On the stability of CaS in liquid steel containing alumina or spinel inclusions

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ABSTRACT

In secondary steel making, calcium treatment is practised to modify the solid alumina or spinel inclusions into liquid or partially liquid calcium aluminates. It has been seen that the dissolved calcium reacts with sulfur or oxygen present in the steel to form CaS or CaO type of transient inclusions. Post calcium treatment these transient inclusions further react with pre-existing alumina or spinel inclusions and modify them. In addition, direct modification of pre-existing inclusions is also reported in the literature.

In the present study, laboratory-scale induction furnace-based experiments are carried out to melt electrolytic iron in an alumina crucible followed by deoxidation with aluminium. The CaS-based composite material, prepared in-house, is added after the aluminium deoxidation to study the stability of CaS at the steelmaking temperature. Multiple steel samples were also taken to track the dissociation of CaS by means of sulfur pick-up in steel. Additionally, inclusion analysis of these steel samples was also performed to track changes in the chemical composition of inclusions in response to CaS addition. It has been seen that the CaS dissociates leading to a gradual pick-up of sulfur in steel. The SEM-EDS analysis reveals that the alumina crucible and floated alumina inclusions are modified into calcium aluminates and the extent of modification depends on the contact time of CaS with the two sources of alumina mentioned earlier. However, the modification of alumina inclusions in the bulk steel did not occur during these experiments.

INTRODUCTION

As the demand for clean steel steadily increases, particularly within the automotive and defence sectors, global steelmakers are not only paying importance to control impurity levels but are also placing a significant emphasis on controlling non-metallic inclusions in the steel. The early works of Hilty and Farrel (1975a) and Hilty and Farrel (1975b) on the effect of calcium in aluminium-killed steel for the inclusion modification opened new horizons for controlling non-metallic inclusions in steel. As a result, calcium treatment is a well-established process nowadays at the secondary steelmaking process stage to convert deleterious solid non-metallic inclusions into liquid or partially liquid non-metallic inclusions to enhance castability and improve the mechanical properties of the steel. In aluminium-killed steel, two major types of inclusions are alumina and spinel inclusions. This study primarily focuses on alumina inclusions which can be modified into liquid calcium aluminates with calcium treatment. Verma et al. (2011a)reported the sequence of reactions after calcium additions as Eq. 1-4.

$$\mathrm{Ca(s) \rightarrow Ca(l) \rightarrow Ca(g) \rightarrow [Ca]} \quad 1$$

$$\mathrm{[Ca] + [O] \rightarrow CaO} \quad 2$$

$$\mathrm{[Ca] + [S] \rightarrow CaS} \quad 3$$

$$[\mathrm{Ca}] + \left(\mathrm{x} + \frac{1}{3}\right)\mathrm{Al_2O_3} \rightarrow \mathrm{CaO.xAl_2O_3} + \frac{2}{3}[\mathrm{Al}] \quad 4$$

It can be seen from the reactions that the added calcium first melts, vaporises and then dissolves in the liquid steel. Dissolved calcium reacts with dissolved oxygen and sulphur if present in the liquid steel and forms CaO/ CaS type of inclusions. The extent of formation of CaS or CaO type of inclusions depends on the dissolved sulphur or dissolved oxygen in the liquid steel. Further, the dissolved calcium reacts with the pre-existing alumina inclusions and converts them into liquid calcium aluminates. The expected alumina modification route was reported by Faulring G.M. et al. (1980) as $\mathrm{Al_2O_3} \rightarrow \mathrm{CA_6} \rightarrow \mathrm{CA_2} \rightarrow \mathrm{CA_x}$ (C: CaO, A: Al_2O_3). This route is reported in almost all the literature for the modification of alumina into calcium aluminates. It should be noted here that the activity of alumina in the calcium aluminates decreases with an increase in CaO content in the inclusion. The above mechanism of modification is often referred to as direct modification of inclusion.

