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A STUDY ON CALCIUM TRANSFER FROM SLAG TO STEEL AND ITS EFFECT ON MODIFICATION OF ALUMINA AND SPINEL INCLUSIONS

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Abstract

Aluminum deoxidized steel tends to form solid inclusions (alumina, spinel, partially modified calcium aluminates). These solid inclusions are known to present challenges during casting, cause slivers during mechanical working and act as crack initiation sites for mechanical failure. Calcium injection practice has been used by the industry to transform these solid inclusions into liquid inclusions for several decades. There has been a significant amount of study to understand the mechanism of calcium modification of alumina/spinel inclusions. However, there has been little attempt to understand calcium transfer from slag to steel to inclusions that may modify alumina inclusions. In this study, laboratory deoxidation experiments were conducted using an induction furnace, physically simulating a ladle furnace; samples were taken during these experiments to study the extent of calcium transfer through inclusion analysis. This study shows that in the presence of silicon, there can be significant amount of calcium transfer from slag. Also, as the rate of calcium transfer from slag is limited by mass transfer in steel and slag, it is difficult to modify a large concentration of inclusions. However, an appreciable extent of calcium transfer was found in the case of lower concentration of inclusions (less than 150 ppm area fraction).

Introduction

Aluminum killed steels have a tendency to undergo nozzle clogging during casting due to formation of solid inclusions like alumina, spinel or solid forms of calcium aluminates. The clogging results due to tendency of inclusions to deposit on nozzle walls followed by sintering as explained by Singh [1]. Calcium treatment is a common practice to modify solid alumina inclusions that was started in the late 1960s [2]. Earlier, it was thought that magnesium containing inclusions would not modify with calcium addition [3] [4]. However, recent studies show that modification of spinel inclusions into liquid Ca-Al-Mg-O inclusions can be achieved. Pretorius *et al.* [5] found that calcium modification of spinel inclusion is rather easier for LCAK steels with very low oxygen content. However, Yang *et al.* [6] have concluded from thermodynamic analysis of industrial data that spinel inclusions can be modified into liquid inclusions only if dissolved calcium content in alloy steel is at least 1 ppm.

Early studies on the modification mechanism of alumina inclusions were reported by Hilty *et al.* in 1975 [7], [8]. In 1980, they reported that alumina inclusions follow Ca-modification path as alumina → CA_6 → CA_2 → CA → Liquid calcium aluminate (C: CaO, A: Al_2O_3) [4]. This mechanism is now well accepted in the literature. Ye *et al*. [9] and Han *et al*. [10] concluded that the rate of calcium modification is quite high for smaller inclusions (<10 μm) at the steelmaking temperature. Recent studies on calcium modification of alumina inclusions have been focused on the transfer of calcium to inclusions [11] [12]. Verma *et al.* [11][12] and Holappa *et al.* [13] pointed out the effect of sulfur content in steel on the calcium transfer mechanism from liquid steel to inclusions. Verma *et al.* [12] concluded that CaS and CaO form as intermediate products during calcium transfer to inclusions for high and low sulfur content respectively. However, CaO was not observed in the case of experiments with low sulfur due to very high rate of modification of smaller inclusions (<10 μm) [10]. In contrast to alumina inclusions, spinel inclusions start forming liquid phase immediately upon CaO pick-up [5]. Verma *et al.* [14] also concluded that modification of spinel inclusions occur via partial reduction of MgO followed by partial reduction of Al_2O_3 with formation of CaS as intermediate product. These intermediate modification products are summarized in the Figure 1. It should be noted that reduction of MgO from spinel inclusions increases the dissolved Mg concentration in steel that may cause re-appearance of spinels upon subsequent re-oxidation [6].

