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Abstract

A study has been carried out to understand the modification of alumina inclusions in an Al-Killed high sulphur steel with calcium treatment in 150 tonne steel ladle. To avoid abnormalities during casting, inclusions chemistry needs to be controlled so that these inclusions are in liquid phase during continuous casting of steel. For calcium treatment to be effective, general practice is to desulphurise the steel so as to reach sulphur levels below 0.010% to prevent formation of solid CaS inclusions that are harmful to steel quality and final properties. To avoid this additional desulphurising step which involves cost and is time consuming, the authors have developed a new approach of calcium treatment of steel at an industrial scale. This approach involves treating the liquid steel with calcium treatment at low aluminium levels which enables formation of liquid calcium aluminate inclusions ($C_{12}A_7$) in the melt and then addition of sufficient aluminium for achieving grade requirement (i.e.

splitting of aluminium addition before and after the calcium treatment). It is understood from this study that the complete transformation of alumina inclusions and CaS formation depends on activities of aluminium, sulphur and temperature of liquid steel. Based on this principle, Al-S diagram has been developed and calcium treatment has been modified accordingly. The inclusion transformation and morphology was studied using SEM/EDS analysis. It was observed that completely modified duplex calcium aluminate inclusions of $C_{12}A_7.CaS$ and $C_3A.CaS$ type and partially modified CA.CaS were found in steel samples from billet. The formed CaS is found in the liquid state as confirmed by the its activity value which is less than one. Both of these support our assumptions

1. Introduction

The clogging of SEN (Submerged entry nozzle) due to the deposition of inclusions, such as alumina is a long-witnessed problem in the continuous casting of aluminium-killed low-carbon steels[1]. Inclusions in steels are very harmful as they not only deteriorate the mechanical properties such as fatigue and fracture strength of the final product, but also disrupt the continuous casting by nozzle clogging [2-4]. Hence, modification of inclusions to transform them to liquid inclusions reduces nozzle clogging problems in steel industry [5-9].

The main objective of inclusion modification is to transform solid inclusions to liquid inclusions by changing the chemical and phase composition in aluminium killed steel [10-12]. This modification is usually carried out by calcium treatment of molten steel and the amount of calcium added should be appropriate in order to transform solid alumina inclusions to liquid ones. Researchers have pointed out that the castability problems due to clogging could be

avoided even when inclusions are 50% liquid at casting temperatures [6-7]. However, in case of high sulphur steels, if dissolved sulphur is greater than 100ppm, then sulphur reacts with calcium resulting in CaS inclusions which are solid inclusions and are found to be more detrimental than Al_2O_3 inclusions[13].

Adequate information about the modification of alumina inclusions by calcium treatment in low sulphur Al-killed steel melts is available. Verma et al. reported that increased sulphur contents (in the range 40–100ppm) had little effect on the extent of modification of Al_2O_3 inclusions in a Ca-treated steel [14]. However, very limited research work was carried out on modification of oxide inclusions in high sulphur Al-killed steels by Ca-treatment. This study presents the research work on modification of oxide inclusions in the Al-killed high sulphur steels by Ca-treatment in industrial scale in a 150 tonne ladle furnace.

2. Experimental Procedure

Industrial trials with calcium treatment were carried out in high sulphur Al-Killed steel of 150 tonne during closed casting in a billet caster machine. After completion of secondary metallurgy operations, calcium treatment and aluminium additions were made as discussed below.

1. Addition of calcium to transform the solid alumina to liquid alumina at high sulphur and low aluminium as per the Al-S diagram (discussed later). CaO forms here instead of CaS because we added only small amount of aluminium so still there will be dissolved oxygen in the steel melt which can react with excess Ca available.

2. After four to five minutes of modification interval, remaining aluminium is added to meet the grade requirement and retain the modified alumina inclusions from step 1

The flow chart below shows (Figure 1) the conventional and adopted new approach of modification of inclusions in high sulphur steels.
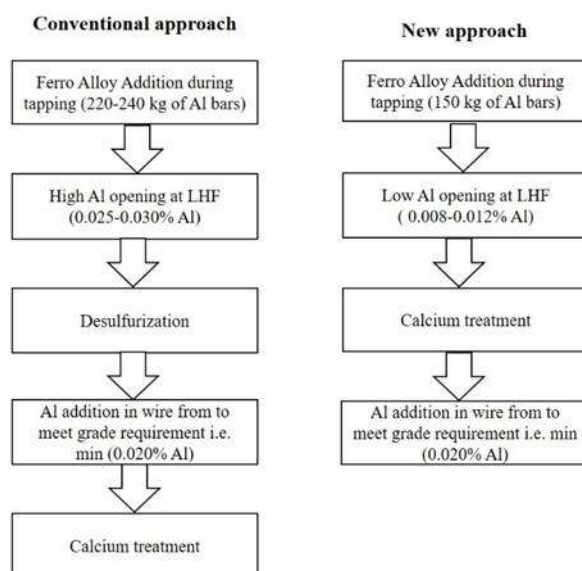

Figure 1. Flow chart of conventional and new calcium treatment approach

Typical chemical composition of steel samples of four different heats before and after calcium treatment was presented in Table 1 and 2 respectively.