Turkdogan T (1988) observed the formation of a CaS layer around the calcium aluminate in high sulphur steels and concluded that the CaS layer hinders the extent of modification of alumina inclusions. (Lu 1994, Higuchi 1996, Ye 1996, Ren 2014) also reported an increase in CaS or CaO content immediately following calcium treatment, followed by a subsequent decrease, suggesting the formation of CaS/CaO as transitional products. They also suggested that the high sulphur and oxygen can enhance the calcium absorption rate. Verma et al. (2011b) reported that apart from being CaS or CaO a transient phase they also play a critical role in alumina inclusion modification. They observed that in high sulphur steels, these transient CaS inclusions tend to nucleate on alumina inclusions and destabilise the alumina inclusions and later modify them by the reaction as shown by Eq. 5. This modification can be referred to as indirect modification of alumina inclusion and the schematic is shown in Figure 1

$$3CaS + Al_2O_3 \rightarrow 3(CaO) + 2[Al] + 3[S] \quad 5$$

It should be noted here that the above reaction involves three condensed phases, two solid and one liquid steel phase. It is expected that the reaction will occur via the liquid steel phase. The reaction mechanism can be

1) CaS dissociates into calcium and sulphur.
2) Calcium transfer to alumina inclusion through liquid steel and sulphur rejection in liquid steel
3) Alumina inclusion modification to liquid calcium aluminates.

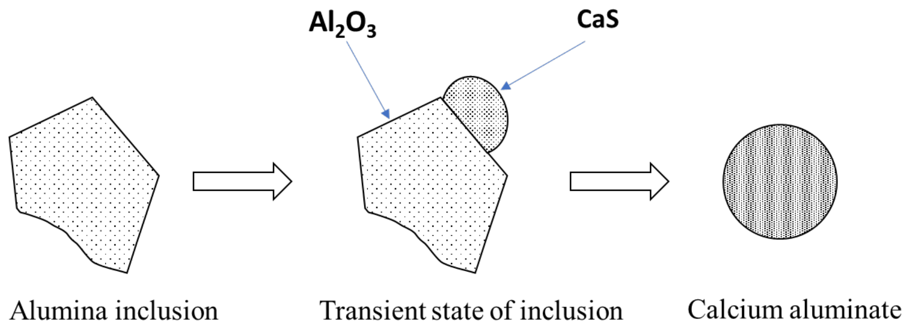

Figure 1 Schematic of indirect modification of alumina inclusion showing CaS evolution as a transient phase Verma et al. (2011b)

As previously mentioned, the CaS is a transient inclusion. This work focuses on examining the stability of CaS in liquid steel containing alumina inclusions. Thermodynamic calculations were also conducted to explore the conditions determining the stability or dissociation of CaS. The Fe-CaS-based composite material was prepared in-house, and its stability was investigated through various experiments involving different durations of experimentation.

EXPERIMENTAL PROCEDURE

The Fe-CaS-based composite material was prepared by melting pure calcium and iron sulphide in an induction furnace under an argon atmosphere. The density of the composite material was measured using a helium pycnometer. Microstructural characterization and elemental composition of the composite lump were carried out using scanning electron microscopy equipped with energy-dispersive x-ray spectroscopy (SEM-EDS, Make and Model: Jeol JSM IT800).

The schematic of the experimental setup and sampling apparatus is shown in Figure 2. Two sets of high-temperature experiments (No.1 and No.2) were performed in the induction furnace by varying the experimentation time. In both experiments, about 800 grams of electrolytic iron flakes (containing dissolved oxygen of about 300 ppm and dissolved sulphur of 30 ppm) were kept in the alumina crucible (OD-57 mm, Height-87 mm and capacity-170 mL). The alumina crucible with electrolytic iron was then placed inside the induction furnace chamber. The chamber was evacuated with a rotary vacuum pump followed by continuous backfilling with pure argon (purity-99.99%) at 1-3 l/min to prevent reoxidation of the liquid steel. The sample was then heated to 1600 ^{0}C and held at that temperature for homogenization. Based on the preliminary experiments, a holding time of 15 min was chosen to ensure homogenisation (uniform temperature and composition of bath).