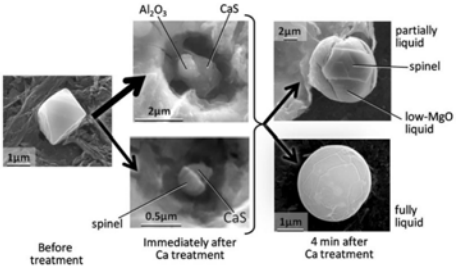

Figure 1 Spinel modification route after calcium treatment in Al-killed steels [14]. **With permission of Springer.**

Due to relatively high activity of CaO in typical secondary steelmaking slag and high activity of aluminum in steel, aluminum can reduce CaO at the steel-slag interface. This would result into dissolved calcium in steel [6]. The dissolved calcium may in turn react with alumina or spinel inclusions resulting in partial modification of these solid inclusions [5] [6]. Although calcium transfer from slag to steel to inclusions has been indirectly reported in the literature [5], [7], [15]; there has not been any systematic study to quantify the extent and rate of calcium transfer from slag to inclusions via steel. The present study focuses on developing a better understanding of mass transfer of calcium to inclusions. As part of this study, experiments were conducted in a laboratory induction furnace to estimate the extent of calcium transfer from slag to steel to inclusions.

Methodology

Experiments were conducted in an induction furnace to study the extent of calcium transfer from slag to steel. Calcium enrichment of alumina or spinel inclusions was used as an indication of this calcium transfer. The schematic of the setup is shown in **Figure 2**. The experiments were conducted in an argon atmosphere in MgO crucibles (61 mm diameter) or yttria stabilized zirconia crucibles (31 mm diameter). 600 g (in MgO crucible) or 100g (in ZrO_2 crucible) of electrolytic iron containing 350 ppm of oxygen and 7 ppm of sulfur was melted and then deoxidized by adding aluminum at ~1600°C. Two compositions of slag were used for these experiments as shown in Table 1. The experiments are described in Table 2. Samples were taken at required intervals using fused-quartz tubes of 4 mm inner diameter and a suction tube. Tubes were flushed with argon before sampling to avoid any reoxidation due to entrapped air in the tube.

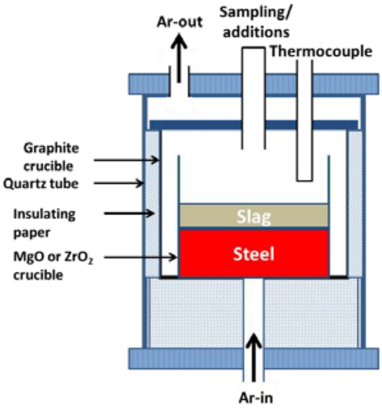

Figure 2 Schematic of induction furnace setup

Table 1 Slag compositions used for experiments

	Slag composition (wt%)			
	CaO	Al_2O_3	MgO	SiO_2
Slag-1	47.50	36.40	7.10	9.10
Slag-2	50.30	42.30	7.40	0

Table 2 Experiment summary

Exp. #	Crucible	Additions
1	MgO	Al (0.3%, t=0), slag-1 (200 g, t=11 min)
2	MgO	Al (0.3%, t=0), Fe-Si (1% Si), slag-1 (200 g, t=6min)
3	ZrO_2	Al (0.15%, t=0), slag-2 (15 g, t=0)

Samples taken during these experiments were used to measure kinetic changes in inclusion composition and chemical composition of steel. Total oxygen concentration in steel was analyzed using LECO and Si, Al, Ca, and Mg in steel were analyzed using ICP at a third party laboratory. Compositions and concentrations of inclusions were measured automatically on polished sample sections using automatic feature analysis and energy-dispersive X-ray microanalysis available in an FEI/ASPEX scanning electron microscope. These analyses were conducted at 10 kV with 16-17 mm working distance and 40% spot size. Specific inclusions of interest were also analyzed at higher resolution in field-emission gun scanning electron microscopes. Some samples were electrochemically etched to reveal three-dimensional morphology of inclusions, especially clusters, using the method suggested by Tan & Pistorius [16].

Results and Discussion

In the first experiment, steel was deoxidized by adding 0.3 wt% of aluminum. Dissolved aluminum in steel reduced silica in slag which resulted into silicon pick-up in steel, as shown in **Figure 3**. A kinetic model was developed using the macro-feature available in the 'Equilib' module of FactSage 6.4 [17]. The mass transfer coefficient of steel (k_{steel}) to the slag-steel interface is the only unknown parameter in such a model assuming that k_{steel} is 10 times larger than k_{slag}. The experimental data (Al and Si content in steel with time) was used to find the product $k_{steel} \times A$ (A: slag-steel interfacial area) for mass transfer in steel, as the value of $k_{steel} \times A$ for which the calculated composition fitted the experimental results. It should be noted here that it is not possible to measure k_{steel} independently because steel-slag interface may not be planar [18].