Table 1. Steel composition (wt. %) during the calcium treatment

Sample ID	Amount of calcium addition (kg)	Overall chemical composition						
		C	Mn	P	S	Si	Al	Ca (ppm)
Heat A	20	0.170	0.730	0.022	0.023	0.216	0.004	37
Heat B	20	0.160	0.710	0.014	0.019	0.240	0.008	33
Heat C	17	0.160	0.880	0.017	0.023	0.210	0.012	32
Heat D	17	0.180	0.740	0.015	0.023	0.190	0.006	30

Table 2. Final steel composition (wt. %) after calcium and aluminium addition

Sample ID	Overall chemical composition						
	C	Mn	P	S	Si	Al	Ca (ppm)
Heat A	0.170	0.790	0.023	0.015	0.202	0.028	26
Heat B	0.170	0.700	0.016	0.010	0.220	0.039	24
Heat C	0.160	0.860	0.016	0.013	0.200	0.030	19
Heat D	0.180	0.720	0.015	0.007	0.230	0.032	23

Samples of calcium treated Al-killed steel were collected from the solidified billet. Characteristics (composition and morphology) of inclusions in steel samples were examined using a Tungsten filament Carl Zeiss EVO 18 scanning electron microscope (SEM) fitted with an Oxford Instruments energy dispersive spectroscopy (EDS). Modification of inclusions with detailed SEM/EDS analysis and ternary diagrams are discussed in the following section.

3. Results and Discussions

3.1 Al-S Phase diagram:

Figure 2 represents the Al-S equilibrium relationship with liquid calcium aluminate inclusions at 1550°C. The final sulphur content in steel for all heats is above the optimum level, i.e. 100ppm as shown in Table 1. The minimum aluminium content required for all these heats is 0.02%, which is typical of Al-killed steels. To increase the size of the liquid inclusion window, experiment was conducted at high oxygen ppm (i.e. at low Al) and high sulphur hence as per the Al-S diagram (as shown in Figure 2) and calcium treatment has been advanced before the addition of further aluminium required to meet the grade specification.

By comparing the experimental data of Choudhary et al.,[15] and Geldenhuis et al.,[16] with the calculation results in the present work, a good agreement was observed as shown in Figure.2. Therefore, [Al]–[S] equilibrium diagram in the present article can be used to evaluate modification of inclusions effectively.
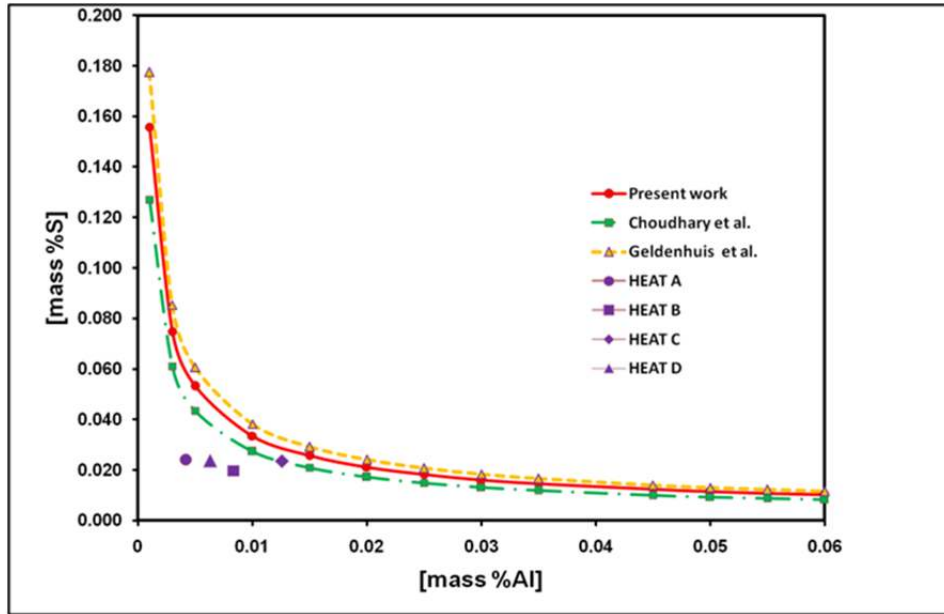
Figure 2. [Al]-[S] equilibrium relationship of liquid calcium aluminate saturated with CaS assuming activity of CaS is equal to one at 1823 K (1550°C)

It is known that elements such as Al, Ca and S affect the modification of alumina inclusions and the sulphide formation in steels [3], [15]. To avoid nozzle clogging in the casting process, calcium is usually injected at the end of refining period to modify oxide inclusions and to control sulfide inclusion formation in the steel. However, in high sulphur Al-killed steel, if calcium treatment process is not properly controlled, then it can result in formation of oxide and sulphide inclusions which usually have higher melting points than the liquid steel and could result in nozzle clogging during continuous casting. Jie Xu et al [17] derived the equilibrium relationship of [Ca]-[S] to form CaS at different temperatures. It was found that when the dissolved sulphur in steel is 0.025%, then the amount of calcium that is required to form CaS inclusions is 0.00425% at steelmaking temperatures (1600°C). But measurement of the activity of calcium or dissolved calcium content in the steel is not easy and equally it is difficult to determine the precipitation kinetics of CaS formation based the [Al] and [S] content in the liquid steel. For better understanding of our steel melt (high sulphur Al-killed steel), the equilibrium relationship between [Al] and [S] with liquid calcium aluminate saturated with

CaS 1823K(1550°C) was developed as shown in Figure 2 based on the reaction as shown in equation (6). Table 3 shows the free energy data of various reactions considered in the present work.

