflects inadequacies of the current calcium treatment practice. Commonly, varieties of calcium aluminates originate during the Ca-treatment due to variation in the local concentrations of Ca and O in liquid steel. Such variations in inclusion composition have been reported by others also viz., Larsen and Fruehan and Tiekink et al.

In addition to Ca, Al and S, there are other elements in steel which can influence the type of inclusions formed. Presence of Si in steel is expected to affect the composition of inclusions formed in steel. The grade of steel considered in the present case for comparing the theoretical predictions, contained 0.02 mass% Al, 0.5 mass% Mn and 0.02 mass% Si. Inclusions formed in the steel contained 2 to 17 mass% SiO2. This amount of SiO2 is likely to lower the activity of CaO, Al2O3 and C12A7, and slightly affect the predictions. In addition to this, Mn content of steel is ex-

| Inclusion SEM-EDS Elemental analysis (atom%) | Calculated oxide and Sulfides (mole%) | CaO/Al2O3 | Expected inclusion type |
|---|---|---|---|
| 1. Al:56.4, Si:2.9 Ca:33.4, Mn:0.0 S:2.7, Mg:4.5 | Al2O3=40.9, SiO2=4.2 CaO=44.5, MnO=0.0 CaS=3.9, MgO=6.5 | 1.09 | CA+CaS |
| 2. Al:36.0, Si:1.6 Ca:26.6, Mn:11.3 S:22.9, Mg:1.5 | Al2O3=30.5, SiO2=2.8 CaO=25.5, MnO=19.2 CaS=19.6, MgO=2.5 | 0.84 | CA2+CaS+MnS |
| 3. Al:4.6, Si:0.4 Ca:15.6, Mn:33.5 S:44.7, Mg:1.2 | Al2O3=4.3, SiO2=0.7 CaO=8.3, MnO=63.3 CaS=21.1, MgO=2.2 | 1.91 | C12A7+MnS+MnO |
| 4. Al:53.1, Si:6.3 Ca:34.5, Mn:0.0 S:1.9, Mg:4.96 | Al2O3=36.7, SiO2=8.7 CaO=42.6, MnO=0.0 CaS=1.5, MgO=6.9 | 1.26 | CA+CaS |
| 5. Al:25.8, Si:4.3 Ca:33.2, Mn:4.3 S:29.4, Mg:3.0 | Al2O3=22.3, SiO2=7.4 CaO=14.1, MnO=7.5 CaS=43.4, MgO=5.3 | 0.63 | CA2+CaS+MnS |
| 6. Al:53.5, Si:4.5 Ca:25.8, Mn:1.7 S:8.1, Mg:6.4 | Al2O3=41.1, SiO2=6.9 CaO=29.7, MnO=2.6 CaS=9.9, MgO=9.8 | 0.72 | CA2+CaS+MnS |
| 7. Al:56.0, Si:5.9 Ca:33.9, Mn:0.0 S:11.1, Mg:3.0 | Al2O3=39.5, SiO2=8.3 CaO=46.2, MnO=0.0 CaS=1.6, MgO=4.3 | 1.17 | CA+CaS |

Table 4. Composition of some of the representative inclusions observed in steel samples.

Fig. 9. Comparison of duplex inclusions found in plant samples with theoretical predictions ($a_{CaS}$=0.8).
pected to affect the composition of sulfide phase. The higher the concentration of Mn, the greater the concentration of MnS in CaS–MnS inclusions. This lowers the CaS activity, and hinders the modification of oxide inclusions as indicated by Eq. (13). However, the presence of Mn and Si have only minor effects on inclusion modification during calcium treatment in most of the Al-killed steel.

4. Conclusions

In the present work a thermodynamic model has been developed for predicting the formation of oxide–sulfide duplex inclusions arising out of competitive reactions between [O], [S] and [Ca] in [Al]-killed steel. The same was compared with literature and plant data. Salient findings of the work are as follows.

(1) Based on the stoichiometry of various compounds in CaO–Al₂O₃ system, relationship between [Ca] total with [O] total of steel was deduced for different calcium aluminate inclusions in the form of plots. Such plots have advantage that these can be used to get an approximate idea of the type of oxide inclusion present in steel without microscopic examination.

(2) Good castability requires completely liquid calcium aluminate inclusion without forming any sulfide. The results indicated that in order to achieve it the sulfur content of liquid steel must be low. With increasing S content of liquid steel, complete modification of alumina inclusions into liquid calcium aluminate becomes difficult and the liquid window for successful casting becomes narrower.

(3) The model predictions were compared with those available in literature as well as with the types of inclusions observed in steel samples collected from the plant. Reasonably good agreements amongst these have been observed.

(4) The sulfide inclusions are often a solid solution of CaS and MnS. Thermodynamic analysis for this system was also carried out. Based on the analysis in the present work, it is possible to predict the influence of sulfide composition on formation of duplex inclusions.

(5) The higher the temperature, the easier it is to form liquid calcium aluminate inclusions. Therefore, it is desirable to carry out calcium treatment at higher temperatures for successful inclusion modification.

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