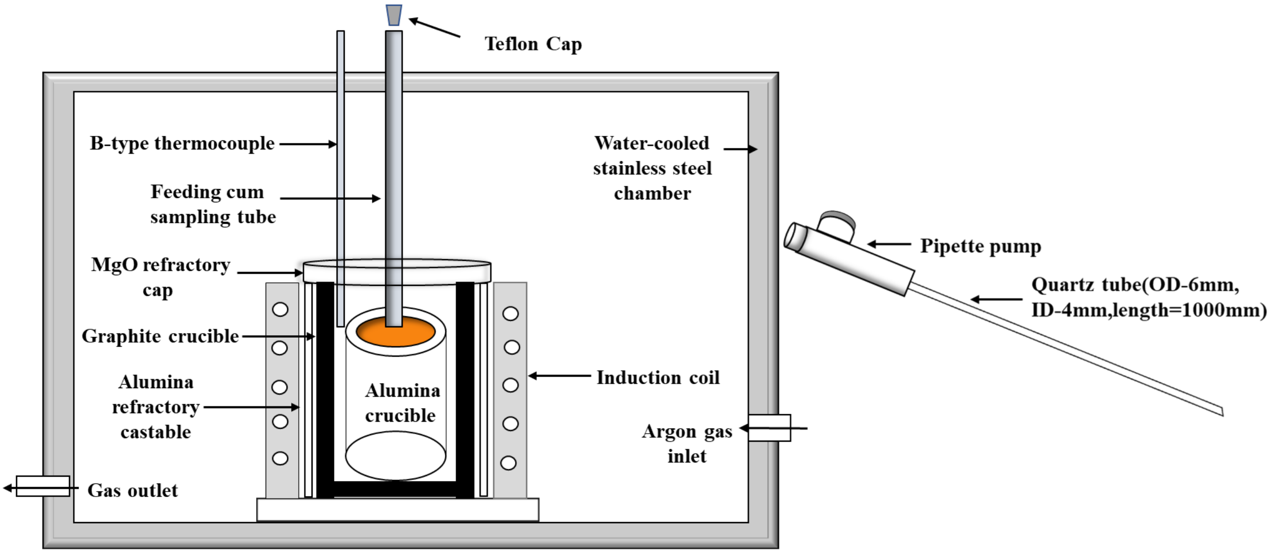

Figure 2 Schematic of the Induction furnace and sampling apparatus

After homogenization, 0.1 wt% of pure aluminium chunks (purity>99%) were added through a feeding cum sampling tube to deoxidise the steel melt. The time of Al addition was taken as a reference time and is denoted as t=0. Experimentation time for experiment 1 was 15 min, whereas 60 min for experiment 2. The addition sequence and the sampling timelines for both experiments are shown in Figure 3. After the deoxidation of the steel melt, a predetermined amount of the Fe-CaS-based composite material powder wrapped in a mild steel foil was dropped into the liquid steel through the feeding tube. Samples from the bulk steel melt were taken at various time intervals by inserting the fused quartz tube (OD-6mm, ID-4mm and length-1000mm) followed by water quenching of the quartz tube containing the steel sample. The sampling cum feeding tube, which was sealed with a Teflon cap during the entire heating cycle to ensure an air-tight chamber; was opened for a very short duration for additions and sampling.

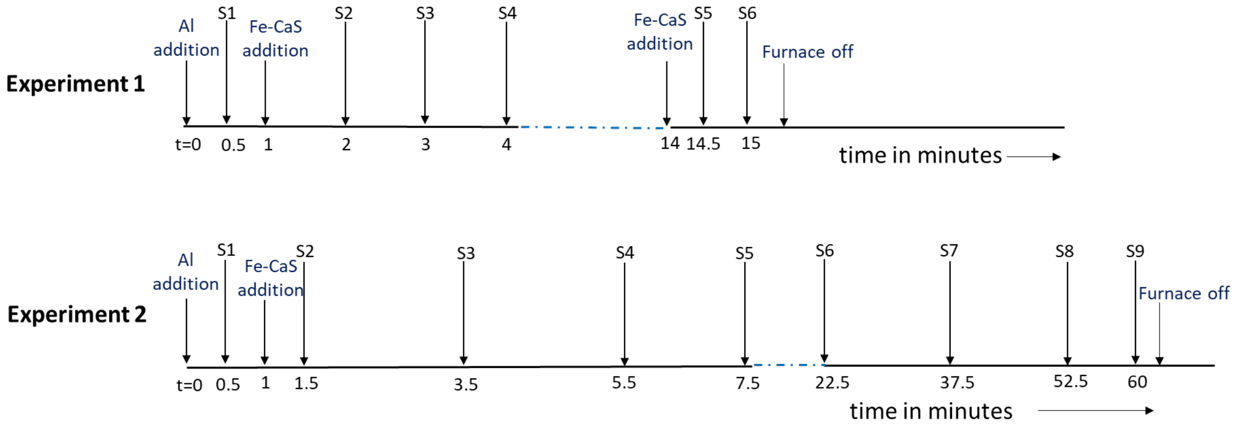

Figure 3 Sampling timelines and additions for experiments 1 and 2

The added amount of electrolytic iron, pure aluminium and composite material for both experiments are shown in Table 1**.**