Table 3. Free energy data of reactions considered in the present work

Equation number	Reaction	ΔG, J mol-1	ΔG_{1873}, KJ mol-1	Reference
1	$2[Al] + 3[O] = Al_2O_{3(s)}$	-1205090 +387.73T	-479.0	[18]
2	$[Ca] + [O] = CaO_{(s)}$	-629998 + 144.75T	-359.0	[15]
3	$[Ca] + [S] = CaS_{(s)}$	-542531+124.15T	-310.0	[15]
4	$12CaO_{(s)} + 7Al_2O_{3(s)} = 12CaO.7Al_2O_{3(l)}$	617977-612T	-528.0	[15]
5	$CaO_{(s)} + Al_2O_{3(s)} = CaO.Al_2O_{3(s)}$	-19246 - 18T	-53.0	[15]

$$\left(\frac{4}{5}\right)(12CaO.7Al_2O_3) + 2[Al] + 3[S] \rightarrow \left(\frac{33}{5}\right)(CaO.Al_2O_3) + 3(CaS) \qquad (6)$$
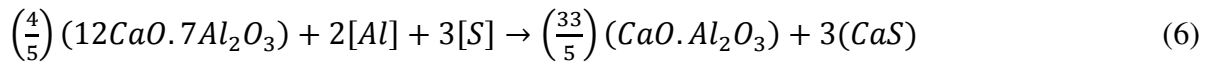
[Al]-[S] equilibrium diagram is calculated from Equation (6), which is deduced by combining the equations listed in Table 3. Table 3 presents the corresponding free energy data of various reactions considered in the present work. a_i is the activity of i(where i =CaO·Al$_2$O$_3$, 12CaO·7Al$_2$O$_3$ or CaS) with respect to the pure standard state, and $[h]_j = f_j[W]_j$ (j = Al and S) is the activity for the 1 wt% standard state. f_j is the Henerian activity coefficient of elements dissolved in liquid steel.

In order to form liquid C$_{12}$A$_7$ inclusion, the Al and S contents of liquid steel must be less than those for the equilibrium of reaction (6). The merit of considering equation (6) is that it only depends on [Al] and [S] contents and not on the [Ca] content as discussed earlier. Equilibrium constant of reaction (6) is given by:

$$K = \frac{a_{CaO.Al_2O_3}^{33/5} a_{CaS}^3}{a_{12CaO.7Al_2O_3}^{4/5} h_{Al}^2 h_S^3}$$

Figure 3 to Figure 6 show that the inclusions composition distribution on ternary $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-CaS$ plots. The inclusions are typically mixtures of CaO, Al_2O_3, MgO and CaS. For $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-CaS$ plots, mole fractions of CaO, Al_2O_3 and CaS was normalized to 100% after deducting sulphur from the available calcium from the EDS data. Inclusions of at least approximately 50% liquid (indicated by a dashed line) at 1823 K (1550°C), are plotted in Figure 3(a) and 3(b).

The composition of inclusions from one sample (Heat A) is plotted on the ternary diagrams as shown in Figure 3 to understand the castability behaviour. It is observed that the alumina inclusions formed during de-oxidation process converted into complex oxy-sulfide non-metallic inclusions i.e. calcium aluminate and calcium sulfide type as shown in Table 4.

In the new approach calcium was added at high-S and low-Al levels as per equation 6 which favours the formation of liquid calcium aluminates. Due to the availability of higher oxygen content (de-oxidation not complete) and high sulphur, formation of CaO and CaS are inevitable. Addition of aluminium for meeting the grade requirement has been carried out after 4 to 5 minutes of calcium treatment along with mild purging. Such a treatment could cause a shift of equilibrium towards products of the reaction (right side of the equation). But in actual practice, this shifting was not visible. This could be attributed to previously formed liquid calcium aluminates joining the slag phase during the treatment period (from continued purging), and the lower quantity of alumina formation due to less availability of dissolved oxygen at that point. This is also supported by the decrease in sulphur content in the steel after calcium treatment and final aluminium addition as shown in Table 2.The alumina formed during second stage of aluminium addition might have taken care by the transient phases of CaO or CaS [18-20] or by already formed liquid calcium aluminate as per the equation (7). This possibility remains to be studied further. However, no adverse effect on the castability behaviour was observed in our case.