The fitted value of $k_{steel} \times A$ was equal to 1.3×10^{-7} m^3/s which is of the same order of the observed value in the past for a similar setup [19]. It is important to note here that the kinetic model over-predicts the concentration of dissolved calcium (3.0 ppm) in steel. This problem arises due to large uncertainty regarding calcium solubility in liquid steel as shown in Figure 4.

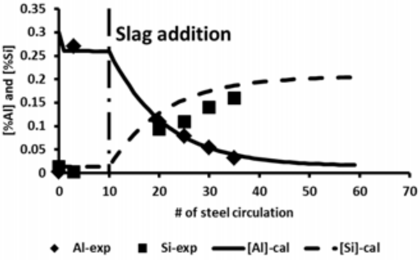

Figure 3 Experimental and calculated variation in total aluminum and silicon contents of steel

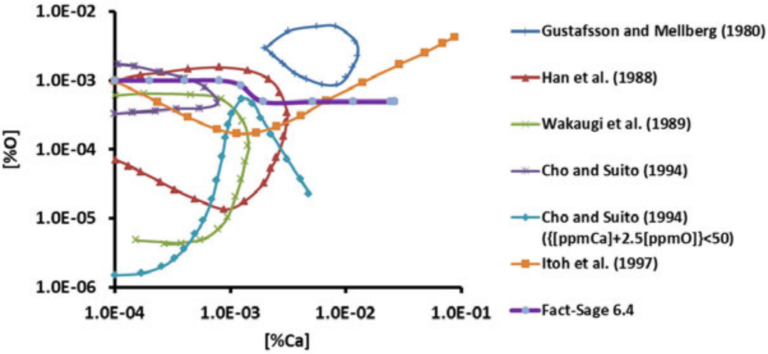

Figure 4 Reported relationships between dissolved oxygen and dissolved calcium in liquid steel at 1873 K. Redrawn after reference [20]

Inclusion analysis results of three samples taken during experiment 1 (in MgO crucible) are shown in Figure 5 (a, b and c) using proportionate symbol plots. In these plots, the area of each small dark triangle is proportional to the area fraction of inclusions present in sample with that composition. The results clearly show increasing magnesium content in inclusions with time. The sample taken before slag addition also shows significant magnesium content in inclusions (see Figure 5 (a)) which indicates magnesium pick-up from crucible as well. In samples taken at longer times, the average mole fraction of MgO in inclusions (~0.60) was higher than typical spinel phase. This large MgO concentration (higher than stoichiometric spinel) indicates partial transformation of spinel inclusions into MgO (resulting from Mg pick-up in steel from both slag and the crucible). The inclusion size and concentration did not change much among these samples. The average size of the inclusions was in the range of 3-4 µm and the corresponding oxygen content in inclusions was in the range of 110-160 ppm by mass.

It should be noted here that the induction furnace used for these experiments did not have any forced mechanical stirring mechanism like Ar-purging. In the absence of forced stirring, flotation of inclusions, especially alumina clusters is expected to be slower due to their higher effective density [21]. These clusters also transform into spinel clusters as shown in Figure 6.

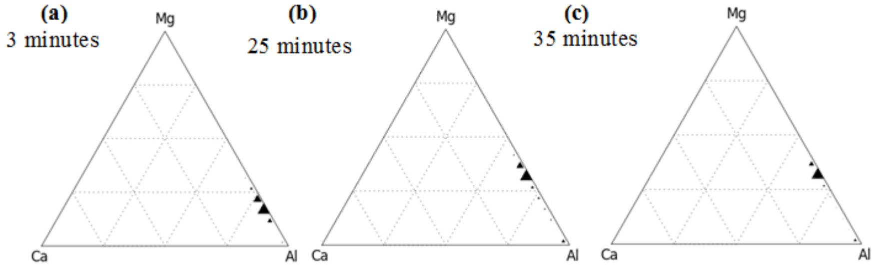

Figure 5 Inclusion composition in samples taken during Experiment 1 (steel with 0.3% Al initially; MgO crucible; Slag 1). Plotted as normalized mass fractions.