Table 1 Raw material and additions for experiments 1 and 2

Experiment #	Electrolytic iron (grams)	Aluminium (grams)	Fe-CaS composite(grams)
1	800	0.8	1.44
2	800	0.8	0.72

The bulk steel cylindrical samples aspirated using the quartz tube were then cut into smaller sections approximately 6-12 mm in size. These sections were hot-mounted in the longitudinal direction and subsequently grinded using SiC emery papers of grit sizes of 200, 400, 600, 800, 1000, 1200,1500 and 2000 respectively. Following this, the samples were mirror polished using 3-micron and 1-micron diamond paste and washed with ethanol. It should be noted that the CaS particles are fairly hydrophilic, so water was not used during the final polishing. Microstructural investigation of these samples was carried out using SEM-EDS for the analysis of inclusion morphology (two-dimensional) and composition. Additionally, the top surface of the solidified steel ingot obtained from experiments no.1 and 2 was also analysed using SEM-EDS, as floated alumina inclusion is expected at the top portion of the solidified ingot.

Furthermore, the alumina crucible used in both experiments was broken, and the inner surface of the alumina crucible, which had been in contact with the solidified steel ingot, was analyzed using SEM-EDS. The sulphur content of samples collected at different time intervals (experiment 2) was measured using a LECO CS744 carbon sulphur analyser at a third-party laboratory.

RESULTS AND DISCUSSION

The microstructural features of the composite material are illustrated in Figure 4. Notably, pure CaS microparticles and pure iron particles are embedded within the Fe-CaS network. The sizes of the CaS microparticle vary from 10-100 microns. The average size of CaS particles was determined through ImageJ software, revealing an average particle size of 50 microns. It should be noted the composite material produced was highly brittle and, thus, difficult to polish. Therefore, the composite material lump was mechanically grinded for SEM analysis, as evidenced by a few scratch marks in the electron image.

The composite material has an average density of 3.95 g/cc, nearly half that of liquid steel, as determined through a helium pycnometer.

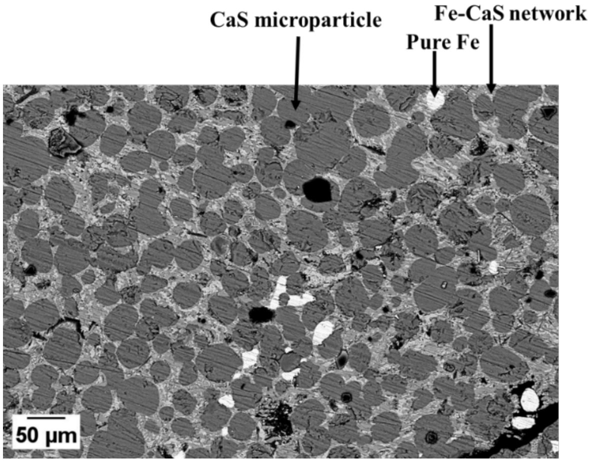

Figure 4 Microstructure of the Fe-CaS composite material

In both experiments, the Fe-CaS-based composite material was added one minute after the aluminium deoxidation. The duration of Experiment 1 and Experiment 2 were 15 minutes and 60 minutes, respectively. The SEM-EDS analysis of bulk steel samples, obtained through a quartz tube at different time intervals for both experiments to track changes in inclusions composition is shown in Figure 5. The EDS spectra reveal the irregular morphology and unmodified alumina inclusions within the specified time frame. The CaS particles are expected to have a very short residence time in the liquid steel due to density differences and shallow melt depths of 30-40 mm. It should also be noted here that the CaS particles were not observed in any bulk steel samples during SEM-EDS analysis. The sampling methodology (aspirated through quartz tube) to track changes in inclusion composition has been widely reported in the literature.