$$(CaO)_{(liquid)} + X\, Al_2O_{3(solid)} = (CaO.XAl_2O_3)_{(liquid)}\ ^{[21]} \qquad\qquad (7)$$
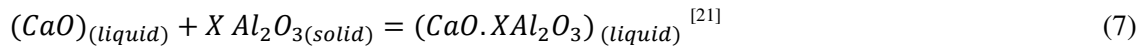
From a ternary diagram of CaO-Al$_2$O$_3$-MgO in Figure 3(a) it was observed that most of the calcium aluminate inclusions are in liquid region (C3A+ C$_{12}$A$_7$ type). The same may be deduced from Figure 3(b). In this case, we considered MgO because the slag of these steel making heats is supersaturated with MgO for operational reasons and it is also observed from EDS data that most of the inclusions contain MgO which is coming from either carryover slag or from refractory erosion as ladle lining is composed of Mag carbon bricks. Even with high sulphur content, it can be seen that the formation of CaS is low, from this new approach. It is observed that most of the inclusions are completely transformed to calcium aluminates with a small amount of MgO. Story et al. [22] have discussed the effect of MgO in increasing the liquid fraction of CaO-Al$_2$O$_3$ type inclusions. From Figure 3(b), some of the inclusions (including sulfides) are outside the 50% liquid region and with minimum CaS content. From this Figure 3(b), clogging would be expected during the casting of this heat. But, no clogging was observed and the slide gate behaviour was stable. This effect of MgO, as discussed by [22] can also be seen here. Thus, it can be seen that most of the solid alumina inclusions have been effectively modified, and those that are only partially modified do not cause issues with nozzle clogging. After inclusion transformation, average "modified $\frac{Ca}{Al}$ ratio" $= \frac{Ca-(S-2)}{Al}$, of Heat A was 0.44. The number "2" in the "modified $\frac{Ca}{Al}$ ratio" represents the approximate solubility of S in liquid calcium aluminates. This also indicates that stable casting can be ensured as suggested by Story et.al [23].
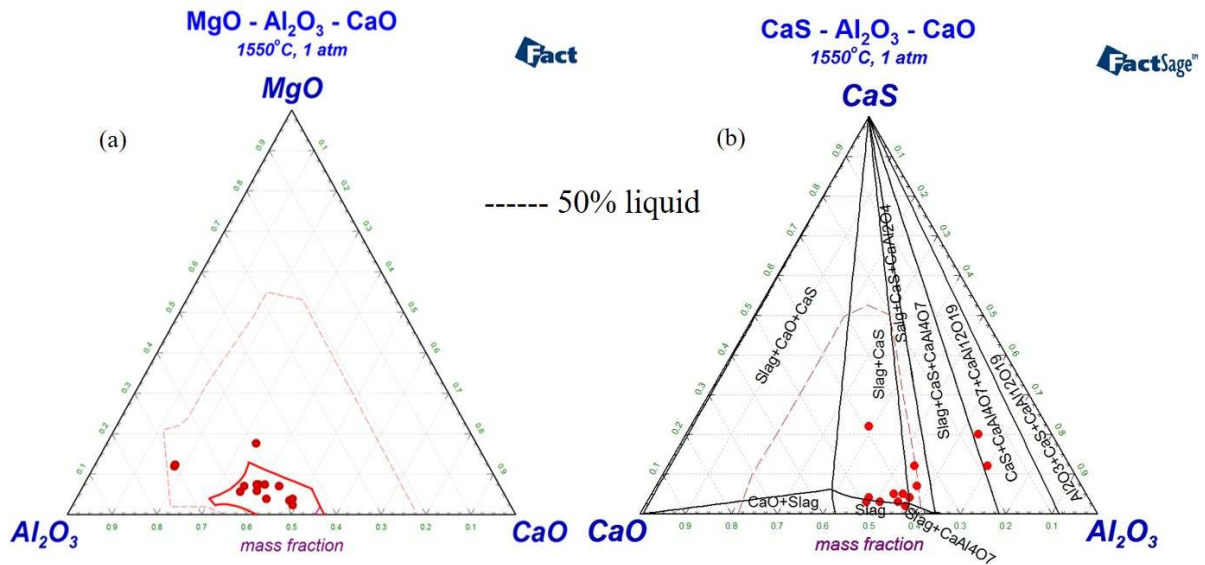
Figure 3. Ternary plot of inclusions of a Heat A

The inclusions plotted on the ternary diagrams of Heats B, C and D are shown in Figure 4, Figure 5 and Figure 6 respectively. In all these cases, most of the calcium aluminate inclusions follow the same trend like in Heat A, where inclusions lie in the 50% liquid region. From Figure 4(a), Figure 5(a) and Figure 6(a) of the $CaO-Al_2O_3-MgO$ ternary diagrams, most of the inclusions are in the complete liquid ($C_3A+ C_{12}A_7$) or semi liquid range ($C_{12}A_7+CA$) type.