Calcium transfer from slag to inclusions via steel was not observed from the inclusion analyses of samples from experiment 1. It appears unlikely that there was no calcium transfer from slag to steel, as calcium containing inclusions have been reported in the past in steel samples taken before calcium treatment [5], [6], [15]. Possible reasons for the lack of measurable calcium transfer are a low rate of transfer (due to the low equilibrium calcium concentration and the large steel circulation time = ~30minutes as can be seen from **Figure 3**) and a relatively large concentration of inclusions in the steel.

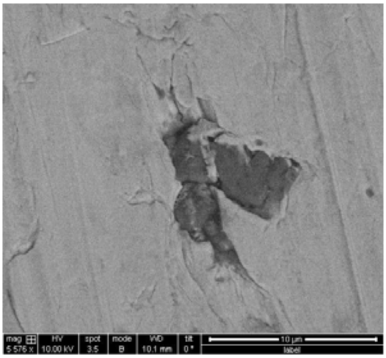

Figure 6 Alumina cluster transforming into spinel observed in the sample taken at t=20 min

Silicon (in steel) is known to increase calcium retention during calcium injection [22]. 1% Si was added after aluminum addition during experiment 2 to test the effect of silicon on calcium pick up from slag. Figure 7 (a, b and c) shows changes in inclusion composition with time. In this experiment, aluminum and slag were added at t=0 and t = 6 minutes respectively. Similar to experiment 1, magnesium pick-up in steel was observed (from MgO-containing inclusions) in all samples. Pure MgO inclusions were also present in the sample taken 55 minutes after Al-deoxidation (see Figure 7 (c)). The presence of MgO inclusions has been reported in literature as well [14]. A spinel inclusion transforming into an MgO inclusion was observed in the final sample from experiment-2 (Figure 8). Figure 7 (c) clearly shows the presence of calcium containing inclusions that formed most likely due to calcium transfer from slag to steel. Calcium containing inclusions were present as both oxide and sulfide. The final oxygen content in steel due to detected inclusions was only 50-70 ppm, less than in experiment 1. It was probably due to better flotation of some partially liquid inclusions. The average size of inclusions observed across samples in experiment 2 was in the range of 2-4 µm, smaller than in experiment 1.

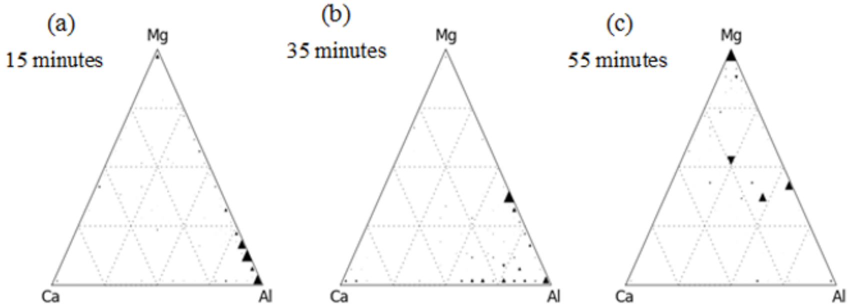

Figure 7 Time dependence of inclusion compositions during experiment 2 (steel with 1% Si and 0.15% Al initially; MgO crucible; slag 1). Plotted as normalized mass fraction.