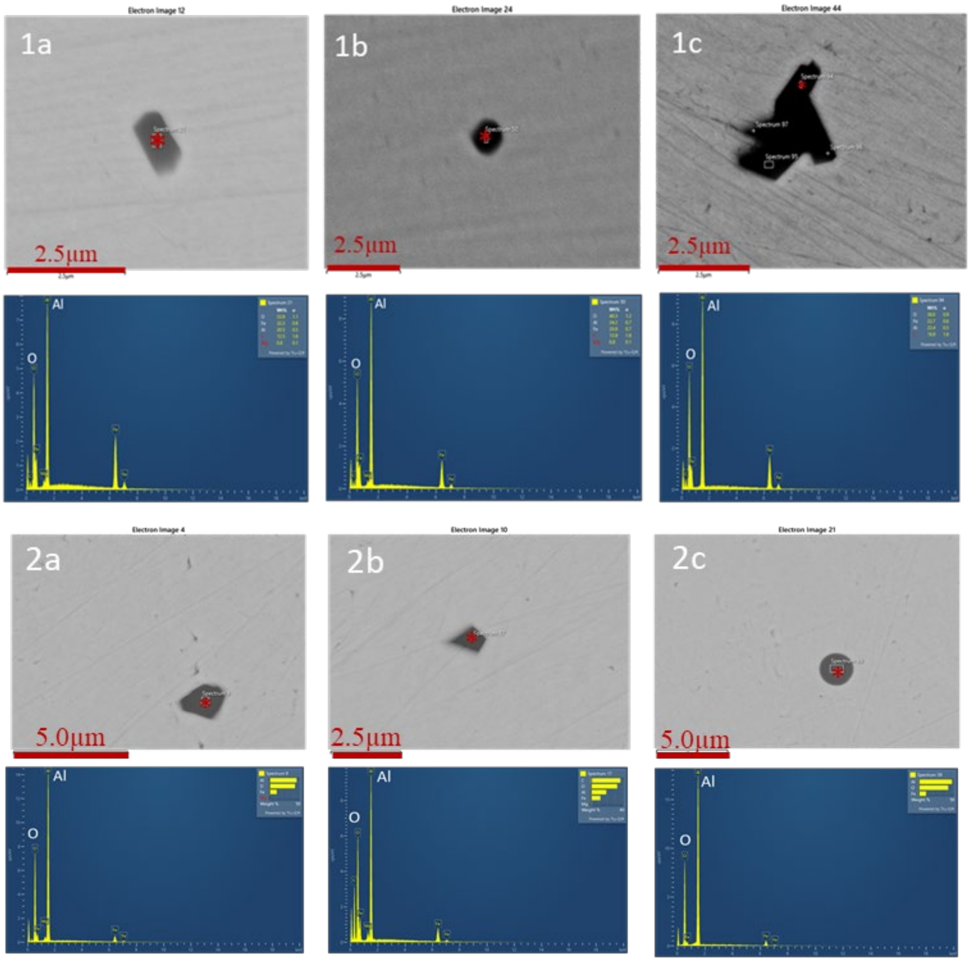

Figure 5: SEM-EDS spectra of bulk steel samples for experiments 1 a)1 min. b) 2 min c)14 mins and experiment 2 a)0.5 min b)2.5 min c)21.5 mins after composite material addition

To investigate the dissociation of CaS in the liquid steel the alumina crucible was carefully observed for both experiments. The microstructure and SEM-EDS spectra of the inner surface of the alumina crucible after 15 minutes and 60 minutes of contact time with liquid steel treated by the composite material are shown in Figure 6.