From the inclusions plotted on a $CaO-Al_2O_3-CaS$ ternary diagrams, it is evident that the inclusions were duplex, consisting of a calcium aluminate phase and calcium sulfide phase. Most of the inclusion compositions fall in a suitable region (50% semi-liquid region) to maintain stable castability. The CaS content in calcium aluminate inclusions was low as is evident from Figure 4(b), Figure 5(b) and Figure 6(b), which is indicative of a ample modification due to sufficient amount of calcium addition in these heats. After inclusion transformation, the average-modified $\frac{Ca}{Al}$ ratio of Heats B,C and D was 0.54,0.47 and 0.58 respectively, which again indicates that stable casting can be ensured as suggested by Story et.al [23].
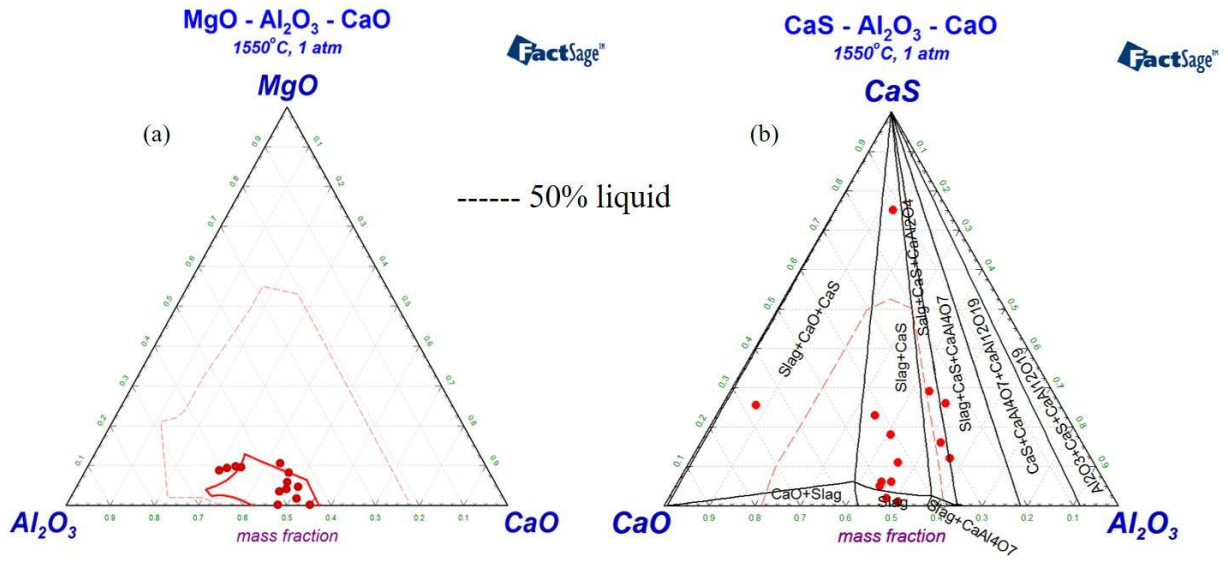
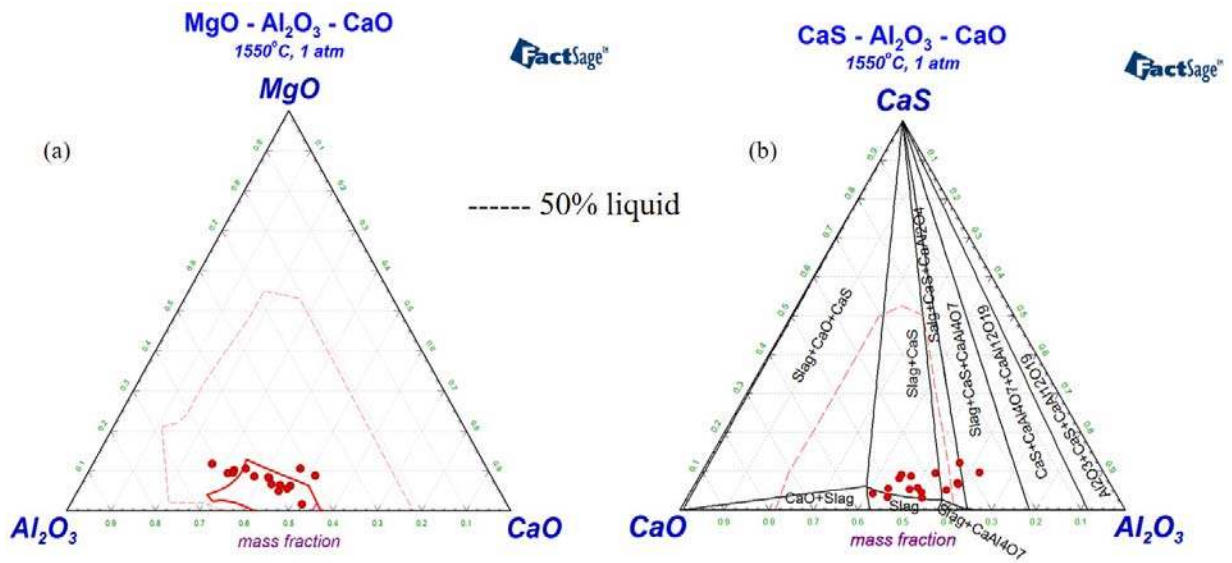Figure 4. Ternary plot of inclusions of a Heat B

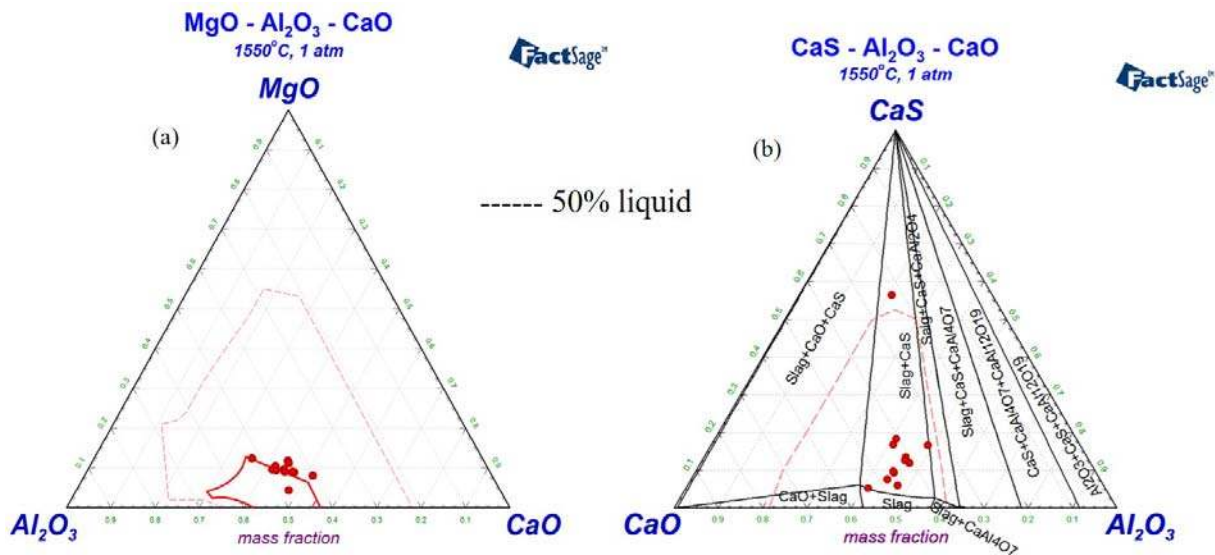Figure 5. Ternary plot of inclusions of a Heat C