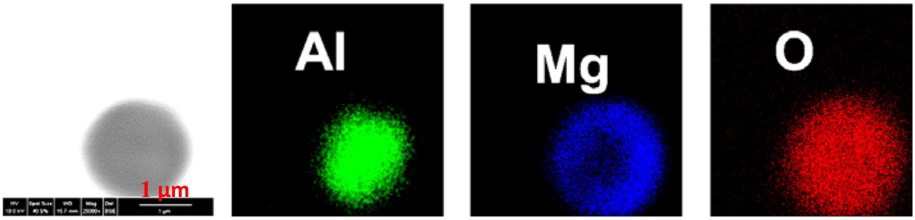

Figure 8 Partial transformation of spinel inclusion to MgO

Experiment 3 was conducted in a zirconia crucible to find the extent of magnesium transfer from slag and also to find the extent of calcium transfer while using a ZrO_2 crucible instead of a MgO crucible (For these experiments, the aluminum addition was 0.15% and the slag contained no SiO_2). The typical inclusions found in the samples taken after 20 minutes were of the following types: Al-Mg-O (Mg:Al = 0.5 by mass), Al-Mg-Zr-O, and Al-Mg-Zr-Ca-O. The average composition (wt %) of Al-Mg-Zr-O inclusions was 65% Al_2O_3, 13% MgO, and 22% ZrO_2; there was significant transfer of magnesium from slag and zirconium from crucible. Hence, it can be concluded that the source of magnesium in experiment 1 was both MgO crucible (Figure 5(a)) and slag (Figure 5 (b and c)). A larger extent of magnesium transfer from slag to steel in comparison to calcium is likely due to the low equilibrium concentration of calcium in steel as compared to magnesium. A typical calcium containing inclusion is shown in Figure 9. These inclusions were rich in Al, Mg and Zr but lean in Ca (<5% by mass). Some CaS containing inclusions attached to oxide inclusions were also observed (see Figure 10). The steel produced in this experiment was very clean as the oxygen concentration in steel from analyzed inclusions was just 7 ppm. This may be due to two reasons: there was just 100 g of steel (in the smaller zirconia crucible) which means that the flotation distance for inclusions to reach to slag was smaller compared to other experiments; due to flotation of larger inclusions the average size of inclusions observed was just 1-2 µm. Secondly, due to the small diameter of the crucible (which precluded making additions after melting the steel), aluminum and slag were placed in the crucible with electrolytic iron at the beginning of the experiment. This is expected to have resulted into liquid slag covering solid iron pieces before melting of the iron (as slag melts at a lower temperature than steel); such good mixing likely promoted inclusion removal.

Summary and Conclusions

The experiments conducted in this work aimed to understand the mechanism of calcium transfer to alumina/spinel inclusions in aluminum killed steel. Aluminum deoxidation experiments were conducted in an induction furnace in MgO and ZrO_2 crucibles to find the extent of calcium transfer from slag to inclusions via steel. The effect of silicon addition on calcium transfer was also analyzed by adding 1 wt% Si after Al-deoxidation. The extent of calcium transfer was analyzed with the help of automated inclusion analysis using SEM-ASPEX. The following conclusions can be drawn from this work:

1. Changes in aluminum and silicon content in steel can be used to calculate mass transfer coefficient in steel (k_{steel}) for steel-slag reaction with the help of a kinetic model using FactSage 6.4. In this case, $k_{steel} \times A = 1.3 \times 10^{-7}$ m^3/s.
2. The addition of 1% silicon can enhance calcium transfer from slag to steel and hence to inclusions. However, reduction of MgO may compete with CaO reduction and may limit calcium pick-up.
3. The steel with a large concentration of inclusions may not exhibit measurable calcium transfer from slag to inclusions due to the slower rate of calcium transfer from slag.
4. MgO crucible and MgO containing slag are significant source of magnesium transfer to steel for these experimental conditions.

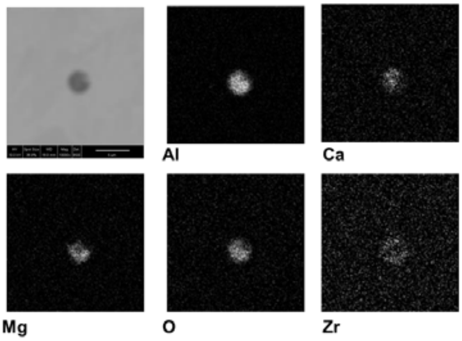

Figure 9 Calcium containing inclusion observed in experiment-3

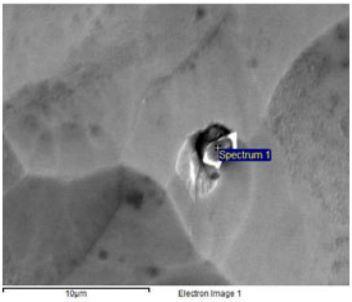

Figure 10 CaS-MgO inclusion observed in sample from experiment-3

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