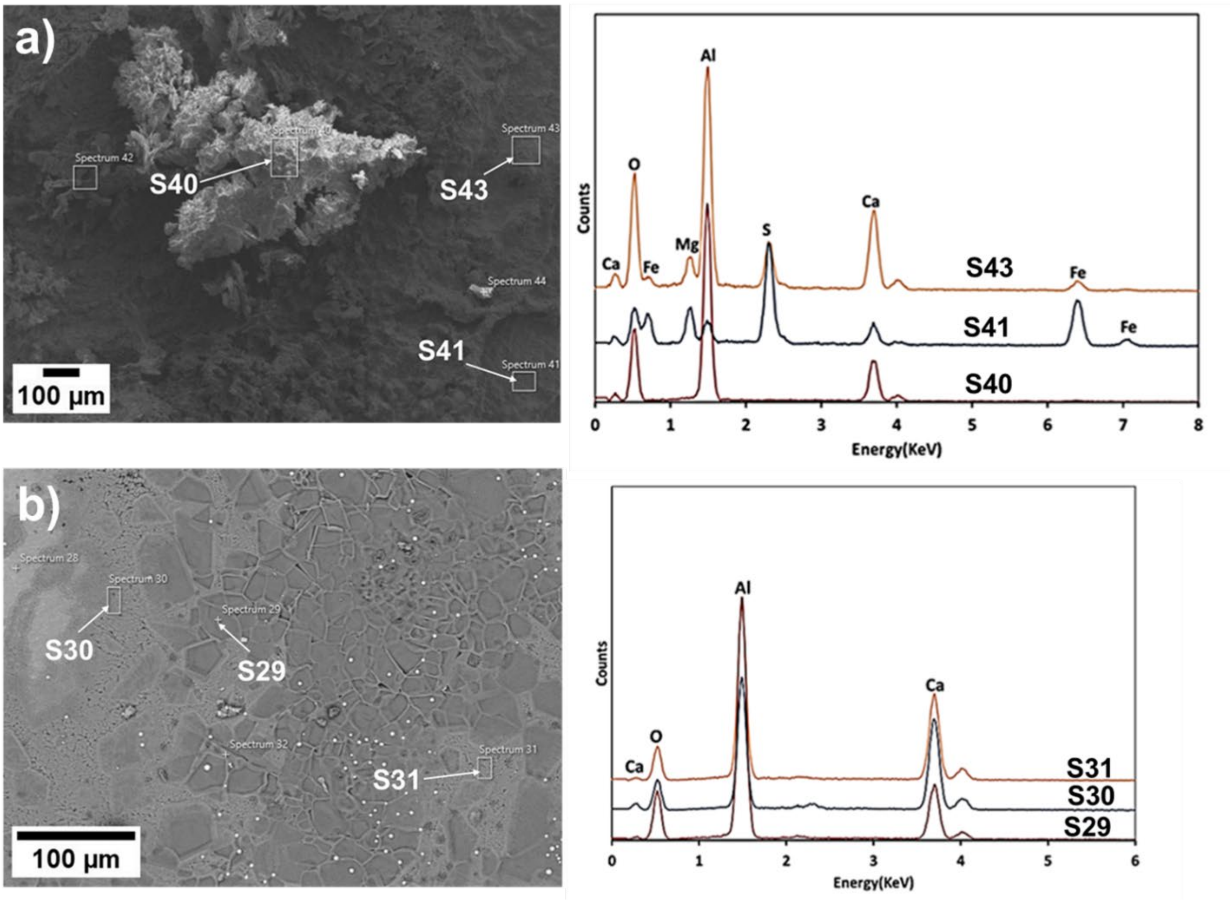

Figure 6 SEM-EDS analysis of the crucible in contact with the solidified ingot for a) Experiment no. 1: contact time -15 minutes b) Experiment no. 2: contact time-60 minutes

Location S40 in Figure 6 a) clearly shows the presence of a significant amount of CaO and no sulfur. The nearby regions S41 and S42 show a mixture of calcium aluminate and calcium sulfide. However, in experiment no.2 where the experimentation time was 60 minutes (see Figure 6 b). A thin layer of liquid calcium aluminates across the crucible's inner surface can be seen. The modification of alumina into calcium aluminates is visible at all locations in Figure 6 b). Also, the absence of sulphur peaks at all locations indicates that sulphur must have dissolved in liquid steel. These results indicate that the reaction between CaS and alumina is kinetically driven; that is, the CaS particles in the composite material for experiment no.1 had insufficient time for complete dissociation and complete modification of alumina, whereas the CaS particles had sufficient time to dissociate and modify alumina crucible for experiment no. 2. To further confirm these findings, (a) the inclusion analysis of the top portion of the solidified ingot and (b) sulphur pick up in the bulk steel sample at different time intervals for experiment no. 2 have been investigated.

The top surface of the solidified ingot has also been examined to observe the CaS particle floatation and their interaction with floated alumina inclusions. It should be noted here that the top surface also contains floated alumina inclusions after aluminium deoxidation. Upon investigating the solidified steel ingot, the SEM-EDS analysis for experiment no.1, shown in Figure 7 a), reveals partial modification of floated alumina inclusions. The locations S18 and S21 in the SEM micrograph show the floated unmodified alumina inclusions and locations S19 and S20 show the modified alumina inclusions. The SEM-EDS analysis for experiment no.2. is shown in Figure 7 b), which shows that the floated alumina inclusions are modified to calcium aluminates, and CaS particles were not observed on the top of the solidified ingot.