Figure 6. Ternary plot of inclusions of a Heat D

3.2 Morphologies and Compositions of Inclusions

In general, Al_2O_3 inclusions containing a trace of MgO and SiO_2 are the main inclusions after tapping at BOF station. With the slag/steel interfacial reaction in the ladle heating furnace (LHF) during the refining process, the MgO content in the inclusions increases and the inclusions may change to $MgO-Al_2O_3-SiO_2$ system. After the calcium addition, most of these inclusions change into $CaO-Al_2O_3-MgO$ system inclusions with small amount of Si as a trace compound in the inclusions as shown in EDS data from the Figurers 7 to 9. Some of these are already in the composition of liquid region. Most of these inclusions are very close to low melting point calcium-aluminate region.

The typical morphologies and EDS spectra of inclusions in the calcium treated samples are shown in Figure 7 to 9. The inclusions are composed of $CaO-Al_2O_3-MgO-CaS$ type (oxy-sulfide inclusions). Normally, calcium is injected in the secondary refining process in order to modify the harmful Al_2O_3 inclusions to liquid calcium-aluminates. However, in the present study, the dissolved sulphur content in the liquid steel is more than the acceptable sulphur limit. Hence during solidification, solubility of sulphur decreases in the liquid inclusion resulting in

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the precipitation of extra sulphur as CaS around the inclusions as shown in Figure 9. The EDS data from the inclusions shows sulphur as a peak in Figure 7, Figure 8 and Figure 9. These types of calcium-aluminate inclusions are mainly observed after calcium treatment in the solidified billet samples. Characteristically these inclusions are blocky or spherical/globular in nature.
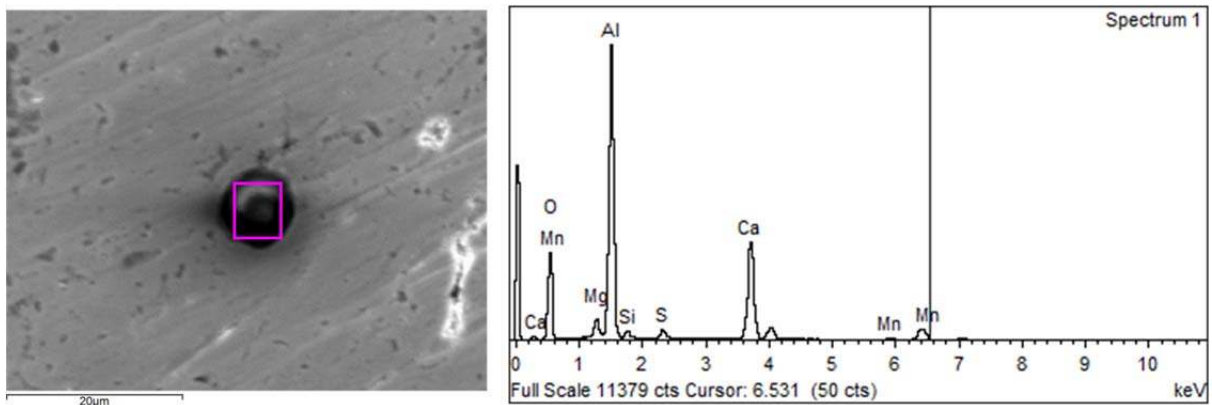

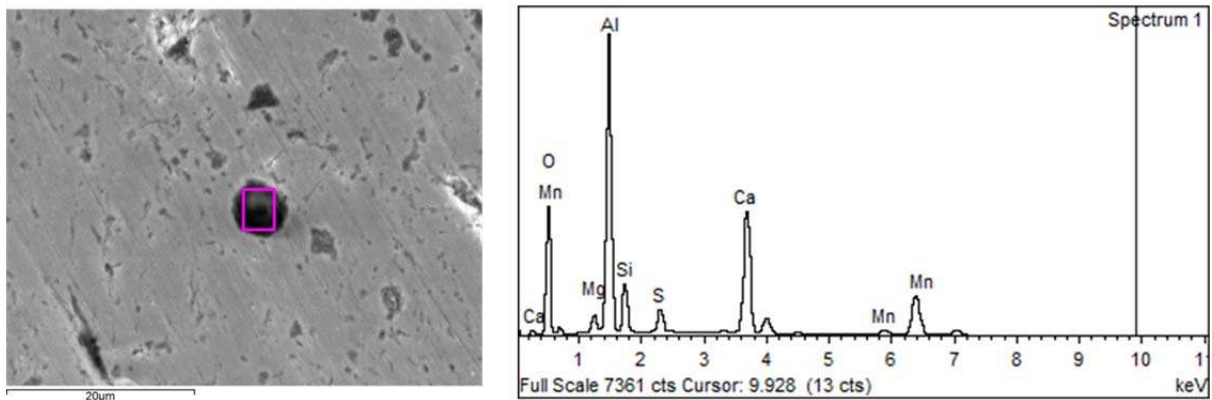Figure 7.SEM and EDS analysis of Typical CaO-MgO-Al$_2$O$_3$ inclusions in Heat A

Figure 8.SEM and EDS analysis of Typical CaO-MgO-Al$_2$O$_3$ inclusions in Heat C
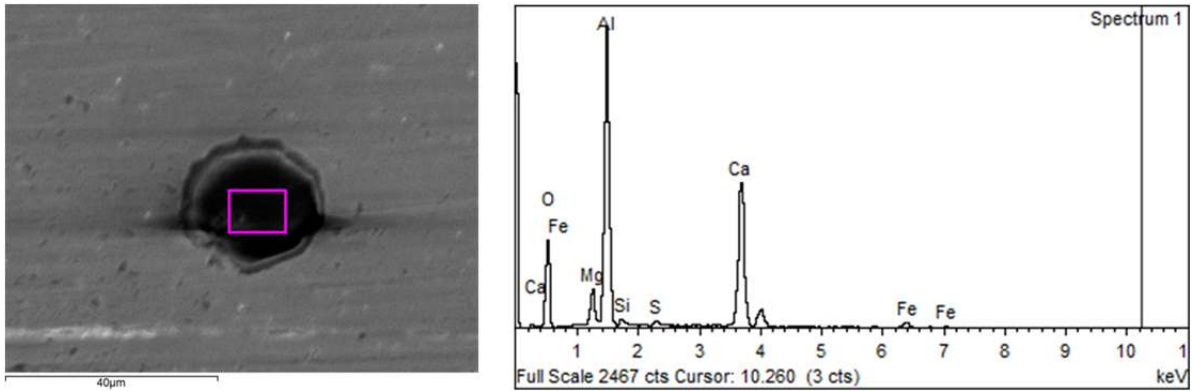
Figure 9. SEM and EDS analysis of Typical CaO-MgO-Al$_2$O$_3$ inclusions in Heat D

Figure 10 shows the elemental mapping of typical inclusions in billet sample after calcium treatment in liquid steel. A typical oxy-sulfide inclusion was observed in this billet sample and is composed of a sulphide ring of CaS outer layer and a CaO-Al$_2$O$_3$ core phase, indicating that calcium reacts with sulphur after the formation of calcium-aluminates. As the steel cools, the solubility of sulphur in the calcium-aluminate inclusions decreases and sulphur is rejected into the liquid [15,24]. During this separation, the excess sulphur reacts with calcium and forms CaS that surrounds the calcium-aluminates. A decrease in S content was also observed before and after calcium treatment in the steel samples. The decrease in sulphur content may be due to the flotation of oxy-sulfide inclusions during argon purging and joins the slag phase.
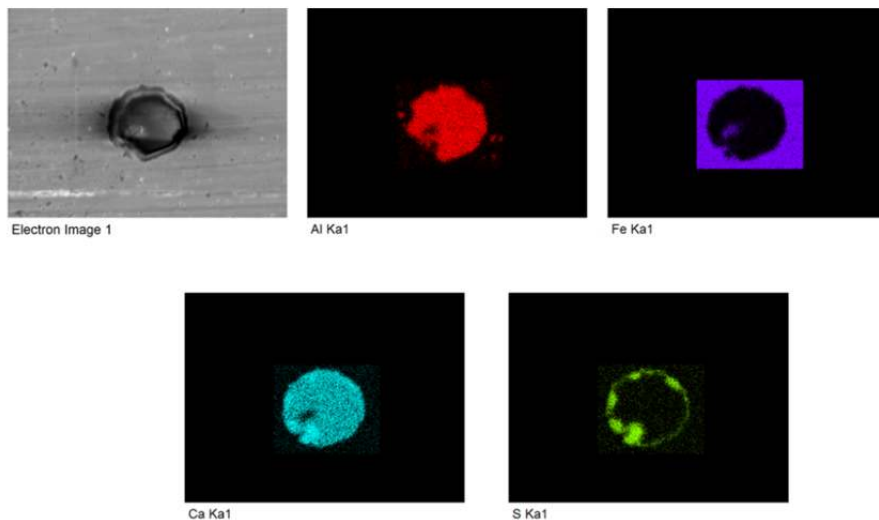

Figure 10 Elemental map of calcium treated oxide inclusion in steel sample collected from billet

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

S.No	SEM-EDS Elemental Analysis (at.%)	Calculated Oxide and Sulfides (Mole %)	CaO/Al_2O_3	Inclusion type
1	O=65.93, Mg=3.75, Al=21.04, S =0.69, Ca =7.88, Mn =0, Si = 0.71	MgO =3.75, Al_2O_3 =10.52, CaO =7.19, CaS =0.69, MnS = 0, SiO_2 = 0.71	0.68	$CA+C_{12}A_7+SiO_2+CaS$
2	O=66.55, Mg=0.75, Al=20.95, S =1.2, Ca =9.23, Mn =0.29, Si =1.03	MgO =3.75, Al_2O_3 =10.52, CaO =7.19, CaS =0.69, MnS = 0, SiO_2 = 0.71	0.79	$CA+C_{12}A_7+SiO_2+CaS$
3	O=61.98, Mg=0.78, Al=18.97, S =4.25, Ca =13.67 ,Mn =0.0, Si = 0.35	MgO =0.78, Al_2O_3 =9.49, CaO =9.42, CaS =4.25, MnS = 0.0, SiO_2 = 0.35	0.99	$C_{12}A_7+SiO_2+CaS$
4	O=65.57, Mg=0.0, Al=14.16, S =5.22 ,Ca =13.54 ,Mn =0.39, Si = 1.12	MgO =0.0, Al_2O_3 =7.08, CaO =8.71, CaS =4.83, MnS = 0.39, SiO_2 = 1.12	1.23	$C_3A+C_{12}A_7+SiO_2+CaS$
5	O=64.99, Mg=1.07, Al=17.32, S =2.3 ,Ca =10.41 ,Mn =0.52, Si = 3.39	MgO =1.07,Al_2O_3 =8.66, CaO =8.63, CaS =1.78, MnS = 0.52, SiO_2 = 3.39	1.00	$C_{12}A_7+SiO_2+CaS$
6	O=67.27, Mg=1.81, Al=15.68, S =1.21 ,Ca =11.11 ,Mn =0.37, Si = 2.56	MgO =1.81,Al_2O_3 =7.84, CaO =10.27,CaS =0.84, MnS = 0.37, SiO_2 = 2.56	1.31	$C_3A+C_{12}A_7+SiO_2+CaS$
7	O=63.8, Mg=1.83, Al=18.81, S =1.42 ,Ca =13.37 ,Mn =0.16, Si =0.59	MgO =1.83, Al_2O_3 =9.41, CaO =12.11, CaS =1.26, MnS = 0.16, SiO_2 = 0.59	1.29	$C_3A+C_{12}A_7+SiO_2+CaS$
8	O=68.84, Mg=1.52, Al=15.93, S =2.63 ,Ca =8.87 ,Mn =0.60, Si =1.61	MgO =1.52, Al_2O_3 =7.97, CaO =6.84, CaS =2.03, MnS = 0.60, SiO_2 = 1.61	0.86	$C_{12}A_7+CA+SiO_2+CaS$