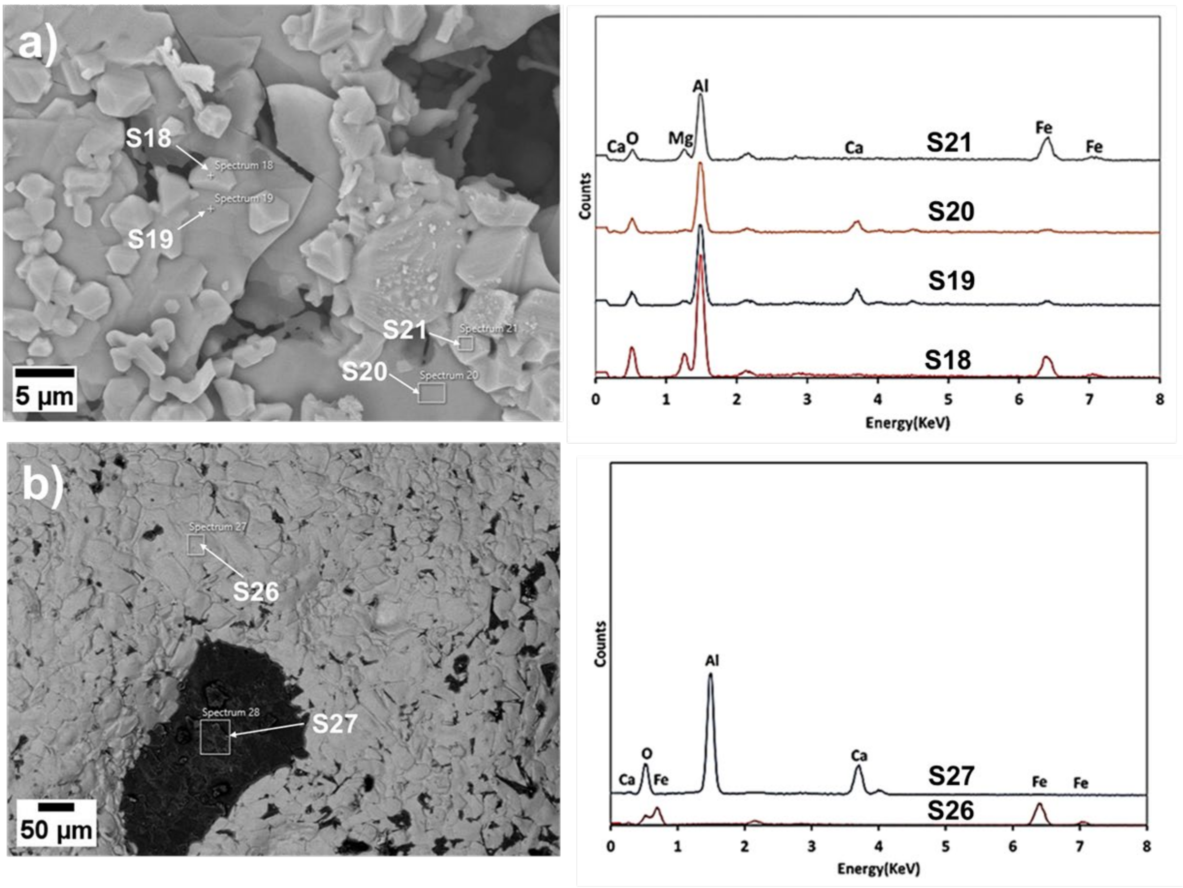

Figure 7 SEM-EDS analysis of the solidified ingot top a) Experiment no.1 b) Experiment no. 2

Furthermore, the steel samples for experiment no.2 were collected at different time intervals to track the sulphur pick-up in the liquid steel, as shown in Figure 8**.** The rate of sulfur pick-up is very large at early times, followed by a steady increase in the sulfur concentration. It is evident that the CaS-based composite material undergoes dissociation, facilitating the transfer of calcium to liquid steel for the modification of oxide inclusions and rejecting the sulphur into the liquid steel.