Compositions of inclusions shown in Table 4 have been determined from elemental analysis based on the stoichiometry of each compound. Most of the inclusions are of duplex type with core of spinel and outer boundary layer composed of $CaO-Al_2O_3$ and CaS layers as shown in Figure 10. In all duplex inclusions, lower modification of calcium aluminates (CA) were also observed in addition to C_3A and $C_{12}A_7$.

Table 5 first order interaction coefficient e_j^i of elements dissolved in liquid steel used in the present work (from [23])

i/j	C	Si	Mn	P	S	Al	O	Ca
Al	0.091	0.0056	0.0056	0.033	0.03	0.045	-6.6	-0.047
Si	0.11	0.063	-0.026	0.29	-0.028	0.035	-0.27	-269

Table 6. f_{Al}, f_S of inclusions in different heats

Heat No	f_{Al}	f_S
Heat A	1.055	1.042
Heat B	1.054	1.047
Heat C	1.051	1.029
Heat D	1.056	1.049
Avg	**1.054**	**1.041**

Table 7. Activity of CaS in calcium aluminate inclusions in different heats

Heat No	$a_{CaS_{Before\ Ca\ addition}}$	$a_{CaS_{after\ Ca\ and\ Al\ addition}}$
Heat A	0.40	0.96
Heat B	0.52	0.80
Heat C	0.82	0.86
Heat D	0.52	0.49
Avg	**0.57**	**0.78**

$$\log f_i = \sum_{j=2}^{n} e_i^j \left[W_j \right] \tag{7}$$

Table 5 [25] depicts the first order interaction coefficient e_j^i of elements dissolved in liquid steel used in the present work. Henrian activity coefficients(f_i, where i = Al and S) can be determined by Wagner interaction formalism equation (7). The calculated Henrian activity coefficients for Al, S and activity of CaS in different heats are given in Table 6 and Table 7 respectively. It can be observed that the average activity of CaS is 0.57 and 0.78 before the calcium treatment and after complete process (after calcium and aluminium addition) respectively. The precipitation of CaS is not solid at steel making temperature because the activity of CaS < 1 and it is due to the formation of duplex inclusion of CaS or CaS-MnS and calcium aluminate as shown in Table 4. It indicates precipitation of CaS on liquid calcium aluminate inclusion and is partially in liquid state at the casting temperature i.e. 1550 deg c.

Ideally, for stable casting, most of the inclusions should be of $CA+C_{12}A_7$ type. The presence of $C_3A+CA+C_{12}A_7$ in most of the cases reflects adequate amount of calcium is added in the current calcium treatment practice.

Conclusions

A new approach has been developed for successful casting of high sulphur, Al-killed heats without an extra desulphurization step at an industrial scale. This successful attempt is based on the concept of Al-S diagram. During calcium addition, presence of high sulphur in liquid steel results in the formation of duplex calcium aluminate with calcium sulfide. But the formed CaS is found in the liquid state as confirmed by the its activity value which is less than one. Both completely modified duplex calcium aluminate inclusions of $C_{12}A_7.CaS$ and $C_3A.CaS$ type and partially modified CA.CaS were found in steel samples from the billet. This clearly indicates that the added calcium is adequate for complete modification of solid alumina inclusions into liquid calcium aluminates. The sulphide inclusions are often found has a solid solution of CaS and MnS, with average activity of CaS as 0.78. SEM-EDS analysis of calcium treated Al-killed steel samples indicates that most of the inclusions are of the oxy-sulfide type, in which the spinel forms at the core and the outer layer surrounded by calcium aluminate and CaS layers. From ternary diagrams plotted for some of the inclusions from the samples, indicate formation of calcium or CaS-rich aluminates. These phases may have taken care of additionally formed alumina during the extra aluminium addition after calcium treatment. Based on the results of industrial trials, it can be concluded that optimum addition of 0.11-0.14kg calcium per ton of liquid steel is sufficient to transform solid alumina inclusions to liquid inclusions. In High sulphur Al-killed steel, by following this new approach, it is possible to modify the solid alumina inclusions to liquid alumina inclusions with minimal CaS formation.

Further studies are being conducted separately to characterise these inclusions to give a better idea on their formation in high sulphur steels.

Acknowledgement

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