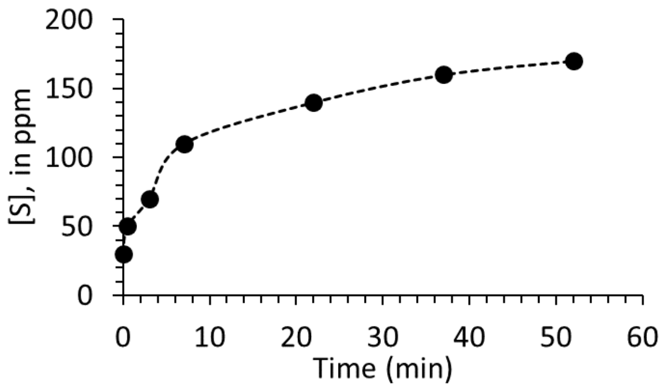

Figure 8 Sulphur analysis of steel samples at different time intervals for experiment 2

The thermodynamic stability of CaS in liquid steel was evaluated using the FactSage 8.1 thermodynamic software Bale et al. (2016) . The calculations were performed using Factsage8.1 (Equilib module, Databases: FactPS, FactOxid and FTMisc) at 1600 ^{0}C temperature and 1 atm pressure. The activity of CaS was set to 1 for these calculations. The saturation line representing the equilibrium concentration for S content and total oxygen at which CaS activity is one is shown in Figure 9. The concentration (sulphur, oxygen) region above this line represents CaS is stable, whereas, CaS will dissociate below this saturation line. Both the stability region and dissociation region are depicted in Figure 9.

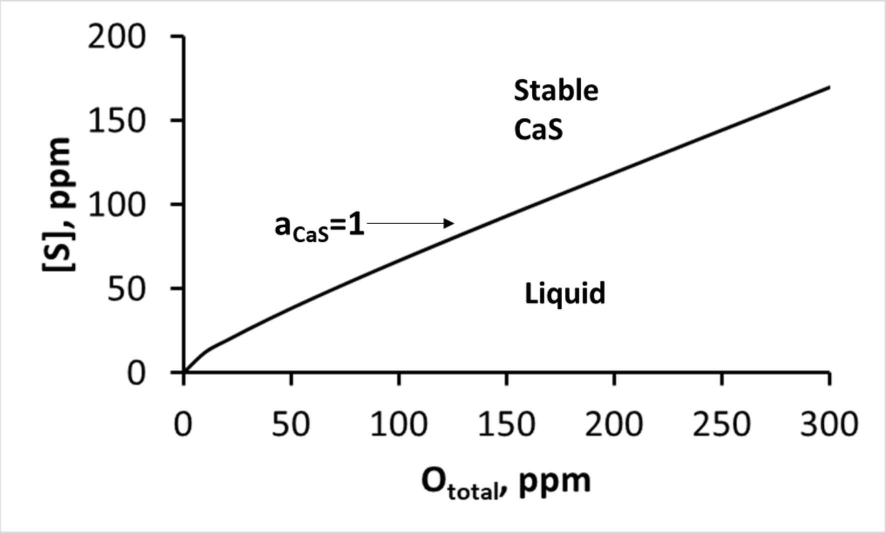

Figure 9 CaS stability diagram at 1600^{0}C using Factsage8.1

It can be seen from Figure 9 that a high total oxygen content favours CaS dissociation. The total oxygen in the present system comes from the steel (Fe-Al-Ca-O-S), and the Al2O3 crucible interface is expected to have a high oxygen content. Consequently, CaS dissociation is feasible for a wide range of sulfur content, which reasonably aligns with the experimental results. As observed in the experiments, the dissociation of CaS into liquid steel, followed by the transfer of calcium to inclusions and sulfur to melt, depends not on dissolved oxygen but rather on the total oxygen content.

SUMMARY AND CONCLUSIONS:

In the current study, laboratory experiments and thermodynamic calculations were performed to investigate the CaS stability in the liquid steel containing alumina inclusions. Experiments were conducted by adding Fe-CaS-based composite material and the following conclusions can be obtained.

1. As expected, since the CaS-Al_2O_3 interaction involves three condensed phases, two solid phases and a liquid steel phase the transfer of chemical species occurs via liquid phase.
2. The dissociation of CaS, subsequent calcium transfer to alumina inclusions, and sulfur transfer to the melt are influenced by the total oxygen content from both dissolved oxygen in the melt and oxygen present in the inclusions.
3. The CaS dissociation is a kinetic-driven process. The dissociation and subsequent chemical species transfer can depend on the mass transfer coefficients of the species in the liquid steel.

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